C.—*Studies of Electrolytic Polarisation. Part VIII. Complex Cyanides:* (b) *Copper.*

By Samuel Glasstone.

The behaviour of a copper electrode in potassium cyanide solution when submitted to the action of an alternating current is quite different from that of silver: Le Blanc and Schick (*Z. physikal. Chem.*, 1903, **46**, 213; *Z. Elektrochem.*, 1903, **9**, 636) found that the latter did not dissolve to any appreciable extent, but the rate of dissolution of the former only decreased slowly with increasing frequency of current alternations, and was quite considerable even at frequencies of 38,000 per minute. The explanation offered by them was that copper, like silver, ionises during the anodic intervals of the alternating current and readily forms a complex cuprocyanide ion; this, however, unlike the argentocyanide ion, does not come into equilibrium rapidly with its simpler ionic constituents. Hence, during the cathodic pulses the supply of cuprous ions in the vicinity of the electrode will not be sufficient to meet the requirements of the current. Hydrogen ions will then be discharged to an appreciable extent, and more copper will dissolve during the anodic intervals than is replaced during the cathodic periods; the electrode will therefore dissolve under the influence of the alternating current.

Before accepting the views of Le Blanc and Schick concerning the rate of dissociation of the cuprocyanide ion, it is important to remember that copper can dissolve spontaneously in cyanide solutions with the liberation of hydrogen. This has been known for some time (compare Goyder, *Chem. News*, 1894, **69**, 268) and is due to the fact that the concentration of copper ions in a cyanide solution is so low that the electrode potential Cu|KCN is of the order of $-1{\cdot}05$ volts, whereas the reversible potential H_2(1 atm.)|KCN is about $-0{\cdot}65$ volt. For the same reason, hydrogen will be deposited in preference to copper during the cathodic intervals irrespective of the rate of dissociation of the cuprocyanide ion, provided there is an excess of free cyanide in the electrolyte. It is clear, therefore, that a copper electrode is bound to dissolve to some extent in potassium cyanide solution under the influence of alternating current. Le Blanc and Schick found a decrease in the rate of dissolution with increasing frequency of alternations: this may well be due to the decreased opportunities for the cuprocyanide ions to diffuse away from the electrode, so that appreciable amounts of copper, as well as hydrogen, are deposited during the cathodic pulses. At high frequencies, too, some of the hydrogen deposited during the cathodic intervals will redissolve during the anodic pulses, and so the rate of dissolution of the copper will decrease. It appears, therefore, that the work of Le Blanc and Schick throws no light on the fundamental problem of the rate of dissociation of cuprocyanide ions. In confirmation of this view, it may be mentioned that Brochet and Petit (*Z. Elektrochem.*, 1904, **10**, 916) found that zinc, nickel, and cobalt electrodes behaved like copper when subjected to the action of alternating current electrolysis in cyanide solutions, whereas mercury and cadmium resembled silver. The first three metals, like copper, dissolve spontaneously in cyanide solutions and liberate hydrogen (compare Goyder, *loc. cit.*), but the other two, like silver, do not react in this manner.

