

# THE IODOMETRIC DETERMINATION OF COPPER AND ITS USE IN SUGAR ANALYSIS.

## I. EQUILIBRIA IN THE REACTION BETWEEN COPPER SULFATE AND POTASSIUM IODIDE.

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(Received for publication, November 29, 1920.)

In the course of a comparative study of several methods for the determination of sugar in blood, the results of which will be recorded elsewhere, it became desirable to investigate the reaction between copper sulfate and potassium iodide which is concerned in a number of methods for sugar determination (Bang (1), Maclean (2), Scales (3), Lehmann (4), Riegler (4), Peters (4), Kendall (5)).

In certain of these methods (Bang, Maclean, Scales) the cuprous oxide formed by the oxidation of the sugar is dissolved in acid<sup>1</sup> and reoxidized to cupric salt by a known amount of standard iodine—potassium iodide, the excess of iodine being then titrated with thiosulfate. The oxidation takes place in the presence of considerable excess of cupric salts which under the conditions does not appear to inhibit the oxidation, the latter going apparently to completion.

Essentially the same reaction between cupric salts and potassium iodide is the basis of the well known method for the iodometric determination of copper introduced by De Haen in 1854, the details of which have been studied especially by Gooch and Heath (6) who give the earlier literature. But in this case cupric salt is reduced to cuprous iodide in the presence of an excess of potassium iodide, with the liberation of free iodine

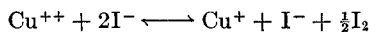
<sup>1</sup> In Bang's micro method the cuprous salt is held in solution by the presence of a large amount of potassium chloride.

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equivalent to the amount of copper reduced. Under the conditions laid down by Gooch and Heath the reduction is complete, and correct results are obtained.

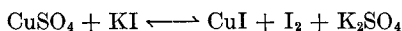
This latter reaction, the reduction of cupric to cuprous salt, also has been utilized in the determination of sugar, the excess of cupric copper, after filtering off the cuprous oxide, being determined in this way in methods described by Lehmann, Riegler, Peters, and others (4).

Both procedures outlined above are based upon the reversible reaction



which under slightly different conditions appears to run, for practical purposes, to completion in either direction. It has long been known that this reaction is reversible and it has been shown by Bray and MacKay (7) to obey the mass law within certain limits in dilute solutions. It therefore seemed rather remarkable that conditions should exist which permit the complete removal of free iodine, one of the active factors in the reaction without perceptibly disturbing the equilibrium at *both* extremes.

In order to permit an intelligent use of the reaction in both directions we have undertaken the determination of the points of equilibria of the reaction



at various initial concentrations of  $\text{CuSO}_4$  and  $\text{KI}$  and at various ratios of  $\text{CuSO}_4$ :  $\text{KI}$ . Our results indicate the conditions under which the reaction may be utilized for the determination of either cupric or cuprous salts with ease and accuracy.

The experimental procedure was to mix the solutions of copper sulfate and potassium iodide in definite molecular ratios at widely varying concentrations. After standing at room temperature samples of the supernatant liquid (which contained the liberated iodine, unreduced cupric copper, excess potassium iodide, and a minute quantity of cuprous iodide in solution) were carefully pipetted out, and the extent of the reduction, and thus the equilibrium attained, was determined by titrating the amount of free iodine by standard thiosulfate solutions. Since according to the reaction



1 atom of iodine is liberated for each atom of copper which is reduced, one may readily calculate the amount of cuprous salt formed and this subtracted from the total copper gives the amount of cupric salt unreduced. It was clear, however, that this method of determining the equilibrium point would not work unless the equilibrium were in some way stabilized; for, on removal of iodine by titration, the equilibrium is rapidly shifted to the right by the now unbalanced cupric and iodide ions; the blue starch-iodide end-point returns very rapidly; and the results indicate much too great reduction. This was avoided simply by measuring the samples for analysis directly into an equal volume of water containing an excess of sodium hydroxide. The cupric copper which remains is precipitated as the hydroxide and removed by filtration while the iodine is converted into hypoiodite and iodide and is recovered on acidifying the filtrate.

With both cupric and cuprous salts<sup>2</sup> removed the reaction cannot take place, and the equilibrium attained is represented by the amount of iodine, which after acidification is titrated with thiosulfate. Under these conditions the end-point is sharp. The results are given in Table I. The details of procedure and the method of calculating the results are given below.

