	B.-p. C.	B.-p. abs.	V. p. change. obsd. mm.	V. p. change. calc. mm.
Benzene	80°	353°	24	24.1
Naphthalene	218	491	17	17.3
Chloroform	62	335	25.2	25.4
Carbon disulphide	46	319	24.7	26.6
Aniline	184	457	19.5	18.6
Methyl acetate	57.5	330.5	26.8	25.7
Methyl formate	32.3	305.3	28.8	27.8
Amyl *n*-butyrate	178.6	451.6	19	18.8
Ether	34.6	307.6	27	27.6
Mercury	357	630	13.6	13.5
Sulphur	445	718	12.2	11.8
Water	100	373	27.2	27.3[1]
Alcohol	78.4	351.4	30.3	28.9[1]
Acetic acid	119	392	24	26.0[1]

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 52.]

THE CONDUCTANCE AND IONIZATION OF POTASSIUM TRI-IODIDE, AND THE EQUILIBRIUM BETWEEN IODINE, IODIDE, AND POLYIODIDES IN AQUEOUS SOLUTION.

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This investigation was undertaken in order to determine the equivalent conductance of the tri-iodide ion, I_3^-; for a knowledge of this quantity is needed in the study of the equilibrium between iodine, iodide, and polyiodides in aqueous solution. Our own experimental work deals only with dilute solutions; but so much experimental evidence relating to this equilibrium in more concentrated solutions is available that it has seemed worth while to consider the results of several of these investigations from a single point of view. Accordingly, after presenting our own results, we have attempted to calculate the proportion of iodide, tri-iodide, and higher polyiodide present in a normal KI solution saturated with iodine.

The only careful determination of the conductance of tri-iodide ion, Λ_{I_3}, is that of Burgess and Chapman,[2] who calculated, from transference experiments, that $\Lambda_{I_3}/\Lambda_I = 0.566$. If we accept the value $\Lambda_I = 76.5$ at 25°, as given below, then Λ_{I_3} is found to be 42.5. We have recalculated these results[3] and have found the same mean value for Λ_{I_3}, although

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[1] Constant here 10200, for the others 8500.

[2] Burgess and Chapman, *J. Chem. Soc.*, 85, 1305 (1904).

[3] The share of transport of tri-iodide ion, $C_{I_3^-} \times \Lambda_{I_3} / (C_{I_3^-} \times \Lambda_{I_3} + C_{I^-} \times \Lambda_I + C_{K^+} \times \Lambda_K)$ equals $\frac{1}{2}(B/A - 1)$ and may be obtained directly from the values of B/A given by these authors in the table on page 1316. The concentration ratio $C_{I^-}/C_{I_3^-}$ is given as C_2/C_1 in the tables on page 1309, the degrees of ionization of KI and KI_3 being assumed equal.

the separate values do not agree perfectly with the original calculations. These experiments are, it is true, open to the objection that concentration changes are referred to a constant volume of solution instead of to a definite weight of water. But we have estimated, on the assumption that the partial volume of 1 gram of dissolved iodine (as explained below) is 0.2376 cc. and that of 1 gram dissolved potassium iodide is 0.283 cc., that the error introduced in this way is less than 0.2 per cent.

The method which we have used in determining Λ_{I_3} depends upon the measurement of the change of conductance produced by dissolving iodine in a solution of potassium iodide. A few incidental measurements of this kind have been made by LeBlanc and Noyes[1] and by Burgess and Chapman,[2] from which the last named authors calculated that the average value of the ratio Λ_{I_3}/Λ_I is 0.553. This close agreement with the results of their transference experiments is purely accidental; for the individual values (eight in all) derived from the conductance measurements vary irregularly between 0.51 and 0.60, corresponding to a variation of Λ_{I_3} between 39 and 46. The inaccuracy of these measurements is doubtless due to the fact that the amount of KI_3 present was much smaller than that of KI. We have avoided this source of error as far as possible by saturating the KI solution with iodine, and thus obtaining a concentration of KI_3 nearly equal to that of the uncombined KI.

The fundamental assumption which is made in interpreting any of these experimental results is that the only polyiodide present is KI_3. This depends upon the measurements of the equilibrium $I_3^- = I^- + I_2$ made by Jakowkin[3] at 25° and Dawson[4] at 13.5°, in which the concentration of I_2 as such in the aqueous solution was varied and determined by partition experiments, and the additional dissolved iodine was assumed to be present as KI_3. The values of the equilibrium constant[5]

$$K = \frac{(I_2)(I^-)}{(I_3^-)} = \frac{C_{I_2}\gamma C_{\Sigma I}}{\gamma' C_{\Sigma I_3}}$$

could not be directly determined but the values of the expression

$$K_1 = \frac{C_{I_2}C_{\Sigma I}}{C_{\Sigma I_3}}, \text{ where } K = \frac{\gamma K_1}{\gamma'}$$

We have also assumed that Λ_K at 25° = 74.8, and that $C_{\Sigma I}C_{I_2}/C_{\Sigma I_3} = 0.00138$. The values of Λ_{I_3} calculated from the separate experiments, and given in the same order as on page 1309, are 42.3, 42.9, 42.6, 42.5, 41.9, 42.4, and 43.3.

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[1] LeBlanc and Noyes, *Z. physik. Chem.*, **6**, 402 (1890).

[2] Burgess and Chapman, *Loc. cit.*, 1310.

[3] Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

[4] Dawson, *J. Chem. Soc.*, **79**, 238 (1901).

[5] Concentrations are represented by means of parentheses, or by the letter C. $C_{\Sigma I}$ means the total concentration of iodide. γ and γ' are the degrees of ionization of KI and KI_3 respectively.

were found to be remarkably constant when the concentrations of I_2, KI and KI_3 were greatly varied. We have collected in the following table some additional values of K_1 at 25° which we have calculated from the experimental data of Maitland.[1] A few of Jakowkin's results are also presented for comparison. The first column shows the concentration in mols per liter of the total potassium salt present, $C_{\Sigma K} = C_{\Sigma I} + C_{\Sigma I_3}$. The values of K_1 and the corresponding values of C_{I_2} are arranged in horizontal rows:

TABLE I.—VALUES OF $K_1 = C_{I_2}C_{\Sigma I}/C_{\Sigma I_3}$ AT 25°.

