146. *Studies on Some Metal Electrodes. Part I. Oxide-film Formation on Copper, and the Evaluation of the Standard Electrode Potential of the Metal.*

By A. Riad Tourky and S. E. S. El Wakkad.

Oxide-film formation on the surface of a metal immersed in a solution of its ions is liable to obstruct the regular transfer of ions to and from the metal, with the result that the thermodynamic potentials are not attained. We tried to study this effect on the evaluation of the standard electrode potential of copper, taking into consideration that with an oxide film on its surface it may respond to variations in pH and that the oxide may be removed by subjecting the electrode to hydrogen and to high vacuum at high temperatures. By comparing the results obtained in and out of contact with air in buffers initially free from copper ions, a set of conditions could be chosen leading to the evaluation of the true standard electrode potential. In air, the electrode was found to behave as an indicator electrode for hydrogen ions from pH 4·65 to 8·0 with $\Delta E/\Delta$pH and E_0 values coinciding practically with those for a Cu–Cu_2O electrode. Out of contact with air, an oxide was found to form on the metal between pH 6·77 and 8·0. This and the subsequent behaviour of the electrode in solutions of higher pH are discussed in the light of the amphoteric properties of cuprous oxide.

By evaluating the standard electrode potential of copper under conditions not favouring the formation of an oxide, a value of 0·3457 v. as compared with 0·3420 v. in air was obtained. With the help of the former value the activity coefficients of some copper sulphate solutions were obtained.

The establishment of a true thermodynamic equilibrium between a metal and its ions in solution imposes the condition that no other process than the reversible transfer of metal ions between metal and solution should take place. Local action processes, due, *e.g.*, to oxide-film formation on the surface of the metal, should therefore be absent as this may obstruct the regular transfer of ions to an extent depending on the properties of both film and solution (Müller, *Monatsh.*, 1936, **69**, 437; *Z. Elektrochem.*, 1936, **42**, 789, 830; 1937, **43**, 561; *Kolloid-Z.*, 1938, **86**, 150). The non-recognition of this factor by many previous investigators, or the application of less efficient means for removing oxide films, is responsible, at least in part, for the discrepancies observed in the values of many standard electrode potentials.

A metal with an oxide film on its surface is liable to respond to variations in pH in solutions free from the metal ions. It should therefore be possible, from a study of the electrodic behaviour in such solutions, to ascertain whether or not the potentials set up in solutions containing the metal ions are the pure metal–metal ion potentials. Copper was chosen for this investigation on account of the comparative ease with which an oxide film formed on its surface can be removed by reduction with hydrogen. Its electrodic behaviour can therefore be studied in buffer solutions initially free from the metal ions in and then out of contact with air after removal of the oxide film from its surface. In the light of the results obtained, that set of conditions can be chosen which is capable of leading to the evaluation of the true standard electrode potential.

EXPERIMENTAL.

Copper Electrodes.—In order to eliminate differences due to variations in the physical state of the metal, the electrodes were prepared by electrodeposition according to the method of Lewis and Lacey (*J. Amer. Chem. Soc.*, 1914, **36**, 804; see also Getman, *Trans. Amer. Electrochem. Soc.*, 1914, **26**, 67; Denham and Pennycuick, *J. Amer. Chem. Soc.*, 1923, **45**, 1355; Oku, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, **1**, 84). The electrodes so prepared were considered to be satisfactory in every respect save for occluded hydrogen, to which were mostly attributed variations in the standard potential of the metal.

FIG. 1.

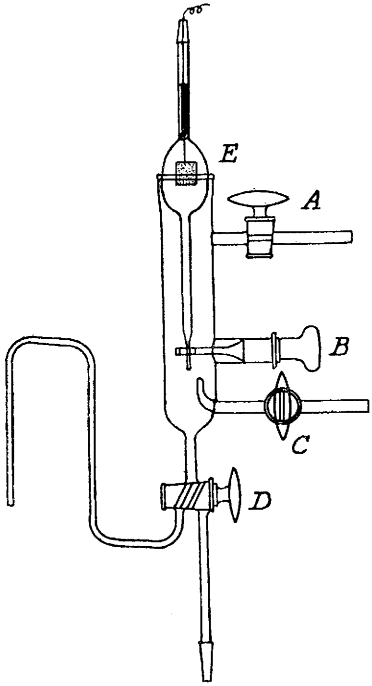
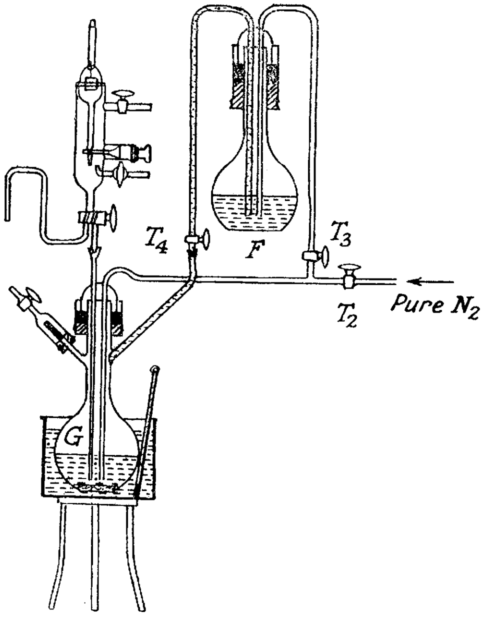


FIG. 2.



