

### 147. Studies on Some Metal Electrodes. Part II. The Behaviour of the Copper Electrode in Dilute Copper Sulphate Solutions.

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By plotting the equilibrium potentials obtained with the spongy copper electrode in copper sulphate solutions of different dilutions ( $3.85 \times 10^{-1}$  to  $3.8 \times 10^{-6}$  M) against  $\log a_{\text{Cu}^{++}}$ , curves are obtained which manifest a sudden break at  $a_{\text{Cu}^{++}} \sim 10^{-4}$ . This is nearly always the case irrespective of whether the measurements are made in or out of contact with air. In copper sulphate solution in contact with the metal there are cupric and cuprous ions. By plotting the calculated  $\text{Cu}/\text{Cu}^{++}$  and  $\text{Cu}/\text{Cu}^+$  potentials, the former for activities higher and the latter for activities lower than  $1 \times 10^{-6}$ , against  $\log a_{\text{Cu}^{++}}$  of the original solutions, a theoretical curve is obtained showing the same break at  $\sim 10^{-6}$ , the difference being attributed to uncertainties in the activity values, the volumetric dilutions, etc. Taking  $\sim 10^{-4}$  instead of  $10^{-6}$  as the equilibrium constant for the reaction  $\text{Cu} + \text{Cu}^{++} \rightleftharpoons 2\text{Cu}^+$ , a break in the theoretical curve far removed from that in the experimental one is obtained, indicating that the lower value is probably the more correct. From the present study it is concluded that in order for an electrode to function as indicator electrode for its ions in solution, the activity of these ions ought not to be smaller than the activity provided by the solubility of the oxide on the metal. One must, therefore, be guided by the pH range within which the oxide persists on the metal, the solubility of that oxide, and, in cases such as that of copper, by the equilibrium constant of the reaction between the different ions in contact with the metal.

CONSIDERABLE interest has recently been taken in the study of the behaviour of metal electrodes in very dilute aqueous solutions of their ions (McAulay and Spooner, *Proc. Roy. Soc.*, 1932, *A*, **138**, 494; Müller and Durichen, *Z. physikal. Chem.*, 1938, *A*, **182**, 233, where other references may be found). Investigations along these lines are not only of significance for providing information as to the limits of applicability of the Nernst equation to the different electrode systems, but are also of value in that they may throw light on the general problem of electrode mechanism.

#### EXPERIMENTAL.

Owing to the increased solubility of mercurous sulphate in dilute copper sulphate solutions, it was not possible to use the same type of cell without liquid junction as that used in Part I. Instead, a cell involving the use of the saturated calomel electrode was used, the procedure described in Part I being followed. The copper sulphate solutions used were  $3.85 \times 10^{-1}$  to  $3.8 \times 10^{-6}$  M. Their copper content was determined whenever possible by electrodeposition. Otherwise, the solutions were prepared only by volumetric dilution using the device described in Part I. In order to minimise uncertainty due to the process of dilution, each solution was prepared at least twice from two more concentrated ones the copper content of which was accurately known. The dilutions were then only considered valid when the measured e.m.f. values agreed with each other within reasonable limits. The activities of the more concentrated solutions were calculated from a graph plotted according to data obtained in Part I. The measurements were carried out either in or out of contact with air. In the latter case the same procedures described in Part I were applied.

## RESULTS AND DISCUSSION.

By plotting the equilibrium potential values as referred to the standard hydrogen electrode against  $\log a_{\text{Cu}^{++}}$ , a curve as shown in Fig. 1 ( $A-B$ ) is obtained. This reveals a sudden break at an activity of  $\text{Cu}^{++} = 10^{-4}$ . Repeated experiments with solutions diluted from different copper sulphate solutions always indicated the same break at about the same activity. This occurred also when the measurements were made in air. Calculations of the standard potential from measurements obtained with the protected electrode before the break (line  $A$ ), yielded a value which approached very closely the value previously obtained out of contact with air (Part I). After the drop, in the more dilute solutions, the measured potentials varied in a normal manner and were found to lie on a more or less straight line  $B$ , possessing a steeper slope than the line  $A$ . In air the curve corresponding to  $B$  was not so straight and was in general less steep ( $B'$  in Fig. 2).