The work of Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) on the variation with *C.D.* of cathodic potential of copper in cuprocyanide solutions at ordinary temperatures, suggested that there was a considerable polarisation during the deposition of the metal; Foerster (*ibid.*, 1907, **13**, 561) correlated this with the supposed slow dissociation of the cuprocyanide ion as suggested by Le Blanc and Schick (*loc. cit.*). Brunner (see Foerster, *loc. cit.*) found that at higher temperatures (*e.g.*, 75°) the cathodic polarisation during copper deposition from cuprocyanide solutions is greatly decreased, and Foerster attributed this to an increased rate of decomposition of the complex ion. It is interesting to note in this connexion, however, that Le Blanc and Schick concluded from their observations that the temperature coefficient of the rate of decomposition of the cuprocyanide complex is very small. More recently, Höing (*ibid.*, 1916, **22**, 286) has determined the deposition potentials at 25° from a solution which was said to be $M/10$ with respect to potassium cuprocyanide, $KCu(CN)_2$, and contained no appreciable excess of free cyanide; it was found in these circumstances that an increase of *C.D.* caused very little cathodic polarisation, and the behaviour was very much the same as that observed by Brunner (*loc. cit.*) during silver deposition. Höing found, however, that the addition of a very small excess of potassium cyanide to the cuprocyanide solution resulted in a considerable polarisation, which he attributed to the presence of the more complex ion $Cu(CN)_3''$ formed by the reaction $Cu(CN)_2' + CN' \longrightarrow Cu(CN)_3''$. According to Foerster's interpretation of the origin of polarisation in the case under discussion, it would be concluded from these results that whilst the $Cu(CN)_2'$ ion dissociated rapidly, the $Cu(CN)_3''$ dissociated only slowly, and even had a tendency to retard the dissociation of the former ion. In the course of the present work it was found that an "$M/10$-solution of $KCu(CN)_2$" probably does not exist at 25°, and that even the solution in which Höing found no appreciable polarisation contains a large proportion of the $Cu(CN)_3''$ ion. In view of the unsatisfactory nature of the position concerning the electrochemical properties and behaviour of cuprocyanide solutions, a more complete investigation seemed desirable, especially as a similar investigation with silver (preceding paper) had yielded interesting results. The conditions were kept as uniform as possible with those existing in the previous work, so the results are comparable. Cathode-potential and current-efficiency measurements were made at various *C.D.*'s, and an electrometric titration of cuprous cyanide with sodium cyanide solution was carried out.

For convenience the results of the latter experiments will be described first.

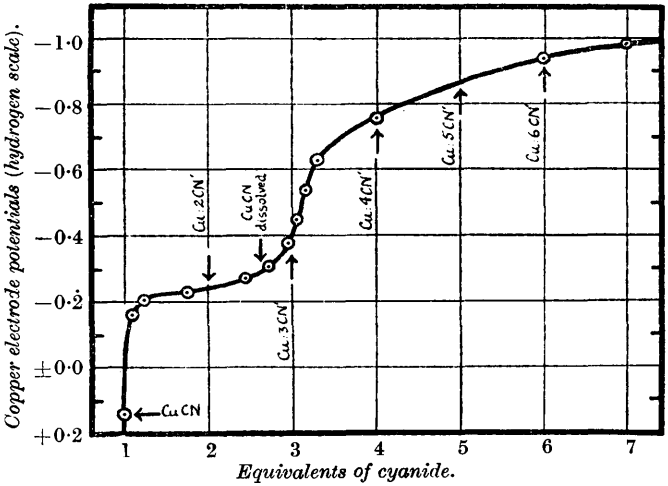
EXPERIMENTAL.

Electrometric Titration of Cuprous Cyanide by Sodium Cyanide.—Kunschert (*Z. anorg. Chem.*, 1904, **41**, 359) and Spitzer (*loc. cit.*) both found that reproducible measurements of copper potentials in cuprocyanide solutions were not easily obtained, and this was confirmed in the present work. During the electrometric titration a current of hydrogen was passed through the liquid; in this way more satisfactory results were obtained with solutions containing an excess of alkali cyanide. Although the general nature of the results was quite reproducible, the actual electrode potential values were not very exact; for the present purpose, however, the latter are not essential.

In accordance with the observations of Spitzer (*loc. cit.*) and Höing (*loc. cit.*), it was found most satisfactory to precipitate cuprous cyanide by adding the correct amount of sodium or potassium cyanide solution to a hot solution of copper sulphate; care was taken to boil off all the cyanogen produced in the reaction. For the electrometric titration, a known amount (about 0·2 g.) of cuprous cyanide thus prepared was transferred to a wide tube together with about 10 c.c. of water and 0·05 g. of sodium sulphate (the latter being used to increase the conductance of the system). The tube was fitted with a cork through which passed a connexion to the copper electrode, a potassium chloride tube for connecting with the calomel half-element used as a standard, the hydrogen lead-in tube, an outlet tube, and the tip of the burette. A standard solution of sodium cyanide was added gradually to the suspension of cuprous cyanide, and the mixture well shaken; the electrode potential of the copper was measured after each addition. Since the actual values are inexact, they need not be given, but some typical results which serve to show the general tendency are plotted in Fig. 1. It may be mentioned that the more limited observations of Spitzer (*loc. cit.*) and of Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 111) are in agreement with those made in the present work.