The deposition was made on platinum plates 1 × 1 cm. each sealed to glass tubes partly filled with mercury. They were always freshly prepared and were carefully rinsed with redistilled water and with the solution to be used immediately before immersion.

Buffer Solutions.—We first used as series of buffers nine acetic acid–acetate mixtures covering the pH range 3·62—5·61, which approximately coincides with the same range of copper sulphate solutions of ordinary dilutions. These were made each of the constant ionic strength 0·04 according to Cohn's method (*J. Amer. Chem. Soc.*, 1927, **49**, 173; Cohn, Heyroth, and Menkin, *ibid.*, 1928, **50**, 696). Later another series was used consisting of the dipotassium hydrogen phosphate–borax buffer of pH 6·0 (Kolthoff), the boric acid–borax buffers of pH values 6·77, 7·09, 8·08, and 9·11 (Paletzsch), and the boric acid–sodium hydroxide buffer (Clark and Lubs; cf. Clark, " The Determination of Hydrogen Ions ", London, 1928, pp. 192 *et seq.*). All buffers were prepared as recommended by the respective authors and their pH values were carefully checked by means of the hydrogen electrode. Owing to inherent difficulties, the second series could not be made of the same ionic strength.

Preparation of Electrodes and Solutions for Measurements out of Contact with Air.—In order to eliminate the effect of atmospheric oxygen on electrode and solution, a device was constructed, in which the electrode could be alternately heated in a vacuum and subjected to the action of hydrogen at ~350°, a temperature which was considered high enough to ensure the reduction of any oxide on the metal and the removal of adsorbed gases. Another device (Fig. 1), essentially similar to that used by Müller and Dürichen (*Z. physikal. Chem.*, 1938, *A*, **182**, 233), served for holding electrode and oxygen-free solution.

The hydrogen, supplied from a cylinder, was purified as recommended by Noyes (*J. Amer. Chem. Soc.*, 1907, **29**, 1718).

The electrode jacket holding the electrode E was ground from outside in such a manner so as to fit tightly into the vessel to hold the solution. After being sealed off at the capillary constriction, the electrode jacket was fitted into the vessel with the capillary end passing through the loop-hole of the joint B. When this was turned, it broke the capillary tip and allowed the solution to fill the evacuated electrode jacket. Taps C and A served as inlet and outlet for pure nitrogen, which was bubbled through the solutions to ensure the removal of any traces of dissolved oxygen.

Before introduction of the solution through D, the vessel was alternately evacuated and filled with pure nitrogen several times so as to ensure that the traces of gas remaining after evacuation consisted only of that gas. The tube connected to tap D served as lead to the other half-cell used.

After thorough washing to remove any adhering liquid from the electrolysis cell, the freshly prepared electrode was sealed into the high-vacuum device so as to form a capillary constriction. Evacuation was then started, and in the meantime, the electric oven packed with asbestos and holding the electrode jacket was gradually heated to $\sim$350°. It was kept at that temperature for at least $\frac{1}{2}$ hour before hydrogen was introduced. As the gas was not made to flow through the device, a process which aids in the removal of water vapour from the electrode surface, the apparatus was subjected to high vacuum once every two hours at the same high temperature after the electrode had been subjected to the reducing action of the gas for about one hour. The operation was repeated at least three times before the electrode was sealed off at the capillary constriction and left to cool.

Copper Sulphate Solutions.—" AnalaR " Copper sulphate was twice recrystallised. The oxygen-free solutions were prepared by means of the device shown in Fig. 2 as follows : Flask F was removed, filled to about two-thirds of its capacity with boiling conductivity water, and brought to its original position. Pure nitrogen was then allowed to bubble through till the water had cooled. It was then sucked out from a joint below T_4 till the tube was filled, and T_4 was then closed. A weighed amount of the copper sulphate stock solution was also introduced into the calibrated flask G before it was connected to F and the electrode vessel. Nitrogen was then bubbled into flask G through T_2 for some time and was kept bubbling while T_4 was turned round, allowing the conductivity water to run into G till it was filled to just below the mark on the constricted neck. A small water thermostat adjusted at 30° (temperature at which the flask was calibrated) was then placed in position, immersing flask F to the neck. After equilibrium had been attained, and the well-mixed solution adjusted to the mark, T_2 was closed and the solution was now ready for admittance into the carefully evacuated copper electrode half-cell.

The gram-molarities of the solutions were further checked by determining electrolytically the copper content of accurately weighed portions at least three times in each case. The density of each solution was determined also at least thrice at 30° pyknometers with platinum hooks being used. The results of some density measurements are shown in Table I.

TABLE I.

Molarity, M	1·1040	0·4071	0·1764	0·1076	0·0559	0·0067
Density	1·1644	1·0599	1·0236	1·0130	1·0040	0·9966

By plotting these values together with others obtained from the International Critical Tables (1928, III, p. 67) against composition, a straight line was obtained connecting all points.