#### *Preparation of CuSO<sub>4</sub>-KI Mixtures.*

An approximate 1.25 M solution was made of Kahlbaum's "Zur Analyse" CuSO<sub>4</sub>·5H<sub>2</sub>O. After filtering from suspended particles this was carefully standardized by titrating 20 cc. portions of a 1:10 dilution with 0.1 N thiosulfate after adding KI under the conditions described by Gooch and Heath. From the original CuSO<sub>4</sub> solution, an exactly molecular solution was made by dilution. The concentration of this solution was checked by diluting 50 cc. to 500 cc., when 20 cc. portions titrated with thiosulfate gave 20.05 cc.  $\times$  0.0997 N = 19.99 cc. 0.1 N. Potassium biiodate was used to standardize the thiosulfate. From the M CuSO<sub>4</sub>, other dilutions were made as needed.

<sup>2</sup> The amount of cuprous iodide in solution is negligible except in the presence of high concentrations of potassium iodide. Bodländer and Storbeck (8) calculate the solubility product of (Cu<sup>+</sup>). (I<sup>-</sup>) as  $5 \times 10^{-12}$  according to which value the concentration of cuprous salt in dilute solutions of potassium iodide would be less than  $2.2 \times 10^{-6}$  M.

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TABLE I.  
Equilibria of  $\text{CuSO}_4 + \text{KI}$ .

Experiment No.	Initial concentration of $\text{CuSO}_4$ .	Initial concentration of KI.	Thiosulfate titration of 10 cc. of mixture.			At equilibrium.	
			Found at equilibrium.	Calculated for complete reduction to $\text{CuI}$ .	Thiosulfate.	Cuprous salt.	Cupric salt.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	<i>millimolar</i>	<i>millimolar</i>	1CuSO <sub>4</sub> :1KI			<i>per cent</i>	<i>per cent</i>
1	2.5	2.5	0.00	25.0	0.001 N	0.00	100.00
2	5.0	5.0	0.00	50.0	0.001 "	0.00	100.00
3	6.0	6.0	0.03	60.0	0.001 "	0.05	99.95
4	7.0	7.0	0.05	70.0	0.001 "	0.07	99.93
5	8.0	8.0	0.15	80.0	0.001 "	0.19	99.81
6	9.0	9.0	0.50	90.0	0.001 "	0.56	99.44
7	10.0	10.0	0.80	100.0	0.001 "	0.80	99.20
8	11.0	11.0	1.20	110.0	0.001 "	1.09	98.91
9	12.0	12.0	1.80	120.0	0.001 "	1.50	98.50
10	20.0	20.0	19.75	200.0	0.001 "	9.88	90.12
11	50.0	50.0	11.74	50.0	0.01 "	23.48	76.52
12	100.0	100.0		100.0	0.01 "	36.50	63.50*
13	200.0	200.0		200.0	0.01 "	40.40	59.60*
			1CuSO <sub>4</sub> : 2KI				
14	2.5	5.0	0.00	25.0	0.001 N	0.00	100.00
15	3.0	6.0	0.00	30.0	0.001 "	0.00	100.00
16	4.0	8.0	0.20	40.0	0.001 "	0.50	99.50
17	5.0	10.0	0.50	50.0	0.001 "	1.00	99.00
18	6.0	12.0	1.00	60.0	0.001 "	1.67	98.33
19	7.0	14.0	0.25	7.0	0.01 "	3.57	96.43
20	8.0	16.0	0.50	8.0	0.01 "	6.25	93.75
21	9.0	18.0	0.75	9.0	0.01 "	8.33	91.67
22	10.0	20.0	1.10	10.0	0.01 "	11.00	89.00
23	11.0	22.0	1.50	11.0	0.01 "	13.64	86.36
24	12.0	24.0	2.00	12.0	0.01 "	16.67	83.33
25	13.0	26.0	2.40	13.0	0.01 "	18.46	81.54
26	14.0	28.0	2.85	14.0	0.01 "	20.36	79.64
27	15.0	30.0	3.60	15.0	0.01 "	24.00	76.00
28	16.0	32.0	4.18	16.0	0.01 "	26.13	73.87
29	17.0	34.0	4.58	17.0	0.01 "	26.94	73.06
30	18.0	36.0	5.15	18.0	0.01 "	28.61	71.39
31	19.0	38.0	5.80	19.0	0.01 "	30.53	69.47

\* Determination of precipitated cupric hydroxide.

TABLE I—Continued.