One can attribute the break either to the removal of cupric ions by hydrolysis and formation of colloiddally dispersed phase, or to the progressive formation of cuprous ions by interaction

FIG. 1.

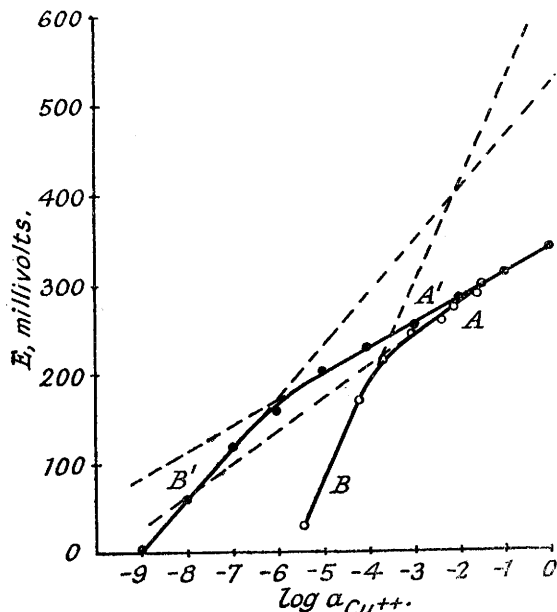
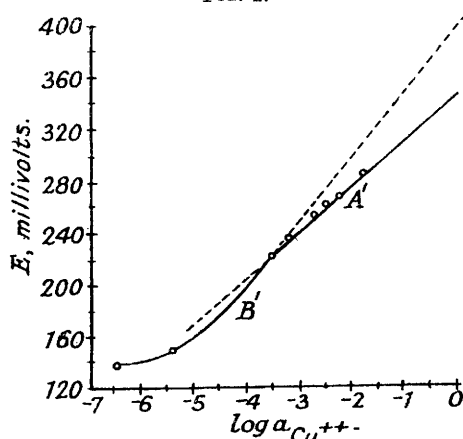


FIG. 2.



between electrode and electrolyte solution. Trials to prevent the first possible effect, by addition of quantities of sulphuric acid just sufficient to repress hydrolysis without making the solution too acid, failed to effect any noticeable change, so one has only to consider the effect of cuprous-ion formation.

The equilibrium constant of the reaction  $\text{Cu} + \text{Cu}^{++} \rightleftharpoons 2\text{Cu}^+$  has been determined by Luther (*Z. physikal. Chem.*, 1901, **36**, 385), Bodländer and Storbeck (*Z. anorg. Chem.*, 1907, **31**, 1, 458), and Fenwick (*J. Amer. Chem. Soc.*, 1926, **48**, 860), giving the respective values  $1.5 \times 10^{-6}$ ,  $1.6-2.0 \times 10^{-4}$ , and  $4 \times 10^{-6}$ . Luther worked with sulphate solutions in which he titrated the cuprous salt formed; he neglected the influence of complexes which, as Abel (*Z. anorg. Chem.*, 1901, **26**, 361) has pointed out, are not negligible in such solutions. Bodländer used a solubility method in chloride and bromide solutions for which it was necessary to make somewhat uncertain corrections. Both authors calculated their results on the basis of ionic concentrations. Fenwick carried out her measurements in perchlorate and sulphate solutions and calculated the results in terms of activities. The agreement between the values of Luther and of Fenwick can, therefore, be considered as more or less fortuitous. If now we calculate with the help of Fenwick's value the cuprous-ion activity in the copper sulphate solutions in contact with the metal, we obtain values such as those in col. 2 of the table. In col. 3 of this table are contained the calculated potentials if the solutions contained only the calculated amounts of cuprous ions. In these calculations  $E_0$  was set equal to 0.522 at 30°. The redox potentials as calculated from

