sulphate titration will doubtless be settled in the near future by the investigation of the oxalate and ferrous sulphate titrations now in progress at the Bureau of Standards. The author takes pleasure in thanking Dr. W. F. Hillebrand and Mr. R. S. McBride, of the Bureau of Standards, for their kindness in reading and criticizing this note before its publication.

BOSTON, July, 1910.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 55.]

THE EQUILIBRIUM BETWEEN SOLID CUPROUS IODIDE AND AQUEOUS SOLUTIONS CONTAINING CUPRIC SALT AND IODINE.

BY W. C. BRAY AND G. M. J. MACKAY.

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This investigation was originally undertaken in order to test the generally accepted view that the cuprous ion is monatomic (Cu^+), rather than diatomic (Cu_2^{++}), and especially to check the results of Bodländer and Storbeck[1] on this subject. The work, however, was interrupted two years ago and has not been continued; the results then obtained are presented in the present article as an investigation of the law of mass action in dilute aqueous solutions.

Cuprous iodide is difficultly soluble in water, but in the presence of iodine a considerable amount dissolves, owing to the formation of cupric iodide and tri-iodide. The following two equilibria are involved:

$$CuI\ (solid) + \tfrac{1}{2}I_2 = Cu^{++} + 2I^-, \text{ and } I_3^- = I_2 + I^-.$$

From the experimental results at 25° presented below, values have been determined, under widely different conditions, for the two equilibrium functions:

$$(Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}} = K', \text{ and } (I^-)(I_2)/(I_3^-) = K.$$

Bodländer and Storbeck have reported a single, apparently not very accurate experiment at room temperature (18–20°), in which 1 liter of solution saturated with both cuprous iodide and iodine was found to contain 0.01666 gram molecule of cupric salt, and 0.00946 equivalent of dissolved iodine.

The *cuprous iodide* was prepared according to the directions of Bevan Lean,[2] by adding one formula weight of potassium iodide dissolved in 150 cc. of water to a solution of one formula weight of copper sulphate dissolved in 1500 cc. of water saturated with sulphur dioxide. The resulting precipitate was washed several times with water containing sulphur dioxide, and finally with pure water until all trace of sulphate

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[1] Borländer and Storbeck, *Z. anorg. Chem.*, **31**, 469 (1902).

[2] *J. Chem. Soc.*, **73**, 149 (1898).

had disappeared. In each of our equilibrium experiments a large excess (about 20 grams) of solid cuprous iodide was present.

The experimental methods of obtaining saturated solutions, removing known volumes for titration, making conductance measurements, etc., were the same as were used in determining the solubility of iodine in potassium iodide solutions.[1]

The concentration of *iodine*, whenever the solid was present, was assumed to be 0.00132 molecule I_2 per liter, as determined in a recent investigation.[2] In the three remaining experiments (Nos. 1–3), in which solid iodine was absent, the equilibrium was investigated in the presence of carbon tetrachloride. The concentration of iodine in this phase was determined by titration; that in the aqueous phase was calculated by means of the partition-coefficient of iodine between carbon tetrachloride and water. The determinations of the latter were made in the presence of iodine; after 24 hours' rotation the ratio of the concentration in carbon tetrachloride to that in water was found to be 90.8 and 89.3. The smaller value agrees fairly well with that determined by Yakovkin,[3] 89.55, in the presence of solid iodine. After taking into consideration the fact that, on account of the hydrolysis of iodine in the aqueous solution, these values should be increased by about 0.08 per cent., the value 90 was chosen. Yakovkin's results, however, show a decrease of the partition coefficient with decreasing iodine concentration, and, even after correcting for hydrolysis, it is possible that a value as low as 86.5 should be used in our experiments. The calculations for exps. Nos. 1–3 were accordingly repeated, using this partition coefficient and the results are given in Table II as experiments Nos. *1a*, *2a*, and *3a*.

