[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE POTENTIAL OF A PROPOSED STANDARD FORM OF COPPER AND THE ACTIVITY OF COPPER SULFATE[1]

BY RALPH F. NIELSEN AND DENTON J. BROWN

RECEIVED JUNE 6, 1927 PUBLISHED OCTOBER 5, 1927

This research was undertaken in connection with the attempt to find a standard form of copper for use in potential measurements involving various compounds of copper. The potential of the copper electrode in copper sulfate solution has been measured by numerous investigators, using various forms of copper, and the results always depended on the method of preparing the electrodes. Lewis and Lacey[2] give the value 0.3928 volt for the electromotive force of the cell Cu | $CuSO_4(0.05\ M)$ | Hg_2SO_4 | Hg, using a copper sponge prepared by rapid electrolysis of copper sulfate on a platinum point. They found a considerable number of cells to agree within several tenths of a millivolt, using various current densities in preparing the copper. We have been unable to obtain reproducible results using copper prepared by their method, and invariably the copper lost its reducing activity slowly upon standing under concentrated copper sulfate solution. The following table gives the relative potentials of a sample of copper prepared by this method at the time indicated.

TABLE I

RELATIVE POTENTIALS

Day	11/19/26	11/23/26	11/29/26	12/3/26
E.m.f.	0.1595	0.1551	0.1531	0.1523

In addition, pieces of wire and sheet were heated to a temperature near the melting point of copper in an atmosphere of nitrogen and slowly cooled. These gave values somewhat lower, although we could not obtain constant results. These facts are in agreement with a rather generally accepted theory that metals freshly precipitated by violent reduction are abnormally high in their reducing power. In fact, a copper sponge obtained by the action of zinc dust on copper sulfate solution gave exceptionally high values. All our values were admittedly higher than those of Lewis and Lacey, but we can see no reason why their values should be selected as standard.

It became necessary to find a form of copper which gave constant results that could easily be reproduced by any investigator, and we finally

---

[1] This paper is an abstract of part of the work done by Ralph F. Nielsen toward the degree of Doctor of Philosophy at the University of Nebraska. The problem of the determination of free energies of copper compounds was selected by him at the suggestion of Professor Merle Randall of the University of California, and the work of this paper was found necessary in carrying out the problem.

[2] Lewis and Lacey, THIS JOURNAL, **36**, 804 (1914).

decided to use a two-phase electrolytic amalgam in our work. By accurately determining the standard potential of this form of copper, we can easily correct our subsequent data on various copper compounds when a justifiable standard form of copper is found. We made a number of measurements involving copper sulfate solution, making use of this amalgam. The copper amalgam was prepared by electrolysis of a half-molal solution of copper sulfate, slightly acidified, using about five amperes per square decimeter of mercury surface and a copper anode. The amalgam was kept under this solution after preparation. Mercurous sulfate was prepared by electrolysis of a 25% solution of sulfuric acid, using about five amperes to a square decimeter and a rapid stirrer which just grazed the mercury surface, according to the method of Hulett.[3] The copper sulfate used had been recrystallized from an acidified solution of the best C. P. crystals obtainable, and the solutions were made up gravimetrically from a stock solution standardized iodimetrically with metallic copper as primary standard. Molality is taken as moles per kilogram of water in vacuum. Conductivity water and distilled mercury were used in preparing the reagents. Measurements were made on a Leeds and Northrup "Type K" potentiometer, using a new Weston cell with a Bureau of Standards Certificate. The thermostat consisted of a bath of distilled water maintained at 25 ± 0.05°. The mercurous sulfate electrodes were always placed in glass-stoppered flasks, rotated in the thermostat for several hours and then put into dry electrode vessels of the usual type. All heating and regulating circuits were shut off during the measurements and all connections were made by means of mercury. We measured the following cells, each value being the mean of four different cells, none deviating more than a tenth of a millivolt from the mean. The four cells were obtained by cross combinations among two electrodes of each kind.

TABLE II

CELL MEASUREMENTS

Cu (amalgam) | $CuSO_4$ (0.05 M) | Hg_2SO_4 | Hg	0.3874 volt
Cu (amalgam) | $CuSO_4$ (0.1 M) | Hg_2SO_4 | Hg	.3784 volt
Cu (amalgam) | $CuSO_4$ (0.2 M) | Hg_2SO_4 | Hg	.3697 volt
Cu (amalgam) | $CuSO_4$ (0.4 M) | Hg_2SO_4 | Hg	.3592 volt

The cell Cu(amalgam) | $CuSO_4$(sat.) | Hg_2SO_4 | Hg has been measured by Cohen, Chattaway and Tombrook,[4] by Obata[5] and by Öholm[6] using reagents prepared as above. The mean value from the last two investigators is 0.3467 volt ± 0.0001. As a check on our preparations we re-

---

[3] Hulett, *Phys. Rev.*, **32**, 32 (1900).

