XCIX.—*Studies of Electrolytic Polarisation. Part VII. Complex Cyanides :* (a) *Silver.*

By SAMUEL GLASSTONE.

DURING the course of an investigation of the rates of dissolution of various electrodes under the influence of alternating current, Le Blanc and Schick (*Z. Elektrochem.*, 1903, **46**, 213; *Z. physikal. Chem.*, 1903, **9**, 636) observed that with potassium cyanide as electrolyte the rate at which a silver electrode dissolved fell off rapidly with increasing frequency of the current alternations, and even when the frequency was quite small a negligible amount dissolved. Since the silver ions formed during the anodic pulses of the current probably combine readily with cyanide ions to form complex argentocyanide ions, Le Blanc and Schick suggested that the latter must in turn dissociate rapidly so that silver may be deposited during the cathodic pulses in amounts almost identical with those which dissolved when the electrode was acting as an anode. This view appeared to obtain confirmation from the work of Brunner on the variation of cathodic potential with increasing current density (*C.D.*) during the direct current electrolysis of com plex cyanide solutions (*Diss.*, Zurich, 1907; see Foerster, *Z. Elektrochem.*, 1907, **13**, 561). With a solution containing $N/10$-potassium argentocyanide and $N/5$-potassium cyanide it was found that the deposition potential of silver varied only slightly with *C.D.*, and Foerster (*loc. cit.*) explained this observation by the aid of the conclusion of Le Blanc and Schick concerning the rate of dissociation of argentocyanide ions. If the latter come rapidly into equilibrium with free silver and cyanide ions, then the concentration of silver ions in the immediate vicinity of the electrode will not change appreciably during the process of electrodeposition, and hence there should be very little concentration polarisation even at high *C.D.*'s.

In the present paper it is shown that the apparent absence of polarisation, as observed by Brunner (*loc. cit.*), does not necessarily mean that the argentocyanide ion dissociates rapidly, but calcultions made during the course of this work tend to confirm that view. It is also shown that the complex ion may dissociate rapidly even when cathodic polarisation appears to be considerable, because under certain conditions a small decrease in the silver-ion concentration may cause a large change in the electrode potential.

Silver and copper are supposed to behave differently during deposition from complex cyanide solutions, but the observations were made by different authors and not necessarily under the same conditions; thus it is not certain if the solutions were always stirred during the course of cathode-potential measurements made by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345), Höing (*ibid.*, 1916, **22**, 286), and Brunner (*loc. cit.*). Further, in every case, the so-called "direct" method of measurement with the polarising current flowing was used, and this method, especially with solutions of low conductance, is liable to give erroneous results at high *C.D.*'s (see Glasstone, J., 1924, **125**, 250); such errors may mask important changes in the true cathodic potential. Since the published work on the change of deposition potentials of various metals from complex cyanide solutions is of limited scope, a further investigation seemed desirable, especially in view of the importance of such solutions for electroplating and for the electrodeposition of alloys. In this work the commutator-extrapolation method was used for measuring cathode potentials (Glasstone, *loc. cit.*), and the general conditions were kept as uniform as possible. As part of the comparative studies now being made on the electrochemical properties of solutions containing complex ions, the present paper contains an account of the results obtained during the electrolysis of argentocyanide solutions.

In the course of the present work it became desirable to know how the reversible, or static, potential of a silver electrode against an argentocyanide solution varied with the amount of free cyanide present. For this purpose a rough electrometric titration of silver nitrate with a sodium cyanide solution was performed using a silver indicator-electrode. Treadwell (*Z. anorg. Chem.*, 1911, **71**, 219) and Müller and Lauterbach (*ibid.*, 1922, **121**, 178) have titrated solutions containing potassium cyanide with silver nitrate, but these authors were seeking an accurate end-point for the titration rather than the actual potential values; in the present work the exact end-point was a minor consideration, but the static electrode potential values were important.

In order to make this investigation of argentocyanide solutions reasonably complete, the current efficiencies for metal deposition were determined under various conditions. The influence of certain ions, which are supposed to affect the nature of the silver deposit, has been examined, and the theory of silver deposition discussed.

EXPERIMENTAL.