In addition to molecular iodine, the solutions contained three constituents to be determined: copper, ΣCu; iodide, ΣI; and tri-iodide, $\Sigma I_3'$; and three separate analyses were made in each case.

The *copper* was determined, usually in 100 cc. of solution, by evaporating the solution with 5–10 cc. of dilute sulphuric acid and a few drops of nitric acid until white acid fumes were given off. Ammonia was then added in slight excess, and the solution boiled to expel the excess of ammonia. Finally 50 cc. of 25 per cent. acetic acid and 5 grams of potassium iodide were added, and the mixture was titrated with sodium thiosulphate solution according to the method investigated by Gooch and Heath.[4] Another portion of the saturated solution was titrated in a similar manner directly with thiosulphate, which gave the *total dissolved iodine* and copper. Finally, in a third portion, the *total iodine* was de-

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[1] Bray and MacKay, THIS JOURNAL, **32**, 918 (1910).

[2] Bray, THIS JOURNAL, **32**, 936 (1910).

[3] Yakovkin, *Z. physik. Chem.*, **18**, 585 (1895).

[4] Gooch and Heath, *Am. J. Sci.*, **24**, 65 (1907); *Z. anorg. Chem.*, **55**, 119 (1907).

termined by the method described in the preceding paper. Thus the three analyses were referred to a single thiosulphate solution, and the error in determining differences reduced to a minimum. The thiosulphate was standardized by comparison with a known arsenious acid solution, and checked against a known copper sulphate solution, as explained in the first group of analyses in the preceding article.

The method of calculating the concentrations of the separate substances is illustrated by the following example (Expt. No. 4):

$$\begin{array}{ll} \text{Total iodine} & \Sigma I + 3\Sigma I_3 + 2I_2 = 0.08490 \\ \text{Direct titration} & \Sigma Cu + 2\Sigma I_3 + 2I_2 = 0.06432 \\ & \Sigma Cu = 0.02068 \\ & 2I_2 = 0.00264 \end{array}$$

From these four equations ΣI_3 and ΣI are calculated to be 0.02050 and 0.02076, respectively.

In the solutions to which no copper salt or iodide had been added a check is furnished upon the accuracy of our analyses by the stoichiometric relation that the equivalent concentration of copper should equal the sum of the concentrations of iodide and triiodide,[1] $2\Sigma Cu = \Sigma I + \Sigma I_3$. In the above example these numbers are 0.04136 and 0.04126, respectively; this difference corresponds to an error of only 0.12 per cent. in the determination of the total iodine, or to larger and less probable errors in the determination of copper or in the direct thiosulphate titration. Accordingly, we have adopted the value of 0.02086 instead of 0.02076 for the value of ΣI, and have applied similar corrections to ΣI in the other experiments in which this stoichiometric relation could be used, except in that with nitric acid (No. 11) where the deviation is much larger and may be accounted for by a reaction between hydriodic acid and oxygen.

The experimental results are presented in Table I. The values given in the column "ΣI calculated" are derived from the relation $2\Sigma Cu = \Sigma I_3 + \Sigma I$, and have been adopted in the calculations described below. The values of "specific conductance, calculated" are derived from the concentrations of the separate ions given in Table II, by means of the

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[1] We have neglected the cuprous copper in solution; this is present as cuprous iodide and as a complex ion, CuI_2^-, formed by the union of cuprous iodide and iodide ion. With regard to the first substance, Bodländer and Storbeck (*loc. cit.*, page 427) have calculated from electromotive force measurements, that the solubility product $(Cu^+)(I^-)$ is equal to 5×10^{-12}; since in our experiments the concentration of I^- never is less than 0.0088, it is evident that the concentration of Cu^+ cannot exceed 0.6×10^{-9}. The same authors have shown (page 475) that the ratio $(CuI_2^-)/(I^-)$ in the presence of solid CuI is not greater than 7.8×10^{-4}. This complex is therefore present in greatest amount in expt. No. 7, where I^- has its maximum concentration, and the amount does not exceed 2×10^{-5} g. molecule CuI_2^- per liter; this corresponds to only 0.2 per cent. of the total copper present, and its neglect does not seriously alter the final results.

following equivalent conductances at 25°, $\Lambda_{Cu} = 56.0$, $\Lambda_{I} = 76.5$, $\Lambda_{I_3} = 41.5$, $\Lambda_{K} = 74.8$, $\Lambda_{NO_3} = 70.6$.