Experiment No.	Initial concentration of $\text{CuSO}_4$ .	Initial concentration of KI.	Thiosulfate titration of 10 cc. of mixture.			At equilibrium.	
			Found at equilibrium.	Calculated for complete reduction to $\text{CuI}$ .	Thiosulfate.	Cuprous salt.	Cupric salt.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	<i>millimolar</i>	<i>millimolar</i>	$1\text{CuSO}_4:2\text{KI}$			<i>per cent</i>	<i>per cent</i>
32	20.0	40.0	6.45	20.0	0.01 N	32.25	67.75
33	30.0	60.0	12.35	30.0	0.01 "	41.17	58.83
34	40.0	80.0	19.18	40.0	0.01 "	47.95	52.05
35	50.0	100.0	2.62	5.0	0.10 "	52.40	47.60
36	100.0	200.0		10.0	0.10 "	67.25	32.75*
37	200.0	400.0		20.0	0.10 "	72.50	27.50*
38	300.0	600.0		30.0	0.10 "	75.50	24.50*
			$1\text{CuSO}_4:3\text{KI}$				
39	2.5	7.0	0.00	25.0	0.001 N	0.00	100.00
40	5.0	15.0	0.35	5.0	0.01 "	7.00	93.00
41	10.0	30.0	3.30	10.0	0.01 "	33.00	67.00
42	20.0	60.0	11.62	20.0	0.01 "	58.10	41.90
43	50.0	150.0	3.87	5.0	0.10 "	77.40	22.60
44	100.0	300.0	9.07	10.0	0.10 "	90.70	9.30
45	200.0	600.0	19.17	20.0	0.10 "	95.85	4.15
46	400.0	1,200.0	38.69	40.0	0.10 "	96.72	3.28
			$1\text{CuSO}_4:4\text{KI}$				
47	2.5	10.0	0.25	25.0	0.001 N	1.00	99.00
48	5.0	20.0	0.90	5.0	0.01 "	18.00	82.00
49	10.0	40.0	5.47	10.0	0.01 "	54.70	45.30
50	20.0	80.0	14.77	20.0	0.01 "	73.85	26.15
51	50.0	200.0	4.62	5.0	0.10 "	92.40	7.60
52	100.0	400.0	9.77	10.0	0.10 "	97.70	2.30
53	200.0	800.0	19.67	20.0	0.10 "	98.35	1.65
54	400.0	1,600.0	39.57	40.0	0.10 "	98.93	1.07
			$1\text{CuSO}_4:5\text{KI}$				
55	2.0	10.0	0.00	20.0	0.001 N	0.00	100.00
56	3.0	15.0	0.85	30.0	0.001 "	2.83	97.17
57	4.0	20.0	3.88	40.0	0.001 "	9.70	90.30
58	5.0	25.0	10.00	50.0	0.001 "	20.00	80.00
59	6.0	30.0	18.25	60.0	0.001 "	30.42	69.58
60	8.0	40.0	33.95	80.0	0.001 "	42.44	57.56
61	10.0	50.0	5.77	10.0	0.01 "	57.70	42.30

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TABLE I—*Concluded.*

Experiment No.	Initial concentration of $\text{CuSO}_4$ .	Initial concentration of KI.	Thiosulfate titration of 10 cc. of mixture.			At equilibrium.	
			Found at equilibrium.	Calculated for complete reduction to $\text{CuI}$ .	Thiosulfate.	Cuprous salt.	Cupric salt.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	<i>millimolar</i>	<i>millimolar</i>	1 $\text{CuSO}_4$ :5KI			<i>per cent</i>	<i>per cent</i>
62	20.0	100.0	17.00	20.0	0.01 N	85.00	15.00
63	30.0	150.0	26.72	30.0	0.01 "	89.06	10.94
64	40.0	200.0	3.70	4.0	0.10 "	92.50	7.50
65	50.0	250.0	4.80	5.0	0.10 "	96.00	4.00
66	60.0	300.0	5.78	6.0	0.10 "	96.33	3.67
67	100.0	500.0	9.77	10.0	0.10 "	97.70	2.30
68	200.0	1,000.0	19.72	20.0	0.10 "	98.60	1.40
69	300.0	1,500.0	29.56	30.0	0.10 "	98.53	1.47
70	400.0	2,000.0	39.34	40.0	0.10 "	98.35	1.65
			1 $\text{CuSO}_4$ :10KI				
71	1.0	10.0	0.00	10.0	0.001 N	0.00	100.00
72	2.5	25.0	6.00	25.0	0.001 "	24.00	76.00
73	3.0	30.0	12.50	30.0	0.001 "	41.67	58.33
74	4.0	40.0	23.90	40.0	0.001 "	59.75	40.25
75	5.0	50.0	3.72	5.0	0.01 "	74.40	25.60
76	8.0	80.0	7.00	8.0	0.01 "	87.50	12.50
77	10.0	100.0	9.57	10.0	0.01 "	95.70	4.30
78	20.0	200.0	19.57	20.0	0.01 "	97.85	2.15
79	50.0	500.0	4.97	5.0	0.10 "	99.40	0.60
80	100.0	1,000.0	9.62	10.0	0.10 "	96.20	3.80
81	200.0	2,000.0	17.62	20.0	0.10 "	88.10	11.90
82	300.0	3,000.0	22.12	30.0	0.10 "	73.73	26.27