Although Fig. 1 is a typical electrometric titration curve similar to the one obtained for silver cyanide (see previous paper, Fig. 2), yet a closer examination reveals important differences. Since the break corresponding approximately to $Cu:3CN'$ is not very sharp, it appears that although nearly the whole of the copper is present in solution in the form of the $Cu(CN)_3''$ ion, or possibly $[Cu(CN)_3(H_2O)]''$, this is not a very stable ion. On the other hand, the sudden increase of negative potential, *i.e.*, the large reduction in the concentration of cuprous ions, resulting from the addition of a small amount of alkali cyanide to cuprous cyanide alone, suggests the presence of a stable complex ion, which must presumably be $Cu(CN)_2'$. The titration curve, however, shows no break at a point corresponding to Cu : 2CN′, and hence it must be concluded that when cuprous cyanide is dissolved in sodium cyanide both complex ions $Cu(CN)_2'$ and $Cu(CN)_3''$ are formed simultaneously in comparable amounts. If the $Cu(CN)_2'$ ion were completely formed prior to the formation of appreciable amounts of $Cu(CN)_3''$, then we should expect 1 equiv. of cuprous cyanide to be dissolved by 1 equiv. of alkali cyanide, and the titration curve should show a break at this point as in the case of silver cyanide; similarly if only the $Cu(CN)_3''$ ion were formed, then 1 equiv. of the cuprous salt would require 2 equivs. of alkali cyanide for complete dissolution. In practice it is found, however, that about 1·5 equivs. of the latter are actually required, and so it is clear that the resulting solution contains both complex ions in almost equivalent amounts. Kunschert (*loc. cit.*) stated that 2·5 equivs. of alkali cyanide are required to dissolve 1 equiv. of cuprous cyanide, but, as indicated by Spitzer (*loc. cit.*), this is probably a misprint for 1·5.

Fig. 1.



When 2 equivs. of cyanide ions have been added per equiv. of cuprous cyanide, we may conclude from the curve in Fig. 1 that nearly the whole of the copper is present in the form of the $Cu(CN)_3''$ complex; beyond this point, addition of free cyanide can only have a very gradual influence on the ions present in solution.

The titration of cuprous cyanide with potassium cyanide gives results almost identical with those given by sodium cyanide, except that a slightly larger proportion of alkali cyanide is required to effect complete dissolution of the precipitate; this fact is probably connected with the limited solubility of $KCu(CN)_2$ (see below).

Höing (*loc. cit.*) claimed to have worked with an *M*/10-solution of $KCu(CN)_2$ at 25°, but in the author's opinion such a solution does not exist at this temperature. The solubility of cuprous cyanide in *N*/10-sodium and potassium cyanides has been determined at 25° and found to be 0·085 and 0·045 g.-equiv. per litre respectively. The value for sodium cyanide tends to confirm the view that both $Cu(CN)_2'$ and $Cu(CN)_3''$ are formed, but with potassium cyanide it would appear that only the latter ion is present. The result is, however, probably connected with the low solubility of the salt $KCu(CN)_2$; Spitzer (*loc. cit.*) gives the value as 0·04 mol. per litre at 25°, but it is probably much less than this, since it seems impossible to prepare a solution of the salt free from cyanide,* and the latter undoubtedly increases the solubility. The presence of both cuprocyanide complexes in the solution of cuprous cyanide in potassium cyanide is suggested by the fact that in *N*/20-solution 1 equiv. of potassium cyanide dissolves 0·65 equiv. of the copper salt; this confirms the view that the smaller relative solubility in the more concentrated potassium cyanide is accounted for by the low solubility of the complex salt. In any case it is clear that the electrolyte used by Höing was probably not an *M*/10-solution of $KCu(CN)_2$ alone, and hence his conclusions regarding the relative rates of dissociation of the two cuprocyanide complexes are not justifiable.