The time of rotation of two days was adopted after preliminary experiments with water alone, in which it was found that the concentration of copper salt after 24 hours was a few tenths of a per cent. less than that obtained after 48 hours. In No. 5 the equilibrium was approached from undersaturation, and in No. 4 from supersaturation, attained by first rotating the mixture for several hours at 35°. The agreement shows that the equilibrium is actually reached in 2 days. This conclusion is further justified by the similar results obtained in experiments Nos. 9 and 10, where the times of rotation differed by 2 days.

TABLE I.—EXPERIMENTAL RESULTS.

				Concentrations, millimols per liter.					Specific cond. × 10^6.	
No.	Solid phases.	Solvent.	Days rotated.	I_2.	Σ Cu.	Σ I_3.	ΣI expt.	ΣI calc.	Measured.	Calculated.
1	CuI	Water and CCl_4 (part. coeff. = 90).......	2	0.1007	8.18	1.125	15.18	15.24	1853	1824
2	"	(Part. coeff. = 90)....	2	0.1501	9.01	1.76	16.20	16.26	1979	1980
3	"	(Part. coeff. = 90)....	2	0.8040	15.78	11.58	19.83	19.98	3139	3098
4	CuI, I_2	Water alone.........	2	1.32	20.68	20.50	20.76	20.86	3848	3834
5	"	Water alone.........	2	1.32	20.71	20.53	20.76	20.89	3877	3840
6	"	Acetic acid (0.1*N*)...	2	1.32	27.16	21.29	20.78	21.03	....	....
7	"	KI solution.........	2	1.32	10.03	31.75	31.77	.....	6923	6913
8	"	$CuSO_4$ solution......	2	1.32	101.7	15.67	16.01	.....	....	....
9	"	$Cu(NO_3)_2$ solution....	2	1.32	100.0	12.41	13.14	.....	1721	1749
10	"	$Cu(NO_3)_2$ solution....	4	1.32	111.3	11.89	12.78	.....	1892	1926
11	"	HNO_3 (0.113*N*).....	2	1.32	24.11	23.90	23.31	.....	....	....
12	"	$Mg(NO_3)_2$ (0.1*F*)....	2	1.32	25.77	24.77	26.69	26.77	....	....
13	"	$Mg(NO_3)_2$ (0.1*F*).. HNO_3 (0.005*N*)...	2	1.32	25.77	24.58	26.73	26.96	....	....

The concentrations of the separate ions and of the various un-ionized substances were calculated by the method of approximations which has already been explained in publications from this laboratory.[1] This depends upon the assumption that the "ionization function" of a given salt, *K* = (anion)(cation)/(un-ionized salt), for example $(Cu^{++})(I^{-})/(CuI_2)$ for cupric iodide, depends only on the equivalent ion concentration, and has the same value in a mixture as at the same ion concentration in a solution of the pure salt.

In the present instance accurate conductance data at 25° are not available, and the calculations are based on the following assumptions: The ionization values for CuI_2, $Cu(I_3)_2$, $Cu(NO_3)_2$, $Cu(Ac)_2$, and $Mg(NO_3)_2$ are equal to the values for $MgCl_2$ calculated from the data of Kohlrausch and

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[1] Cf. THIS JOURNAL, **31**, 754 (1909).