The nitrogen used as the inert atmosphere was supplied from a cylinder and contained a small amount of oxygen but hardly any carbon dioxide. It was purified by allowing it to pass slowly through three tubes packed with copper filings and heated electrically to $\sim$400°, then through a train of bubblers containing successively in pairs pyrogallol, dilute sulphuric acid, potassium hydroxide, silver nitrate, and concentrated sulphuric acid, and lastly through a long tube packed with asbestos wool. It was not necessary to modify the device so as to saturate the gas with water vapour at the vapour pressure of the solutions as these were checked by analysis after each dilution.

Electrical Measurements.—Measurements in the buffer solutions were performed in the usual manner, using a saturated calomel half-cell as the reference electrode. In order to avoid its preparation according to exact specifications, we did not make use of any assigned E_0 value but determined, following the suggestion of Harned and Owen (" The Physical Chemistry of Electrolytic Solutions ", New York, 1943, pp. 316 *et seq.*), its experimental E_0pH value under the prevailing conditions in buffers with acids of known dissociation constants. The experimental E_0pH involving all necessary corrections amounted to 0·2413 v. at 30° as compared, *e.g.*, with Clark's value of 0·2420 v. (*op. cit.*, p. 455). The reference half-cell was kept during the whole experimental period in an air thermostat at the working temperature of 30° $\pm$0·02°. An N.P.L. calibrated cadmium cell and an Onwood mirror galvanometer having a sensitivity of 190 mm./microamp. were used. Unless greater accuracy was required (as for the evaluation of the standard electrode potential of the metal) the potentials were measured to the nearest millivolt.

Measurements in the copper sulphate solutions were performed against a mercury–mercurous sulphate half-cell, the mercury of which was purified as recommended by Hullet and Minchin (*Physical Rev.*, 1905, **21**, 388). The mercurous sulphate was prepared according to the method of Partington and Stonehill (*Trans. Faraday Soc.*, 1935, **31**, 1357) by electrolysis of a sulphuric acid solution between a platinum cathode and an anode of purified mercury.

RESULTS AND DISCUSSIONS.

(1) *The Behaviour of the Electrode in Solutions of Varying* pH *and Initially Free from Copper Ions in Air.*—(A) *The behaviour of the electrode after immersion.* On examining the electrode in solutions of varying pH in air it was observed that :

(i) Except in the most alkaline solutions used, steady-state potentials are attained in the unstirred solutions within 1—2 hours. These remain practically constant in the more acid solutions ($<$pH 4·7) for the next 20 hours, but as the solutions become less acid they undergo a gradual change, the extent of which varies from one electrode to the other and does not seem to depend in a regular manner on the pH values of the solutions.

(ii) The immersion as well as the steady-state potentials approach each other closely in the more acid solutions (pH 3·62—4·83). They correspond within that pH range at the steady state to comparatively high copper-ion activities, the mean value being lower only by ~120 mv. than the standard $Cu–Cu^{++}$ potential. With increasing pH up to 9·11 the potentials decrease both on immersion and at the steady states.

(iii The manner in which the steady-state potentials are approached depends on the pH values of the solutions. For instance, from pH 3·62 to 4·83 they are approached chiefly from smaller, whereas from pH 5·00 to 8·08 they are mostly approached from higher initial values.

The fact that the potentials approach each other in the more acid solutions below ~ pH 5·0, attaining high values which then decrease with increasing pH, points to a considerable break down of the film below, and an increase in its area, probably by precipitation or oxidation above that pH. The potential-determining ions within the former range may be thought of as consisting mainly of Cu^{++} and Cu^+ ions originating presumably from the anodic dissolution of the metal by local action processes, or in the case of Cu^+ ions from the dissolution of cuprous oxide, the stable oxide in contact with the metal (Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529; Evans, *J.*, 1925, **127**, 2484; Haase, *Metallw.*, 1932, **11**, 516; Bengough *et al.*, *J. Inst. Metals*, 1913, **10**, 13; 1916, **15**, 27; 1919, **21**, 37; 1920, **23**, 97; 1924, **32**, 108). The relative amounts of both ionic species will be governed by the equilibrium constant of the reaction $Cu + Cu^{++} \rightleftharpoons 2Cu^+ (K = 10^{-6})$ provided that both ions can come freely in contact with the metal and that the solution at the interphase has been freed from dissolved oxygen.

Assuming now that the relations which govern ionic equilibria in the bulk solution can be applied to equilibria at the interphase, that the ionic product $S_{Cu(OH)_2} = 5{\cdot}6 \times 10^{-20}$ (cf. Latimer, "Oxidation Potentials", New York, 1938, p. 174) and $S_{CuOH} = 7{\cdot}18 \times 10^{-14}$ (unpublished), and by taking E_0 of the $Cu–Cu^{++}$ couple as 0·3457 v. (Section 3), and 0·236 v., the steady-state value at pH 3·62 (Table II) as representing a pure metal–metal ion potential with a minimum of polarisation, then at the interphase $a_{Cu^+} = 1{\cdot}712 \times 10^{-5}$ and $a_{Cu^{++}} = 2{\cdot}205 \times 10^{-4}$.