For most of the work sodium cyanide was used, as a good specimen was available, although previous workers in this field used the potassium salt; reference is made below to the possible differences in behaviour of these two salts. The silver nitrate was a recrystallised commercial product.

Cathode-potential Measurements.—The silver cathodes were generally of about 10 sq. cm. exposed area, and were made by depositing a thick layer of the metal, from an argentocyanide bath, on thin sheets of copper cut to the requisite size; the anode consisted of a short piece of platinum wire. No attempt was made to separate the anode and cathode compartments except in some preliminary work in which measurements were made in an atmosphere of hydrogen; as the results obtained in this way were very similar to those obtained ordinarily, the more complicated procedure was not continued. In order to avoid the possible influence of the nitrate ion acting as a depolariser, the electrolytic solutions were prepared as follows. A known amount of silver nitrate solution was precipitated with the theoretical quantity of cyanide solution; the silver cyanide was filtered off, washed quickly, and dissolved in the requisite amount of standard sodium cyanide solution. For the preparation of solutions containing equimolar amounts of sodium and silver cyanides, the solution of sodium cyanide was vigorously shaken for some time with excess of silver cyanide; the latter was then filtered off and the clear liquid used. In the measurement of the cathode potentials, the polarising current was increased by stages and held constant for a minute or two before the back *E.M.F.* of the electrode was measured by means of the commutator described previously (J., 1923, **123**, 2926); the results were extrapolated by the method described in connexion with the work on zinc alloys (J., 1927, 642). The reference electrode was in every case a calomel half-element containing a saturated solution of potassium chloride; no allowance was made for diffusion potentials.

Current Efficiencies.—The current efficiencies for silver deposition were investigated in a separate series of experiments, in which a bulk of electrolyte was used sufficient to prevent any appreciable alteration in the concentration of the solution during the process of deposition. Since silver dissolves slowly in cyanide solutions in the presence of oxygen, an allowance was made for this on the weight actually deposited on the cathode; the correction required was never very considerable and was determined by a separate experiment with each solution used.

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 cathodic potentials (*C.P.*) and percentage current efficiencies (*C.E.*) for silver deposition at various *C.D.*'s from an *N*/10-sodium argentocyanide [$NaAg(CN)_2$] solution (I), and from such a solution containing in addition *N*/10 (II), 3*N*/10 (III), 6*N*/10 (IV) and 9*N*/10-sodium cyanide (V). The results for solutions I and V are plotted in Fig. 1.

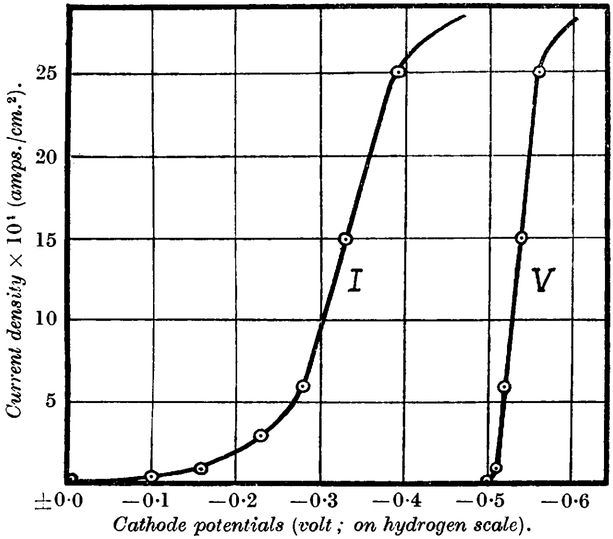
TABLE I.

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.*
—	±0·00	—	−0·33	—	−0·42	—	−0·46	—	−0·50	—
0·5	−0·10	100	−0·34	100	−0·43	100	−0·47	100	−0·51	100
1·0	−0·16	,,	—		—		—		—	
3·0	−0·23	,,	—		—		—		—	
6·0	−0·28	,,	−0·36	100	−0·44	100	−0·48	100	−0·52	100
15	−0·33	,,	−0·41	,,	−0·47	,,	−0·50	,,	−0·54	,,
25	−0·39	,,	−0·49	,,	−0·52	,,	−0·54	,,	−0·56	,,
50	−0·63	75	−0·66	76	−0·64	76	−0·65	78	−0·69	79
100	−1·18	59	−1·26	60	−1·10	62	−1·09	58	−1·12	58
200	−1·42	44	−1·42	44	−1·44	44	−1·45	44	−1·50	43

