Thesis

THE EQUILIBRIUM BETWEEN CUPROUS AND CUPRIC IONS
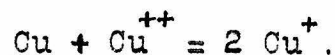# AND COPPER

BY

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THE EQUILIBRIUM BETWEEN CUPROUS AND CUPRIC IONS
AND COPPER.

The object of this investigation is to determine the equilibrium constant of the reaction between cuprous and cupric salts and metallic copper, as represented by the equation

$$\underline{Cu} + Cu^{++} = 2\ Cu^{+}.$$

With the aid of this constant, and the specific electrode potential of metallic copper against cupric ion, the specific electrode potential of metallic copper against cuprous ion may be calculated by the relation

$$E(Cu^{+}) = E(Cu^{++}) + \frac{RT}{F} \log \sqrt{K}.$$

Here $E(Cu^{+})$ denotes the specific electrode potential of cuprous ions, $E(Cu^{++})$ the specific electrode potential of cupric ions against metallic copper, and K the equilibrium constant of the above reaction.

This equilibrium has already been investigated by a number of chemists. Their results are not concordant, the values found varying from 4×10^{-5} to 7×10^{-7}.

PREVIOUS WORK

Luther[1] used a copper sulfate solution, and, after equilibrium had been established, determined the cuprous content by titrating with potassium permanganate. He found the constant, $\frac{(Cu^{+})^2}{Cu^{++}}$, to have the value 7×10^{-7}.

1 - Zeit. phys. Chem. 34, 488, (1900) and 36, 385, (1901).

Abel[1] hung a strip of metallic copper in cupric sulfate solutions of varying concentrations, which in addition contained about two equivalents of sulfuric acid per liter. The amount of cuprous salt formed was derived from the decrease in weight of the copper strip. He considered the questions of the formation of complex ions and of the valence of the cuprous salt. It was decided that experiments of this nature could not throw light upon the complexity of the ions, but the results indicate that the cupric ion is monovalent. For the ratio, $\frac{(cuprous\ salt)^2}{cupric\ salt}$, Abel obtained the value, 4×10^{-5}, at $25°$.

Bodlander and Storbeck[2] employed solutions of cuprous chloride in both hydrochloric acid and potassium chloride solutions, in the attempt to determine the complexity of the cuprous ion. Like Abel, they decided that the problem could not be definitely settled by experiments of this nature. They afterwards investigated solutions of cuprous bromide. In this work the total copper was determined electrolytically, and the cupric copper by titrating with sodium thiosulfate in the presence of a large excess of potassium iodide. The cuprous copper was then determined by difference. Their results confirm the conclusion of Abel, namely, that the cuprous ion is monovalent. For the ratio, $\frac{(Cu^+)^2}{Cu^{++}}$, they obtained the value 5×10^{-5}.

1 - Zeit. fur anorg. Chem. 26, 387, (1901)

2 - Zeit. fur anorg. Chem. 31, 1, and 400, (1902)

Chiu[1] shook solutions of cupric perchlorate for several days with finely divided copper. One portion of this equilibrium mixture was then used for the determination of cuprous ion by titrating with iodine, using carbon disilfide as an indicator. A second portion was taken for the electrolytic determination of total copper. The cupric copper was determined by difference.

Considerable difficulty was encountered because of the fact that the oxygen, dissolved in the very dilute iodine solutions, tended to oxidize the cuprous ion to cupric. During the preliminary experiments it was found that the cuprous ion was oxidized as fast as it was run into the iodine solution. Even after taking all ordinary precautions to overcome this source of error, the results obtained were not very concordant, varying from 1.1×10^{-6} to 1.9×10^{-6} at 25°. Preliminary experiments of the present investigation indicated that equilibrium is not established even after shaking the solutions for more than three months at 25°.

PROCEDURE EMPLOYED.

In this investigation the general outline of Chiu's work has been followed, in that solutions of cupric perchlorate were shaken with finely divided copper until equilibrium was established, and also that the total copper was determined electrolytically. But a new method was employed for the determination of cuprous copper.

1 - Mass. Inst. Tech. Theses, (1916).

The method finally adopted makes use of the fact that cuprous ions reduce quantitatively silver nitrate to free silver in boiling ammoniacal solution. The problem then was an accurate determination of very small amounts of silver. Two methods presented themselves. One[1] was the titration of silver solutions with potassium iodide, in the presence of palladous nitrate, depending upon the fact that an excess of KI forms a precipitate of palladous iodide, easily visible one part in a million. The objection to this method is the large volume of the solutions involved relative to the small concentration of the silver. The other method is likewise an iodimetric one, it being an adaptation of a method published by McLean and Van Slyke for the determination of small amounts of halide as silver halide. The latter method was chosen for this investigation.