A 5 M KI solution was made by dissolving in a volume of 1,000 cc. 830 gm. of a pure preparation, previously powdered and dried at 80°C. for 18 hours. The solution was filtered and from it other dilutions were made. Calibrated pipettes and burettes, the latter of 25 cc. capacity, small bore, and marked in 0.05 cc., were used throughout.

The copper sulfate and potassium iodide solutions were mixed in a uniform way in volumetric flasks. Distilled water was first added to the flasks leaving only slightly more room than needed for the solutions to be added. The  $\text{CuSO}_4$  was then

added by pipette, the solution mixed, the KI measured in, and finally water added to the mark. After being stoppered and mixed by shaking, the flasks stood in a dark closet at 25–30°C. from 2 to 5 days to insure the attainment of equilibrium. During this time the precipitated CuI settles to the bottom so that it is possible to pipette off samples of the clear supernatant liquid without disturbing the precipitate. 20 cc. samples of the solutions were measured into small flasks containing exactly 20 cc. of *N* NaOH. After being mixed, the solutions were filtered from the precipitated cupric hydroxide, and 20 cc. of the filtrates, equivalent to 10 cc. of the CuSO<sub>4</sub>-KI mixtures, were measured into small flasks and acidified with about 5 cc. of 5 *N* H<sub>2</sub>SO<sub>4</sub>. The iodine liberated was then titrated with the same thiosulfate (or dilutions made from it) which was used in standardizing the CuSO<sub>4</sub> solution (Column 4, Table I).

The use of sodium hydroxide makes necessary the application of a small correction for the amount of iodine which is removed by some impurity in the alkali, the correction being added to the amounts of thiosulfate used. The correction in these experiments amounted to 1.11 cc. of 0.01 *N* iodine.

At the same time other 10 cc. portions of the supernatant liquids were in most cases titrated directly with thiosulfate after adding an excess of KI. The results so obtained are equivalent to the *total* copper originally in solution and serve as an additional check upon these values. In all but a few cases the results for total copper agreed well with the calculated values.

The following example illustrates the procedure above described.

10 cc. of 1 *M* CuSO<sub>4</sub> were mixed with about 175 cc. of water in a 200 cc. volumetric flask, 10 cc. of 5 *M* KI added, and the solution was diluted to the mark. The mixture had therefore as the initial concentrations, 50 millimolar Cu and 250 millimolar KI (Experiment 65, ratio 1CuSO<sub>4</sub>.5KI, Table I). After standing 3 days a 20 cc. sample of the supernatant liquid was pipetted out, added to 20 cc. of *N* NaOH, and filtered.

	0.1 <i>N</i> thiosulfate.
	<i>cc.</i>
20 cc. filtrate, acidified (= 10 cc. original solution).....	4.69
Correction for NaOH.....	0.11
	<hr style="width: 10%; margin-left: auto; margin-right: 0;"/>
(Column 4, Table I).....	4.80
10 cc. original solution + excess KI = total copper (Column	
5).....	5.00

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Since 1 atom of iodine is liberated from each atom of copper reduced, 10 cc. of 0.05 *M*  $\text{CuSO}_4$  when fully reduced by KI should yield 10 cc. of 0.05 *N* or 5.0 cc. of 0.1 *N* iodine, which is the amount found by titration. The amount found at equilibrium (4.80 cc.) divided by the amount from total reduction (5.00) gives the proportion reduced (0.96 or 96.0 per cent) (Column 7). The remainder (4 per cent) is the proportion of cupric salt (Column 8).