$a_{\text{Cu}^{++}}$	$a_{\text{Cu}^+}$	$\text{Cu}/\text{Cu}^+$	$\text{Cu}^+/\text{Cu}^{++}$	$\text{Cu}/\text{Cu}^{++}$
1	1 $\times 10^{-3}$	0.342	0.349	0.3455
$1 \times 10^{-1}$	$3.162 \times 10^{-4}$	0.312	0.319	0.3155
$1 \times 10^{-2}$	1 $\times 10^{-4}$	0.282	0.289	0.2855
$1 \times 10^{-3}$	$3.162 \times 10^{-5}$	0.252	0.254	0.2555
$1 \times 10^{-4}$	1 $\times 10^{-5}$	0.222	0.229	0.2255
$1 \times 10^{-5}$	$3.162 \times 10^{-6}$	0.192	0.213	0.2025
$1 \times 10^{-6}$	1 $\times 10^{-6}$	0.162	0.151	0.1565
$1 \times 10^{-7}$	2 $\times 10^{-7}$	0.120	—	—
	( $3.162 \times 10^{-7}$ )			
$1 \times 10^{-8}$	2 $\times 10^{-8}$	0.060	—	—
	(1 $\times 10^{-7}$ )			
$1 \times 10^{-9}$	2 $\times 10^{-9}$	0.000	—	—
	( $3.162 \times 10^{-8}$ )			

the relation  $E = 0.169 - 0.060 \log a_{\text{Cu}^{++}}/a_{\text{Cu}^+}$  at 30°, and which should be set up owing to the presence of both species of ions, are shown in col. 4. In these calculations  $a_{\text{Cu}^{++}}$  was put equal to the total copper-ion activity, as it remained practically unchanged by subtracting the amounts transformed into  $\text{Cu}^+$  owing to their comparatively low values. At higher dilutions ( $\text{Cu}^{++} = 1.0 \times 10^{-5}\text{N}$ ), this was no longer permissible. The value of 0.169, representing  $E_0$  for the  $\text{Cu}^+-\text{Cu}^{++}$  couple, was obtained by subtracting the standard potential of the  $\text{Cu}-\text{Cu}^+$  from twice the standard potential of the  $\text{Cu}-\text{Cu}^{++}$  couple as obtained in Part I. In the last column are contained the calculated  $\text{Cu}-\text{Cu}^{++}$  potentials for each solution as calculated from  $\frac{1}{2}(E_{\text{Cu}, \text{Cu}^+} + E_{\text{Cu}^+, \text{Cu}^{++}})$ .

From the reaction  $\text{Cu} + \text{Cu}^{++} \longrightarrow 2\text{Cu}^+$ , it is evident that half the amount of  $\text{Cu}^+$  is supplied from the metal and the other half from the  $\text{Cu}^{++}$  ions. At  $a_{\text{Cu}^{++}} = 1 \times 10^{-5}$  and  $1 \times 10^{-6}$ , respectively, where it was not permissible to use the original total  $\text{Cu}^{++}$  for calculating the redox potential  $\text{Cu}^+-\text{Cu}^{++}$ ,  $a_{\text{Cu}^{++}}$  was calculated by subtracting half the amount of  $a_{\text{Cu}^+}$  from the original total  $a_{\text{Cu}^{++}}$ . At greater dilutions than  $a_{\text{Cu}^{++}} = 1 \times 10^{-6}$ , half the calculated amount of  $a_{\text{Cu}^+}$  exceeded the original total  $a_{\text{Cu}^{++}}$ , so the method fails. At such dilutions it was necessary to assume that the total amount of  $\text{Cu}^{++}$  has been transformed into  $\text{Cu}^+$ , the amount of which was accordingly set equal to twice  $a_{\text{Cu}^{++}}$  (figures in parentheses in col. 2) and the electrode was supposed to function only as a  $\text{Cu}-\text{Cu}^+$  electrode. By plotting the calculated  $\text{Cu}-\text{Cu}^{++}$  and  $\text{Cu}-\text{Cu}^+$  potentials, the former for activities higher and the latter for activities lower than  $1 \times 10^{-6} a_{\text{Cu}^{++}}$ , against the logarithms of  $a_{\text{Cu}^{++}}$  of the original solutions, we obtain the curve shown in Fig. 1 ( $A'-B'$ ) which we shall designate as the theoretical curve for differentiation from the experimental curve in Fig. 1 ( $A-B$ ). As can be seen, both curves are of the same shape, the drops occurring, however, at  $a_{\text{Cu}^{++}} = 1 \times 10^{-5}$  in the theoretical curve instead of about  $2.0 \times 10^{-4}$  in the experimental one.