The method as developed by McLean and Van Slyke[2] is as follows: To the solution of halide (or silver) to be titrated is added a solution containing sodium citrate and sodium nitrate, with starch as an indicator. The silver, which had been dissolved in nitric acid was then titrated with standard potassium iodide. The first action taking place is the precipitation of the silver as the iodide, according to the reaction

$$AgNO_3 + KI = \underline{AgI} + KNO_3.$$

As soon as there is the slightest excess of potassium iodide solution the iodine is released by the action of the

1 - Science   46, 1199, 622, (1917)
2 - Jour. Amer. Chem. Soc. 37, 1128, (1915)

sodium nitrite, and the strong blue color, characteristic
of the iodo-starch reaction, is easily visible,

$$2 \text{ KI} + 2 \text{ HNO}_2 = 2 \text{ NO} + 2 \text{ KOH} + I_2$$
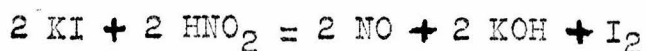
The purpose of the citrate is to regulate the acidity of
the solution. About four cc. of the reagent (see below)
are added to the silver solution before titration for each
gram of free nitric acid contained therein. As four cc. of
concentrated nitric acid were used to dissolve the free
silver, and 1 cc. of 16 N. acid contains approximately 1
gram of free HNO_3, sixteen cc. of the reagent were necessary.

The reagent itself was made up according to the formula
given by McLean and Van Slyke as follows:

Trisodium Citrate, $Na_3C_6H_5O_7$ $5H_2O$.........446.0 grams

Sodium Nitrite, $NaNO_2$ 19.0

Soluble Starch 2.5

Water to ....1000.0 cc.

It was found advisable in this work to employ a slightly
stronger concentration of the starch than the formula called
for, so to each mixture just before titration five cc. of
starch solution were added. In all other respects the pro-
ceedure as given was followed.

As may be at once apparent, the method developed has a
manipulation very similar to the Volhard titration for silver
There are two very important differences however, interdepen-
dent upon each other. First, the reagent that is added and
second, the Volhard titration requires one drop of a 0.1 N

solution (about 0.05 cc.) for its end point, while because
of the careful regulation of conditions and the simplicity
of this method, a single drop of a 0.01 N solution gives an
excellent and easily observed end point. It is at once ap-
parent that smaller volumes will allow of a sharper end
point. To this end, the volumes of the solutions in the ti-
trations were kept down to 50 cc. at the beginning of the
titration.

The pipette employed for withdrawing the samples was
provided with a small tubular glass wool filter on the end .
Preliminary experiments showed the necessity of this precau-
tion in order to prevent fine metallic copper from being
withdrawn with the sample. Any free copper on being boiled
with the ammoniacal silver solution containing free silver,
would tend, first, to oxidize the copper to cupric ion and,
second, to displace the equilibrium, with the greater forma-
tion of cuprous ion and so of free silver. Experiments with
equilibrium solutions containing 1 milligram of metallic
copper showed that a very material error is introduced by
the presence of even this small amount of copper.

Another series of preliminary experiments were preformed
upon solutions of ammoniacal silver nitrate to determine
whether the silver was quantitatively reduced from the same
by the cuprous ion reaction. These were carried out by adding
a measured quantity of a freshly standardized solution of
cuprous chloride to a boiling solution of ammoniacal silver

nitrate. The silver precipitated out as free silver with
that precipitated as the chloride was filtered off on a
Gooch crucible. The free silver was dissolved in dilute
nitric acid, and the filter well washed. The silver chloride
remaining was weighed as such. The silver nitrate in the
mixed solutions was precipitated with hydrochloric acid and
filtered off on the same Gooch filter. From the combined
weights of the silver chloride, the excess of silver nitrate
was calculated. These results showed a quantitative reaction
between the silver ion and the cuprous ion.

The determination of total copper was in all cases made
by depositing the copper out of a solution containing a def-
inite concentration of nitric acid. This was found necessary
in order to obtain a clean pure deposit; depositions made
from perchloric acid solutions were naturally inadvisable
owing to the nature of the gases evolved. The proceedure
followed was approximately that recommended by Talbot's
Quantitative Analysis.

PREPARATION OF THE SUBSTANCES.

