CLIX.—*Studies of Electrolytic Polarisation. Part IX. Complex Cyanides: (c) Zinc, Cadmium, and Mercury.*

By SAMUEL GLASSTONE.

FROM previous studies (J., 1929, 690, 702) it was concluded, in contrast to the views of Le Blanc and Schick (*Z. Elektrochem.*, 1903, **9**, 636; *Z. physikal. Chem.*, 1903, **46**, 213) and of Foerster (*Z. Elektrochem.*, 1907, **13**, 561), that the cathode potential–*C.D.* curves and the current efficiency for metal deposition in the electrolysis of complex cyanides depend on (*a*) the variation of electrode potential with increasing ratio of cyanide to metal in the solution, and (*b*) the relation of the potential in the presence of excess of cyanide to that at which hydrogen evolution occurs. If the solution under examination is one in which an increase of the cyanide concentration causes an appreciable alteration of potential, *i.e.*, if it corresponds with a position on the metal ion–cyanide titration curve where there is a marked inflexion, polarisation should be appreciable. On the other hand, very little polarisation should result when the addition of cyanide has only a small influence on the electrode potential; this occurs when the solution already contains an excess of cyanide. If the cathode potential remains below that requisite for the evolution of hydrogen, the efficiency for metal deposition is 100%; but if the *C.D.* exceeds a value at which the rate of deposition of metal is greater than the rate of diffusion of the appropriate ions to the electrode, the cathode potential rises rapidly, the efficiency for metal deposition falls off, and hydrogen evolution commences. If the hydrogen potential is attained before the limiting *C.D.* is reached, the current efficiency decreases at this point, but there is no rapid increase of cathode potential. Since all the polarisation observed in the electrolysis of complex cyanides is due ultimately to concentration changes, and not to the slowness of any chemical reaction, it can be decreasd by vigorous stirring of the electrolyte.

The above views, based on observations on complex silver and copper cyanides, have now been tested and confirmed by similar experiments involving electrometric titrations of salts of zinc, cadmium, and mercury with sodium cyanide solutions, together with cathode-potential and current-efficiency measurements at various *C.D.*'s.

Zinc dissolves spontaneously in alkali cyanide solutions with the evolution of hydrogen, since the electrode potential Zn|KCN is about −1·25 volts; hence the electrolytic behaviour of complex zinc cyanide solutions was expected to be similar to that of the cuprocyanides (J., 1929, 702). Cadmium and mercury are not attacked by potassium cyanide solution in the absence of air; on electrolysis their complex cyanides were, therefore, expected to give results similar to those obtained with argentocyanide solutions (J., 1929, 690). The limited observations made by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) and by Höing (*ibid.*, 1916, **22**, 286) on zinc, and by Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 111) on cadmium, were seen to support these conclusions.

EXPERIMENTAL.

The experimental methods were similar to those already used for the study of silver and copper complex cyanides. With zinc and cadmium the electrometric titrations were performed on the corresponding sulphates in *N*/5-solutions; the electrolysis solutions were made from the same salts by the addition of appropriate amounts of cyanide. Sodium cyanide was used almost exclusively throughout this work; independent experiments showed that potassium cyanide gave exactly similar results. For the observations with the mercury cathode, a pure specimen of mercuric cyanide was used; as this substance is almost a non-electrolyte, a small amount of sodium sulphate was added to the solution.

It is noteworthy that mercuric cyanide is stable in contact with metallic mercury, whereas under these conditions most other mercuric salts are unstable and tend to form mercurous salts. Mercurous cyanide, however, is unstable and decomposes immediately into mercuric cyanide and mercury (Abel, *Z. anorg. Chem.*, 1901, **26**, 379). The explanation of this behaviour lies in the fact that mercuric cyanide yields only a very small concentration of mercuric ions in solution; from observations made in the course of the present work the mercuric-ion concentration (assumed equal to the activity) is about 10^{-21} g.-ion per litre in $N/5$-solutions of the cyanide. According to Abel (*loc. cit.*, p. 375), $[Hg_2^{\cdot\cdot}]/[Hg^{\cdot\cdot}]$ is equal to 120 when mercuric and mercurous ions are in equilibrium with metallic mercury; hence the concentration of mercurous ions in the mercury–mercuric cyanide system is about 10^{-19} g.-ion per litre. Mercurous salts are generally more highly ionised than corresponding mercuric salts (compare Lowry, *Trans. Faraday Soc.*, 1928, **24**, 1), and so only an extremely small concentration of mercurous cyanide can co-exist with mercuric cyanide and mercury. The latter salt is, therefore, stable and the former unstable.

