concentration of 0.1 normal; and that the conductances at 25° of iodide ion and tri-iodide ion are 76.5 and 41.0, respectively, that of potassium-ion being assumed equal to 74.8.

Burgess and Chapman, by means of transference experiments, have made an independent determination of A_{I_3} and found a value only slightly greater than ours, namely 42.5. We have therefore adopted an intermediate value, 41.5, as the most probable value of A_{I_3}.

It has also been found that in potassium iodide solutions saturated with iodine the ratio $C_{I^-}/C_{I_3^-}$, which according to the law of mass action should be a constant, decreases from 1.16 to 0.99 between 0.0 and 0.1 normal; thus showing that an effect due to the presence of potassium iodide, which has been known to exist in more concentrated solutions, is not negligible even in these very dilute solutions.

Finally we have attempted to determine the composition of concentrated solutions of potassium iodide saturated with iodine, and have illustrated the usefulness of the concept of "activity," as defined by Lewis, in dealing with deviations from the law of mass action. An examination of the existing solubility and electromotive force data has shown that the problem may be solved if the relation between the activity and concentration of iodide ion in solutions saturated with iodine is known. By concentration of an ion is understood the value ordinarily calculated from conductance measurements. Although the somewhat conflicting nature of the evidence prevents an exact solution of the problem, the conclusion is reached that the ratio of activity to concentration for iodide ion is nearly independent of the concentration, that the same ratio for tri-iodide ion decreases rapidly in the concentrated solutions, and that probably higher polyiodide ion show this abnormality in an even higher degree. In a normal potassium iodide solution saturated with iodine, the concentration of KI_5 is calculated to be about 0.08 molal, if this is the only higher polyiodide present.

BOSTON, May, 1910.

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THE HYDROLYSIS OF IODINE AND OF BROMINE.

BY W. C. BRAY.

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I. The Hydrolysis of Iodine.

During the investigation described in the preceding paper, we were confronted with the problem of how to account for the conductance of aqueous iodine solutions. From calculations based on Sammet's[1] de-

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[1] *Z. physik. Chem.*, **53**, 687 (1905).

terminations of the equilibrium constants, we were led to conclude that both of the following reactions must be considered:

$$(1)\quad I_2 + H_2O = H^+ + I^- + HIO, \text{ and}$$

$$(2)\quad 3I_2 + 3H_2O = 6H^+ + 5I^- + IO_3^-;$$

and we could predict that the conductance would rise very rapidly at first (reaction (1)), and continue to rise slowly (reaction (2)) to a much higher value than we had found in our preliminary experiments. This prediction has been completely verified by the results of the conductance and solubility measurements described below.

The experimental methods employed were the same as in the experiments described in the preceding article. All measurements were made at 25°. In the final conductance experiments three different portions of powdered iodine were used; these were rotated with frequently renewed portions of water over a period of about three weeks to ensure the removal of all soluble impurities. The conductance then showed a constant value when measured after two hours' rotation. The measurements were made in a low resistance cell with smooth electrodes. The conductance of the water used varied between 0.4 and 0.9×10^{-6}; it was determined in each case and subtracted from the measured conductance. Some experiments with water alone showed that under the regular experimental conditions its conductance changed very little; in 16 hours from 0.89 to 0.94×10^{-6}; in 41 hours 0.58×10^{-6}, unchanged; in 54 days from 0.44 to 1.5×10^{-6}.

The conductance measurements for aqueous solutions are given in Table I:

TABLE I.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN AQUEOUS SOLUTIONS.

Hours rotation.	1/4.	2.	4.	8.	15.	16.	18.	21.	40.	(54×24.)
Portion I	3.8	...	...	...	...	...	4.9	4.7	...	19.1
Portion II	...	4.0	4.3	4.7	4.9	4.8	...	...	...	63.9(?)
Portion III	3.8	3.9	4.0	4.0	4.5	4.6	...	...	5.4	..

These results show that the specific conductance of aqueous iodine solutions rises rapidly to 4.0×10^{-6}, and continues to rise very slowly for a long period of time. The results obtained with Portion II are uniformly high, which is due to the fact that the stopper of the bottle did not fit properly; the introduction of an organic impurity and the resulting formation of an iodide would explain the very high result (63.9).