At higher temperatures the solubility of cuprous cyanide in alkali cyanides is increased, presumably because there is less tendency for the $Cu(CN)_3''$ complex to be formed as the temperature is raised. When the solution is cooled, cuprous cyanide, and, particularly in the case of potassium, some complex salt are precipitated.

Cathode-potential and Current-efficiency Measurements.—The electrolytic solutions were prepared by dissolving cuprous cyanide, precipitated as described above, in the requisite volume of standard sodium cyanide solution. During the course of the work it was found that the presence of a small concentration of sulphate ions (*e.g.*, *N*/10) had no appreciable influence on any of the measurements made; hence the alkali cyanide solution was generally added to the cuprous cyanide suspension without filtering the latter. The so-called " *N*/10-cuprocyanide " solution was made by saturating *N*/10-sodium cyanide solution with cuprous cyanide and filtering off the excess of the solid; the clear liquid apparently contained

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* Compare Bassett and Corbet, J., 1924, **125**, 660.

0·06 g.-ion of $Cu(CN)_2'$ and 0·02 g.-ion of $Cu(CN)_3''$ per litre. Cathodic potentials were measured at increasing *C.D.*'s by the method described in the previous paper. The determination of current efficiencies presented some difficulty owing to the tendency of copper to dissolve in cyanide solution, particularly in the presence of air. Separate experiments were made in order to determine the normal loss in weight of the copper electrode in each of the solutions used in this work, and a correction was applied to the actual weight of the deposit (compare Field, *Trans. Faraday Soc.*, 1909, **5**, 172). The rate of dissolution was greatest in those solutions in which the current efficiency was least, and so the results for solutions containing an excess of free cyanide, especially at high *C.D.*'s, can only be regarded as approximate. In some instances, in fact, the cathode actually lost in weight during the electro-deposition, because it was dissolving spontaneously faster than it was being deposited. Owing to such difficulties as these, the current efficiencies were only determined down to a *C.D.* of 0·0004 amp./cm.^{2}.

Unless otherwise stated, experiments were carried out at room temperature (15°). All electrode-potential measurements are expressed on the hydrogen scale.

Results.—Table I gives the cathode potentials (*C.P.*) and percentage current efficiencies (*C.E.*) for deposition of copper as a univalent metal, at different *C.D.*'s from the so-called "*N*/10-cuprocyanide" solution (I), and from four other solutions which can be represented by the general formula *N*/10-[CuCN,*n*KCN], where *n* is equal to 2 (II), 3 (III), 5 (IV) and 7 (V). The results of the cathode-potential measurements in solutions I and II have been plotted in Fig. 2.

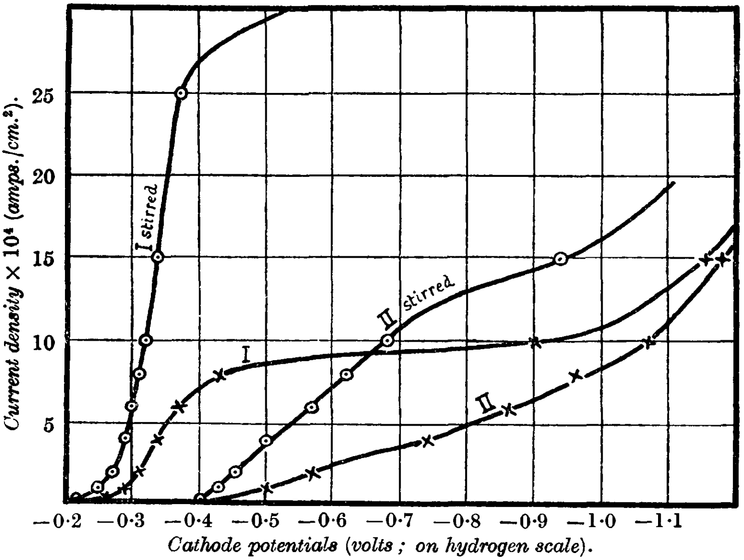
TABLE I.