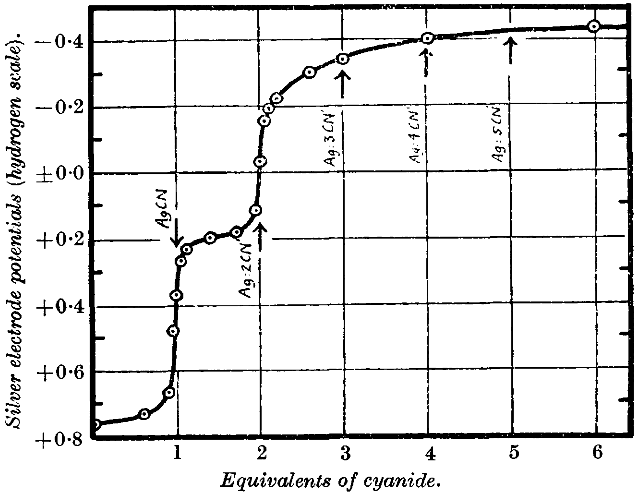
Electrometric Titration of Silver Nitrate with Sodium Cyanide.—A known volume of *N*/5-silver nitrate solution was placed in a wide tube fitted with a cork carrying a connexion to the silver indicator-electrode, a tube containing potassium chloride solution for connecting with a standard electrode, and the end of a burette containing *N*/5-sodium cyanide. Definite quantities of the latter solution were added to the silver nitrate, the mixture shaken and the electrode potential of the silver measured. It was found essential to shake the mixture vigorously for some time before taking a measurement, otherwise very misleading results were obtained. As the detailed values are not required for the purposes of the present work, they are omitted, but the variation of electrode potential with increasing amounts of added cyanide is plotted in Fig. 2. Points corresponding to important ratios of silver cyanide to sodium cyanide are marked on the curve.

FIG. 1.



A preliminary examination of the *C.D.*–*C.P.* curves in Fig. 1 would suggest that in a solution of sodium argentocyanide not containing any excess of free cyanide (solution I), there is considerable polarisation during metal deposition, since the cathodic potential increases fairly rapidly with increasing *C.D.* If an appreciable excess of free cyanide is present in the solution, as in (V), however, there is very little variation in the cathode potential for *C.D.*'s below 0·0025 amp./cm.^{2}, and the polarisation during silver deposition appears to be negligible. In the latter solution the free silver-ion concentration, as calculated from the static potential (— 0·50 volt), is apparently much less than in the former solution in which the potential of a silver electrode is ± 0·0 volt, and hence one would expect the polarisation effects to be reversed. The explanation of this anomaly can be found in the electrometric titration curve (Fig. 2). The potential of a silver electrode in an argentocyanide solution containing no excess of free cyanide is represented by a point near the centre of the second vertical portion of the curve. It is clear, therefore, that any small decrease in the ratio of silver ions to cyanide ions will cause the silver electrode potential to become rapidly more negative until a value of about − 0·3 volt is reached; beyond this point a further decrease in this ratio will result in a gradual increase in the negative potential of the silver until a value of about − 0·55 volt—the static potential in an *N*/2-cyanide solution containing no added silver ions—is reached. During the electrolysis of the argentocyanide solution (I), the deposition of even a small amount of silver on the cathode will cause a slight change in the Ag/CN′ ratio in its immediate vicinity, and hence the cathode potential will rise rapidly. As the *C.D.* is increased, the rate of silver deposition is further increased, and the reduction of the Ag/CN′ ratio will continue; the cathode potential will thus rise fairly rapidly to − 0·3 volt, and then more slowly to about − 0·5 volt. The *C.D.–C.P.* curve thus gives in this case the impression of considerable polarisation, especially at low *C.D.*'s. With solution (V), which already contains a large excess of cyanide, the static potential is represented by a point on the long horizontal part of the electrometric titration curve; any change in the Ag/CN′

FIG. 2.



ratio will, consequently, cause very little alteration to the electrode potential. In this case, therefore, although silver ions may be removed from the solution quite rapidly as a result of electrodeposition, no appreciable change occurs in the cathodic potential, and hence there is apparently no polarisation with increasing *C.D.*