By extrapolating the part  $B'$  of the theoretical curve to  $\log a = 0$ , we obtain the value of 0.542 v. as compared with the value of 0.522, the standard  $\text{Cu}-\text{Cu}^+$  electrode potential. The difference is to be attributed to the fact that the potentials were plotted against  $a_{\text{Cu}^{++}}$  throughout the whole range instead of  $a_{\text{Cu}^+}$  at concentrations below  $1 \times 10^{-6}$ . By making the necessary corrections and plotting against  $a_{\text{Cu}^+}$  after the break, extrapolation leads to the value of 0.522, which is the standard  $\text{Cu}-\text{Cu}^+$  electrode potential. In the case of the experimental curve, extrapolation of the portion  $B$  leads to the value of 0.602 v. The difference between both curves is to be expected owing to the uncertainties involved in evaluating the activities, the volumetric dilution, and the functioning of the electrode at the greater dilutions (where the pH values approach neutrality) as a metal-metal oxide electrode.

By using Bodländer and Storbeck's value of  $K$  for calculating the cuprous-ion activity in contact with the metal and proceeding in the same manner as above, two lines are obtained which intersect at a point far removed from the experimentally found one (between  $a_{\text{Cu}^{++}} = 1 \times 10^{-6}$  and  $1 \times 10^{-7}$  on the abscissa of the theoretical curve). The present measurements provide therefore a further substantiation for the lower equilibrium constant due to Luther and Fenwick.

By comparing the potential set up in the most dilute solution of  $3.8 \times 10^{-6}\text{M}$ -copper sulphate with the potential set up in pure water it is found that the difference amounts only to 11.1 mv. McAulay and Spooner (*loc. cit.*) found that the potential of a cadmium electrode was independent of the concentration of the cadmium ions in solutions lower than  $10^{-4.25}\text{M}$ ; they advanced a theory according to which the strongly polar water molecules, owing to their heat motion, bombard the metal, with the result that a stream of ions is drawn into the solution to a mean distance,  $l$ , from the electrode surface. Equilibrium is then reached when their removal is balanced by their migration back under the field produced by their abstraction. As a

consequence, the electrode potential will be independent of all changes in the character and constitution of the solution provided that the concentration of the electrode metal ions in the bulk solution is less than that in the layer. Müller and Durichen (*loc. cit.*), on the other hand, attributed the value found by McAulay and Spooner to the formation of a cadmium hydroxide film on the electrode, giving a cadmium-ion concentration of  $10^{-4.22}$  as calculated from the solubility product of cadmium hydroxide, *i.e.*,  $2.1-2.4 \times 10^{-13}$ . It is, therefore, reasonable to assume that, in an ideal case, the potential set up between an electrode and a very dilute solution of its salt is governed by the solubility product of its oxide, provided of course that the oxide under the prevailing conditions can persist in the medium. Otherwise expressed, when an electrode is immersed in a solution of such a dilution that the ions present are greater than the ions supplied by the solubility product of the metal hydroxide, then the electrode will respond accurately to the activity of these ions. If, on the other hand, the ion activities are made less, the electrode will not respond to their variations, since it will always respond to the ions originating from the solubility of its oxide.

From the evaluation of the solubility product of cuprous hydroxide in contact with the metal even out of contact with air (Part I), there is a copper-ion activity close to the metal in water amounting to about  $10^{-7}$ . This value closely approaches the limiting values at which the electrode does not seem to show variations in potential with decreasing activities of copper ion. This is shown by the horizontal trend of the extension of the curve *B'* in Fig. 2 at the maximum dilution. We conclude, therefore, that the present study shows that, in applying a metal electrode as indicator electrode for its ions in solution, one must be guided by the pH range within which the oxide can persist on the metal, the solubility of that oxide, and, as in the case under consideration, the equilibrium constant of the reaction between the different ions in contact with the metal.

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