[4] Cohen, Chattaway and Tombrook, *Z. physik. Chem.*, **60**, 706 (1907).

[5] Obata, *Proc. Phys. Math. Soc. Japan*, [3] **2**, 223 (1920).

[6] Öholm, *Medd. Vetenskapsakad. Nobelinst.*, **5**, N:04, 1 (1919).

peated these measurements and obtained 0.3468 volt ± 0.0001. Since we were afraid that we had not washed all the acid from the crystals of copper sulfate before making up our solutions, we recrystallized some from a neutral solution and repeated the measurements at 0.2 *M* concentration. We obtained perfect agreement, however, with the above. Since we found that we could not avoid the formation of a green precipitate at the mercurous sulfate electrode in the case of the 0.05 *M* solution, this solution contained a drop of nitric acid in a liter of the solution. This should not affect the activity coefficient noticeably if the degree of hydrolysis is small; and, indeed, it was found to have no effect in the 0.1 *M* solution. We did not think it advisable to carry these measurements into more dilute solutions owing to the solubility of mercurous sulfate.

As a further check on our activity coefficients we combined our electrodes in the following way,

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{CuSO_4}(0.1\ M) \mid \mathrm{Cu(amal.)} \mid \mathrm{CuSO_4}(0.05\ M) \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$$
$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{CuSO_4}(0.5\ M) \mid \mathrm{Cu(amal.)} \mid \mathrm{CuSO_4}(0.2\ M) \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$$
$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4} \mid \mathrm{CuSO_4}(0.5\ M) \mid \mathrm{Cu(amal.)} \mid \mathrm{CuSO_4}(0.1\ M) \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$$

These cells gave, respectively, 0.0089 volt ± 0.0001; 0.0105 volt ± 0.0001; 0.0190 volt ± 0.0001.

Employing the values of the two tables, we obtain the following series of activity coefficients:

TABLE III

ACTIVITY COEFFICIENTS

M....................	0.05	0.1	0.2	0.5	1.38
γ....................	.216	.153	.107	.064(4)	0.0378

The value of 0.216 for the 0.05 *M* solution was taken from Lewis and Randall.[7] These values are about three per cent. lower than theirs, but are undoubtedly more nearly correct, since their calculations from freezing point measurements were not corrected for the heat of dilution.

For the standard potential of copper amalgam we obtain —0.3502 volt, based on the mean activity of the ions in copper sulfate solution. The copper amalgam used above seems to be a good standard form of copper for use in potential measurements. It is easily reproducible and, since it is a two-phase amalgam, its potential is independent of the relative quantities of copper and mercury within rather wide limits. The General Electric Company has prepared single, unstrained crystals of copper, and we attempted to obtain some from them, to see if they would give the same potential as the amalgam. They had none on hand, however, which had not been strained, so we did not perform this experiment.

---

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York City, 1923.

Summary

The choice of a standard form of copper for use in potential measurements was discussed.

The standard potential of copper amalgam and the activity coefficients of copper sulfate over a limited range were determined.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 42]

THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC GOLD[1]

BY ARTHUR F. BENTON AND JOSEPH C. ELGIN[2]

RECEIVED JUNE 13, 1927 PUBLISHED OCTOBER 5, 1927

Introduction

In a previous communication[3] evidence was presented to show that the mechanism of water formation over a reduced silver catalyst involves collisions of gaseous hydrogen with adsorbed oxygen on that fraction of the surface not covered by adsorbed water. In this case the reaction kinetics proved to be relatively simple.

Metallic gold like metallic silver does not form definite compounds by direct combination at ordinary pressures with either hydrogen or oxygen.[4] Their similarity in chemical properties would lead one to expect that the reactions in contact with the two metals would exhibit similar kinetics and mechanism. The present investigation shows that this is not the case, although the adsorption phenomena for the two metals are similar.

Bone and Wheeler[5] have studied the hydrogen-oxygen combination in contact with gold gauze at 250° by a circulatory method. They state that the results for gold and silver were analogous; namely, that the rate of reaction was roughly proportional to the pressure of hydrogen, but independent of the pressure of oxygen, and that the activity of the catalyst was greatly stimulated by previous heating in hydrogen but not in oxygen. This latter effect was further investigated by Chapman, Ramsbottom and Trotman.[6]

The experimental method and the conclusions of Bone and Wheeler have been discussed and criticized in other places.[3] The difficulties

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society held at Richmond, Virginia, April 11-16, 1927.

[2] Du Pont Fellow in Chemistry during the period covered by this investigation.

[3] Benton and Elgin, THIS JOURNAL, **48**, 3027 (1926).

[4] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, **1923**, Vol. III, pp. 525-526, 577.

[5] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906).

[6] Chapman, Ramsbottom and Trotman, *Proc. Roy. Soc. (London)*, **107A**, 29 (1925).