In all solutions a condition must be reached in which the silver ions are being deposited on the cathode as fast as they are being brought up to it by diffusion and by other processes; at this point the thin layer of electrolyte in direct contact with the electrode may be regarded as virtually a solution of sodium cyanide containing no silver ions. The electrode potential of silver in such a solution is about − 0·5 volt, and hence, when this cathodic potential is reached, as a result of increasing the *C.D.*, the silver is being deposited at its maximum rate under the particular conditions of the experiment. This occurs in general for a solution containing *N*/10-argentocyanide, with or without excess of free cyanide, at a *C.D.* of 0·0025 amp./cm.^{2}; for an *N*/50-solution the limiting *C.D.* is about 0·0005 (see below). If the *C.D.* is increased beyond this point, then silver ions cannot be brought up to the cathode sufficiently rapidly to satisfy the requirements of the current, and so another process must commence; this is undoubtedly the discharge of hydrogen ions, which, if it occurred reversibly, should set in at a potential of about − 0·65 volt in the solutions under discussion (p_H approx. 11). As a result of hydrogen overvoltage at a silver cathode, however, the gas is not liberated freely until a potential of − 0·85 volt is reached (compare Watts and Brann, *Trans. Amer. Electrochem. Soc.*, 1917, **31**, 303). The cathodic potential of a polarised silver electrode should thus increase rapidly from − 0·55 to − 0·85 volt, and at the same time the current efficiency for metal deposition should fall below 100%. The results obtained in the present work are in complete agreement with these views.

If the *C.D.* is increased beyond the point at which gas evolution commences, it will be seen from Table I that the cathodic potential continues to increase rapidly until a value of about − 1·4 volts is attained; the subsequent increase is, however, not so sudden. The cathodic potentials for hydrogen evolution at a silver electrode in an *N*/2-sodium cyanide solution containing no silver salts have been determined, and the results show that the tendency is exactly the same :

C.D. × 10^4 (amps./cm.^{2})	1	2	3	6	9	15	30
Potential	−0·61	−0·67	−0·94	−1·27	−1·35	−1·43	−1·51

It is not improbable that the rapid increase of potential to − 1·4 volts may be connected with the discharge of sodium ions to form a sodium–silver alloy; the current is carried to the cathode almost entirely by these ions and they will accumulate in its immediate vicinity. At high *C.D.*'s some may be deposited, only, however, in the form of an alloy in which the free energy of the sodium is very much below its normal value (compare Haber and Sack, *Z. Elektrochem.*, 1902, **8**, 245; Sack, *Z. anorg. Chem.*, 1903, **34**, 286).

Rate of Dissociation of Argentocyanide Ions.—A consideration of the arguments presented above will show that the actual shape of the *C.D.–C.P.* curve does not give any direct information concerning the rate at which the argentocyanide ion comes into equilibrium with silver and cyanide ions; if the process occurred slowly, the *shape* of the curve would not be altered, but the limiting *C.D.* beyond which the current efficiency drops below 100% would be affected. From the results of the present work it is possible, however, to obtain some idea of the rate of dissociation of argentocyanide ions into simpler ions from which silver deposition can occur.

If the diffusion constant of argentocyanide ions and the thickness of the diffusion layer (compare Glasstone, J., 1925, **127**, 1824) are known, the maximum rate of diffusion of these ions to the cathode can be calculated by the aid of Fick's law. At the ordinary temperature the diffusion constants of most simple salts are between 1·0 and 1·5 (Öholm, *Z. physikal. Chem.*, 1904, **50**, 309), and hence we shall probably not be greatly in error if we take the value for the argentocyanide ion as 1·2. The thickness of the diffusion layer in the vicinity of an active electrode has only been determined in a few cases (Brunner, *ibid.*, 1904, **47**, 56; Wilson and Youtz, *J. Ind. Eng. Chem.*, 1923, **15**, 603), but the result obtained by Wilson and Youtz for an unstirred solution, *viz.*, 0·05 cm., may be taken as typical. From these values, and upon the assumption (used by the latter authors) that the concentration of ions at the electrode in the limiting case is zero, it may be calculated that from an $N/10$-argentocyanide solution, assumed to be completely dissociated, the maximum rate of diffusion of these ions to the electrode is 0·0024 g.-equiv. per day per sq. cm. of electrode surface. On the other hand, it may be calculated from the value of the limiting *C.D.*, which is in the present case 0·0025 amp./cm.^{2}, that the rate of silver deposition under these conditions is 0·0022 g.-equiv./day/cm.^{2}. In view of the approximate nature of the calculations, the agreement between the maximum rate of diffusion of argentocyanide ions to the electrode and the rate of silver deposition is very striking, and indicates that the argentocyanide ions come into equilibrium almost instantaneously with simpler ions from which silver is deposited on the cathode.