$C_{\Sigma K}$.					
0.0625	$C_{I_2} \times 10^4$	0.754	1.59	5.71	Jakowkin
	$K_1 \times 10^3$	1.38	1.40	1.41	
0.100	$C_{I_2} \times 10^4$	0.453	1.855	4.190	Maitland
	$K_1 \times 10^3$	1.39	1.38	1.36	
0.200	$C_{I_2} \times 10^4$	0.474	1.179	4.02	Maitland
	$K_1 \times 10^3$	1.41	1.39	1.35	
0.400	$C_{I_2} \times 10^4$	...	1.33	...	Maitland
	$K_1 \times 10^3$	...	1.32	...	
0.500	$C_{I_2} \times 10^4$	0.541	1.114	3.60	Maitland
	$K_1 \times 10^3$	1.37	1.33	1.27	
1.00	$C_{I_2} \times 10^4$	0.484	1.013	2.904	Maitland
	$K_1 \times 10^3$	1.30	1.26	1.08	

It is evident that Maitland's results are in good agreement with those of Jakowkin, and that in the dilute solutions the amount of polyiodides higher than KI_3 must be extremely small. In the concentrated KI solutions, however, the values of K_1 are smaller and show a steady decrease with increasing concentration of I_2.[2]

The expression K_1 is related to the equilibrium constant K by the equation $K = (\gamma/\gamma')K_1$, where γ and γ' are the degrees of ionization of KI and KI_3, respectively. Dawson concluded from the constancy of K_1 that $\gamma = \gamma'$, but this is not necessarily true. It has been found, from conductance measurements, that in a mixture of two salts with a common ion the degree of ionization of each salt depends only on the total ion concentration and for highly ionized salts changes only very slowly with the ion concentration. Since, moreover, the degrees of ionization of KI and KI_3 do not differ greatly, it follows that the degree of ionization of potassium iodide, γ, will not be changed appreciably when a portion of it is converted into tri-iodide by dissolving iodine in its solution, and that also, in the different solutions which may be prepared from a given potassium iodide solution, the degree of ionization of KI_3 will have a definite, constant value, γ'.[3]

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[1] Maitland, *Z. Elektrochem.*, 12, 264 (1906).

[2] This will be considered later; the corresponding values of K_1 for solutions saturated with I_2 are given in Table V, γ' being then assumed equal to γ.

[3] This conclusion, that for such a series of solutions γ/γ' is a constant, was reached

Upon the basis of the conclusion that the ionization γ of KI is unchanged by the addition of iodine, the results of our conductance measurements may be represented by the following equations, where L and L' represent respectively the specific conductances of the potassium iodide solution and of the same saturated with I_2:

$$1000\, L = \gamma C_{\Sigma I}\, (\Lambda_K + \Lambda_I)$$

$$1000\, L' = \gamma C'_{\Sigma I}\, (\Lambda_K + \Lambda_I) + \gamma' C'_{\Sigma I_3}\, (\Lambda_K + \Lambda_{I_3}).$$

Furthermore, since the change of volume on dissolving the iodine is negligible in dilute solutions we have:

$$C_{\Sigma I} = C'_{\Sigma I} + C'_{\Sigma I_3}.$$

For the simple case that $\gamma = \gamma'$ the difference between the two conductances then becomes:

$$1000\, (L - L') = \gamma C'_{\Sigma I_3}\, (\Lambda_I - \Lambda_{I_3});$$

for the general case, however, the difference assumes the form

$$1000\, (L - L') = (\gamma - \gamma')\, C'_{\Sigma I_3}\, (\Lambda_K + \Lambda_I) + \gamma' C'_{\Sigma I_3}\, (\Lambda_I - \Lambda_{I_3}).$$

Since $\gamma - \gamma'$ approaches zero with decreasing concentration, the two expressoins will become identical at the limit. In other words, if we calculate the difference between the conductances, $\Lambda_I - \Lambda_{I_3} = \dfrac{1000(L - L')}{\gamma C'_{\Sigma I_3}}$ assuming as a first approximation that $\gamma = \gamma'$, then the limiting value approached in dilute solutions will be a true measure of $\Lambda_I - \Lambda_{I_3}$. We have therefore made a series of determinations in which the initial potassium iodide concentration was varied from 0.1 to 0.001 normal in order to obtain the limiting value of the ratio $1000\, (L - L')/(I_3^-)$.

Preparation of the Substances and Solutions.

The *potassium iodide* solutions, 0.1 and 0.01 normal at 25°, were made by dissolving the requisite amount[1] of the pure salt (Kahlbaum's guaranteed reagent), powdered and dried to constant weight, and diluting (at 25°) to 2 liters. The remaining solutions were prepared from these by dilution by means of a calibrated 200 cc. pipette and a series of calibrated measuring flasks. The strength of the two stock solutions was checked to within 0.1 per cent. by liberating the iodine and titrating

by Osaka (*Z. physik. Chem.*, 38, 743 (1901)), but he made the assumption that the law of mass action could be applied to the ionization of these two salts. Osaka found in his preliminary measurements of the freezing points of 0.5–1.0 normal solutions of potassium iodide before and after adding iodine that after the addition of iodine the freezing point is distinctly higher than before, and concluded that KI_3 is somewhat less ionized than KI. But since the behavior of these concentrated solutions is in general so different from that of more dilute solutions it is not justifiable to conclude that in dilute solutions the degree of ionization of KI_3 is less than that of KI.

[1] The International Atomic Weights of 19.08 were used. No correction, however, was applied for buoyancy.

it by a method to be described in a subsequent paper, thus proving the absence of chloride or other impurity.

The *water* used was prepared by redistilling ordinary distilled water from an alkaline solution of potassium permanganate; it had a specific conductance of from 0.4 to 0.8 × 10^{-6} reciprocal ohms at 25°. The conductance of the water was in each case subtracted from the conductance of the weaker solutions.

The *sodium thiosulphate* solution used in titrating "free iodine" in the three more concentrated solutions was 0.07348 normal. It was standardized by comparison with an iodine solution which had been titrated against a weighed quantity of As_2O_3 according to the directions of Washburn.[1] For the titration of the more dilute iodine solutions this standard thiosulphate solution was diluted just before use to five times its volume.

The *iodine* used was obtained by purifying commercial resublimed iodine. This was ground with about one-quarter of its weight of potassium iodide and carefully sublimed; the iodine thus obtained was again sublimed without the addition of any potassium iodide.