Cathode-potential measurements were made by the methods described in previous papers of this series. Attempts were made to determine the current efficiencies for metal deposition, but only with cadmium was a systematic study possible. Zinc dissolves so readily in solutions containing the slightest excess of free cyanide that even at high *C.D.*'s there was a net *loss* in weight of the cathode. A rough indication of the efficiencies can, however, be obtained from the cathode-potential measurements. A satisfactory investigation of the current efficiency with a mercury cathode was prevented by experimental difficulties, but approximate determinations were made with an amalgamated copper electrode as well as with one of liquid mercury; the results indicated that the metal was discharged almost entirely as bivalent ions.

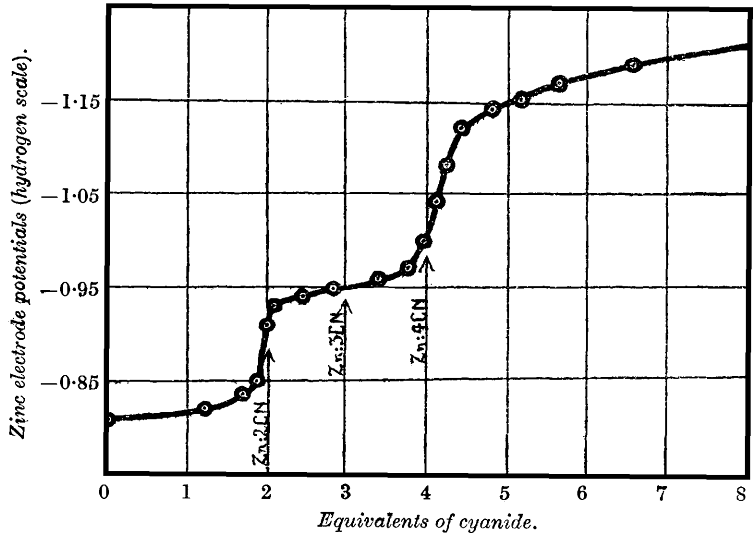
Unless otherwise stated, experiments were carried out at room temperature (15°). All electrode-potential measurements are expressed on the normal hydrogen scale.

Results.

Zinc.—The electrometric titration curve of zinc sulphate solution with sodium cyanide, a zinc electrode being used as indicator, is shown in Fig. 1. The precipitate of zinc cyanide dissolves completely when the ratio Zn : CN = 1 : 4, in approximately $N/10$-solutions (see Treadwell, *Chem.-Ztg.*, 1914, **38**, 1230; Corbet, J., 1926, 3190); this fact, together with the shape of the titration curve, suggests that $Zn(CN)_4''$ is the chief complex ion present in solution. The

p_H of the $Na_2Zn(CN)_4$ solution is about 10, and the reversible potential of a hydrogen electrode in it is −0·57 ; the reversible zinc potential is −0·99 volt. In the electrolysis of such a solution, therefore, hydrogen may be expected to be liberated at the cathode instead of metal, but the high overvoltage of hydrogen at a zinc cathode prevents this happening. Actually, it has been observed that hydrogen bubbles appear at a zinc electrode in a complex cyanide solution at a potential of −1·18 volts; even at less negative potentials, however, some of the current will be utilised in the discharge of hydrogen ions, since the resulting atoms are removed by diffusion or by depolarisation with air. It is clear, therefore, that 100% efficiency for zinc deposition is not to be expected from solutions containing cyanides.

FIG. 1.