Finely divided copper was made by electrolyzing a
slightly acid, approximately 0.3 N copper sulfate solution.
A strip of copper served as the anode, and by employing a
platinum wire as the cathode a high current density was ob-
tained. The copper prepared in this way can be removed by
gently tapping the platinum wire. This copper was boiled

for a few minutes in a solution of copper sulfate and sulfuric acid to remove traces of impurities that might have been deposited with the copper, and also to remove any cupric oxide that might have been formed by the action of the air. After boiling it was washed several times with distilled water to remove the copper sulfate. Finally it was washed with 0.1 N cupric perchlorate, and then with a solution of the same concentration as that of the equilibrium mixture into which it was to be placed. About ten grams of the metal so prepared was added to each equilibrium bottle.

Cupric perchlorate was chosen because of the fact that it is the salt of a strong oxygen acid, hydrolysis being thus less likely to occur. The cupric salt was prepared by dissolving cupric oxide in pure perchloric acid. The cupric oxide was made by heating finely divided copper prepared as above in a Rose crucible. It was found that the action was never complete by heating in air, so the oxidation was carried on in a current of oxygen. Thus a very pure copper oxide was obtained. This cupric oxide was weighed out and a sufficient volume of concentrated perchloric acid added to cause the resulting solution to contain about ten percent excess acid. The presence of free perchloric acid serves the purpose of preventing the possible hydrolysis of the salt. The standard stock solution was made about 0.01 M. From the stock solution the more dilute solutions were prepared. Then if hydrolysis does occur, the degree of hydrolysis is always the same.

The containers employed for the equilibrium mixture of cupric perchlorate and copper were 250 cc. laboratory reagent bottles. Before use they were well washed out with a solution of cupric perchlorate of the strength to be contained in them. Before adding the copper and the cupric perchlorate solution, the bottles were filled with carbon dioxide gas. They were finally sealed with sealing wax, and placed in the thermostat.

The thermostat was a metal basin of about 15 gallons capacity, provided with a wooden cover. The heating unit was a 500 c.p. electric globe run continuously, and a 250 c.p. globe connected thru the mercury regulator. The regulator, after lengthy experimentation, proved itself capable of maintaining the temperature within one-tenth of a degree of 75° C or 50° C. The bottles were firmly attached to a central revolving shaft.

METHOD OF PROCEDURE.

At the end of a predetermined period the bottles were removed from the thermostat. Considerable difficulty was experienced during the preliminary experiments in finding an expeditious method of so securing and sealing the bottles that they might be safely opened before sufficient time had elapsed to change the equilibrium. Practice developed a technique whereby less than $1\frac{1}{2}$ minutes intervened between stopping the motor and taking the sample from the bottle.

As cuprous salts are very easily oxidized by air, every possible precaution to guard against this source of error was taken. The bottles were opened in an atmosphere of carbon dioxide. This gas was freed from oxygen by passing it thru two wash bottles containing cuprous chloride, hydrochloric acid, and metallic copper. The pipette employed to draw out the solutions was also connected with the carbon dioxide generator, well washed out and filled with the gas just previous to use. By an arrangement with a three way stop cock on the end of the pipette, suction was applied, and a sample taken without the solution coming into contact with the air. The sample was quickly transferred to a boiling solution of ammoniacal silver nitrate, care being taken to keep the tip of the pipette under the surface of the hot solution.

After boiling for three minutes to coagulate the silver formed by the reaction, the solution was filtered thru a Gooch crucible, and the residue thoroughly washed first with boiling distilled water, then with a 50% solution of ammonium hydroxide, and finally with cold water. The silver on the filter consisted of very fine specks, often not visible to the eye. The condition of the metal enforced great care in the preparation of the Gooch filters to retain it. Only layers of minutely small fibers were successful for the purpose.

The silver so collected was dissolved in four cc. of concentrated nitric acid, in four portions, and the filter

washed free of silver nitrate. In case the volume of the solution, after the washings had been added, was over 40 cc. it was evaporated to that volume on the water bath. The citrate reagent and the starch solution was added, and the sample was ready for titration. The titrations were always carried out in a casserole.

Another sample was taken from the equilibrium bottle for the determination of total copper. Nitric acid was added to give the desired acid concentration, one gram of ammonium nitrate added, and the whole transferred to the platinum crucible. The time allowed for the deposition was from nine to ten hours, and the current regulated accordingly.

EXPERIMENTAL RESULTS.