The Experimental Method.

The *conductance measurements* were made in glass cells of the pipette form, such as have been described in another article from this laboratory.[2] Two were used, one of low resistance for the very dilute solutions, and the other of high resistance for the more concentrated solutions. The cell constants were determined by measuring in the cells at 25° freshly prepared solutions of potassium chloride 0.01 normal at 18°, the specific conductance of which was assumed to be 1413 × 10^{-6} at 25°.[3] The measurements were made in the usual way by means of an accurately calibrated bridge of the Kohlrausch roller pattern.

The *saturated solutions* were prepared as follows: Ten to thirty grams of freshly powdered iodine were placed in a 250 or 500 cc. glass-stoppered bottle of "Resistenz" glass, which had been well steamed out. After washing this iodine with a small quantity of a potassium iodide solution the bottle was filled with a potassium iodide solution of the same concentration, the stopper and neck of the bottle were carefully covered with a rubber tube, the bottles were rotated in a thermostat at 25° for different lengths of time, and finally were hung in the thermostat for a few minutes to allow the iodine to settle.

Portions of the saturated solution were forced by air pressure through a glass tube into the conductivity vessel, which was also immersed in

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[1] Washburn, This Journal, 30, 31 (1908).

[3] Abbott and Bray, This Journal, 31, 732 (1909).

[3] This value is based upon recent measurements made in this laboratory by A. C. Melcher and by F. L. Hunt.

the thermostat; and the conductance was quickly measured. Fresh portions of solutions were then forced into the cell in order that the measurement might be checked.

Other portions of the same solution were withdrawn by pipettes of known volume, run into solutions of potassium iodide, and the free iodine titrated with thiosulphate. In filling a pipette the solution was forced by means of air pressure through a filter of glass wool and asbestos connected with the pipette by a ground glass joint. This use of air pressure in transferring the saturated solutions prevented the error from evaporation of iodine which would have arisen if suction had been used. To avoid this error the measurements were also made as quickly as possible and only one-half, or at most two-thirds, of the solution in the bottle was used.

The Conductance and Solubility Data.

All the experimental data are presented in the following table:

TABLE II.

KI solution.			KI solution saturated with iodine.			Best values.	
Milli-mols per liter.	Equiv. cond.	Spec. cond. $\times 10^6$.	Hours rotation.	Spec. cond. $\times 10^6$.	Milli-mols I_2 dissolved.	Spec. cond. $\times 10^6$.	Total iodine dissolved.
100	130.8	13080	25	11500	51.1	11490	51.35
	130.8	13080	120	11485	51.6		
50	134.75	6737.5	25	5930	25.77	5930	25.77
20	139.4	2788	25	2468	11.13	2468	11.13
10	142.2	1422	20	1259	6.185	1260	6.185
	142.4	1424	54	1261	6.080[1]		
5	144.5	722.5	20	641.0	3.725	641	3.728
	144.8[1]	724.0[1]	54	642.0[1]	3.731		
2	147.0[1]	294.0[1]	4	260.2	2.292[1]	260.8	2.266
	146.7	293.4	20	260.8	2.266		
	146.6	293.2	54	261.2	.....		
1	149.95	147.95	4	131.6	1.772	131.7	1.788
	147.9	147.9	20	131.9	1.788		
	148.0	148.0	48	131.8	1.793		
	147.8	147.8	54	133.2[1]	1.787		

It will be seen that the duplicate measurements of conductance gave concordant results throughout, but the values of "iodine dissolved" in the saturated solutions are somewhat less satisfactory. The maximum variation from the mean is 1 per cent. in the most dilute solution, 0.5 per cent. in the most concentrated, and 0.1 per cent. in an intermediate solution (0.005 mol. KI).

The Equivalent Conductance of Potassium Iodide.

A comparison of the conductance data presented above with those obtained by earlier investigators is afforded by Table III. This con-

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[1] These data were rejected in deriving the best values because they were not consistent with the data at other concentrations.

tains values interpolated from the results at 25° of Ostwald,[1] of Jones and Douglas[2] and Schmidt and Jones,[3] all reduced from Siemann's units to reciprocal ohms by multiplying by 1.066. Values at 25° derived by combining the data of Kohlrausch and Steinwehr at 18° with Déguisne's temperature coefficients[4] and making a slight correction for the expansion of the solution are also included. The table also contains in the last two columns the percentage ionization of potassium iodide at 25° and at 18° derived from our data and those of Kohlrausch, respectively. These columns serve to show the consistency of the data at the two temperatures and the very small effect of temperature on the ionization.

TABLE III.—EQUIVALENT CONDUCTANCE AND PERCENTAGE IONIZATION OF POTASSIUM IODIDE.

	Λ for KI at 25°.					100γ for KI.	
Concentration.	Bray & MacKay.	Ostwald.	Jones & Douglas.	Schmidt & Jones.	Kohlrausch & Déguisne.	(25°).	(18°).
0.1	130.8	...	128.8	133.9	...	86.5	86.95
0.05	134.7	...	133.0	136.7	134.9	89.1	89.45
0.02	139.4	139.3	139.3	140.3	...	92.1	92.30
0.01	142.3	143.1	142.7	142.4	...	94.1	94.20
0.005	144.5	146.2	146.0	144.8	...	95.5	95.60
0.002	146.7	148.7	149.1	146.8	...	97.0	97.05
0.001	147.9	150.0	150.3	148.3	147.9	97.8	97.85
0.0	151.3	...	...	...	...	100.0	100.00

In the last row of the table is given the equivalent conductance at zero concentration. To derive this we have employed a method which has already been described in several publications from this laboratory,[5] which consists in plotting values of $1/\Lambda$ against the corresponding values of $(C\Lambda)^{n-1}$ for different values of n. For the sake of comparison the results of Kohlrausch and Steinwehr on potassium iodide at 18° were plotted on the same diagram. It was found that in both cases a straight line was obtained between the concentrations 0.001 and 0.02 normal for the value $n = 1.45$; that the line expressing the results at 18° met the $1/\Lambda$ axis at a point corresponding to $\Lambda = 131.1$, identical with the value of Λ_0 chosen by Kohlrausch and Steinwehr; and that in the case of the results at 25° the corresponding value of Λ_0 is 151.3 ± 0.1. These results show that between the concentrations 0.001 and 0.02 the dilution law takes the form $(\gamma C)^{1.45}/C(1-\gamma) = \text{const.}$ At higher concentrations a lower value of n than 1.45 must be chosen.[6] This graphical

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[1] Landolt-Börnstein-Meyerhoffer, Tabellen, p. 748.

