704. *The Equilibrium between Copper and Cupric and Cuprous Ions and the Behaviour of the Copper Electrode in Dilute Copper Sulphate Solutions.*

By S. E. S. El Wakkad.

The equilibrium constant of the reaction $Cu + Cu^{\cdot\cdot} = 2Cu^{\cdot}$ has been determined for conditions similar to those at the copper electrode surface immersed in copper sulphate solutions. With the help of the value of K so obtained, the break previously noticed in the potential–activity curve of the copper electrode in dilute copper sulphate solutions is explained. The calculations are also extended to cuprous salt solutions, and it is shown that in cupric salt solutions the potential of the copper electrode tends towards that of the standard potential–activity curve of the Cu–$Cu^{\cdot}$ system at $a_{Cu^{\cdot\cdot}} < \sim 0{\cdot}5 \times 10^{-4}$. On the other hand, in cuprous salt solutions the potential of the copper electrode tends towards that of the standard curve of the Cu–$Cu^{\cdot\cdot}$ system at $a_{Cu^{\cdot}} > \sim 0{\cdot}5 \times 10^{-4}$.

The standard potential of the Cu–$Cu^{\cdot}$ system is determined by two procedures and the results are in satisfactory agreement.

When copper sulphate solutions are shaken with metallic copper, a difference in the pH value of as much as 1·5 units is noticed. The significance of this finding is discussed in so far as it relates to the probable precipitation of cuprous oxide on the copper electrode in very dilute copper sulphate solutions.

The behaviour of the copper electrode in dilute copper sulphate solutions has been studied by Tourky and El Wakkad (*J.*, 1948, 749). Their potential–activity curves showed a break at $a_{Cu^{\cdot\cdot}} \sim 10^{-4}$, which was ascribed to the presence of cuprous and cupric ions in copper sulphate solutions in contact with the metal. The different values assigned by previous authors to the equilibrium constant K of the reaction $Cu + Cu^{\cdot\cdot} = 2Cu^{\cdot}$ were discussed, and 10^{-6} was selected as the most satisfactory value with which to calculate the $Cu–Cu^{\cdot\cdot}$ and $Cu–Cu^{\cdot}$ potentials, the former for activities higher and the latter for activities lower than 10^{-6}. By assuming that at activities lower than 10^{-6} the electrode behaves mainly as a $Cu–Cu^{\cdot}$ electrode, the break in the experimental curve was explained. This procedure was criticised by Mousa (*J.*, 1950, 403), who, however, overlooked the fact that the accepted value of the $Cu–Cu^{\cdot}$ potential had not been determined experimentally but calculated from the equilibrium constant itself (Fenwick, *J. Amer. Chem. Soc.*, 1926, **48**, 860; Bockris *et al.*, *Faraday Soc. Discussion*, 1947, p. 331). A detailed discussion of the method adopted in determining the constant K is therefore necessary. The value of this constant, as stated by Fenwick, is subject to an experimental error of as much as 10%, and this explains why Fenwick's values of both K and the $Cu–Cu^{\cdot}$ potential were taken by Tourky and El Wakkad. These facts also make Mousa's calculation of the value of K to the third decimal in $10^{-5.877}$ meaningless.

The main objective of this investigation was, however, to re-examine the value of K for the reaction $Cu + Cu^{\cdot\cdot} = 2Cu^{\cdot}$ for conditions similar to those at the electrode surface. With the help of the value of K obtained, the potentials of the copper electrodes in cupric salt solutions are calculated. The break obtained in the theoretical curve in this case is found to agree more closely with experiment. The calculations are also extended to cuprous salt solutions, and it is shown that in cupric salt solutions the potential of the copper electrode tends towards that of the standard potential–activity curve of the $Cu–Cu^{\cdot}$ system at $a_{Cu^{\cdot\cdot}} < \sim 0.5 \times 10^{-4}$. On the other hand, in cuprous salt solutions the potential of the copper electrode tends towards that of the standard curve of the copper–cupric system at $a_{Cu^{\cdot}} > \sim 0.5 \times 10^{-4}$.

The standard electrode potential of the Cu–Cu system is also determined by two different procedures and the results are found to be in satisfactory agreement.

The pH values of the original copper sulphate solutions are also determined as well as those of the equilibrated solutions obtained after shaking them with metallic copper; a difference amounting in some cases to ~ 1.5 pH units is noticed. The significance of this finding for the probable precipitation of cuprous oxide or hydroxide on the copper electrode in very dilute copper sulphate solutions is discussed.

EXPERIMENTAL.

Four solutions of cupric sulphate were prepared from twice recrystallised AnalaR salt. The gram-molarities of these solutions were determined both iodometrically and by electrolytic deposition. These solutions were shaken at 21° ± 0·5° with pure electrolytic copper for 5 days in well-stoppered glass bottles in an atmosphere of pure nitrogen. When equilibrium had been attained the solutions were filtered quickly from the copper in an atmosphere of pure nitrogen, and the cuprous sulphate present was determined by titration with standard potassium permanganate.

