basic zirconium phosphate in the absence of added acid, no record was found indicating incompleteness of precipitation of zirconium under these conditions. Investigation showed that phosphates are not efficient in removing zirconium in the absence of added acid.

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THE SINGLE POTENTIAL OF THE COPPER ELECTRODE

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The determination of the normal single potential of a copper electrode has been attempted by many investigators with very discordant results and at the present time its value is not known with certainty within a possible error of 40 millivolts. This work was undertaken, therefore, with the object first of finding the reasons for the variation in the results obtained, and, second, if possible, of removing or circumventing the disturbing factors and determining the true value.

Possible sources of error or of variability of results are: (1) impurities in the electrode, (2) impurities in the electrolyte, (3) variations in the nature of the electrode surface, (4) changes in constitution of electrolyte during measurement, (5) chemical action between electrode and electrolyte producing any or all of the conditions (1) to (4).

1. Most investigators have exercised great care to ensure that the copper electrodes used were free from traces of other metals. Unfortunately one of the most dangerous impurities, hydrogen, which is very frequently present and has a profound potential-disturbing capacity, has been ignored. If two copper plates cut from the same sheet be immersed in dilute acid and a current passed for a few seconds, a potential difference of several millivolts is produced which may persist for several hours. By introducing a third electrode cut from the same sheet at the same time it may be shown that this potential change is mainly due to the cathode.

This cannot be due to deposition of copper on the cathode since the effect is quite unchanged if the three electrodes are placed in separate compartments connected only by narrow tubes.

Lewis and Lacey[1] used electrolytic copper sponge for the determination of the single potential of copper and this was undoubtedly contaminated with hydrogen.

Their attempt to show that occluded hydrogen was not taking part in the electrode process was very unconvincing. They found that the presence of 0.0005 *M* sulfuric acid in the solution had no effect upon the e.m.f.

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

If the hydrogen in the copper exists as unsaturated solid solution, as is probably the case, such a solution will show a single potential intermediate between that of pure copper and of a hydrogen electrode. The effect of change of H-ion concentration will, therefore, be much less than in the case of a hydrogen electrode. Also, the extremely small quantity of acid added by Lewis and Lacey, the buffer action of the salt present and the natural acidity of the copper sulfate solution due to hydrolysis (copper hydroxide being a weak base) all indicate that the change of H-ion concentration due to the addition of the acid must have been very small.

If more concentrated acid is used (say 0.05 M), the tendency for the copper to go into solution becomes marked and a considerable *fall* of potential is observed (5 or 6 millivolts) whether the electrode contains hydrogen or not. With an electrode containing hydrogen in very dilute acid, the two effects tend to balance each other.

Lewis and Lacey's experiment, therefore, fails to prove that the original single potential of the copper was not affected by the presence of hydrogen.

2. The precautions taken by most investigators with regard to the purity of the copper salts and the water used preclude the possibility of any serious errors from this source. Further, preliminary experiments showed that quite appreciable quantities of certain impurities—acid, iron salts, etc.—had very little effect upon the measured potentials.

3. It is remarkable that nearly all workers have been unanimous in ascribing the variations in measured single potentials of copper to variations in the nature of the surface.

Preliminary experiments were carried out in order to examine this effect. Various specimens of copper wire, sheet, ingot, etc., were subjected to the most drastic treatment—heating to near the melting point and cooling in ice water or very slowly in an electric furnace, drawing wire through dies, hammering out to thin plates, cleaning with several grades of emery or glass paper, polishing, burnishing, etc., but the results were entirely negative. In no case could any change of potential be definitely ascribed to mechanical conditions. It is evident, therefore, that this effect has been greatly overestimated.