The procedure of analysis and methods of calculation above described were adhered to throughout, with the following exceptions. In very dilute solutions the iodine liberated is so small in amount that all or most of it was absorbed by the impurity present in the NaOH, the correction for the blank approaching or exceeding the amount of iodine to be determined. In these cases 10 cc. of the supernatant liquid were titrated directly with 0.001 *N* thiosulfate without previously stabilizing the equilibrium. Fortunately at very low concentrations of copper and iodide the small amounts of iodine present can be titrated away without materially shifting the equilibrium within the brief period of making the titration, and the results of direct titration are moderately reliable as proved by a fair agreement of results by the usual procedure and by direct titrations, at the slightly higher concentrations where such comparison was possible.

Another exception to the procedure described was necessary with the higher concentrations of the series, 1  $\text{CuSO}_4$  : 1 KI and 1  $\text{CuSO}_4$  : 2 KI. The results first obtained with the alkaline filtrates from solutions 100 millimolar  $\text{CuSO}_4$  of series 1:1 and of series 1:2 and from solutions of higher concentrations with these ratios, gave values which on being plotted on curves appeared erroneous. On inspection of the precipitate in the flasks, crystals of iodine were observed to be mixed with the cuprous iodide, which explained the low results obtained. The residual iodide, after the equilibrium was reached, was under these conditions not sufficient to hold in solution all the iodine liberated, and the titration of the iodine in solution therefore did not represent the amount formed. In such cases the points of equilibria were located by determining directly the amount of residual cupric copper. The cupric hydroxide precipitated from the supernatant liquid when the latter is run into NaOH was washed free of iodine by repeated centrifugation, decantation, and filtration,



finally dissolved in  $H_2SO_4$ , an excess of KI added, and the solution titrated with thiosulfate under the conditions under which the copper sulfate solutions are standardized. These results proved to be reliable and in agreement with those from the usual procedure in those solutions where such comparison was possible. Data were obtained in this way for the last two mixtures of ratio 1:1 and the last three mixtures of ratio 1:2 as explained in the foot-note to Table I.

#### DISCUSSION.

From the data given in Table I curves have been drawn which show graphically the position of the equilibria under various conditions. In Charts 1 and 2 the percentage of total copper reduced to cuprous salt (the position of equilibrium) is plotted against initial concentration of total copper for each of the molecular ratios 1  $CuSO_4$  :1, :2, :3, :4, :5, and :10 KI. The initial concentration of KI for each curve is readily seen by multiplying the initial copper concentration by the KI ratio of that curve. In Chart 3 the percentage of total copper reduced is plotted against initial concentration of potassium iodide.

Each individual curve of Chart 1 shows the shift of equilibrium with change in volume for a given molecular ratio of the reacting substances. If a mixture of  $CuSO_4$  and KI is made of initial concentrations as indicated and the mixture is progressively diluted the percentage distribution of total copper between precipitated cuprous iodide and cupric salt in solution is shown at any given dilution by the corresponding point on the curve for that molecular ratio. For instance, if equal volumes of 0.2 M  $CuSO_4$  and 1.0 M KI are mixed, the initial concentrations being 100 millimolar  $CuSO_4$  and 500 millimolar KI (1  $CuSO_4$  : 5 KI), about 98 per cent of the total copper is present as cuprous iodide. If the mixture is diluted with 9 volumes of water, the equilibrium is now such that only 57 per cent of the copper exists as cuprous iodide, and on further dilution to 50 times the original volume (total copper 2 millimolar, total KI 10 millimolar) practically all the copper exists as cupric salt and only little if any iodine can be detected by starch.