Grüneisen[1] at 18° taking $\Lambda_0 = 111.4$; those for KI, HI, HI_3, and HNO_3 are the values of KCl at 18° ($\Lambda_0 = 130.1$),[2] which are practically equal to our own values of KI at 25°;[3] and those for $CuSO_4$ are the values of this salt at 18° ($\Lambda_0 = 115.7$).[1] The ionization constant of acetic acid was assumed to be 1.8×10^{-5} at 25°.

The validity of these assumptions may be tested in the case of CuI_2 and $Cu(I_3)_2$ by a comparison of the calculated and measured conductances (Table I) in experiments Nos. 1–5 and 7. Since ordinary distilled water was used in these experiments the measured specific conductances must be reduced by from 2 to 5×10^{-6}, and it is at once evident that the agreement is then a satisfactory one. In experiments Nos. 9 and 10 the agreement is less satisfactory, which indicates that the degree of ionization of $Cu(NO_3)_2$ is less than that of CuI_2; a correction of 2 per cent., however, alters the value of the equilibrium function K' only from 1.62 to 1.59×10^{-4}, since the concentration of I^- remains practically unchanged.

The results of the calculations are presented in Table II. Concentrations are expressed in millimols per liter in the table, but all calculations are based on molal concentrations.

Table II.—Calculation of Equilibrium Functions.

Expt. No.	Solvent.	Concentrations millimols per liter.						
		I_2.	Cu^{++}.	I^-.	I_3^-.	Equiv. Ion.	$K = \frac{(I^-)(I_2)}{(I_3^-)}$.	$K' = \frac{(Cu^{++})(I^-)^2}{(I_2)^{\frac{1}{2}}}$.
1	Water and CCl_4							
	(Part. coeff. = 90)	0.1007	7.01	13.06	0.965	14.02	1.37×10^3	1.19×10^4
2	(Part. coeff. = 90)	0.1501	7.67	13.84	1.50	15.34	1.39×10^3	1.20×10^4
3	(Part. coeff. = 90)	0.8040	12.94	16.38	9.50	25.88	1.39×10^3	1.23×10^4
1*a*	Water and CCl_4							
	(Part. coeff. = 86.5)	0.1047	7.01	13.06	0.96	14.02	1.42×10^3	1.17×10^4
2*a*	(Part. coeff. = 86.5)	0.1562	7.67	13.85	1.49	15.34	1.45×10^3	1.18×10^4
3*a*	(Part. coeff. = 86.5)	0.8364	12.94	16.41	9.47	25.88	1.45×10^3	1.21×10^4
4	Water............	1.32	16.65	16.80	16.50	33.30	1.34×10^3	1.29×10^4
5	Water............	1.32	16.67	16.82	16.52	33.34	1.34×10^3	1.30×10^4
6	Acetic acid (0.1*N*).	1.32	16.97	16.94	17.14	35.35	1.30×10^3	1.34×10^4
7	KI solution.......	1.32	7.76	26.94	26.92	53.86	1.32×10^3	1.55×10^4
8	$CuSO_4$ solution.....	1.32	38.45	11.93	11.68	76.91	1.35×10^3	1.51×10^4
9	$Cu(NO_3)_2$ solution..	1.32	69.85	9.18	8.66	139.70	1.40×10^3	1.62×10^4
10	$Cu(NO_3)_2$ solution..	1.32	76.80	8.82	8.20	153.60	1.42×10^3	1.64×10^4
11	HNO_3 (0.113*N*)....	1.32	16.81	18.63	19.10	128.13	1.29×10^3	1.61×10^4
12	$Mg(NO_3)_2$ (0.1*F*)...	1.32	17.53	18.20	16.86	171.06	1.42×10^3	1.60×10^4
13	$Mg(NO_3)_2$ (0.1*F*). + HNO_3 (0.005*N*)	1.32	17.48	18.36	16.74	174.80	1.45×10^3	1.62×10^4

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[1] Kohlrausch and Grüneisen, *Landolt-Börnstein-Meyerhoffer*, page 745.