When in a mixture containing both ionic species $a_{OH'}$ is progressively increased, cuprous hydroxide alone will be precipitate till $a_{Cu^+}/a_{Cu^{++}}$ has become $\geq S_{CuOH}/S_{Cu(OH)_2} = 1{\cdot}90 \times 10^{-5}$, or when

$$a_{Cu^+} = 1{\cdot}90 \times 10^{-5} \times 1{\cdot}49 \times 10^{-2} = 2{\cdot}8 \times 10^{-7}$$

As the actual value of a_{Cu^+} as calculated is greater, cuprous hydroxide will be precipitated first. Any initially precipitated cupric hydroxide will also be reduced in the presence of the metal, for otherwise no steady-state potential values could be obtained owing to the instability of the $Cu–CuO–OH^-$ couple (Britton, *J.* 1925, **127**, 2796; Maier, *J. Amer. Chem. Soc.*, 1929, **51**, 194). With a value of $a_{Cu^+} = 1{\cdot}712 \times 10^{-5}$ and K_W at 30° $= 1{\cdot}469 \times 10^{-14}$ (Harned and Owen, *op. cit.*, p. 485), we have

$$1{\cdot}712 \times 10^{-5} \times 1{\cdot}469 \times 10^{-14}/a_{H^+} = 7{\cdot}18 \times 10^{-14}$$

hence the pH value at which precipitation begins = 5·46, which compares with the experimental value of ~ pH 5·00 (see below). The lower actual value may be expected owing to the effect of dissolved oxygen which, on being charged, provides the solution at the interphase with hydroxyl ions, making it more alkaline, and owing to the circumstance that a_{Cu^+} might actually be greater (Section 2). In the absence of atmospheric oxygen, the pH value of precipitation as calculated coincides more closely with the experimental one.

(iv) At pH 9·11 and more manifestly at pH 10·00, a continuous drift in potential was observed which only died out after 40—50 hours in the unstirred solutions. The immersion potential at the latter pH, which was smaller in magnitude than any corresponding one at lower pH, increased at first quickly, attaining in one case, for example, the value of 0·197 v. after 2½ hours as compared with the steady-state value of 0·205 v. at pH 5·00 obtained after the same period of time, and then slowly till it ceased at an e.m.f. of 0·222 v., thus approximating to the steady state at pH 4·83. Evidently the irreversible process leading to the drift involves the depletion of the solution at the interphase of its hydroxyl ions. We intend to study this phenomenon in some detail.

The conclusion which can be drawn from the foregoing results is that on immersion an oxide film initially formed on the metal dissolves in solutions with pH values lower than 4·65. Above this limit an oxide persists or is newly formed on the metal. It is now desirable to find out whether, in the presence of an oxide on its surface, the electrode behaves rightly as a metal–metal oxide electrode.

(B) *Behaviour of the electrode as a metal–metal oxide electrode.* Table II contains the results of one representative set of measurements in both series of buffers. In this table E_h represents the steady-state potentials (or, at pH 9·11 and 10·00, the potentials obtained after $2\frac{1}{2}$ hours) as referred to the hydrogen electrode. By plotting these values against pH and extrapolating to pH = 0, an E_{0h} value of 0·507 v. at 30° is obtained. With the help of this value one can calculate the change in potential of the copper electrode per unit pH ($\Delta E/\Delta$pH). The values as shown in Table II are not constant from pH 3·62 to 4·47, but thereafter to pH 8·08 they are practically constant, yielding a mean value of 0·060 v.

TABLE II.

pH	3·62	4·02	4·26	4·47	4·65	4·83	5·00
E_h	0·236	0·228	0·223	0·230	0·227	0·219	0·205
$\Delta E/\Delta$pH	0·075	0·069	0·067	0·062	0·060	0·060	0·060
pH	5·27	5·61	6·00	7·09	8·08	9·11	10·00
E_h	0·188	0·169	0·153	0·083	0·026	(0·020)	(0·197)
$\Delta E/\Delta$pH	0·060	0·060	0·059	0·060	0·060	0·053	0·031

The results indicate that the spongy copper electrode responds to variations in pH from 4·65 to 8·08, a range which coincides in part with that of the more dilute copper sulphate solutions. This cannot be attributed to adsorbed hydrogen, since the pressure of this gas, as calculated from the relation $E = (\boldsymbol{R}T/2\boldsymbol{F}) \log P_1/P_2$ in which E is set equal to 0·507 v., the standard potential at unit a_{H^+}, amounts only to the partial pressure of $1{\cdot}26 \times 10^{-17}$ atm., a negligible quantity with which a hydrogen electrode cannot be conceived to be in equilibrium. The linearity of the potential–pH relation within that range, and the fact that $\Delta E/\Delta$pH is practically identical with the theoretical value, indicates that we have here a well-defined metal–metal oxide electrode which behaves theoretically as a hydrogen electrode. It seemed now desirable to find out whether the electrical measurements confirm the formation of cuprous rather than cupric oxide on the metal. One way of approach is to ascertain whether the oxygen pressure as calculated from the electrical measurements conforms with that of cuprous oxide, the stable oxide in contact with the metal, as calculated from thermal data. Assuming that the thermodynamic relation