The titration curve shows that cathodic polarisation cannot be as marked as with silver and copper, since the sudden rise of potential occurring when the ratio CN : Zn exceeds 4 : 1 is only from −0·99 to −1·14; beyond this, the zinc electrode potential rises gradually to −1·24 volts, which is the value in a 0·5N-sodium cyanide solution. Since the free evolution of hydrogen commences at −1·18 volts, the subsequent change of potential of the zinc cathode should be similar to that in a simple cyanide solution in which hydrogen discharge is the only cathodic process (Table I, last column).

The actual cathode potentials (*C.P.*) and current efficiencies (*C.E.*) recorded in Table I are in agreement with the predictions made from a study of the titration curve. Solution I was $M/10$ with respect to $Na_2Zn(CN)_4$, and Solution II contained in addition $N/5$-sodium cyanide. The current efficiencies, which are in any case very rough, could not be determined for Solution II for the reason given on p. 1239. Experiments were also made with Solution I stirred (500 r.p.m.) at 15°, and unstirred at 70°.

TABLE I.

Cathode potentials and current efficiencies.

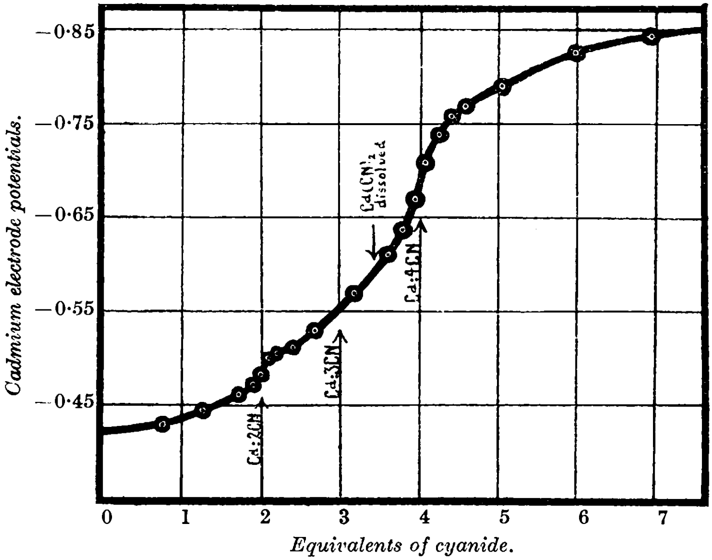
C.D. $\times 10^4$ (amps./cm.^{2}).	Solution I.						Solution II.	$N/5$-NaCN.
	Unstirred at 15°.		Stirred at 15°.		Unstirred at 70°.			
	C.P.	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.P.*
—	−0·99	—	−0·99	—	−0·99	—	−1·22	−1·24
1·0	−1·04	—	—	—	−1·01	—	−1·24	−1·26
2·0	−1·06	—	−1·00	—	−1·02	—	−1·26	−1·27
4·0	−1·09	—	−1·01	—	−1·06	—	−1·29	−1·31
8·0	−1·16	52	−1·03	—	−1·08	—	−1·33	−1·34
12	−1·27	33	−1·07	48	−1·14	51	−1·40	−1·41
20	−1·34	30	−1·14	40	−1·20	41	−1·44	−1·45
40	−1·39	26	−1·24	36	−1·28	36	−1·47	−1·50

It is to be noted that stirring the electrolyte and raising the temperature have not the same marked influence on the current efficiency for zinc deposition as for copper (*loc. cit.*); this is because the polarisation in the former case is smaller, and so stirring and raising the temperature, which tend to decrease polarisation, cannot be relatively so effective. Further, since the cathode potential for zinc deposition from cyanide solutions is always more negative than that required for the reversible discharge of hydrogen ions, the removal of accumulated hydrogen as a result of stirring will increase the proportion of current devoted to the discharge of these ions, and the efficiency of zinc deposition must decrease in consequence. Similarly, at high temperatures the overvoltage for hydrogen evolution is decreased, and a larger proportion of the current will be utilised in liberating hydrogen than for the same cathode potential at lower temperatures. All the observed results may, therefore, be explained without the necessity of assuming that the complex zincicyanide ion dissociates *slowly* into its constituents.