Getman[2] investigated this effect and came to a similar conclusion. Unfortunately, however, he rendered his results of doubtful value by polishing his samples with emery cloth after each treatment, thus destroying to some extent the surface he had been preparing. In the above work all cleaning was done before other treatment, the formation of oxide films during heating being avoided by carrying this out in a vacuum, except in the case where sudden cooling was required. In the latter case the oxide film was removed by scraping with a steel knife and is thus open to criticism, but the remaining cases are sufficient to indicate that the theory of surface strains is

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[2] Getman, *Trans. Am. Electrochem. Soc.*, **26**, 67(1914).

inadequate to explain the large changes of single potential observed when copper is placed in a solution of one of its salts or when different forms of copper (massive, sponge, powder, amalgam, etc.) are used.

On the other hand, the nature of the surface certainly affects the speed of the reaction which occurs between electrode and electrolyte (see under 5). If, therefore, thirty minutes be allowed in each case (as was done by Getman) for this reaction to proceed, differences of potential may well be observed, but these are not true normal potentials.

The maximum potential differences found by Method C, described later, between dead, soft and hard hammered copper and between brightly polished and very rough surfaces were of the order of one millivolt, whereas the values found by Getman vary by 30 millivolts in 0.01 *M* solution and by 200 millivolts in 0.001 *M* solution.

4. The stability of copper sulfate solutions is open to question. It is frequently observed that a bottle of the solution standing for some months in the laboratory deposits a pale blue precipitate. O'Sullivan[3] observed a marked drift of the potential of a quinhydrone electrode in neutral copper sulfate solution amounting to over 20 millivolts in seven days, but accounted for this by the reducing action of the quinhydrone on the copper sulfate. He found that no change was observable in copper sulfate solution which had been kept for a month. From experiments carried out in connection with the present work, it appears probable that if he had used a solution three to six months old, a change would have been observed.

A sample of 0.5 *M* copper sulfate which had been kept in a stoppered measuring flask for three months was compared with a fresh solution by measuring the single potential of a clean copper rod against a mercurous sulfate electrode first in the old solution and then in the new. The rod was cleaned before each immersion and rotated during measurements and a definite difference of potential of 2 to 4 millivolts was observed as a result of about 24 measurements. This would appear to involve a change of the order of 17 to 37% in the concentration of the copper ions in solution. A similar sample of solution which had been kept in a partly filled stoppered bottle for nearly a year and which showed a visible precipitate, gave a value of the single potential of copper 20 millivolts lower than that in a fresh solution. This would imply a reduction of the copper-ion concentration to one-fifth of that in a fresh solution—a very improbable effect. It is possible that crystalline copper sulfate may consist largely of a complex cupri-sulfuric acid and that the real concentration of copper ions in solution is very small and easily disturbed without producing any marked visible effect in the solution as a whole. Possibly also the solution may tend to decompose with the formation of cuprous salt which remains in colloidal solution, and alkali dissolved from the glass container may affect

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[3] O'Sullivan, *Trans. Faraday Soc.*, **23**, 52 (1927).

either of these conditions. In any case, the action under ordinary conditions is a very slow one and cannot account for the rapid changes of 2 millivolts in two minutes frequently observed when a clean copper electrode is placed in old or fresh solution.

5. In order to ascertain whether the electrolyte reacted with the electrode, small copper rods or strips of foil were prepared in various ways and placed in solutions of cupric sulfate, chloride, nitrate and acetate. In every case visible chemical action occurred and the electrodes were coated with basic salts. In some cases, notably with rough electrodes in chloride solutions, the effect was visible after a few seconds' immersion, in other cases it was much slower. A highly polished strip of foil completely covered with a half molar solution of pure copper sulfate and enclosed in a weighing bottle containing only a small quantity of air was not visibly affected during the first twenty-four hours. After four weeks a fairly thick, hard-red deposit was formed on the copper near the surface of the liquid and along minute scratches left by the polishing, but most of the surface was still bright and untarnished. The admission of air materially hastened the formation of further deposit.

In some solutions, crusts a millimeter thick containing visible faces of dark green crystals were formed in less than a week.