$$E = E' + \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln P_{\text{H}_2} + \frac{\boldsymbol{R}T}{4\boldsymbol{F}} \ln P_{\text{O}_2}$$

in which E is set equal to 0·507 and E' is assumed to have the theoretical value of 1·221 v. at 30°, is obeyed, P_{O_2} will amount to $2{\cdot}512 \times 10^{-48}$ atm. For computing P_{O_2} at the same temperature from thermal data, one can proceed as follows : Assuming that the course taken on decomposition is represented by $2\text{Cu}_2\text{O} \rightleftharpoons 4\text{Cu} + \text{O}_2$, we have $P_{\text{O}_2}(a_{\text{Cu}}{}^2/a_{\text{Cu}_2\text{O}})^2 = K$. Provided that no solid solutions are formed, K will equal P_{O_2}. One can now substitute in the familiar relation

$$\boldsymbol{R}T \ln K = \Delta F = \Delta H - T\Delta S$$

by setting $T = 303{\cdot}15°$ and $\Delta H = 39{\cdot}900$ kcals./mole (" International Critical Tables ", 1929, Vol. 5, p. 187). In evaluating this latter quantity, 25° was referred to as the standard temperature. As for most purposes, however, the effect of a few degrees on heats of formation is unimportant, ΔH of the reaction can be considered the same at 30° as at 25°. We have further

$$\Delta S_{303\cdot15} = S_{4\text{Cu}} + S_{\text{O}_2} - S_{2\text{Cu}_2\text{O}} = 32{\cdot}292 + 49{\cdot}146 - 48{\cdot}546 = 32{\cdot}892 \text{ kcals./degree-mole}$$

the entropies being corrected to 303·15° from Latimer's values at 298·15° (*op. cit.*, p. 170) by integration between both temperatures, using C_p values of 6·2, 6·92, and 16·4 for copper, oxygen, and cuprous oxide respectively. Hence $\boldsymbol{R}T \log P_{\text{O}_2} = 79{\cdot}800 - 32{\cdot}892T$ and $P_{\text{O}_2} = 4{\cdot}47 \times 10^{-51}$ atm. The deviations are probably due to the assumptions made and the uncertainties in the quantities used. By proceeding in the same manner for cupric oxide, a value of the order of 10^{-35} atm. is obtained, which deviates greatly from the value computed from the electrical data.

(2) *The Behaviour of the Electrode in Solutions of Varying* pH *and Initially Free from Copper Ions out of Contact with Air.*—In examining the electrode in oxygen-free solutions of varying pH after subjecting it alternately to hydrogen gas and high vacuum at ~350°, the following facts were observed :

(i) The immersion as well as the steady-state potentials for any pH are always lower than those attained in air. The steady-state values in the first eight buffers (pH 3·62—5·61) approach the redox potential of the Cu^+–Cu^{++} couple, the maximum deviations from the hitherto accepted value of 0·187 v. amounting only to 16 mv. This may be ascribed to the circumstance that, in the absence of an oxide film to provide the solution with copper ions and of dissolved oxygen to function as an electron-acceptor from the metal, the process at the interphase in the more acid solutions will mainly be limited to metal dissolution and hydrogen-ion discharge. As in other cases of hydrogen evolution through copper, the process may be looked upon as being due to a negative metal–metal ion potential relative to that of the hydrogen electrode under the given set of conditions (Schikorr, " Die Zersetzungserscheinungen der Metalle ", Leipzig, 1943; Ann Arbor, Michigan, 1945, p. 12). When dissolved in initially copper-ion-free solutions, cupric ions will first be released from the metal, the potential caused by their accumulation at the interphase becoming increasingly positive and approaching that of the Cu–Cu^+ couple. Cuprous ions will then pass into solution until both potentials have become equal, a condition which is satisfied when the redox potential of the system Cu^+–Cu^{++} has been attained. Now under normal conditions the reaction $Cu \rightarrow Cu^+$ is opposed by the equilibrium reaction $2Cu^+ \rightleftharpoons Cu^{++} + Cu$, which leads to a considerable decrease in the activity of cuprous ions. However, since hydrogen evolution on copper is subject to a certain amount of overvoltage, it is likely that a stable film permeable only to electrons will cover the metal, rendering it an inert electrode in a redox system. A similar state of affairs might occur in air, in which case the relative amount of cupric ions and correspondingly the potential set up will be greater owing to oxidation through atmospheric oxygen.