Cathode Potentials and Current Efficiencies.

C.D. × 10^4 (amps./cm.^{2}).	I.		II.		III.		IV.		V.	
	C.P.	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·22	—	−0·40	—	−0·75	—	−0·94	—	−1·00	—
1·0	−0·29	—	−0·50	—	−0·77	—	−0·96	—	−1·02	—
2·0	−0·31	—	−0·57	—	−0·79	—	−1·01	—	−1·05	—
4·0	−0·34	100	−0·74	65	−0·93	62	−1·08	50	−1·08	43
6·0	−0·39	81	−0·86	44	−1·05	36	−1·15	26	−1·15	17
10	−0·90	—	−1·07	—	−1·20	—	−1·28	—	−1·28	—
15	−1·13	47	−1·18	32	−1·27	21	−1·32	13	−1·32	9
25	−1·32	33	−1·26	28	−1·34	13	−1·36	6	−1·36	5
50	−1·38	28	−1·37	22	−1·39	11	−1·40	3	−1·40	1·7
100	−1·41	22	−1·41	13	−1·43	9	−1·43	1·5	−1·43	0·4

A comparison of the results given in Table I with those obtained for argentocyanide solutions (see previous paper) suggests that the general behaviour is entirely different in the two cases. On the whole, there is much more polarisation in the cuprocyanide solutions; the current efficiencies for metal deposition are considerably lower and very much affected by an increase in the free cyanide content of the electrolyte. At first sight it would appear, therefore, that the conclusions of Le Blanc and Schick (*loc. cit.*) and of Foerster (*loc. cit.*) concerning the slow decomposition of the cuprocyanide complex are correct. There are, however, two important differences in the behaviour of copper and silver in cyanide solutions that must be taken into consideration. First, an examination of the curve in Fig. 1 shows that any increase of the CN′/Cu ratio above 2 to 1 causes the copper electrode potential to increase at first gradually from —0·2 to —0·35 volt, and then more rapidly to —0·9 volt; the electrode potential change is, therefore, much greater than in the case of silver. Secondly, the reversible potential for hydrogen evolution in a *N*/10-cyanide solution is about —0·65 volt, and hence in all solutions in which the ratio CN′/Cu exceeds 3·4 the reversible copper potential is more negative. In such solutions hydrogen evolution can thus occur simultaneously with copper deposition, and the current efficiency for the latter cannot be 100%. Although the hydrogen overvoltage at copper raises the actual potential for hydrogen evolution to —0·85 volt, yet during the course of electrodeposition such a potential is soon reached as a result of a small decrease in the cuprous-ion concentration.

FIG. 2.



The divergence of the current efficiency from 100% is not necessarily due to simultaneous hydrogen evolution only; there is evidence that sodium cyanide can act as a depolariser at a copper cathode, possibly with the resulting formation of methylamine, and hence some of the current may be employed in this reduction process.

In solution I we should expect the cathode potential to increase steadily from —0·22 to about —0·4 volt, whilst the current efficiency remains at 100%; beyond this point the potential should rise rapidly to about —1·0 volt with the simultaneous evolution of hydrogen and lowering of current efficiency. This is in agreement with the actual results (see Table I). In solution II the reversible potential is already —0·4 volt, and hence the cathodic potential should increase rapidly from the beginning as the *C.D.* is increased; the results in Table I and the curve in Fig. 2 show this to be the case. The current efficiency, as would be expected, even at the lowest *C.D.* investigated is below 100%. In the other solutions used in this work hydrogen discharge can occur from the commencement; in fact, the cathode potentials for solution V are very similar to those for hydrogen evolution at a copper cathode in an *N*/2-sodium cyanide solution.