[2] Kohlrausch and Maltby, *Ibid.*, page 744.

[3] This Journal, 32, 920 (1910).

An examination of the values of the equilibrium function $K = (I^-)(I_2)/(I_3^-)$ shows that in the first three experiments the values based on the partition coefficient 90 are lower and in better agreement with the remaining values than those based on the partition coefficient 86.5. Accordingly the results tabulated at Nos. 1-3 are accepted rather than Nos. *1a*-*3a*. In neutral solutions the values of *K* lie between 1.32 and 1.42×10^{-3} while in acid solution (Nos. 6 and 11) the values are slightly lower.[1]

In agreement with the results in potassium iodide solutions,[2] the deviations from the law of mass action are in the direction that the values of *K* decrease with increasing iodide concentration. Thus when the total concentration of salt (iodide and tri-iodide) increases from 0.018 (Exp. 2) to 0.063 (Exp. 7) the values of *K* are 1.39 and 1.32×10^{-3}, respectively—in good agreement with the corresponding values in the potassium iodide solutions, 1.38 and 1.33×10^{-3}. From the present experiments it is evident that the presence of other salts, as copper nitrate in Nos. 8 and 9 or magnesium nitrate in No. 12, does not cause a similar decrease in the value of *K*. In the earlier investigation with potassium iodide solutions the conclusion was reached that the decrease of *K* with increasing concentration of the salt was due mainly to a decrease in the ratio of the activity[3] of tri-iodide ion to its concentration. The present experiments enable the additional conclusion to be drawn that in this reaction this influence of the salt is not general for all salts but is an individual effect for iodide-tri-iodide solutions.

From the values of the second equilibrium function $K' = (Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}}$, it is evident that this reaction conforms to the law of mass action as far as the influence of iodine is concerned. Thus *K'* is increased only 9 per cent. as a result of a 13-fold increase in the concentration of iodine (Expts. 1 and 4). Furthermore *K'* is almost unaltered by the presence of acetic acid (Nos. 5 and 6).

In the remaining experiments, however, the deviations from the law of mass action are very marked. Thus *K'* shows a 19 per cent. increase when the concentration of iodide ion is increased 60 per cent. (Nos. 5 and 7), and a 26 per cent. increase when the concentration of cupric ion is increased 4.6-fold (Nos. 5 and 10). Finally there is the striking effect of the presence of a salt without a common ion, as magnesium nitrate or nitric acid, which results in a 23 to 25 per cent. increase in *K'* (No. 5 and Nos. 11-13).

A closer examination of these results leads to the conclusion that in this reaction there is a relationship between the deviation from the mass

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[1] Cf. Dawson, *J. Chem. Soc.*, **79**, 238 (1907).

[2] Bray and MacKay, THIS JOURNAL, **32**, 924 (1910).

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

law and the total ion or salt concentration. Thus the values of K' show a steady increase with increasing equivalent ion concentration, which is roughly independent of the nature of the salts present. To enable this relation to be easily seen, the experiments have been arranged in the table in the order of increasing ion concentration.

This result is in perfect agreement with the results of other investigations in aqueous solutions, such as the determination of the electromotive force of concentration cells, or the effects of salts on the solubility of another salt. Thus, as pointed out in an earlier paper,[1] existing evidence indicates that in the case of a single ion the activity (A) increases somewhat less rapidly than its concentration (C) (when the latter is derived from conductance measurements), or in other words, that the ratio A/C decreases with increasing ion concentration. By taking into consideration the law (based on the definition of activity) that the activity function $A_{\text{Cu}^{++}} \times A^2_{\text{I}^-}/A^{\frac{1}{2}}_{\text{I}_2}$ is constant under all conditions, it could have been predicted as probable that the equilibrium (concentration) function $K' = C_{\text{Cu}^{++}} \times C^2_{\text{I}^-}/C^{\frac{1}{2}}_{\text{I}_2}$ would increase with increasing ion concentration, which is the experimental result derived from the present measurements.