(ii) The steady-state potentials are approached from lower initial values up to pH 5·61 and from higher values from pH 6·77. It can be readily shown that the copper electrode behaves as a metal–metal oxide electrode between the latter pH and pH 8·08, the same upper limit in air. It behaves also as such, as will be shown below, in more concentrated alkali hydroxide solutions from pH 10·83 to 13·91. In that latter set of solutions the carefully protected electrode was found to attain gradually the tint characteristic of cuprous oxide. This led us to the view that the reaction $4OH^- \longrightarrow 2H_2O + O_2 + 4\varepsilon$ was enhanced at the electrode surface, leading to its oxidation and to the observed decreasing trend of the potentials with time. A similar phenomenon was observed in this laboratory by A. Mousa with arsenic electrodes, prepared either by subliming the metal or by decomposing arsine under hydrogen, even when they were immersed in acid buffers of comparatively low pH. If this were the case, hydrogen- as well as hydroxyl-ion discharge should be considered as possible processes taking place at the protected electrode surface, the predominance of either depending upon the pH of the solution and in turn upon the solubility product of the hydroxide. By proceeding as in Section 1, taking 0·180 v. as an average steady-state potential, $a_{Cu^+} = a_{Cu^{++}}$ and $E_{Cu-Cu^{++}} = 0{\cdot}3457$ v., we find that the pH value at which precipitation should occur is 6·2, *i.e.*, between pH 6·00 and 6·77 (see Fig. 3). In order to find whether the pH limits between which the protected copper electrode behaves as a metal–metal oxide electrode were not merely accidental, depending on the presence of a trace of the oxide sufficient to saturate the solution at the interphase, the experimental conditions were varied but mainly substantiated the same results : seven different electrodes were subjected at varying temperatures between 300° and 400° for prolonged periods of time to hydrogen so as to ensure in each case the attainment of equilibrium, and were used singly in carefully prepared and checked buffers.

(iii) Above pH 8·00 the electrode does not respond readily to variation in pH, probably owing to the small extent of ionisation near the isoelectric point and the scarcity of the metal ion caused by varying the pH. At pH 10·00, it manifested the same continuous drift with time towards more positive values as in air. The drift ceased, however, after 20 hours at a value of 0·186 v., *i.e.*, at the same limiting value above which the electrode functions as a metal–metal oxide electrode and below which it functions as an inert electrode in a redox system.

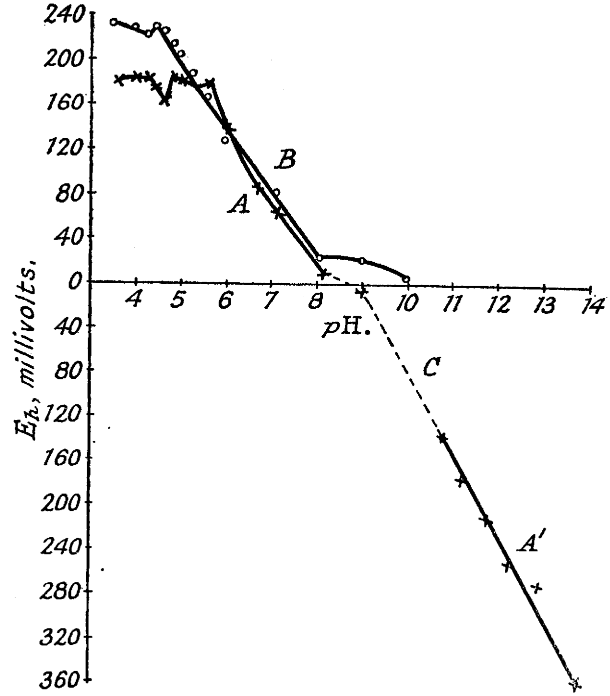
In order to complete the picture on the behaviour of the electrode in solutions of varying pH, and owing to the stability of the Cu–Cu_2O–OH^- couple out of contact with air, the electrode behaviour was studied in solutions more alkaline than pH 10·00. For this purpose, and owing to the difficulty of obtaining suitable buffers, sodium hydroxide solutions of various concentrations (1·709 N to $1{\cdot}99 \times 10^{-4}$ N) were prepared by accurate volumetric dilution in the absence of carbon dioxide and were checked by titration against standard hydrochloric acid. Their pOH values were calculated by using activity coefficients at 30° (Harned and Owen, *op. cit.*, p. 560), and the corresponding pH values were obtained by subtraction from pK_w at the same temperature. The results of one set of measurements are recorded in Table III, in which the figures in the lower row represent the steady states, or otherwise, when drifting took place (figures in parentheses) the values obtained after 2½ hours. The drift during 20 hours at pH 10·30 was 0·100 v. but decreased steadily to the minimum value of 2 mv. at pH 10·83. From this pH up to pH 13·91, the electrode functioned again as a metal–metal oxide electrode, yielding steady-state potentials that were approached from more positive values after about one hour.

TABLE III.

pH	13·93	13·01	12·31	11·83	10·85	10·81	10·63	10·37	10·30	10·13
E_h	−0·360	−0·273	−0·251	−0·174	−0·136	(0·107)	(0·132)	(0·088)	(0·082)	(0·122)

The results of measurements out of contact with air throughout the whole range from pH 3·6 to 13·9 are represented in Fig. 3 by the curve *AA′*. For comparison, the results of measurements in air are also shown by curve *B*. The region above pH 8·08 through which the electrode does not respond regularly to variations in pH is represented by the broken line *C*.

FIG. 3.



In order to account for the behaviour of the protected copper electrode as represented by the curve *AA′*, one should consider the manner in which cuprous oxide dissolves and dissociates in solutions of different pH values. It can be deduced from Laue's work (*Z. anorg. Chem.*, 1927, **165**, 305) on the amphoteric properties of metal hydroxides that the isoelectric point of cuprous hydroxide should be on the alkaline side somewhere below that of silver hydroxide, *i. e.*, below pH 12. When dissociating as a base, a_{Cu^+} in solution will decrease with increase of pH till a limiting value is reached at the isoelectric point, whereupon the hydroxide begins to dissociate as an acid with increasing dissociation as the pH is further increased.