During the course of this work, it was noted that zinc sulphate solution dissolves appreciable amounts of zinc cyanide: 1 l. of M-solution dissolves about 0·003 g.-mol. at 15°, and 0·01 g.-mol. at 70°. This suggests, as in the case of silver (see Hellwig, *Z. anorg. Chem.*, 1901, **25**, 157), that a complex zinc cyanide *kation*, possibly $[Zn_2(CN)_2]^{\cdot\cdot}$, is formed; these complex ions, rather than simple zinc ions, may be actually discharged at the cathode during the electrolysis of cyanide solutions (compare J., 1929, 700, 712).

Cadmium.—The electrode potential–titration curve for $M/5$-cadmium sulphate solution with sodium cyanide and a cadmium electrode, is shown in Fig. 2; the slight inflexion corresponding with the formation of $Cd(CN)_2$ indicates that this substance is comparatively soluble. The electrode potential of cadmium in the system containing cadmium and cyanide in the ratio 1 : 2 is —0·49 volt; hence the solubility of cadmium cyanide in water is of the order of 10^{-3} g.-mol. per litre. This is of a similar order to the solubility of zinc cyanide, but is appreciably greater than that of silver and copper cyanides. It is of interest that at least 1 c.c. of N-sodium cyanide solution must be added to 10 c.c. of N-cadmium sulphate solution before a permanent precipitate of cadmium cyanide is formed; the latter is thus appreciably soluble in the sulphate solution, possibly as a result of the formation of a complex kation of the type $[Cd_2(CN)_2]^{\cdot\cdot}$. The shape of the titration curve when the ratio CN : Cd exceeds 2 : 1, and the fact that the precipitate of cadmium cyanide dissolves completely when the ratio is *ca.* 3·5 :1 (see also Corbet, *loc. cit.*), suggests that at least two complex ions, $Cd(CN)_3'$, or perhaps $[Cd(CN)_3(H_2O)]'$, and $Cd(CN)_4''$ are present in solution (see also Pines, *J. Czech. Chem. Comm.*, 1929, **1**, 387).

FIG. 2.



During electrolysis, the cathodic polarisation of cadmium in a solution containing Cd : CN = 1 : 4 should be of the same order as with zinc; a rapid rise of potential can occur only between —0·67 and −0·82 volt, and this will be followed by a more gradual rise to about −0·95 volt, the potential of cadmium in $N/2$-sodium cyanide solution. There is, however, an important difference between cadmium and zinc as regards hydrogen evolution; it has been found that the gas commences to be evolved freely from a cadmium cathode in sodium cyanide solution at a potential of about −1·1 volts, a value distinctly more negative than that of cadmium in the same solution. It is clear, therefore, that during the electrolysis of complex cadmicyanide solutions the metal should be deposited at almost 100% efficiency, unless the *C.D.* is such that the rate of deposition exceeds the rate of diffusion of cadmium compounds to the cathode. At this limiting *C.D.* the potential will rise and the current efficiency for metal deposition fall. It may be calculated by the method described in a previous paper (J., 1929, 697) that for an $M/10$-solution of a cadmium salt the limiting *C.D.* at which the rates of deposition and diffusion are equal is about 0·0055 amp./cm.^{2}. This value, as in the case of argentocyanide solutions, should be independent of the amount of free cyanide present,* but should depend on (*a*) the concentration of the cadmium salt, (*b*) the temperature of the solution, and (*c*) whether the solution is stirred or not. Raising the temperature or stirring the electrolyte should raise the limiting *C.D.* for 100% deposition, but dilution should bring about a decrease.

The results obtained in the investigations on the electrolysis of cadmium cyanide solutions are given in Table II. Solution I contained Cd and CN in the ratio of 1 to 4, and in Solution II the ratio was 1 to 6; the concentration of cadmium salt was $M/10$ in each original electrolyte.