Finally, it is interesting to note that, when solid CuI and I_2 are both present, the equilibrium function $(\text{Cu}^{++})(\text{I}^-)^2$ has the same form as the solubility product of a hypothetical, difficultly soluble cupric iodide. It is therefore to be expected that the results of the present investigation will be similar to those derived from investigations of the solubility of a salt in the presence of other salts. Accordingly the increase in the value of K' in Expts. 5–13 indicates that under similar conditions the solubility product of a difficultly soluble salt will not be constant, but will increase with increasing ion concentration. This conclusion is in agreement with the results of solubility investigations already obtained in this laboratory, which will soon be published.

Summary.

The equilibrium

$$\text{CuI(solid)} + \tfrac{1}{2}\text{I}_2 = \text{Cu}^{++} + 2\text{I}^-$$

has been investigated at 25° under widely different conditions. The ionic concentrations in the various mixtures were calculated by means of the empirical relations derived from conductance measurements.

The values of the equilibrium function $K' = (\text{Cu}^{++})(\text{I}^-)^2/(\text{I}_2)^{\frac{1}{2}}$ show that this equilibrium conforms with the law of mass action only as far as the influence of iodine is concerned, and deviates from it when cupric salt, iodide, or other salt is added. In all these cases, however, the de-

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[1] Bray and MacKay, *Loc. cit.* In the e. m. f. measurements of concentration cells by Jahn and by Lewis and von Ende, formerly cited as examples of this rule, the ratio A/C was practically constant at low concentrations, but the decrease was marked in 0.1 normal solutions.

viations are of such a nature that K' increases with increasing ion concentration.

This result, when examined from the standpoint of activity, as defined by Lewis, furnishes another illustration of the apparently general rule that when the concentration of an ion is based on conductance measurements the ratio of its activity to its concentration decreases somewhat with increasing ion concentration. An important consequence of this rule is that the solubility product of a salt will not be exactly constant but will increase with increasing ion concentration.

Values were also calculated for anothor equilibrium function $K = (I^-)(I_2)/(I_3^-)$. The results confirm the conclusion reached in an earlier paper that K decreases with increasing concentration of iodide, but show that other salts do not produce a similar effect.

Conductance measurements were also made with a number of the equilibrium solutions. These show that cupric iodide and cupric tri-iodide are ionized to the same extent as magnesium chloride, and that cupric nitrate is ionized to a somewhat less extent.

BOSTON, July, 1910.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY.]

THE POTENTIAL OF IRON CALCULATED FROM EQUILIBRIA MEASUREMENTS.[1]

BY ARTHUR B. LAMB.

Knowing the dissociation pressure of a metallic oxide, its heat of formation, the change of its heat of formation with the temperature, the solubility of its oxide in water, and finally, knowing the single potential of the oxygen electrode, it is possible to calculate on the basis of the fundamental laws of energetics and the concentration law the potential of the metal against a normal solution of its ions.[2]

Many metals give fairly definite and easily measurable potentials, especially when an amalgamated electrode can be employed.[3] When this is the case, an indirect calculation, such as the one just outlined, depending upon measurements of such difficulty as the dissociation pressures of metallic oxides at high temperatures, would be disadvantageous. The reverse calculation, that is, the calculation of dissociation pressures from electromotive forces, would be more rational, and indeed, has most often been made. This is not, however, always the case. Many solid metals give rather variable potentials, and certain

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[1] Presented in preliminary form before the New York Section, Dec. 11, 1908.

[2] van't Hoff, Ostwald's Klassiker No. 110, pp. 76 and 103 (1885); also Lewis, THIS JOURNAL, 28, 162 (1906). *Z. physik. Chem.*, 55, 470 (1906).

[3] Lewis, THIS JOURNAL, 32, 732 (1910).