In order to determine the effect of the presence of hydrogen ion the preceding experiments were repeated with approximately 0.001 *N* HCl and HNO_3. In each case the iodine was first washed with the acid and then rotated over night with it before making measurements, in order to eliminate changes due to adsorption. The first two experiments in Table II were performed with the iodine of Portion I in a cell with platinized electrodes which had been heated;[1] the remaining two were preliminary experiments made at an earlier date by Mr. Mackay in a cell with platinized platinum electrodes. The conductance of the acid was measured at the time the acid was added to the iodine.[2]

TABLE II.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN 0.001 *N* ACID SOLUTIONS.

Acid used. Hours rotation	HCl. 3.	HCl. 15.	HCl. 42.	HNO_3. 42.
Acid + iodine	420.0	420.2	419.4	417.4
Acid alone	418.8	419.3	418.1	416.3
Difference	1.2	0.9	1.3	1.1

These values for the conductance of iodine are the differences between two large numbers and are therefore much less accurate than the determinations in aqueous solutions. But these results, obtained under widely different circumstances, make it almost certain that the specific conductance of iodine in acid solution is about 1×10^{-6}, which is much smaller than the value obtained in pure water.

These experiments were also repeated with 0.001 *N* NaCl solution, using the iodine of Portion III, Table I, in order to determine if the decreased conductance of iodine in the acid solution was due merely to the presence of an ionized substance:

TABLE III.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN 0.001 *N* NaCl SOLUTION.

Hours rotation.	1/2.	3.	7.	14.	(55×24.)
NaCl + iodine	130.2	130.4	130.4	131.0	137.3
NaCl alone	127.1	127.1	127.1	127.0	127.0
Difference	3.1	3.3	3.3	4.0	10.3

The conductance of iodine in dilute sodium chloride is thus seen to increase in a manner very similar to that observed in water solutions, though the values obtained are somewhat smaller. The specific conductance (× 10^6) rises rapidly to 3.3 (in water 4.0) and remains nearly constant for several hours; in 14 hours it reaches the value 4.0 (in water 4.6); and in 54 days increases to 10.3 (in water 19.1).

The probable explanation of these results is that the initial value of the conductance of aqueous iodine solutions is mainly due to the rapidly occurring hydrolysis:

$$I_2 + H_2O = H^+ + I^- + HIO,$$

and that this hydrolysis is driven back almost completely in acid solutions.[3]

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[1] Whetham and Griffiths, *Phil. Trans.*, 194A, 330 (1900).

[2] In two blank experiments in which the hydrochloric acid alone was rotated in the thermostat for two days the conductance remained unchanged.

[3] It is possible that the conductance of iodine in acid solution, 1×10^{-6}, is due to the presence of the ions $I^- + I^+$ (cf. W. A. Noyes, THIS JOURNAL, 23, 463 (1901); Stieglitz, *Ibid.*, 23, 797 (1901); Walden, *Z. physik. Chem.*, 43, 415 (1903)). If this is true, then in KI solutions the concentration of I^+ would be reduced to a very small value.

As a check on this result, the relative solubilities of iodine in water and dilute hydrochloric acid have been determined, and also the change of them with the time. The saturated solution was forced into a 100 cc. pipette through an asbestos filter connected with it by a ground-glass joint; the 100 cc. were run into a potassium iodide solution containing sulphuric acid, and the titration was made with freshly prepared (approximately) *N*/200 thiosulphate. The thiosulphate solutions were not accurately standardized, since the measurements desired were only comparative. The value adopted for the total solubility of iodine at 25° was that of Hartley and Campbell,[1] 0.001337 mol I_2 per 1000 grams water, or 0.001333 mol per liter; the solubility, after two hours' rotation, being assumed to have this value. After each experiment extending over a long period of time, the iodine was washed with water and its solubility again determined by rotating it two hours with fresh water. The iodine used in the experiments with 0.001 *N* HCl was Portion III; in the aqueous solutions Portions I and II. In these experiments only the first 100 cc. portion from each 250 cc. bottle was used, since the second portion, when taken, gave somewhat lower results.

TABLE IV.—RELATIVE SOLUBILITY OF IODINE IN WATER AND IN HYDROCHLORIC ACID SOLUTIONS.