These results are in agreement with the views already expressed; the limiting *C.D.* for 100% efficiency of metal deposition is about 0·006 amp./cm.^{2} in the $M/10$- and 0·00055 in the $M/100$-solutions. As in the work on silver, the effect of stirring at 500 r.p.m., or of raising the temperature to 70°, is to increase the limiting *C.D.* in the dilute solution four- or five-fold. It is of interest that the limiting *C.D.* for 100% efficiency of metal deposition in an $M/10$-cadmium sulphate solution is 0·006 amp./cm.^{2}; this result indicates, in agreement with expectation, that the simple $Cd^{\cdot\cdot}$ and the complex $Cd(CN)_4''$ ions diffuse at almost the same rate. The limiting *C.D.* is thus independent of the actual concentration of $Cd^{\cdot\cdot}$ ions, but depends primarily on the total cadmium concentration.

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* If the solution contains a large excess of free cyanide the efficiency may be somewhat lowered, since hydrogen ions may be discharged to replace the gas removed by diffusion and depolarisation.

TABLE II.

Solution I.

C.D. $\times 10^4$ (amps./cm.^{2}).	Unstirred.		Stirred.		Diluted 10-fold.		Diluted and stirred.		Diluted, at 70°.	
	C.P.	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·67	—	−0·67	—	−0·65	—	−0·65	—	−0·65	—
1·0	−0·72	—	—	—	−0·69	—	—	—	—	—
2·0	−0·75	—	—	—	−0·76	—	−0·69	—	−0·70	—
3·0	−0·77	—	—	—	−0·84	—	—	—	—	—
4·0	−0·78	—	−0·73	—	−0·89	100	−0·71	—	−0·74	—
5·0	—	—	—	—	−0·93	—	—	—	—	—
6·0	—	—	—	—	−1·19	54	−0·74	—	−0·78	—
10	−0·82	—	−0·76	—	−1·37	22	−0·79	—	−0·81	—
20	−0·86	—	−0·78	—	−1·46	18	−0·83	100	−0·85	100
30	−0·89	—	—	—			−1·15	82	−1·20	80
50	−0·91	100	−0·80	—			−1·36	57	−1·28	65
60	−1·00	—	—	—			−1·44	30	−1·35	38
70	−1·30	90	—	—						
100	−1·40	83	−0·84	100						
170			−0·89	—						
200			−1·26	92						

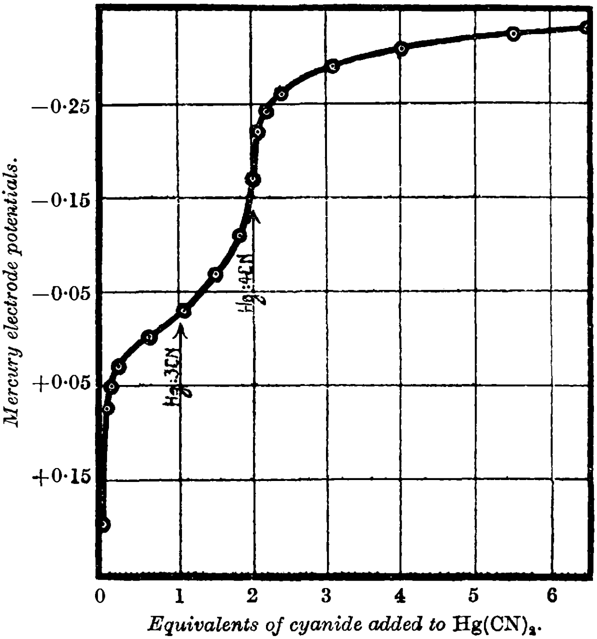
Solution II.

C.D. $\times 10^4$ (amps./cm.^{2}).	Unstirred.		Diluted 10-fold.		Diluted and stirred.		Diluted, at 70°.	
	C.P.	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*	*C.P.*	*C.E.*
—	−0·84	—	−0·80	—	−0·80	—	−0·80	—
1·0	—	—	−0·85	—	−0·81	—	—	—
2·0	—	—	−0·89	—	—	—	—	—
3·0	—	—	−0·92	—	—	—	—	—
4·0	−0·90	—	−0·96	—	−0·85	—	—	—
5·0	—	—	−0·99	100	—	—	—	—
6·0	—	—	−1·27	73	−0·90	—	—	—
10	−0·92	—	−1·35	48	−0·93	—	−0·91	—
20	−0·94	—	−1·45	30	−0·98	100	−0·99	100
30	−0·95	—			−1·30	74	−1·28	70
50	−0·98	100			−1·45	35		
70	−1·32	91						
100	−1·41	84						