Experiments were run at both 50° and 75° C., as noted in the table below. By obtaining the equilibrium constant at these two temperatures, the constant, and hence the specific electrode potential, at lower temperatures can be calculated. The equilibrium mixture was approached from both sides in both series of experiments. Checks were run on the determination of cuprous copper during the first experiments with 0.0102 M and 0.00102 M solutions of potassium iodide. A later test of the stronger solution showed the presence of KIO_3, and these results had to be discarded. Checks were not run on the total copper determination.

In correcting the value of the equilibrium constant for the dissociation of the salts involved, no data are available for the dissociation of the copper salts of perchloric acid, so curves were plotted from the data given by Noyes[1] for the average value of the ionization of salts of the uniunivalent and unibivalent types. From these curves the values of the ionization of the various concentrations of cuprous and cupric salts herein involved were read off, and the specified correction made.

The pipette used for drawing the sample for the cuprous copper determination delivered 99.38 cc. at 50° C., and that for the total copper sample 49.91 cc. In calculating the results the volumes of both were computed to 100 cc. The other data was calculated to mols per liter. The concentration of the KI used in the titration of the experiments at 50° was 0.00102 M., and for those at 75° was 0.00106 M.

1 - Noyes and Sherrill - Gen. Prin. Chem.p. 56, (1916) ed.

The average values of the equilibrium constant of the reaction

$$\underline{Cu} + Cu^{++} = 2\ Cu^{+}.$$
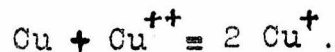
are 7.12×10^{-6} and 15.24×10^{-6} at 50° and 75° respectively. From these data may be calculated, with the aid of the van't Hoff equation, the heat of the reaction and the equilibrium constant at 25°. The heat evolved when the above reaction proceeds from left to right was found to be -6800 calories and the equilibrium constant at 25° to be 2.9×10^{-6}.

The specific electrode potential of cuprous ions against copper at 25° may now be calculated by the aid of the equation given at the beginning of this report[1]. Employing -0.35 volt[2] as the specific electrode potential of the copper, cupric ion electrode, the value -0.51 is obtained for that of the copper, cuprous ion electrode. In addition, the specific electrode potential of the cuprous ion, cupric ion electrode, $E(Cu^{+}, Cu^{++})$, may be calculated by means of the relation

$$E(Cu,\ Cu^{+}) + E(Cu^{+},\ Cu^{++}) = 2\ E(Cu,\ Cu^{++}).$$

The value thus obtained is -0.19 volt.

1 - Page 1.
2 - Lewis and Lacey. J. Am. Chem. Soc. 36, 804. (1914)

TABLE No. 1 - - 50°.

No.	Total copper gm./100 cc.	C.C. of KI	Cuprous salts M./li x10^5	Cupric salts M./li x10^3	Cu M./li x10^5	Cu M./li x10^3	K x10^6
1.	0.2475	10.74	1.102	1.941	1.083	1.481	7.10
2.	0.3001	11.52	1.182	2.354	1.158	2.024	6.65
3.	0.1716	9.26	0.9504	1.345	0.931	1.158	7.46
4.	0.1602	8.91	0.9065	1.255	0.892	1.085	7.34
5.	0.1481	8.63	0.8857	1.161	0.873	1.001	7.50
6.	0.0960	9.61	0.9863	1.508	0.968	1.286	7.29
7.	0.1685	9.02	0.9258	1.321	0.910	1.133	7.16
8.	0.2407	10.84	1.113	1.887	1.091	1.590	6.83
9.	0.0894	6.64	0.6815	0.6969	0.673	0.658	6.87
10.	0.0541	5.12	0.5255	0.4228	0.5196	0.3796	7.11
11.	0.5995	17.10	1.755	4.707	1.703	3.921	7.39
12.	0.3292	12.11	1.243	2.582	1.218	2.149	6.90
13.	0.3173	12.17	1.269	2.489	1.243	2.104	7.35
						Mean	7.12

TABLE No. 2 - - 75°.

No.	Total copper gm./100 cc.	C.C. of KI	Cuprous salts M./li x10^5	Cupric salts M./li x10^3	Cu M./li x10^5	Cu M./li x10^3	K x10^6
14.	0.2376	4.65	4.959	1.844	4.849	1.558	15.10
15.	0.5261	6.87	7.327	4.104	7.144	3.362	15.18
16.	0.3594	5.66	6.237	2.794	5.898	2.250	15.46
17.	0.1785	4.09	4.362	1.382	4.271	1.188	15.35
18.	0.1779	3.99	4.316	1.378	4.226	1.182	15.11
						Mean	15.24