Solvent.	Water.		0.001 *N* HCl.		0.001 *N* NaCl.
Time.	Iodine.	Iodate.	Iodine.	Iodate.	Iodate.
1.5 hours	2.664	..	...	..	...
2 hours	2.666[2]	0.002 or less	2.639	..	...
2 hours	..	..	2.639	..	...
3 hours	2.666	..	...	..	...
16 hours	2.668	..	2.653	..	...
41 hours	2.666	0.010 or less	2.665	0.010 or less	...
48 hours	2.665	..	...	..	...
27 days	2.80	..	2.72	0.017 or less	...
27 days	2.83	0.017	...	..	...
54 days	..	0.027	...	..	0.025

The iodate concentration was also determined approximately by adding 100 cc. of the saturated solution to a potassium iodide solution containing sodium hydrogen carbonate and an excess of carbonic acid, decolorizing with thiosulphate, adding excess of sulphuric acid, and titrating after 3–5 minutes the iodine now liberated by the action of HIO_3

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[1] *J. Chem. Soc. Trans.*, 93, 741 (1908). These authors made an extended series of measurements at different temperatures and used carefully purified iodine and conductivity water. Other determinations (in mols per liter) are, Jakowkin, 0.001337; Noyes and Seidensticker, 0.001342; Sammet, 0.001341.

[2] Value derived from several concordant experiments.

on HI.[1] By determining roughly the rate at which iodine is subsequently liberated by the action of oxygen on hydriodic acid, the very small error due to this reaction was eliminated. The iodate was also determined in a single experiment in which the solvent was 0.001 *N* NaCl (in which iodine, Portion III, was used). The results are given in Table IV, in milliequivalents (of $^1/_2I_2$ and $^1/_6HIO_3$) per liter.

The solubility of iodine in the acid solution is (after two hours) just one per cent. less than in water, which is at any rate qualitatively in agreement with the conductance results. The solubility increased slightly in two days in the acid, but remained practically constant in the aqueous solution; and later increased steadily in both cases.[2]

If we assume that the initial solubility in the acid solution is a measure of the true solubility of iodine as I_2, then this value is 1.320 millimols per liter. From the 41-hour experiment, after correcting for the iodate and the tri-iodide due to the iodide formed in the reaction, the value 1.320 is again obtained. The most probable source of error is the presence of iodide (and consequently tri-iodide), and the results are therefore more likely to be too high than too low.

Another method of calculating the true solubility is to correct the value found in pure water by means of the conductance data, Table I. Assuming that the conductances, 4.0, 4.6, and 5.4, after 2, 16, and 41 hours, respectively, are due solely to the acid (mainly HI) formed by the reactions (1) and (2), then the ion concentrations obtained by dividing them by $\Lambda_H + \Lambda_I = 425$ are approximately 0.0094, 0.0108 and 0.0127 millimol per liter. The corresponding iodine concentrations (in equivalents), which are to be subtracted from the solubilities are approximately three times these values; since for each equivalent of H^+ there are two oxidation equivalents of HIO (or IO_3^-) and roughly one oxidation equivalent (= 0.5 mol) of I_3^- (since about one-half of the iodide ion originally formed is converted into tri-iodide ion). The true solubilities after 2, 16 and 41 hours are therefore 1.320, 1.318 and 1.314 millimols I_2 respectively. These results may be too low if the conductance is not wholly due to the acid formed in the reactions (1) and (2).

The agreement between these two independent methods confirms the correctness of both, and the value 1.32 millimols I_2 per liter was therefore chosen as the true solubility at 25° of iodine as such.

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[1] Bray, *Z. physik. Chem.*, 54, 470 (1905). The amount of dilute thiosulphate required in the first stage of the titration was always considerably less than the theoretical amount, but increased when the concentration of potassium iodide present increased. This phenomenon is probably due to direct oxidation of the thiosulphate to sulphate (cf. *Ibid.*, 472).

[2] The unexpectedly high values for the 27-day experiments may be due to an experimental error, since all depend on a single (comparative) determination of the solubility of iodine after two hours; but are more probably due to the entrance of some organic matter through the stoppers.

It is now possible to calculate the equilibrium constant of the hydrolysis: $I_2 + H_2O = H^+ + I^- + HIO$, from the above given value of the H^+ concentration. Since it seems probable that the initial conductance 4.0×10^{-6} of an aqueous solution is a measure of the hydriodic acid formed in this reaction, $(H^+) = (I^-) = (HIO) = 0.94 \times 10^{-5}$ mols per liter, and the equilibrium constant

$$(H^+)(I^-)(HIO)/(I_2) = 0.6 \times 10^{-12}.$$

This value is much smaller than the limiting values, 10^{-8} to 10^{-10} esti mated by Sammet; but he considered his results to be of very little value and gave no details of his measurements.