[2] *Am. Chem. J.*, 26, 445 (1901).

[3] *Ibid.*, 42, 73 (1909).

[4] Landolt-Börnstein-Meyerhoffer Tabellen, p. 744 and 755.

[5] See for example THIS JOURNAL, 31, 745 and 1010 (1909).

[6] The conductance measurements at 18° for solutions more dilute than 0.001 normal indicate that n has a higher value than 1.45 in these very dilute solutions, and

method has also shown that our individual measurements are consistent with one another, and that the lower value (144.5) found for the equivalent conductance of the 0.005 normal solution is more nearly correct than the higher value (144.8).

It will be seen that the two conductance values of Kohlrausch and Déguisne agree almost completely with ours, and that the ionization values at 18° and 25° run closely parallel, those at 18° being uniformly slightly higher and by an amount that increases gradually as the concentration increases. The results of Ostwald and of Jones and Douglas agree with ours only at 0.02, being considerably higher at the lower concentrations, owing probably to errors introduced by the method of dilution employed. Those of Schmidt and Jones at the lower concentrations (0.01 to 0.001 normal) are much lower than those of Jones and Douglas and fairly concordant with our values; but at the higher concentrations (0.1 to 0.02) the results of Schmidt and Jones are widely divergent from all the others.

The most probable values of the conductances Λ_I and Λ_K of the separate ions were considered to be 76.5 and 74.8, respectively, the sum of which is of course equal to Λ_0 = 151.3. These values are based upon some unpublished conductance measurements at 25° which will be discussed in a later publication.

The Equivalent Conductance of Potassium Tri-iodide.

Before the data for the solutions saturated with iodine could be interpreted it was necessary to determine whether any correction should be made for the conductance of iodine in pure water. The results of experiments on the hydrolysis of iodine described in the following article show that the initial conductance of an iodine solution in water is due mainly to the acid formed by the hydrolytic reaction, $I_2 + H_2O = HIO + H^+ + I^-$, and that this hydrolysis is driven back almost completely in the presence of a dilute acid. Since an iodide may be expected to have the same effect, no correction has been made for the conductance of iodine in pure water.

It will also be shown in that article that the solubility of iodine as I_2 is 0.00132 mols per liter—a value that will be used in the following calculations.

To the measured conductances of the more concentrated solutions a small correction must, however, be applied on account of the increase of volume when the iodine is dissolved; for in determining the change of conductance resulting from the transformation of KI into KI_3, it is necessary to compare solutions of the same concentration with respect to potassium. Mr. R. C. Tolman, of this laboratory, has kindly furnished

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that therefore the values of Λ_0 chosen at 18° and 25° are somewhat too high. For the sake of uniformity however, we have retained the Kohlrausch value.

us with the results of his preliminary measurements on the specific gravities of solutions obtained by dissolving varying amounts of iodine in a 0.25 normal KI solution. The volume-increase of 1 liter of the potassium iodide solution was found to be 0.2376 cc. per gram of iodine dissolved in it. It was calculated that the total concentration of potassium salts in the three most concentrated solutions saturated with iodine differed from the original round concentrations by 0.31, 0.16 and 0.05 per cent., respectively, thus giving 0.9969, 0.04992 and 0.01999 mols per liter. The specific conductances of pure potassium iodide solutions at the same concentrations were therefore calculated to be 0.013040, 0.006727 and 0.002786, respectively, and these values have been used in determining the decrease of specific conductance (Table IV, column 6).

In Table IV the final results and some quantities calculated from them are presented. Concentrations are expressed in the table in millimols per liter at 25°, but all calculations are based upon molal concentrations. The *first* column gives the total concentration of the potassium salts in the solutions, the values in the three most concentrated solutions having been obtained by correcting the values given in Table II as just described. The *third* column gives the concentration of the tri-iodide ($\Sigma I_3 = I_3^- + KI_3$), obtained by subtracting the solubility of I_2 (1.32) from the "total iodine dissolved," as given in the last column of Table II. The *second* column gives the concentration of iodide (ΣI) determined by taking the difference between the two concentrations just referred to ($\Sigma K - \Sigma I_3$). The *fourth* column gives the concentration of tri-iodide ion, (I_3^-), calculated under the assumption that the degree of ionization of KI_3 is the same as that of KI in the initial KI solution. The *fifth* column contains the ratio $\Sigma I_3/(\Sigma I + \Sigma I_3) = r$. The *sixth* and *seventh* columns show the decrease in specific and equivalent conductance, $L - L'$ and $\Delta\Lambda$, respectively, produced by replacing the iodide by exactly the same amount of tri-iodide. The *eighth* column contains the values of the ratio, $1000\,(L - L')/(I_3^-)$, which should be constant, and equal to $\Lambda_I - \Lambda_{I_3}$, if the ionization of KI_3 is the same as that of KI. The *ninth* column shows the values of the ratio, $\Delta\Lambda/\gamma$, which would equal the decrease of equivalent conductance if all the KI were replaced by KI_3, no assumption in regard to degree of ionization of the KI_3 being involved. The *tenth* column contains the values of Λ_{KI_3} calculated by subtracting $\Delta\Lambda/\gamma$ from the values of Λ_{KI} given in Table III, and the *last* column gives the corresponding values of the percentage ionization of KI_3, $100\gamma_{KI_3}$, calculated on the assumption that Λ_0 for KI_3 is equal to 115.8.

An inspection of the table shows that all the results are concordant except the value $r = (\Sigma I_3)/(\Sigma I + \Sigma I_3) = 4.90$ for the second solution, which is evidently too low. Since this value is based upon only a single titration of "total iodine dissolved," a more probable value, 4.97, has been obtained by interpolation, and the corresponding values of γ_{KI_3}, etc., calculated. These values are enclosed in brackets in the table.

TABLE IV.