Influence of Dilution, Temperature, and Stirring.—The cathode-potential and current-efficiency measurements at various *C.D.*'s were repeated, at ordinary temperatures, in solutions (I) and (V) in which was placed a stirrer rotating at 500 r.p.m. A similar series of observations was also made on these solutions at 70°, without stirring. The results of these experiments are given in Table II. In order to determine the effect of dilution, solution (V) was diluted with water to five times its original volume, and series of measurements were made in the stirred and unstirred solutions at ordinary temperatures and in the latter at 70°. The results are given in Table III.

TABLE II.

	Solution stirred.				Solution at 70°.			
	I.		V.		I.		V.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·00	—	−0·50	—	0·02	—	−0·50	—
0·5	−0·05	100	−0·51	100	−0·02	100	−0·51	100
1·0	−0·09	,,	—		−0·06	,,	—	
3·0	−0·15	,,	—		−0·15	,,	—	
6·0	−0·20	,,	—		−0·21	,,	—	
15	−0·25	,,	−0·53	100	−0·26	,,	−0·52	100
25	−0·31	,,	−0·54	,,	−0·29	,,	−0·53	,,
50	−0·38	91	−0·58	90	−0·33	99	−0·54	,,
100	−0·44	73	−0·65	72	−0·60	81	−0·66	83
200	−1·05	60	−1·10	59	−1·10	65	−1·00	68

TABLE III.

Solution (V) diluted five times.

	Temperature 15°.				Temperature 70°.	
	Unstirred.		Stirred.		Unstirred.	
C.D. × 10^4 (amps./cm.^{2}).	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·45		−0·45		−0·46	
2	−0·47	100	−0·46	100	−0·47	100
4	−0·48	,,	—			
6	−0·50	85	−0·49	100	−0·48	
8	−0·52	—	—			
10	−0·56	—	—			
15	−0·72	52	−0·52	100	−0·50	
25	−1·09	40	−0·54	85	−0·52	89
50	−1·42	25	−0·91	34	−0·70	55
100	−1·49	23	−1·45	28	−1·25	40
200	−1·55	—	−1·51	—	−1·29	—

Since agitation of the solution increases the rate of diffusion of ions to the electrode, probably as a result of a thinner diffusion layer, it is to be expected that if the electrolyte is stirred the limiting *C.D.* at which the efficiency for metal deposition is 100% will be raised. Under the conditions of the present work, with stirring at the rate of about 500 r.p.m., the limiting *C.D.* has been approximately doubled in the *N*/10-solutions (Tables I and II), but increased about four-fold in the *N*/50-solution (Table III). The effect of raising the temperature to 70° appears to be almost the same as that of the particular type of stirring used in these experiments. Since the argentocyanide ion is already dissociating rapidly into simpler ions at the ordinary temperature, an increase of temperature can have relatively little influence in this connexion, and hence the effect of raising the temperature is merely to increase the velocity of ionic diffusion, and possibly to decrease the thickness of the diffusion layer.

For the *N*/50-argentocyanide solution it can be calculated, on the basis of the assumptions stated above, that the maximum rate of diffusion of the complex ions to the electrode is 0·00048 g.-equiv./cm.^{2}/day, whilst the rate of deposition of silver at the limiting *C.D.* is 0·00044 g.-equiv. The agreement is again good and confirms the view that the argentocyanide ion dissociates rapidly, even in dilute solution.