The pH values of the original copper sulphate solutions and of the equilibrated solutions were determined with the glass electrode (Marconi pH meter). In this case three more diluted solutions were also examined.

RESULTS AND DISCUSSION.

Table I summarises the results obtained. The equilibrium constant in each case was obtained after calculating the activity of the cuprous ion from a knowledge of the ionic strength of the solution, the activity coefficient of the cuprous ion being taken as identical with that of the silver ion at the same ionic strength. The activities of the cupric ions were obtained from data given by Tourky and El Wakkad (*J.*, 1948, 740) for copper sulphate solutions. From these results it is clear that the mean value for the equilibrium constant K is 1×10^{-5} as compared with 1×10^{-6} obtained by Fenwick (*loc. cit.*) and 0.5×10^{-4} by Bodlander and Storbeck (*Z. anorg. Chem.*, 1907, **31**, 458).

TABLE I.

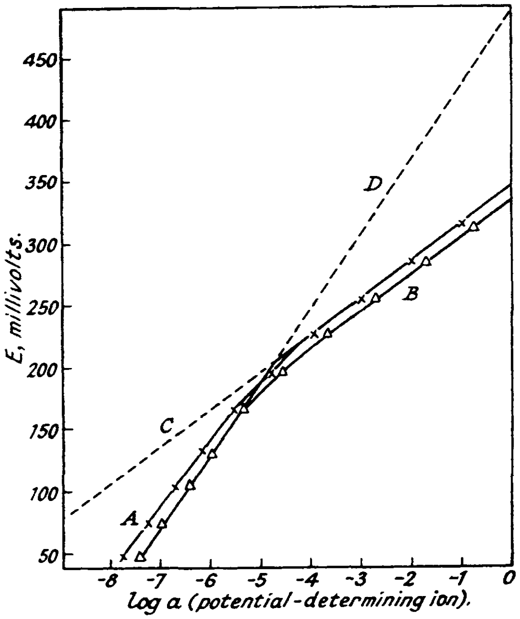
$CuSO_4$, M.	Cu_2SO_4, M($\times 10^4$).	$10^5K = 10^5a^2_{Cu^{\cdot}}/a_{Cu^{\cdot\cdot}}$.	$CuSO_4$, M.	Cu_2SO_4, M($\times 10^4$).	$10^5K = 10^5a^2_{Cu^{\cdot}}/a_{Cu^{\cdot\cdot}}$.
0·2027	4·2	0·9	0·0510	2·1	0·9
0·1019	3·1	1·0	0·0100	1·3	1·1

With this value of K, 1×10^{-5}, the cupric and the cuprous activities in contact with metallic copper in cupric sulphate solutions of different concentrations were calculated, and the corresponding potentials were also obtained as shown in Table II. In these calculations the standard potential of the $Cu–Cu^{\cdot\cdot}$ system was taken as 0·3457 v. (Tourky and El Wakkad, *loc. cit.*).

TABLE II.

$a_{\mathrm{Cu}^{\cdot\cdot}}$, original.	$a_{\mathrm{Cu}^{\cdot\cdot}}$, equil.	$a_{\mathrm{Cu}^{\cdot}}$, equil.	$a_{\mathrm{Cu}^{\cdot}}$, original.	*E*.
1·0016	1	$3·162 \times 10^{-3}$	2·0032	0·3457
$1·005 \times 10^{-1}$	1×10^{-1}	$1·000 \times 10^{-3}$	$2·010 \times 10^{-1}$	0·3157
$1·016 \times 10^{-2}$	1×10^{-2}	$3·162 \times 10^{-4}$	$2·032 \times 10^{-2}$	0·2857
$1·050 \times 10^{-3}$	1×10^{-3}	$1·000 \times 10^{-4}$	$2·100 \times 10^{-3}$	0·2557
$1·116 \times 10^{-4}$	1×10^{-4}	$3·162 \times 10^{-5}$	$2·316 \times 10^{-4}$	0·2257
$1·500 \times 10^{-5}$	1×10^{-5}	$1·000 \times 10^{-5}$	$3·000 \times 10^{-5}$	0·1957
$2·581 \times 10^{-6}$	1×10^{-6}	$3·162 \times 10^{-6}$	$5·162 \times 10^{-6}$	0·1657
$6·000 \times 10^{-7}$	1×10^{-7}	$1·000 \times 10^{-6}$	$1·200 \times 10^{-6}$	0·1357
$1·681 \times 10^{-7}$	1×10^{-8}	$3·162 \times 10^{-7}$	$3·362 \times 10^{-7}$	0·1057
$5·100 \times 10^{-8}$	1×10^{-9}	$1·000 \times 10^{-7}$	$1·020 \times 10^{-7}$	0·0757
$1·591 \times 10^{-8}$	1×10^{-10}	$3·162 \times 10^{-8}$	$3·182 \times 10^{-8}$	0·0457