Concentrations × 10^3.					Decrease in cond.					
$(\Sigma I + \Sigma I_3)$.	(ΣI).	(ΣI_3).	(I_3^-).	$r = \frac{(\Sigma I_3)}{(\Sigma I + \Sigma I_3)}$.	$(L - L')10^6$.	$\Delta\Lambda$.	$\frac{1000(L - L')}{(I_3^-)}$.	$\Delta\Lambda/r$	Λ_{KI_3}.	$100\gamma_{KI_3}$.
99.69	49.66	50.03	43.28	0.502	1550	15.5	35.8	30.9	99.9	86.3
49.92	25.47	24.45	21.79	0.490	797	15.9	36.6	32.5	102.3	88.3
49.92	...	...	...	(0.497)[1]	...	..	(36.0)	(32.0)	(102.8)	(88.8)
19.99	10.18	9.81	9.04	0.491	320	16.0	35.4	32.6	106.8	92.2
10.00	5.135	4.865	4.58	0.486	163	16.3	35.6	33.5	108.8	94.0
5.00	2.592	2.408	2.30	0.482	81.5	16.3	35.4	33.8	110.7	95.6
2.00	1.054	0.946	0.918	0.473	32.6	16.3	35.5	34.5	112.2	96.9
1.00	0.532	0.468	0.458	0.468	16.2	16.2	35.4	34.6	113.3	97.8
0.00				0.462	0.0	16.4	35.5	35.5	115.8	100.0

A comparison of the values of γ_{KI_3} with those of γ_{KI} (Table III) shows that the degree of ionization of potassium tri-iodide is practically identical with that of KI up to a concentration of 0.1 normal. Each of the ratios $1000 (L - L')/(I_3^-)$ is therefore a separate determination of $(\Lambda_I - \Lambda_{I_3})$, the difference between the equivalent conductances of the tri-iodide ions. The average value of $\Lambda_I - \Lambda_{I_3}$ is 35.5, from which it follows that

$$\Lambda_{I_3} = 41.0 \text{ and } \Lambda_0 \text{ for } KI_3 = 115.8.$$

The limiting value (at zero concentration) of the ratio $\Delta\Lambda/r$ is equal to $\Lambda_I - \Lambda_{I_3}$, and the limiting values of $\Delta\Lambda$ and of r are therefore not independent. In the table $\Delta\Lambda$ is shown to increase slightly with increasing dilution, and the limiting value is probably as high as 16.4. It follows that, in solutions saturated with iodine, the ratio $r = (\Sigma I_3)/(\Sigma I + \Sigma I_3)$ tends toward the value $16.4/35.5 = 0.462$ as the concentration approaches zero.

From the values of this ratio in the different solutions it is seen that the proportion of tri-iodide in a solution saturated with iodine increases steadily with increasing concentration,[2] the whole change between 0.0

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[1] An interpolated value.

[2] A comparison with the values of this ratio $(\Sigma I_3)/(\Sigma I + \Sigma I_3)$ determined by Noyes and Seidensticker (THIS JOURNAL, 21, 217 (1899); *Z. physik. Chem.*, **27**, 359) shows that the agreement is fairly good at 0.1 normal, but that their values at smaller concentrations are always larger than ours and that the difference increases rapidly with increasing dilution. Since, as they point out, their values at the lowest concentrations are apparently affected by large errors, it seems not improbable that their values at higher concentrations are similarly affected, though of course to a smaller

and 0.1 normal being about 8 per cent. This effect is identical in direction with the very marked effect which has been observed in more concentrated solutions, where the ratio of total iodine dissolved in total potassium salt decreases rapidly with increasing salt concentration.

A Deviation from the Law of Mass Action.

This result may be expressed in another way: In potassium iodide solutions saturated with iodine, the ratio $(I^-)/(I_3^-)$, which according to the law of mass action should be constant, decreases from 1.16 to 0.99 when the potassium salt increases from 0.0 to 0.1 normal.

We have used the results of Laurie[1] to calculate at higher concentrations the apparent values of this ratio which are obtained when the same assumptions are made as at lower concentrations, *viz.*, that the solubility of I_2 as such is 0.00132 millimolal, that all the dissolved iodine in excess of this amount is present as tri-iodide, and that KI_3 is ionized to the same extent as KI. In order, however, to allow for the expansion of the solutions when iodine was dissolved in them, approximate corrections have been introduced by the method described above. The concentrations in the saturated iodine solution are thus referred to the volume of solution containing the same number of mols of potassium salt as were present in 1 liter of the original potassium iodide solution. The results, together with our own results at lower concentrations, are included in the following table. The table also contains the corresponding values of the equilibrium "constant" $K = (I^-)(I_2)/(I_3^-)$, obtained by multiplying the ratios $C_{I^-}/C_{I_3^-}$ by the solubility of I_2, 0.00132.

TABLE V.—VALUES OF $(I^-)/(I_3^-)$ AND $(I^-)(I_2)/(I_3^-)$ IN KI SOLUTIONS SATURATED WITH IODINE.

ΣK	1.000	0.850	0.700	0.500	0.344	...	..
ΣI_2 combined, mols per liter.	0.711	0.578	0.440	0.295	0.189	...	..
I_2 combined (mols)	0.742	0.598	0.452	0.300	0.191	...	..
In the volume (cc.)	1043	1035	1027	1018	1011	...	..
$C_{I^-}/C_{I_3^-}$	0.35	0.42	0.55(?)	0.67	0.80	...	..
$K \times 10^3 = 1.32\ C_{I^-}/C_{I_3^-}$	0.46	0.55	0.72	0.88	1.06	...	..
ΣK	0.100	0.020	0.010	0.005	0.002	0.001	0.0
$C_{I^-}/C_{I_3^-}$	0.99	1.04	1.06	1.08	1.11	1.14	1.16
$K \times 10^3 = 1.32\ C_{I^-}/C_{I_3^-}$	1.31	1.37	1.40	1.42	1.47	1.50	1.53

On plotting the values of $(I^-)/(I_3^-)$ against log (ΣK) it was found that a straight line was obtained from 0.001 to 0.1 normal ΣK, and that this line produced to normal concentration gave the value $(I^-)/$

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percentage extent. As a possible source of error in these experiments, the presence of an organic impurity in the water may be mentioned; the reaction of this with iodine would produce an iodide, and the proportion of tri-iodide found would therefore be too great, especially in the dilute solutions.

[1] Laurie, *Z. physik. Chem.*, 67, 627 (1909).