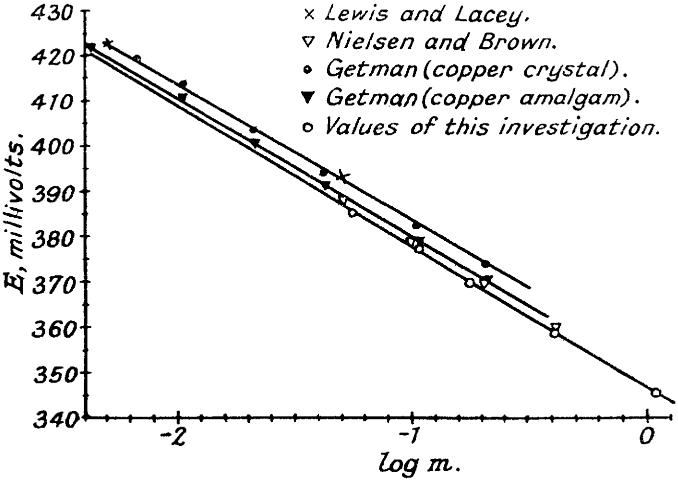
Trials to determine the exact position of the isoelectric point by analytical methods failed on account of the non-response of all known reagents to variations in the copper-ion concentrations at these dilutions. If it were permissible to locate that point within the region of disturbance represented by the dotted line, then it should lie at about pH 9·4.

It may be noted that the drift taking place within the region of the isoelectric point is independent of the nature of the solution used, for it revealed itself not only in the boric acid–sodium hydroxide buffer but in a sodium carbonate–hydrochloric acid buffer, as well as in the sodium hydroxide solutions. It may further be noted that the results did not diverge to any marked extent from those represented by curve *A* when pure cuprous oxide (prepared in the absence of atmospheric oxygen) was introduced in the copper electrode half-cell except perhaps for the attainment of the steady-state potentials more quickly.

(3) *Evaluation of the Standard Potential of Copper.*—The foregoing studies have shown that an oxide film persists on the electrode surface in air above pH 4·65. Out of contact with air, and after the electrode has been subjected to the reducing action of hydrogen and a high vacuum, an oxide film forms on the metal somewhat above pH 6. Accordingly, measurements in copper sulphate solutions under the latter conditions should lead to the evaluation of the true standard electrode potential. For this purpose the copper-electrode potentials were measured in the copper sulphate solutions of the previous molarities (see Table I) in cells without liquid junction of the type Hg | Hg_2SO_4 | xM-$CuSO_4$ | Cu, which were designed to allow the measurements to be taken out of contact with air.

By plotting the equilibrium values usually attained after about 30 minutes, and which were constant and reproducible, against the logarithms of molarity, a straight line is obtained as shown in Fig. 4. For comparison, the values obtained by Lewis and Lacey (*loc. cit.*), by Nielsen and Brown (*ibid.*, 1927, **49**, 2423), and by Getman (*J. Physical Chem.*, 1930, **34**, 1454) are plotted in the same manner.

FIG. 4.



For the reaction occurring in the cell the equation connecting the e.m.f. with the activities of the cell components is as follows :

$$E = E_0 - \frac{RT}{2F} \ln \frac{a_{CuSO_4} a_{Hg}^2}{a_{Cu} a_{Hg_2SO_4}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

which reduces to

$$E = E_0 - \frac{RT}{2F} \ln a_{CuSO_4} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

since mercury, copper, and mercurous sulphate are in their standard states and it is customary to assign the value unity to the activity of such components. Further, since by convention $a_{CuSO_4} = a_{Cu^{++}} a_{SO_4^{--}} = (fm)^2$, equation (2) becomes at 30°

$$E = E_0 - 0{\cdot}06005 \log fm \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Following Lewis and Randall's procedure ("Thermodynamics", 1923, New York and London, p. 334), equation (3) can be rearranged as follows :

$$E_0 = 0{\cdot}06005 \log f + (E + 0{\cdot}06005 \log m) \quad . \; . \; . \; . \; . \quad (4)$$

If we designate the quantity in parentheses as E_0^{I} and plot this against any function of the concentration such as the square root of the ionic product μ, the limit approached by the ordinate at infinite dilution will be equal to E_0, the standard electrode potential. In Table IV are given the values of E_0^{I} calculated by the above equation at rounded concentrations.

TABLE IV.