Rate of Dissociation of Cuprocyanide Ions.—Since the change of CN′/Cu ratio in an electrolyte soon brings the potential of the copper cathode into the region of hydrogen evolution, it is not possible to apply directly the criterion of diffusion velocity which was used in the case of silver; a modified test is, however, possible. If the rate of diffusion of the cuprocyanide ion $Cu(CN)_2'$ is assumed to be the same as that of the $Ag(CN)_2'$ ion, and we assume that the former ion, like the latter, dissociates *rapidly*, then the maximum *C.D.* at which the metal deposition efficiency is 100% should be about 0·0025 amp./cm.^{2} (see previous paper). In solution I, however, this maximum is reached at 0·0005 amp./cm.^{2}, when the cuprocyanide-ion concentration in the vicinity of the electrode must be at least three-fourths of its value in the bulk of the electrolyte. It might appear, therefore, that the cuprocyanide ions are present in sufficient concentration, but that they dissociate slowly into the simpler ions from which copper deposition can occur. If this were the case, then stirring of the electrolyte should have very little influence on the cathode potentials and the current efficiencies. Increase of temperature, on the other hand, might be expected to increase the rate of dissociation of the complex ions, and hence would lead to less polarisation and higher efficiencies. In order to test these points, a number of cathode-potential and current-efficiency measurements were made in solutions I and II whilst they were stirred mechanically at the rate of 500 r.p.m., and also in the same solutions at a temperature of 70°, without stirring. The results obtained are given in Table II; the cathode-potential measurements in the stirred solutions are plotted in Fig. 2 for comparison with those obtained in the unstirred solutions at the same temperature.

TABLE II.

	Solution stirred.				Solution at 70°.			
	I.		II.		I.		II.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·22	—	−0·40	—	−0·22	—	−0·38	—
1·0	−0·25	—	−0·43	—	−0·24	—	−0·40	—
2·0	−0·27	—	−0·46	—	−0·26	—	−0·43	—
4·0	−0·29	100	−0·50	100	−0·28	100	−0·45	100
6·0	−0·30	,,	−0·57	87	−0·30	,,	−0·47	,,
10	−0·32	,,	−0·68	—	−0·39	,,	−0·52	—
15	−0·34	,,	−0·94	64	−0·45	96	−0·58	89
25	−0·47	85	−1·12	44	−0·85	78	−0·80	71
50	−1·13	59	−1·23	33	−1·11	63	−0·98	62
100	−1·33	38	−1·32	28	−1·29	43	−1·25	48

The values in Table II show that stirring of the electrolyte has a very considerable effect in reducing cathodic polarisation and increasing the current efficiency, especially in solution I; the results, therefore, are opposed to the view that the cuprocyanide ions dissociate slowly, unless the assumptions concerning the rate of diffusion of these ions are incorrect. The observations are, however, in harmony with the rate of dissociation being rapid; in this case stirring would be expected to retard the normal increase of the CN′/Cu ratio, and hence the rise of cathode potential at about —0·4 volt, with its corresponding decrease of current efficiency, should occur at a higher *C.D.* This change of potential is bound to occur as soon as the ratio CN′/Cu approaches 3, and so the limiting *C.D.* for 100% efficiency will be below that obtained in *N*/10-argentocyanide solutions. Although cuprocyanide solution I and argentocyanide solution I are not strictly comparable, yet the fact that the limiting *C.D.*'s in stirred solutions are 0·0025 and 0·005 amp./cm.^{2}, respectively, suggests that there is really no essential difference in behaviour : both complex ions probably dissociate rapidly. The influence of stirring is also quite marked in solution II, although the limiting *C.D.* for 100% efficiency is raised only to 0·0005 amp./cm.^{2}; since the static potential of copper in this solution is already —0·4 volt, it is clear that the rapid rise of cathode potential cannot be long delayed even by stirring.