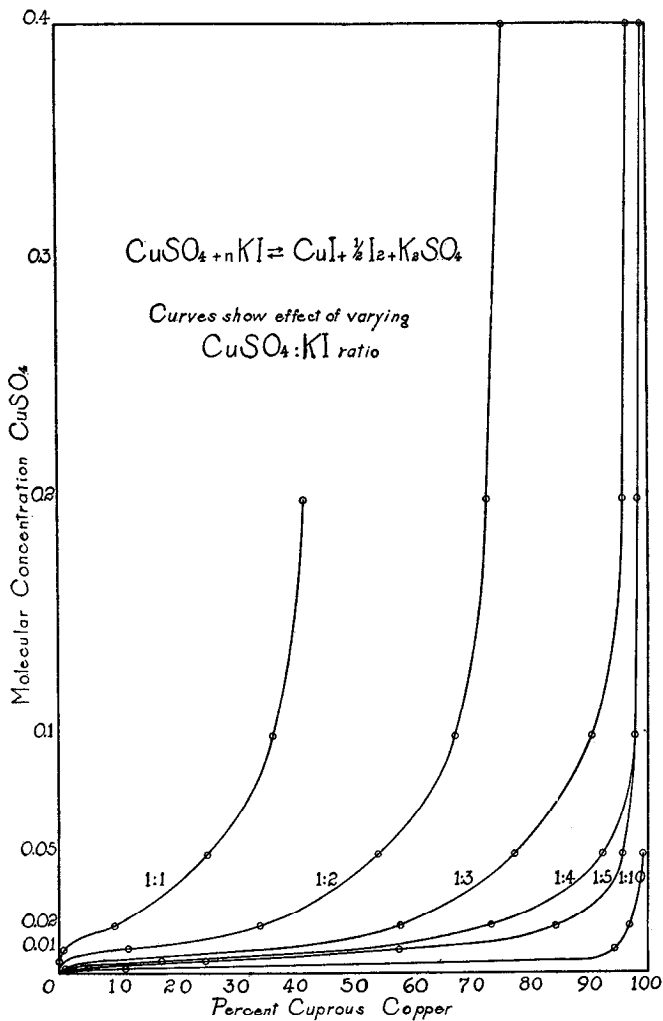


CHART 1. Curves show the position of equilibrium of the reaction between  $\text{CuSO}_4$  and  $\text{KI}$ , expressed as percentage of total copper in the form of cuprous salt, as affected by varying the ratio of  $\text{CuSO}_4:\text{KI}$ , and by concentration (dilution).

The relations are illustrated by the following experiment.

Mix 2.5 cc. of *m* (25 per cent)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 7.5 cc. of *m* (16.6 per cent) KI. Cuprous iodide is immediately precipitated and the solution is dark-colored from the formation of free iodine. On analysis 96 per cent of the copper would be found as cuprous iodide. This mixture had initial concentrations of 250 millimolar  $\text{CuSO}_4$  and 750 millimolar KI or  $1\text{CuSO}_4:3\text{KI}$ . Mix the same amounts in a total volume of 1,000 cc. by adding 2.5 cc. of *m*  $\text{CuSO}_4$  to 990 cc. of water, and to this dilute solution add 7.5 cc. of *m* KI. The mixture now remains clear and gives no iodine reaction with starch.<sup>3</sup> The initial concentrations in this case correspond to 2.5 millimolar  $\text{CuSO}_4$  and 7.5 millimolar KI.<sup>4</sup>

It is evident that the proportion of cupric salt which is reduced to cuprous iodide is determined by the dilution and by the relative excess of iodide in solution. The predominant influence of iodide is indicated by Chart 3. These relations are implied in the mass law equation

$$(\text{Cu}^{++}) \cdot (\text{I})^2 = \sqrt{\text{I}_2} \cdot \text{K}$$

according to which the concentration of cupric ions will vary inversely as the square of the iodide ions and directly as the square root of the free iodine. A discussion of the bearing of our data upon the validity of this equation will be deferred to a later paper, and we shall point out here only their significance for the determination of cupric and cuprous copper, for which purpose the work was undertaken.

<sup>3</sup> Since writing the above the work of Traube (Traube, M., *Ber. chem. Ges.*, 1884, xvii, 1064) has come to our attention. Traube established the existence of cupric iodide in solution and described experiments very similar to those given above showing the effect of dilution upon the formation and precipitation of cuprous iodide from mixtures of copper sulfate and potassium iodide. He pointed out that the mixture of 0.1 per cent KI and 0.075 per cent  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (equivalent to final concentrations of 3 millimolar KI and 1.5 millimolar  $\text{CuSO}_4$ ) or 0.05 per cent KI with 1.0 per cent  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (equivalent to final concentrations of 1.5 millimolar KI and 20 millimolar  $\text{CuSO}_4$ ) remains clear and gives no reaction with starch after 24 hours standing. Our work is thus an elaboration of facts made known 36 years ago.

<sup>4</sup> The same experiment may be more simply performed by diluting the first mixture to a liter, but in this case equilibrium is attained more slowly and the solution contains a small amount of free iodine for some time.