It is interesting to calculate the maximum conductance which should be finally attained by the saturated aqueous solution as a result of reaction (2) from Sammet's (accurate) value of its equilibrium constant: $(H^+)^6(I^-)^5(IO_3^-)/(I_2)^3 = 2.8 \times 10^{-47}$. The concentrations of the other substances are calculated from the known concentration of the iodine to be: $(H^+) = 3.16 \times 10^{-5}$, $(I^-) = 2.63 \times 10^{-5}$, and $(IO_3^-) = 0.53 \times 10^{-5}$, and the corresponding specific conductance is calculated to be 13×10^{-6}. This value is somewhat larger than that obtained in the sodium chloride solution, 10.3×10^{-6}, and somewhat smaller than the value in aqueous solution, 19.1×10^{-6}.

II. The Hydrolysis of Bromine.

It is well known from the comprehensive investigation of Jakowkin[1] that dilute solutions of chlorine are hydrolyzed to a very considerable extent. The hydrolysis constant at 25° is

$$(H^+)(Cl^-)(HClO)/(Cl_2) = 4.48 \times 10^{-4}.$$

Since bromine occupies an intermediate position between chlorine and iodine in so many instances, it is almost certain that bromine solutions will also exhibit hydrolysis. This hydrolysis is mentioned in a recent article by Jakowkin,[2] but no experimental data are given. In the following some preliminary measurements are described:

A large portion of liquid bromine was placed in a 250 cc. bottle and shaken successively with eight portions of fresh water. Conductance measurements were made, and the correction for the specific conductance of water applied, as in the preceding experiments. Portions of each solution were also removed in a small pipette designed to prevent an error due to evaporation; and were added to a concentrated solution of potassium iodide containing sulphuric acid; the liberated iodine was titrated with thiosulphate. The results are presented in the following table In experiments 3(*b*) and 7(*b*) the water was not renewed. In

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[1] Jakowkin, *Z. physik. Chem.*, 29, 613 (1899).

[2] Jakowkin, *Ibid.*, 70, 188 (1910).

the final experiment, the solution was probably not saturated, since the amount of bromine left was very small.

TABLE V.—CONCENTRATION AND CONDUCTANCE OF SATURATED BROMINE SOLUTIONS

No.	Time (hours).	Equiv. conc.	Spec. cond. × 10^6.
2	70	0.506	7440
3*a*	1	0.465	4160
b	20	0.466	4160
4	2	0.440	2210
5	1	0.424	907
6	1	0.424	734
7*a*	1	0.411	726
b	6	0.425	805
8	2	0.411	728

The concentration decreases slightly, and the conductance greatly in the first five experiments, probably owing to the gradual removal of some impurity, such as hydrobromic acid or potassium bromide. The bromine appears, from the approximate constancy of the two series of results, to have been nearly pure in the last four experiments; and the following values are probably not greatly in error: solubility, 0.21 mol Br_2 per liter;[1] specific conductance, 727×10^{-6} reciprocal ohms.

If we assume that the conductance is solely due to the hydrobromic acid formed by the hydrolysis, $Br_2 + H_2O = H^+ + Br^- + HBrO$, then the concentration calculated for $(H^+) = (Br^-) = (HBrO)$ is 0.0017. This corresponds to 0.8 per cent. hydrolysis, and the calculated equilibrium constant is:

$$(H^+)(Br^-)(HBrO)/(Br_2) = 2.4 \times 10^{-8}.$$

This value differs very little from the geometric mean, 1.7×10^{-8}, of the hydrolysis constants of chlorine and iodine.

Summary.

From conductance and solubility measurements of iodine and of bromine in water, the hydrolysis constants $(H^+)(I^-)(HIO)/(I_2)$ and $(H^+)(Br^-)(HBrO)/(Br_2)$ are found to be 0.6×10^{-12} and 2.4×10^{-8}, respectively.

BOSTON, March, 1910.

THE THERMAL DISSOCIATION OF CALCIUM CARBONATE.

BY JOHN JOHNSTON.

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Measurements of the dissociation pressures of calcium carbonate have been made through a range of temperatures by Debray,[2] LeChatelier,[3]

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[1] This value agrees well with that determined by Winkler (Seidell, solubilities, page 67) 3.36 g. per 100 g. soln., or approximately 0.206 mol per liter.

[2] *Compt. rend.*, 64, 603 (1867).

[3] *Id.*, 102, 1243 (1886).