(I_3^-) = 0.92 instead of the much lower value found (0.35). Thus the decrease of this ratio in concentrated solutions is much more rapid than was to have been expected from the results in dilute solutions.

Additional information with regard to this deviation from the law of mass action was obtained by comparing these values of the equilibrium function $K = (I^-)/(I_2)/(I_3^-)$ in saturated I_2 solutions with those obtained at other I_2 concentrations (Table I). On plotting K against the concentration of I_2 as determined from partition experiments, it was evident that in a dilute potassium iodide solution ($\Sigma K = N/16$) the values of K are practically constant and equal to 1.40; that in 0.1 and 0.2 normal solutions K decreases slightly with increasing I_2 concentration; and that this decrease is very pronounced in concentrated potassium iodide solutions. From the results for the most concentrated solutions (normal ΣK) the value of K at zero I_2 concentration was found by extrapolation to be 1.34×10^{-3}, which is almost as large as the values found in dilute potassium iodide solutions. Thus the deviations from the mass action law are very slight when the concentration of I_2 is small.

An obvious explanation of this decrease of K in the concentrated potassium iodide solution, which has frequently been offered, is that a polyiodide higher than KI_3 is formed, and that its concentration increases as I_2 is increased. But a difficulty is at once encountered when we consider the equilibrium in the saturated I_2 solution, *e. g.*, $I_5^- = I^- + 2I_2$. Here the ratio of (I_5^-) to (I^-) should be constant, and yet solid iodine separates when a concentrated solution is diluted. We are led to the result that if a polyiodide is present its concentration cannot be a measure of its "activity"[1] in the reaction. But if this second assumption is necessary even when a higher polyiodide is assumed to be present, then it seems worth while to determine if the assumption of a variation of the ratio of activity to concentration for tri-iodide or iodide is alone sufficient to explain the phenomenon—without the assumption of a higher polyiodide.

This concept of "activity" as introduced by Lewis is of great value in dealing with a problem involving a deviation from the law of mass action. For our purposes it is sufficient to recall that the following law is a thermodynamic consequence of the definition of activity. If the value of the activity (A) of each substance at equilibrium is substituted for its concentration in the mass-action expression, then the resulting activity function is a constant. Thus for the equilibrium, $I_3^- = I^- + I_2$, at constant temperature, $A_{I^-} \times A_{I_2}/A_{I_3^-}$ = constant. For our purposes we may, for the sake of convenience, place the activity (A) of each substance equal to the concentration (C) at infinite dilution.[2] As the con-

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Lewis, *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

This is only justifiable when, as in the present instance, we are dealing with a centration increases the activity will, in general, differ from the concentration, and the ratio of activity to concentration will also be altered when other substances are introduced into the solution. The problem of deviations from the law of mass action is thus resolved into the problem of determining how the ratio of activity to concentration varies for each substance under varying conditions. In the following we shall designate this ratio by the letter

$$\rho = A/C.$$

We shall assume throughout that the concentration of any ion has the value derived from conductance measurements.

In the present example we may therefore conclude that at 25°, in solutions saturated with iodine,

$$A_{\mathrm{I}^-}/A_{\mathrm{I}_3^-} = C_{\mathrm{I}^-}/C_{\mathrm{I}_3^-} \text{ (for } K_{\mathrm{KI}} = 0) = 1.16.$$

It is evident that the activity of I_2 as such is constant in all solutions in equilibrium with solid I_2, and may be considered equal to its solubility in pure water, since the concentration is very small, that is: $A_{\mathrm{I}_2} = C_{\mathrm{I}_2} = 0.00132$. The activity function,

$$K_{\mathrm{A}} = A_{\mathrm{I}^-} \times A_{\mathrm{I}_2}/A_{\mathrm{I}_3^-},$$

has therefore the value $1.16 \times 0.00132 = 0.00153$. This quantity, K_{A}, in virtue of the definition of activity, is, at any given temperature, constant under all circumstances. In the investigations of the equilibrium in solutions unsaturated with iodine (Table I) it is evident that the activity of I_2 in the aqueous phase, and not its concentration, was determined by the partition experiments.[1] The quantity K_1 (Table I), which is equal to K since γ' is now assumed equal to γ, therefore has the form

$$K = C_{\mathrm{I}^-} \times A_{\mathrm{I}_2}/C_{\mathrm{I}_3^-}.$$

From the values of K, given in Tables I and V, we may calculate the values under different conditions of the expression

$$K_{\mathrm{A}}/K = \rho_{\mathrm{I}^-}/\rho_{\mathrm{I}_3^-} = 0.00153/K.$$

Thus in 0.1 and 1.0 normal potassium iodide solutions the limiting values approached by the ratio $\rho_{\mathrm{I}^-}/\rho_{\mathrm{I}_3^-}$ as C_{I_2} approaches zero are $1.53/1.40 = 1.09$ and $1.53/1.34 = 1.14$, respectively; while in 0.0, 0.1 and 1.0 normal potassium iodide solutions saturated with iodine the values are 1.0, 1.17 and 3.34, respectively.

Thus if we can determine how one of the activity-concentration ratios,

single solvent at a constant temperature. In other cases it is best to adhere to the original definition of Lewis, according to which $A = C$ at infinite dilution only in the gaseous phase.

[1] This is exact only when the activity of iodine is proportional to its concentration in the organic solvent used in the partition experiments, which, however, is doubtless true, or nearly so, for CCl_4, $CHCl_3$, and CS_2, the solvents used.

as $A_{I^-}/C_{I^-} = \rho_{I^-}$, varies under different conditions we can at once calculate the corresponding values of the second ratio. As we shall see later, ρ_I^- is nearly constant, whence we conclude that $A_{I_3^-}/C_{I_3^-}$ decreases rapidly:

(1) in saturated I_2 solutions with increasing KI, and
(2) in a normal KI solution with increasing I_2.

Let us illustrate the significance of a variation in this ratio for a given substance. When the substance is at the same concentration in two different solvents, M and N, and has a smaller activity in M, then it will tend to escape from N to M (*e. g.*, through the gaseous phase if it is volatile). In such a case it is frequently stated that M is a "better solvent for the substance." Whenever the addition of any substance to a solution causes a decrease in the ratio of A/C for the original solute, the same idea may be applied by saying that the solution has become a better solvent for that solute.