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With the ratio of 1 Cu : 1 KI reduction is absent or very slight until the concentration reaches about 5 millimolar (Chart 2). With these relative amounts of cupric salt and potassium iodide and at these concentrations no cuprous salt and no free iodine are formed. Furthermore, if cuprous salt is originally

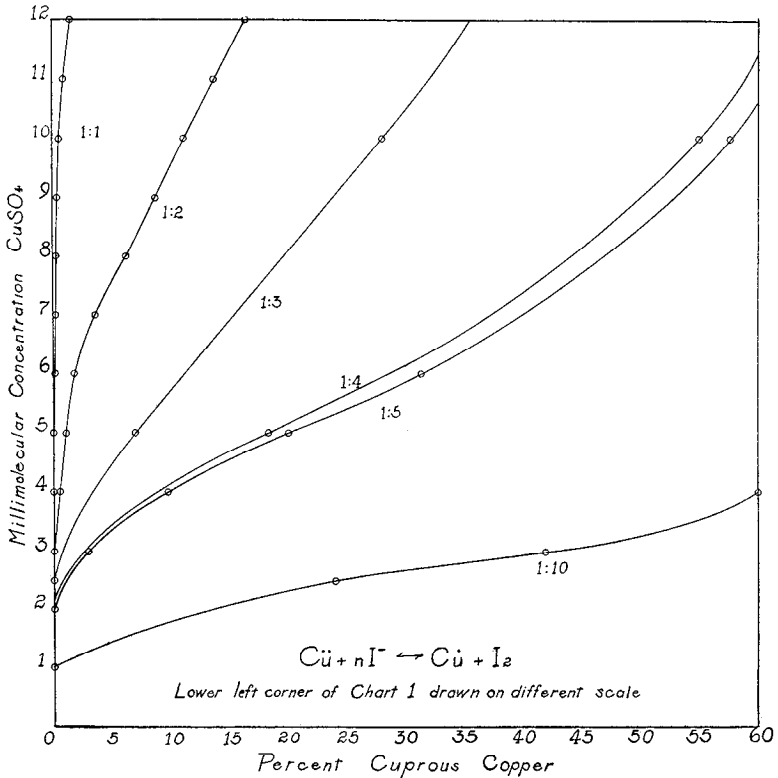


CHART 2. Curves show the same relations as in Chart 1, drawn on a larger scale to indicate the limiting concentrations for the complete oxidation of cuprous to cupric salt.

present it is quickly and completely oxidized to the cupric condition if iodine is added; and since at this concentration there is no tendency for the reaction to run to the right, and thus no cuprous salt and free iodine to form, the excess iodine may be removed by titration with a sharp end-point. The

conditions, therefore, which must be chosen for the determination of cuprous copper by this reaction are a minimum excess of KI and a final (total) concentration of less than about 3 to 5 millimolar copper. (In the following paper means are described by which this limitation is removed.) Cuprous copper will be completely oxidized to cupric salt by an excess of iodine provided the final concentration of copper and iodide do not exceed 5 millimolar each.<sup>5</sup>

These are the conditions which Maclean and Scales found empirically to be necessary for the reoxidation by iodine of cuprous copper formed in the oxidation of sugar. The final concentration of total copper in Maclean's titration is 2.5 millimolar and of iodide 2.9 millimolar (after the amount of iodide necessary for the reaction with the iodate has been subtracted from the original amount present) or 1:1 ratio. In the technique described by Scales the values prove to be 4.5 millimolar iodide and 2.3 millimolar total copper or 1:2 ratio. An examination of Chart 2 shows that both these conditions lie on the ordinate below the intersection of Curves 1:1 and 1:2, where no cuprous salt is present at equilibrium. At concentrations represented by points above the intersection of the respective curves, the end-points would not be sharp and the results would be incorrect. At such higher concentrations a large excess of iodine will, to be sure, oxidize more or less cuprous salt but on removal of the excess of iodine during titration with thiosulfate the equilibrium will shift to the right with the reformation of cuprous iodide and iodine and a consequent running (returning) end-point.

<sup>5</sup> The actual limitation is doubtless a certain value of the product  $(\text{Cu}^{++}) \times (\text{I}^-)^2$ . What this value is we have not determined exactly though our results indicate it to be roughly about 135, the concentrations being expressed in terms of millimolar solutions.