Since an invisible film of no more than molecular thickness may profoundly affect the single potential of the metal, it is evident that this action is the main source of all the difficulties experienced in determining the single potential of copper.

The following experiments were carried out, therefore, with a view to eliminate the effect of this film.

Experimental

(A) The first method of attack consisted in an attempt to determine the single potential of the copper immediately after the passage of a very small current either depositing or dissolving copper from an electrode in a half molar solution of the sulfate. For this purpose the rotating commutator apparatus previously used for overvoltage measurements was employed.[4] A Tinsley vernier potentiometer reading to five significant figures with no slide wire and a galvanometer reading to 10^{-9} amp. were used. The subsidiary electrode was a sheet of pure copper and the standard electrode was mercurous sulfate in half molar sulfuric acid.

When the experimental electrode is made the cathode, pure copper is deposited on it and the single potential of this was measured at such a short interval after interrupting the current that the objectionable film of basic salt has no time to form. The deposited copper, however, always contains hydrogen and the single potential will, therefore, always be too low (negative).

On the other hand, when the experimental electrode is the anode, small quantities of metal will be removed continuously from the surface, thus hindering the formation of a basic film but at the same time oxygen or some oxidizing agent is formed on the surface and the measured single potential will be too high (positive).

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[4] Newbery, *J. Chem. Soc.*, **105**, 2420 (1914).

It was hoped that an extrapolation to zero current would eliminate both of these errors. At the same time errors due to local changes of concentration were eliminated by stirring the liquid by means of a small spiral glass stirrer revolving rapidly in front of the electrode. At first currents of a few micro-amperes were tried, but the single potentials observed were very erratic and indefinite. When heavier currents up to 12 milliamperes per sq. cm. were applied, more consistent results were obtained and these are illustrated by the curve shown in Fig. 1, which gives the average values obtained in four complete series of observations. In this curve ordinates represent the single potential in volts (assuming that of the normal mercurous sulfate electrode to be 0.968 volt at 20°) and abscissas the current density in milliamperes per sq. cm.

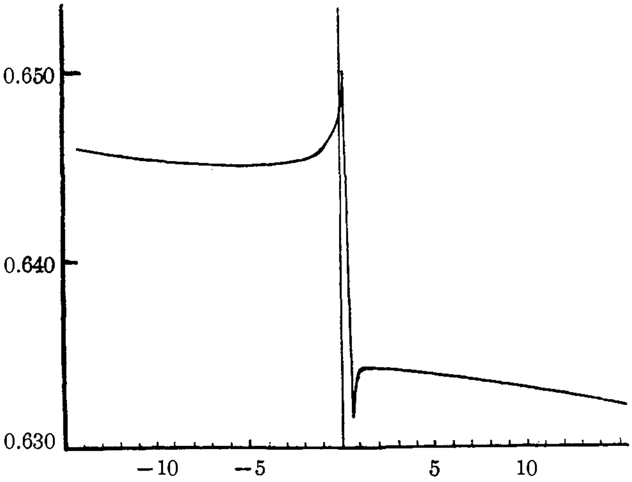

Fig. 1.

It is evident that extrapolation to zero current is quite out of the question with a curve such as this, where the two branches of the curve are pointing in opposite directions instead of approaching each other near the zero line as might have been expected. It is, however, of considerable interest as showing that the production of hydrides or other reducing bodies at the cathode and of oxides or other oxidizing bodies at the anode occurs even at extremely low current densities. In fact, the single potential of the electrode depends greatly upon its previous history for some time past. An attempt was next made to bring the two arms of this curve together by constructing a triple four-part commutator which gave the following cycle: (1) current applied, test electrode cathode; (2) current broken, test electrode connected to potentiometer; (3) current applied, test electrode anode; (4) current broken, test electrode connected to potentiometer. When the commutator gave about twenty complete cycles per second, steady readings were obtained on the potentiometer at all current densities and it was found that these readings were almost unaffected by changes of current density. Nevertheless, the original slow drift of potential again became evident, so it appeared that this treatment could not succeed in preventing formation of films of basic salt.