In the present example we may thus state that a concentrated KI — I_2 solution is a better solvent for tri-iodide than is a pure potassium iodide solution or pure water. This phenomenon is doubtless connected with the mutual solubility of KI and I_2,[1] an idea which has been expressed by Parsons[2] in the phrase "solution in a dissolved solid."

The Composition of Concentrated Potassium Iodide Solutions Saturated with Iodine.

Important evidence relating to the presence of polyiodides higher than KI_3 in concentrated potassium iodide solutions saturated with iodine is furnished by the electromotive force determinations of Laurie.[3] The problem, however, cannot be completely solved without the knowledge, for some substance as I^-, of the variation of the activity concentration ratio in the saturated iodine solutions with increasing potassium iodide concentration. Accordingly, in the following detailed calculations the simple assumption referred to above has been made that $C_{I^-} = A_{I^-}$. Other assumptions are considered later and the complete results are summarized in Table VI.

In Laurie's measurements a half-cell containing 0.0005 mol I_2 dissolved in a potassium iodide solution was combined with another containing the same potassium iodide solution saturated with iodine. The diffusion potentials were eliminated by inserting between the half-cells a 10 times normal solution of ammonium nitrate.[4]

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[1] The great solubility of KI in liquid iodine has been noted by Lewis and Wheeler, *Z. physik. Chem.*, 56, 179 (1906).

[2] Parsons, *J. Physic. Chem.*, 11, 669 (1907).

[3] Laurie, *Z. physik. Chem.*, 67, 627 (1909).

[4] Cumming's tests of this method, *Trans. Faraday Soc.*, 2, 213 (1906) depend upon the agreement between the measured e. m. f. (using 10 N NH_4NO_3), and the value calculated from the Nernst equation; but he used concentrated solutions, such as N

When the electrode reaction is considered to be

$$I^- + \oplus = {}^1/_2 I_2,$$

then the electromotive force (aside from the diffusion potential) is:

$$E = 0.0591\ [\log (A_{I^-})_d/(A_{I^-})_s - {}^1/_2 \log (A_{I_2})_d/(A_{I_2})_s]$$

where the subscripts d and s refer to the dilute and saturated solutions, respectively.

By means of this equation the quantity which we wish to determine $(A_{I^-})_s$ may be calculated, since E was measured by Laurie and the other three activities may be derived as follows:

In the experiment with normal potassium iodide solutions,

$$E = 0.1252 \text{ volts.}^1$$

By our assumption,

$$(A_{I^-})_d = (C_{I^-})_d = 0.79 \times 0.9995 = 0.790,$$

where 0.79 is the degree of ionization of the potassium iodide and 0.9995 its concentration (the remaining K salt, 0.005, being present as triiodide).

The activity of iodine in any phase in equilibrium with solid I_2 has a constant value; as explained above

$$(A_{I_2})_s = 0.00132.$$

Finally $(A_{I_2^-})_d$ may be calculated from the equations

$$(A_{I_3^-})_d = (C_{I_3^-})_d/1.14 = 0.79 \times 0.0005/1.14 = 3.46 \times 10^{-4},$$

and

$$(A_{I_2})_d = K_A(A_{I_3^-})_d/(A_{I^-})_d = 0.00153 \times 3.46 \times 10^{-4}/0.790 = 6.70 \times 10^{-7}.$$

It is to be noted that the assumption is here made that the proportion of higher polyiodide such as KI_5 is negligible in this dilute I_2 solution, but this is evidently justifiable since we shall find that its concentration is small even in the saturated I_2 solution.

On substituting these values in the above electromotive force equation, it is found that $(A_{I^-})_s = 0.267$, which, according to our assumption, is equal to $(C_{I^-})_s$.[2] According to the view adopted early in the

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HCl — 0.1 N HCl, in which it is very doubtful if the Nernst equation will give accurate results. Therefore the accuracy of the NH_4NO_3 method of eliminating potential differences is still unknown; but it is probably sufficiently accurate in the present instance for our purpose.

[1] In Laurie's article, page 632, the "NH_4NO_3 correction" of 0.0008 volt is a misprint for 0.0080.

[2] Laurie considered the electrode reaction $I^- + \oplus = \frac{1}{2}I_2$, and applied the Nernst formula, thus tacitly assuming that $A_{I^-} = C_{I^-}$. It is interesting to note that if he had adopted the equally possible electrode reaction $I_3^- + \oplus = {}^3/_2 I_2$ he would have obtained absolutely different results, since this corresponds to the assumption that $A_{I_3^-} = C_{I_3^-}$. Since Laurie adopted the first view his value for the concentration of I^- (0.264), is almost identical with ours (0.267). But he assumed that the degree of ionization depends upon the actual concentration of potassium iodide present, and his values for $C_{\Sigma I}$ are therefore smaller than ours.

paper the degree of ionization of potassium iodide in this mixture depends on the total ion concentration and therefore is the same as in the pure potassium iodide solution. It follows that the total concentration of iodide, $C_{\Sigma I} = 0.267/0.79 = 0.338$, a value which is obviously independent of the degree of ionization originally assigned to the normal potassium iodide solution.

The total concentration of the potassium salt present in other forms than potassium iodide is therefore $1.000 - 0.338$ or 0.662, while the concentration of combined iodine is 0.742 mol I_2. This result evidently indicates that a small amount of a polyiodide higher than KI_3 is present. If we consider it to be only KI_5, then we have

$$C_{\Sigma I_5} = 0.080 \text{ and } C_{\Sigma I_3} = 0.582.$$

We thus reach a conclusion similar to that of Laurie, that a large part of the dissolved iodine in the normal potassium iodide solution saturated with iodine is present as tri-iodide. A similar treatment of the remaining measurements shows that the amount of higher polyiodide decreases as the potassium iodide concentration is decreased, and becomes negligible in the neighborhood of the 0.1 normal solution.

The activity of the tri-iodide ion in the normal potassium iodide solution saturated with I_2 is given by the equation,

$$(A_{I_3^-})_s = (A_{I^-})_s/1.16 = 0.230.$$

If the KI_3 is ionized to the same extent as KI, then the ratio of $A/C =$ for tri-iodide ion is: $0.230/0.79 \times 0.582 = 0.50$, which, of course, is considerably larger than the value (1/3.34), which we have previously calculated on the assumption that no higher polyiodide was present. Our previous calculations, however, will hold for concentrations of ΣK below 0.1 normal.