Ratio 10:1, 1	Cu	×	(10 I) <sup>2</sup>	=	100
" 5:1, 2	Cu	×	(10 I) <sup>2</sup>	=	200
" 4:1, 2.1	Cu	×	( 8.2I) <sup>2</sup>	=	141
" 3:1, 2.5	Cu	×	( 7.5I) <sup>2</sup>	=	140
" 2:1, 3.0	Cu	×	( 6 I) <sup>2</sup>	=	101
" 1:1, 5	Cu	×	( 5 I) <sup>2</sup>	=	125
Average					135

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For the determination of cupric copper, on the other hand, it is necessary that the cupric salt be completely reduced with the liberation of an equivalent amount of iodine, and, as shown by Chart 1, this condition depends upon the presence of a considerable excess of iodide in solution. The optimum concentration of iodide is about 0.25 to 0.5 M, in which solutions, if the ratio of

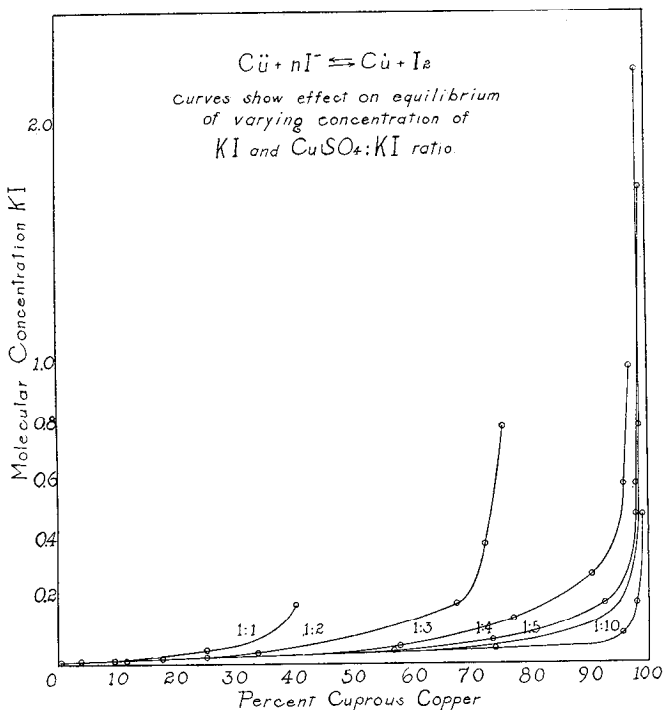


CHART 3. The curves show the predominating influence of KI in determining the equilibrium.

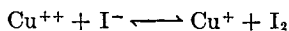
copper to iodide is not greater than 1:5, the copper will be almost completely converted into cuprous iodide at equilibrium, and on removal of the iodine by titration the small remainder of cupric salt is quickly reduced. Equilibrium being close to the right side of the reaction, the titration end-point is sharp. In a volume of 100 cc., 0.25 M potassium iodide (4.2 gm.) allows the correct determination of amounts of copper up to the equivalent of

1.25 gm. of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , or double this amount with 0.5 M KI. With smaller concentrations of iodide, as is apparent from Chart 1, the reduction is less complete at equilibrium, and the titration end-points are in consequence less sharp, the blue color returning as long as cupric salts are present.

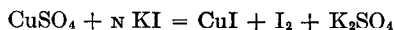
It is doubtless due to the lack of such information as may be derived from Chart 1 that varying opinions have been expressed as to the value of this method for the determination of copper (cited by Gooch and Heath (6)). Those who have favored the method adopted conditions the correctness of which are confirmed by our curves. Moser (9) recommends the addition of 2 gm. of potassium iodide to 50 cc. of a solution containing about 0.6 gm. of cupric sulfate; this is equivalent to about 0.24 M iodide and at least 5 KI:1 Cu. Gooch and Heath recommend the use of 5 gm. of potassium iodide in 100 cc. of solution containing not more than 0.3 gm. of copper. These amounts are equivalent to 0.3 M iodide and at least 6 KI:1 Cu.

#### SUMMARY.

Both cupric and cuprous salts may be determined iodometrically by means of the reversible reaction



The position of equilibrium has been determined for the reaction



at ratios of from 1 to 10 KI:1CuSO<sub>4</sub> at various dilutions.

For the determination of cupric salts potassium iodide must be added to give a *final* concentration of about 0.25 M (4 to 5 gm. per 100 cc. of solution).

For the determination of cuprous salts the solution must be so diluted that the *final* concentration of copper and of iodide does not exceed about 5 millimolar each.

The conditions found empirically by Gooch and Heath (6) for cupric salts and by Maclean (2) and Scales (3) for cuprous salts comply with these requirements.

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