The effect of increasing the temperature is also to decrease the polarisation and to increase the current efficiency; with solution I, as in the corresponding case of silver, the result of raising the temperature to 70° is also the same as stirring under the particular conditions used in this work. This is further confirmation of the view that cuprocyanide ions do not dissociate slowly, for if they did the influence of temperature would be far greater than that of stirring. In solution II, an increase of the temperature to 70° improves the current efficiency somewhat more than does stirring, although the difference is not considerable; this may be connected with the fact, already mentioned, that an increase of temperature tends to retard the formation of the $Cu(CN)_3''$ complex, which probably diffuses more slowly than the $Cu(CN)_2'$ ion.

All the work described above was carried out with sodium cyanide solutions, but as other authors have used potassium cyanide some experiments were made with the latter for purposes of comparison. The electrolyte corresponding to solution I showed slight differences on account of the lower solubility of cuprous cyanide in potassium cyanide (see p. 707); the static potential of copper in this solution was —0·27 volt, as compared with —0·22 volt in the sodium cyanide solution. The cathodic potentials were very similar, but the current efficiencies were, naturally, somewhat lower in the potassium cyanide solution. With the other solutions the results were in general very similar for both cyanides; small differences in cathodic potential were probably due to the difficulty of obtaining concordant results for copper potentials in cyanide solutions.

Theory of Copper Deposition from Cuprocyanide Solutions.—Although the theory of alkali-metal discharge as a primary process in the electrodeposition of copper from cuprocyanide solutions has not been definitely suggested, yet it would seem to be as applicable to this case as to argentocyanide solutions; the same objections, however, apply to both cases (see previous paper). The theory generally accepted is that copper is deposited from cuprous ions produced by the dissociation of cuprocyanide ions, but the objection raised by Haber applies to this case as it does to silver (*Z. Elektrochem.*, 1904, **10**, 433). Foerster ("Elektrochemie Wässeriger Lösungen," 1922, p. 299, footnote), following Bodländer (*Z. Elektrochem.*, 1904, **10**, 604), has suggested that the *anion* $Cu(CN)_4'''$ is discharged at the *cathode*; this, however, seems very improbable. Although there is no independent evidence for the existence of the complex kations $(Cu_2CN)^{\cdot}$ and $(Cu_3CN)^{\cdot\cdot}$, yet it is not improbable that a small concentration of such ions, as postulated in the case of silver (p. 700), is present in cuprocyanide solutions. The discharge of these ions at the cathode would yield copper, in a finely crystalline form, as a secondary product. As soon as the complex ions were removed they would be regenerated from cuprocyanide ions as a result of the displacement of the equilibria $(Cu_2CN)^{\cdot} \rightleftharpoons 2Cu^{\cdot} + CN'$; $Cu(CN)_2' \rightleftharpoons Cu^{\cdot} + 2CN'$; $Cu(CN)_3'' \rightleftharpoons Cu^{\cdot} + 3CN'$.

Summary.

(1) The evidence for the slow dissociation of the cuprocyanide ion is discussed and shown to be inconclusive.

(2) Electrometric titration of cuprous cyanide and solubility measurements in alkali cyanide solutions show that the complex ions $Cu(CN)_2'$ and $Cu(CN)_3''$ can both exist.

(3) The cathode potentials and current efficiencies for copper deposition have been measured in a number of cuprocyanide solutions, and the results discussed.

(4) The effects of raising the temperature and of stirring the electrolyte have been investigated, and shown to be in harmony with the view that the cuprocyanide ion dissociates rapidly.

(5) The difference in behaviour of copper and silver in complex cyanide solutions is shown to be connected with the fact that a small increase in the ratio of cyanide to metal ions in the case of copper raises the electrode potential to a point at which the evolution of hydrogen is possible.

University College, Exeter.
The University, Sheffield.

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