For the sake of comparison with these results a second series has been calculated from the electromotive force measurements in a similar way on the much less probable assumption that $C_{I_3^-} = A_{I_3^-}$. The two sets of results are presented in columns III and I in the following table. This table also contains, in the second column, the corresponding results when, according to the extrapolation from dilute solutions made early in the paper the ratio $C_{I^-}/C_{I_3^-}$ is assumed to be 0.92, and in the last column those obtained from the sole assumption that no polyiodide higher than KI_3 is present.

An inspection of this table shows that this complicated problem has been reduced to the determination of the variation, with increasing potassium iodide concentration, of the ratio of activity to concentration for a single substance, as iodide ion, in a saturated iodine solution. It is evident that, no matter what assumption is made, one or more of the substances involved will show marked deviations from the law of the ideal solution that activity and concentration are equal.

TABLE VI.—ACTIVITIES AND CONCENTRATIONS OF THE CONSTITUENTS OF THE NORMAL KI SOLUTION SATURATED WITH I_2.

	(I) Assuming $C_{I_3^-} = A_{I_3^-}$.	(II) Assuming $C_{I^-}/C_{I_3^-} = 0.92$.	(III) Assuming $C_{I^-} = A_{I^-}$.	(IV) Assuming $C_{\Sigma I_5} = 0$.
A_{I^-}	0.305	...	0.267	...
$A_{I_3^-}$	0.262	...	0.230	...
$C_{\Sigma I}$	0.463	0.408	0.338	0.258
$C_{\Sigma I_3}$	0.332	0.443	0.582	0.742
$C_{\Sigma I_5}$	0.205	0.149	0.080	0.000
$\Sigma_I/\Sigma_{I_3} = C_{I^-}/C_{I_3^-}$	1.39	0.92	0.58	0.35
A_{I^-}/C_{I^-}	0.83	0.89	1.00	1.20
$A_{I_3^-}/C_{I_3^-}$	1.00	0.71	0.50	0.36

In the case of an aqueous solution of a single salt several examples are known in which the activity of a univalent ion increases somewhat less rapidly than its concentration (derived from conductance measurements), and there are at present no exceptions to this rule. This has recently been emphasized by Lewis and von Ende[1] in connection with their work upon the electromotive force of thallous-ion concentration cells. Another illustration is evidently furnished by Jahn's investigations of chloride-ion concentration cells[2] from which he concluded that the degrees of ionization ordinarily calculated from conductance measurements are too high. Some additional examples will be considered in later articles.

From the analogy with Jahn's experiments it is extremely probable that investigations of iodide-ion concentration cells free from iodine, using for example thallium-thallous-iodide electrodes, will yield similar results, and that therefore the activity of iodide-ion in pure potassium iodide solutions increases somewhat less rapidly than its concentration. If this applies in the present case in which the solutions are saturated with iodine, then the composition of the normal solution considered above will probably lie between the values given in the second and third columns of the table, and the solution will contain a greater proportion of higher polyiodide than calculated by Laurie. It is also interesting to note that the activity of tri-iodide ion increases much less rapidly than its concentration, and that this is even more striking when A_{I^-} is equal to or increases more rapidly than C_{I^-}.

But it is by no means certain that the relationship between A_{I^-} and C_{I^-} in potassium iodide solutions free from iodine will be the same as that in solutions saturated with iodine, and the two cases must be considered as two separate experimental problems.

The relation between A_{I^-} and C_{I^-} in dilute potassium iodide solutions saturated with iodine may be determined by combining the results of electromotive force measurements of concentration cells, using iodine

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[1] THIS JOURNAL, **32**, 732 (1910).

[2] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

electrodes, with the values of C_{I^-} determined in the present investigation. Unfortunately, the existing measurements of Crotogino,[1] in which each iodine electrode was measured against a calomel electrode, are probably not very accurate, and the corrections for the diffusion potential cannot be readily calculated. The results[1] show that A_{I^-} increases more rapidly than C_{I^-}, which is an indication that the composition of the normal potassium iodide solution saturated with iodine is intermediate between the values given in the last two columns of Table VI, and that the amount of higher polyiodide present is very small. This conclusion, however, can scarcely be accepted as correct without further experimental investigation.

While this evidence is somewhat conflicting, it would seem that the results given in column III of Table VI cannot be very far wrong. Thus, roughly speaking, the ratio of activity to concentration for iodide ion is independent of the concentration. The same ratio for tri-iodide ion diminishes rapidly with increasing concentration, and in all probability the higher polyiodide ions will be found to show even greater abnormalities in the same direction.

Summary.

In this investigation, conductance measurements at 25° have been made with potassium iodide solutions between 0.1 and 0.001 normal, and of the same solutions when saturated with solid iodine. The solubility of iodine in each solution has also been determined.

These results have led to the conclusions that the degree of ionization of KI_3 in dilute solutions is practically identical with that of KI up to a

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[1] Cf. Sammet, *Z. physik. Chem.*, 53, 674–5 (1905). Crotogino's results, recalculated, are presented in the following table, the potential of the $N/16$ KI electrode being taken as zero. The last column contains the values of E calculated by means of the formula

$$E = 0.0591 \log C'_{I^-}/C''_{I^-},$$

i. e., on the assumption that $A_{I^-} = C_{I^-}$. The values of C_{I^-} are calculated from the data given in Table IV.

ELECTROMOTIVE FORCE MEASUREMENTS OF CROTOGINO.

ΣK.	C_{I^-}.	E measured.	E calc.
$N/1024$	0.000509	−0.122	−0.102
$N/256$	0.001956	−0.081	−0.068
$N/64$	0.00744	−0.040	−0.034
$N/16$	0.0277	0.000	0.000
$N/4$	0.0980	0.0038	0.032

The large differences between E measured and E calculated are partly due to diffusion potentials, since the mobility of K^+ is greater than that of I_3^-. We have calculated approximately that 4 millivolts is the value of the diffusion potential between two solutions where there is a fourfold change in the concentration of ΣK; but, since the measurements were made against a calomel electrode, this value must be too high. It is therefore evident that E measured is always greater than E calculated, and that A_{I^-} increases somewhat more rapidly than C_{I^-}.

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).