Theory of Silver Deposition from Argentocyanide Solutions.—The oldest view concerning the mechanism of silver deposition from cyanide solutions—one which is still held by many authors—is apparently due to Hittorf (see Dean and Cheng, *Chem. Met. Eng.*, 1918, **19**, 83; Hughes, "Modern Electroplating," 1923, p. 115). This theory supposes that the alkali-metal ion is first discharged at the cathode, and that the sodium or potassium then reacts with argentocyanide ions to produce silver, thus: $K^{\bullet} + \ominus \longrightarrow K$; $K + Ag(CN)_2{}' \longrightarrow K^{\bullet} + 2CN' + Ag\downarrow$. According to Dean and Cheng, since silver is produced as the result of a secondary reaction, there is no opportunity for the crystals to grow, and so the metal is deposited at random; this is said to account for the production of small crystals and a smooth deposit. The normal deposition potential of the alkali metals is in the vicinity of – 3·0 volts, and even allowing for a considerable reduction of free energy as a result of alloy formation, it is extremely doubtful if there can be any appreciable discharge of sodium ions at a potential of, say, – 0·3 volt, at which silver deposition from a cyanide solution can occur readily. This theory may therefore be regarded as highly improbable (see also Sanigar, *Rec. trav. chim.*, 1925, **44**, 549). An alternative theory, which has obtained considerable support, is that silver ions produced by the rapid dissociation of argentocyanide ions are directly deposited on the cathode (compare Sanigar, *loc. cit.*), and that the smooth deposit is due to the minute concentration of silver ions in the electrolyte. Haber (*Z. Elektrochem.*, 1904, **10**, 433) has pointed out, however, that since the silver-ion concentration is so small, a reasonable rate of metal deposition would involve electron velocities which must be regarded as impossibly great. Bodländer (*ibid.*, p. 604) then suggested that the complex anion—$Ag(CN)_3''$ is mentioned—takes up a negative charge at the cathode and forms an unstable ion $Ag(CN)_3'''$, which immediately dissociates into $Ag\downarrow$ and $3CN'$. If this mechanism were correct, we should have a case of the deposition of an *anion* on the *cathode !* The possibility of silver deposition occurring through the discharge of a complex kation has not yet been suggested, but this view is not improbable. Transport experiments by Hellwig (*Z. anorg. Chem.*, 1900, **25**, 157) indicated that the double salt $2AgNO_3,AgI$ gave complex kations of the form $(Ag_2I)^{\cdot}$ and $(Ag_3I)^{\cdot\cdot}$ in aqueous solution. The solubility of silver iodide in silver nitrate solution was attributed to the formation of either or both of these complexes. Hellwig found that the solubility of silver cyanide in the nitrate solution is almost the same as that of the iodide, and further, the double salt $2AgNO_3,AgCN$ is known; it appears possible, therefore, that ions such as $(Ag_2CN)^{\cdot}$ and $(Ag_3CN)^{\cdot\cdot}$ may exist in solution. It is now suggested that the presence in an argentocyanide solution of such ions, even if only to the extent of 10^{-4} g.-ion per litre, would account satisfactorily for the deposition of silver from these solutions. The equilibria in the solution would then be $Ag(CN)_2' \rightleftharpoons Ag^{\cdot} + 2CN'$, and $2Ag^{\cdot} + CN' \rightleftharpoons (Ag_2CN)^{\cdot}$. At the cathode we should probably have $(Ag_2CN)^{\cdot} + \ominus \longrightarrow Ag\downarrow + Ag^{\cdot} + CN'$. The deposition of silver, according to this view, is a secondary process, and hence the physical nature of the deposits would be explained. Since the complex kation is in equilibrium with silver and cyanide ions, it can be shown that the potential of a silver electrode against the complex ion would be the same as that of a silver|silver-ion electrode in the same solution, and hence there is no difficulty concerning the deposition from a cyanide solution occurring at the reversible potential for silver.

It has already been assumed that the maximum rate at which argentocyanide ions diffuse up to the cathode is proportional to a *C.D.* of 0·0025 amp./cm.^{2} for an *N*/10-solution; at a *C.D.* of 0·02, however, the current efficiency is about 44%, which means that 0·0088 amp./cm.^{2} is being used to deposit silver. This rate is more than three times the maximum value expected; it might, in fact, have been anticipated that the rate of deposition at the higher *C.D.* would have been smaller than at the lower, since in the former case there will be a greater tendency for the argentocyanide ions to migrate away from the cathode. If, as postulated above, the solution contains complex kations which may be brought up, to some extent, by the current from the bulk of the electrolyte to the electrode, especially at high *C.D.*'s, then the increase in the rate of silver deposition at 0·02 amp. would be expected; this increase may be partly due, however, to the stirring caused by the evolution of hydrogen bubbles.