M.	E.m.f. of cell.	$\mu^{1/2}$.	E_0^{I}.	E_0^{II}.	E_0^{III}.
1·00	0·3473	2·000	0·3473	0·3510	—
0·70	0·3520	1·673	0·3427	—	—
0·50	0·3565	1·415	0·3384	0·3416	—
0·20	0·3685	0·8943	0·3265	0·3292	0·3331
0·10	0·3778	0·6324	0·3177	0·3196	0·3236
0·07	0·3825	0·5291	0·3131	—	—
0·05	0·3868	0·4472	0·3086	0·3108	0·3148
0·02	0·3993	0·2831	0·2972	0·3009	0·3042
0·01	0·4087	0·2000	0·2886	0·2926	0·2961
0·007	0·4135	0·1673	0·2841	—	—
0·005	—	0·1415	—	0·2857	0·2892

The values under E_0^{II} and E_0^{III} were those obtained by Getman with the copper amalgam and the copper crystal electrode, respectively. By plotting the E_0^{I} values against $\mu^{1/2}$ and assuming that E_0^{I} remains a rectilinear function of $\mu^{1/2}$ at greater dilutions, we obtain a limiting value for our cell equal to 0·2654 v. at 30° as compared with 0·2715 v. for the amalgam electrode and 0·2738 v. for the crystal electrode at 25° and with 0·2765 v. for Lewis and Lacey's spongy electrode.

Now, according to Harned and Hammer (*J. Amer. Chem. Soc.*, 1935, **57**, 9), the potential of the mercury–mercurous sulphate electrode is 0·61107 at 30°. From this it follows that the standard potential of the copper electrode in copper sulphate solutions is 0·3457 at 30°. Müller and Reuther (*Z. Elektrochem.*, 1943, **49**, 277) found that $\Delta E/\Delta t$ for the standard potential of the copper electrode between 20° and 50° was only 0·01 mv./degree, which they ascribed to the circumstance that the non-isothermal temperature coefficient of the standard copper-electrode potential was of the same order of magnitude as that of the standard hydrogen electrode. This implies that for a change in temperature from 30° to 25° there will be a change of 0·05 mv., which is beyond the limit of accuracy in our experiments.

In Table V are given the values obtained by different authors. Col. 3 shows the original values assigned by them, and col. 4 contains the corrected values after assigning to the reference electrode the more recent value of Harned and Hammer at the respective temperature. For comparison, another value obtained in this laboratory by following the same procedure as given above but in air with the unprotected spongy copper electrode is also inserted. Under these conditions the E_0^{I}–$\mu^{1/2}$ plot was found to lie below that of the protected electrode.

TABLE V.

Author.	Type of electrode.	E_0.	E_0 (corr.).
Lewis and Lacey [1]	Spongy copper	0·3469	0·3453
Nielsen and Brown [2]	Copper amalgam	0·3502	—
Newbery [3]	Copper amalgam	0·3502	—
Getman [4]	Copper crystal	0·3475	0·3414
Getman [4]	Copper amalgam	0·3498	0·3437
Present value	Spongy copper (protected)	—	0·3457
Present value	Spongy copper (unprotected)	—	0·3420

[1] *Loc. cit.* [2] *Loc. cit.* [3] *J. Amer. Chem. Soc.*, 1929, **54**, 1315. [4] *Loc. cit.*, 1930.

The data in Table V show that the value obtained with Getman's crystal copper electrode approaches closely the value obtained in this investigation in air. The values obtained with the copper amalgam electrodes are somewhat higher and are also very close to each other before correction. The only value which could be corrected by assigning the most recent value to the mercury–mercurous sulphate half-cell is that of Getman, and it is remarkable that it is somewhat higher than the value obtained in air but lower than that obtained out of contact with air in this investigation. It is apparent that the higher values obtained with the amalgam electrodes in air are due to the decreased tendency of copper in them to be oxidised. In this connection reference may be made to the higher and lower potential values obtained respectively with cathodically and anodically polarised copper electrodes (Newbery, *loc. cit.*).

Possible Errors.—All our weights, volumetric apparatus, etc., were carefully calibrated. The standard cell which served as the standard of the electromotive force had been calibrated by the N.P.L. and was correct to 0·0001 volt. The value of the mercury–mercurous sulphate electrode is also accurate to the fourth decimal place. The concentration of each of our solutions as determined by analysis is accurate to 0·01%. The e.m.f. measurements were carried out by using a calibrated metre bridge on which readings accurate to 0·02 cm. could be easily read. From this the accuracy of measured e.m.f. values is limited to 0·0004 v., which is the maximum error.

The Activity Coefficient of Copper Sulphate Solutions.—By introducing the value of E_0 into the equation $E_0 = E - 0{\cdot}06005 \log fm$, the values of the activity coefficients at different concentrations can readily be calculated. The values thus computed are given in col. 2 of Table VI as compared with the values obtained by Getman from the amalgam and the crystal electrode. In col. 5 of the table are given the values of the activity coefficients computed from freezing-point data.

TABLE VI.

M.	From this investn.	From Cu amalgam (Getman).	From Cu crystals (Getman).	From f. p.	M.	From this investn.	From Cu amalgam (Getman).	From Cu crystals (Getman).	From f. p.
1·00	0·043	0·045	0·041	—	0·07	0·161	—	—	—
0·70	0·052	—	—	—	0·05	0·191	0·217	0·203	0·206
0·50	0·061	0·065	0·060	—	0·02	0·296	0·317	0·305	0·295
0·20	0·096	0·105	0·100	—	0·01	0·411	0·438	0·418	0·396
0·10	0·135	0·154	0·144	0·158					

FOUAD I UNIVERSITY, FACULTY OF SCIENCE,
ABBASSIA, CAIRO, EGYPT.

[*Received, April 2nd,* 1947.]