The addition of sulfuric acid up to a concentration equal to that of the copper salt was next tried with both of the preceding methods but no greater consistency was observed.

(B) The electrochemical methods outlined above having failed to prevent the formation of the basic film, purely chemical methods were next tried. When a strongly acid solution of cupric chloride is treated with metallic copper in excess, the remaining copper appears clean and fairly bright. An attempt was therefore made to prepare a cuprous chloride electrode after the style of the calomel electrode. The above solution was precipitated by the addition of air-free water and washed with normal potassium chloride solution. It was found that the pure white precipitate acquired a yellow stain as soon as the acidity fell below a certain limit even in complete absence of free oxygen, evidently due to hydrolysis of the cuprous chloride. The stain was very slight and the following cell was therefore made up: $Cu \mid CuCl_2 \mid M\ KCl \mid Hg_2Cl_2 \mid Hg$. An average value of 0.1385 volt at 20° was obtained, which was fairly constant for two hours, but this rose to over 0.14 volt in forty-eight hours. This change of potential cannot be due to oxidation of the cuprous chloride since that would have lowered the e.m.f. of the cell. Hence, it must be concluded that chemical action is proceeding between electrode and electrolyte. On dismantling the cell, the copper electrode was found to be coated with a dark brown substance. Other relatively insoluble copper salts were tried with similar results and this line of attack was therefore abandoned.

(C) Since chemical and electrochemical methods failed to produce the desired effect, purely mechanical methods were again resorted to. Very rapid stirring of the electrolyte and very rapid rotation of the electrode were found only to retard the rapid change of potential of copper in various solutions of cupric salts. Mechanical cleaning of the electrode while immersed in the electrolyte would be difficult and results obtained would be open to considerable doubts as to the effect of such cleaning on the equilibrium between electrode and its ions. The electrode was therefore arranged in a rotating holder so that it could be easily and rapidly cleaned, and immersed in the electrolyte immediately after. The glass tube leading from a mercurous sulfate electrode in half molar copper sulfate was arranged alongside the freshly cleaned and still rotating copper electrode and immersion of both effected by quickly raising a beaker containing half molar copper sulfate previously placed below the electrodes. Before this was done the electrodes were connected to the potentiometer, which was set as near as possible to the point expected. Raising the beaker then completed the potentiometer circuit and the *first* direction of movement of the galvanometer was noted. Continued repetition of this process, the electrode being washed, dried and cleaned each time, finally gave a limiting value which could be reproduced with different electrodes repeatedly within a few tenths of a millivolt. The electrodes were in the form of small circular rods or thick wires with flat ends, the upper portions being covered with hard sealing wax; the cleaning was effected with No. 000 emery paper or rouge paper. The final value obtained for the cell $Cu \mid 0.5\ M\ CuSO_4 \mid Hg_2SO_4 \mid Hg$ was 0.3630 ± 0.0005 volt at 20°.

Nielsen and Brown[5] have carried out a series of careful determinations using a two-phase copper amalgam as a standard copper electrode. It appeared of interest, therefore, to compare the above result with such an amalgam electrode. Three samples of copper amalgam were prepared by the electrolysis of acidified copper sulfate solution with a mercury cathode, and after thorough washing and heating to destroy any hydride and expel any adsorbed hydrogen present, were used in the above cell to replace the copper electrode. All three samples gave the value 0.3633 ±0.0003 volt at 20°. We thus arrive at the conclusion that within the limits of experimental error the single potentials of pure copper and of two-phase copper amalgam are identical. Nielsen and Brown's claims for the two-phase

[5] Nielsen and Brown, This Journal, 49, 2423 (1927).

amalgam as a standard form of copper are therefore justified in a wider sense than the authors appeared to expect. At first sight it seems remarkable that the presence of a large quantity of mercury should have absolutely no effect upon the single potential of copper but the case is not without parallel. In the case of the hydrogen electrode, the single potential of the base metal—platinum, palladium, etc.—is completely submerged and that of the dissolved and dissociated atomic hydrogen alone determines the observed values.