The presence of complex kations in argentocyanide solutions might account for the abnormal electromotive behaviour of such solutions (compare Bodländer and Eberlein, *ibid.*, 1904, **39**, 226; Frary and Porter, *Trans. Amer. Electrochem. Soc.*, 1915, **28**, 307), and for the fact that no satisfactory stability constant for the $Ag(CN)_2'$ ion could be calculated from the results plotted on Fig. 2 of the present paper.

Influence of Sodium and Potassium Ions.—Although there seemed to be no fundamental reason for supposing that potassium cyanide would behave differently from the sodium salt used in this work, it was desirable to investigate this point in view of the fact that silver deposited from sodium argentocyanide solutions is sometimes regarded as inferior, from the electroplater's standpoint, to that obtained from potassium cyanide solutions (compare Blum and Hogaboom, "Electroplating and Electroforming," 1924, pp. 200 and 292; *Metal Ind.*, 1928, **32**, 214, 235). In all the cases studied, however, there was no appreciable difference in the static potentials of a silver electrode in similar solutions containing either sodium or potassium cyanide, or a mixture of the two salts. There was also no difference in the dynamic potentials under the influence of a polarising current up to a *C.D.* of about 0·002 amp./cm.^{2}, but beyond this point, *i.e.*, in the vicinity of the limiting *C.D.*, slight variations were sometimes observed. Such differences were of the order of 0·02 volt and were probably due to small changes in diffusion rates.

Influence of Carbonates.—It has been found that the addition of carbonates to a silver-plating bath affects the nature of the deposit (compare Sanigar, *Trans. Faraday Soc.*, 1929, **25**, 1), and Hogaboom (Electroplaters' Technical Society, April 18th, 1928) connects such changes with an increase of cathodic potential. In order to verify this, a number of observations were made on solutions of sodium and potassium argentocyanide containing up to 80 g. per litre of the corresponding carbonate. Up to *C.D.*'s of about 0·002 amp./cm.^{2} the carbonate produced no change in the cathode potential, but beyond this point the values were slightly more negative (by 0·02 to 0·03 volt) than in solutions free from carbonate. Exactly the same effect could be produced by adding sodium or potassium *sulphate* to the argentocyanide solution, and so the change in potential is not specific for carbonates, but is connected in some way with the altered cathode environment. It is significant that the *C.D.* used by Hogaboom (*loc. cit.*) would correspond to about

0·0025 amp./cm.^{2} in the present work, when allowance is made for the difference in concentration of the solutions used.

In technical practice it is general to deposit silver at a *C.D.* of about 0·004 amp./cm.^{2} from an approximately *N*/5-argentocyanide solution, using slight agitation; under these conditions the deposition potential is not likely to be influenced appreciably either by changes in the alkali metal or by the addition of carbonates. If there is any difference in the actual deposits obtained, it is probably due to the fact that the silver crystals grow in different environments : it is well known that the external character of a crystal may vary according to the nature of the solution from which it crystallises. The present author has considered the possibility of the presence of a complex ion of the type $(MAgCN)^{\cdot}$, where M is an alkali metal, in argentocyanide solutions; the discharge of these ions would account for the supposed differences in the deposits obtained from sodium and potassium cyanide solutions, but their existence must for the present be regarded as speculative.

Summary.

(1) The cathode potentials and current efficiencies for silver deposition have been measured in a number of argentocyanide solutions, and the results discussed and explained.

(2) The influence of stirring, temperature, and dilution of the electrolyte has been investigated.

(3) It has been shown that the argentocyanide probably dissociates very rapidly into simpler ions.

(4) The theories of silver deposition from cyanide solutions have been discussed and shown to be unsatisfactory; an alternative theory involving a complex kation is proposed.

(5) The possible influence of sodium, potassium or carbonate ions on the form of the silver electrodeposit is discussed.

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