When these potentials were plotted against the log $a_{\mathrm{Cu}^{\cdot\cdot}}$ (original) the curve *A* shown in the figure was obtained, which shows a break at $\sim 0·5 \times 10^{-4}$ in agreement with Tourky and El Wakkad (*loc. cit.*). Column 4 in the same table shows the original $a_{\mathrm{Cu}^{\cdot}}$ necessary to give the potentials in column 5 when a copper electrode is dipped in a solution containing originally only cuprous ions. These results are represented graphically in curve *B*. The standard curves of the Cu–Cu$^{\cdot\cdot}$ and the Cu–Cu$^{\cdot}$ systems are also shown by *C* and *D* respectively. From these curves it is seen that the potential of the copper electrode actually approaches that of the standard Cu–Cu$^{\cdot}$ system in cupric salt solutions of activities less than $\sim 0·5 \times 10^{-4}$; similarly in cuprous salt solutions it approaches the standard curve of the Cu–Cu$^{\cdot\cdot}$ system in solutions of $a_{\mathrm{Cu}^{\cdot}}$ greater than $\sim 0·5 \times 10^{-4}$.



The Standard Potential of the Cu–Cu$^{\cdot}$ *System*.—The value of *K* being taken as 1×10^{-5} and the standard potential of the Cu–Cu$^{\cdot\cdot}$ system as 0·3457 (Tourky and El Wakkad, *loc. cit.*), the standard potential of the Cu–Cu$^{\cdot}$ system will be equal to 0·49 v. This value can be confirmed from a knowledge of the E_0 value of the Cu–Cu$_2$O|H$^{\cdot}$ electrode and the solubility product of cuprous oxide; Tourky and El Wakkad (*loc. cit.*) found that the potential of the Cu–Cu$_2$O electrode at pH 0 is 0·507 v., and the solubility product of cuprous oxide as obtained from conductivity measurements is $7·18 \times 10^{-14}$, whence the standard Cu–Cu$^{\cdot}$ potential will be equal to 0·47 v. These results give a mean value of $0·48 \pm 0·01$ v. for the standard Cu–Cu$^{\cdot}$ potential. It must be stated that, although the equilibrium constant experiments were carried out at 21° and the measurements of the potentials of the Cu–Cu$_2$O system and of the solubility product of cuprous oxide at 30°, yet such a variation in temperature involves a comparatively small change in potential which is believed to be within the limits of error of the stated value. This value for the standard electrode potential of the Cu–Cu$^{\cdot}$ system agrees well with that, *viz.*, 0·47 v., obtained by Gatty and Spooner (" Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford, 1938, p. 190) from the results of Immerwahr (*Z. anorg. Chem.*, 1900, **24**, 269) and Luther (*Z. physikal. Chem.*, 1900, **34**, 488; 1901, **36**, 385).

Concerning the probable precipitation of cuprous hydroxide at greater dilution of copper sulphate solutions owing to the increase of pH of the solution, one must take into consideration the fact that reduction of cupric sulphate to cuprous sulphate in solution will at the same time lead to a decrease in the pH owing to the greater tendency of the latter salt to hydrolysis (O'Sullivan, *Trans. Faraday Soc.*, **1925**, **21**, 319; **1927**, **23**, 52). This has been proved by comparing the pH values of the original cupric sulphate solutions with those of the equilibrated solutions obtained after **5** days' shaking with metallic copper. The results obtained are shown below. In this table are shown also the values of the products $a_{\mathrm{Cu}^{\cdot}} \times a_{\mathrm{OH}'}$ in each case ($a_{\mathrm{Cu}^{\cdot}}$ was calculated from the equilibrium constant $K = 10^{-5}$, and $a_{\mathrm{OH}'}$ from the final pH of the equilibrated

$CuSO_4$, M.	pH, original.	pH, final.	$10^{14}a_{Cu^{\cdot}} \times a_{OH'}$.
0·2027	3·9	3·1	1·40
$1{\cdot}019 \times 10^{-1}$	4·1	3·2	1·46
$5{\cdot}10 \times 10^{-2}$	4·3	3·2	1·23
$1{\cdot}00 \times 10^{-2}$	5·1	3·6	1·98
$1{\cdot}00 \times 10^{-3}$	5·5	4·1	2·45
$1{\cdot}00 \times 10^{-4}$	6·4	4·9	4·80
$1{\cdot}00 \times 10^{-5}$	6·8	5·5	4·93

solution, pK_w being taken as 13·9). From this table it is clear that down to $a_{Cu^{\cdot\cdot}}$ as low as $\sim 10^{-5}$ the product of $a_{Cu^{\cdot}} \times a_{OH'}$ is less than the solubility product of cuprous hydroxide ($7{\cdot}18 \times 10^{-14}$) and thus there will be no tendency for cuprous hydroxide to be precipitated. At greater dilution than $\sim 10^{-5}$ the pH value may become high enough to cause precipitation of the hydroxide and hence the electrode will no longer show a potential varying with $a_{Cu^{\cdot\cdot}}$ but will remain more or less constant at a certain value. This confirms Tourky and El Wakkad's finding (*loc. cit.*), and indicates also that the drop obtained at $a_{Cu^{\cdot\cdot}} \sim 10^{-4}$ has nothing at all to do with the formation of cuprous oxide as suggested by Mousa.

UNIVERSITY OF LIVERPOOL.

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