The action of the mercury in checking the influence of basic films on copper appears to be similar to its action on aluminum, where the softening of the underlying metal allows of easy fracture of the oxide film with consequent exposure of the metal. Formation of a film is not entirely prevented by the mercury in the case of copper amalgam, as may be shown by allowing an amalgam electrode to stand under pure copper sulfate for some hours. A steady drift of potential occurs similar to that in the case of pure copper but very much slower. After a few days a red crystalline deposit appears on the amalgam but the original single potential is restored by stirring the surface. This very slow change of potential of the amalgam is in marked contrast to that of pure copper, where the true single potential is not constant for more than half a second.

The Standard Potential of Copper.—The absolute values obtained in the previous work were not very reliable for two reasons. (1) No thermostat was used owing to mechanical difficulties involved and the room temperature varied ±1° from 20° during the experiments and (2) the mercurous sulfate electrode was not fresh and showed signs of variation. The main conclusion from this work namely, that the single potentials of pure copper and two-phase copper amalgam are identical, is not affected by the above errors; we are therefore justified in using the convenient amalgam for the determination of the standard potential of copper against a normal solution of cupric ions.

This has already been done by Nielsen and Brown with considerable care but one point in their work is open to criticism. They preserved their amalgam under an acid solution of copper sulfate and the presence of this acid may possibly give rise to the appearance of traces of hydrogen in the electrode—a very dangerous impurity. They are well aware of the fact that freshly prepared copper shows abnormally high reducing power but took no precautions to ensure the absence of hydrogen in their amalgam. Their experiments were therefore repeated in the single case of the cell $\mathrm{Cu{\cdot}Hg} \mid \mathrm{CuSO_4} \mid 0.5\ M\ \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$, using a thermostat adjusted to 25 ± 0.02°. All of the materials used were prepared by methods similar to those used by Nielsen and Brown except that the amalgam before use was heated to near the boiling point of mercury. The value obtained for the above cell in this work was 0.3596 volt, whereas Nielsen and Brown obtained 0.3592 volt. The difference between the two results is so small that it is evident that the amalgam prepared by Nielsen and Brown was free from hydrogen and their results may therefore be accepted as standard values for the pure copper electrode with a considerable degree of confidence.

How far their calculations for the potential of the normal copper electrode are justified is open to doubt since the activity equations break down at such high concentrations. If their value of 0.3502 volt referred to the hydrogen electrode be accepted, then taking the absolute potential of the normal hydrogen electrode as 0.285 volt, the absolute potential of the normal copper electrode will be 0.635 volt as compared with the values 0.60 to 0.62 volt previously given in the literature.

In view of the success of the above work it should be possible to determine the absolute potentials of iron, nickel and cobalt electrodes in the same way. Discrepancies in the values assigned to these metals are far greater than in the case of copper. Work along these lines is already in progress.

Part of the preliminary work was carried out in 1926 at this University by Mr. R. C. MacGaffin, to whom the author tenders his thanks.

Summary

The variations in the single potential of a copper electrode have been traced to the formation of insoluble films of basic cuprous or cupric salts on the electrode surface. These films are produced by the chemical action of the electrolyte upon the metallic copper, more rapidly in the presence of air, and may attain a thickness of 1 millimeter in a few days.

A method is described whereby the single potential of the copper electrode is measured before the film has time to form.

The single potential of a two-phase copper amalgam is identical with that of pure copper but much easier to measure with accuracy. Reasons for this are given.

Nielsen and Brown's work on the two-phase copper amalgam may be accepted as standard for pure copper.

The absolute potential of the normal copper (cupric) electrode is 0.635 volt if that of the normal hydrogen electrode is 0.285 volt.

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