Mercury.—Since mercuric salts, other than the cyanide, are unstable in the presence of mercury, an *M*/10-solution of the latter salt was used for the electrometric titration with sodium cyanide and a mercury indicator electrode; the variation of mercury electrode potential with varying Hg : CN ratios is shown in Fig. 3. The shape of the curve indicates that $Hg(CN)_4''$ is the main ion formed when alkali cyanide is added to mercuric cyanide, but the absence of any marked horizontal portion between the Hg : CN ratios 1 : 2 and 1 : 4 (*i.e.*, between 0 and 2 added equivs.) suggests that the ion $Hg(CN)_3'$ is also formed to some extent. Since mercuric cyanide is soluble in water, it is not possible to verify this conclusion by observations on the solubility in the presence of alkali cyanide. From the titration curve, it may be seen also that on electrolysis the cathode potential of mercury in a solution of mercuric cyanide should alter with increasing polarising *C.D.* at first rapidly from 0·18 to 0·03, more slowly to —0·15, rapidly again to —0·25, and finally more gradually to about —0·35 volt. In a solution of $Na_2Hg(CN)_4$, the polarisation should be marked at low *C.D.*'s, since the mercury potential rises from —0·15 to —0·25 for quite small changes in the Hg : CN ratio. If the electrolyte contains excess of free cyanide there should be very little polarisation even at appreciable *C.D.*'s.

As the rate of diffusion of the mercuricyanide ion is probably similar to that of other ions (diffusion coefficient, 1·2 approx.), the limiting *C.D.* for 100% efficiency of mercury deposition should be about 0·006 amp./cm.^{2}; above this *C.D.* some of the current must be utilised in the discharge of hydrogen ions. Since the overvoltage for hydrogen evolution at a mercury electrode is more than 0·7, the cathode potential for the liberation of this gas from cyanide solutions will be about —1·3 volts. Hence, in the electrolysis of mercuricyanide solutions, the potential beyond the limiting *C.D.* must rise rapidly from —0·35 to —1·3 volts, and at the same time the current efficiency should fall. The actual results obtained were in agreement with these anticipations. Cathode-potential measurements made by means of the commutator were trustworthy only up to the limiting *C.D.*, for above this point the rate of fall of potential on switching off the current—as might be anticipated from the factors already mentioned—was too great to allow of accurate extrapolation being made. The potentials in Table III are therefore only for *C.D.*'s at which there is no tendency for hydrogen

FIG. 3.



evolution to occur; the highest *C.D.* quoted for any particular electrolyte may be regarded as the limiting value for 100% efficiency of mercury deposition in that solution. On account of the difficulties of working with a mercury cathode, only a limited number of current-efficiency measurements were made; these, as well as others with an amalgamated copper electrode, indicated that at all *C.D.*'s given in Table III the metal-deposition efficiency was about 100%. Solution I was *M*/10-mercuric cyanide containing some sodium sulphate to increase the conductance; Solution II was *M*/10-$Na_2Hg(CN)_4$, and Solution III contained in addition 0·4*N*-sodium cyanide solution.

TABLE III.

Cathode potentials.

	Solution I.			Solution II.		
C.D. × 10^4 (amps./cm.^{2}).	I.	Diluted 5-fold.	Diluted, at 70°.	II.	Diluted 10-fold.	Solution III.
—	0·18	0·18	0·19	−0·15	−0·13	−0·33
2·0	0·08	0·02	0·09	−0·21	−0·19	−0·36
4·0	—	−0·03	0·04	−0·24	−0·24	−0·37
5·0	—	−0·05	—	—	−0·27	—
6·0	0·01	−0·07	—	−0·27	−0·29	−0·39
8·0	—	−0·15	—	−0·28		—
12	−0·02	−0·31	−0·03	—		—
20	−0·04		−0·06	−0·30		−0·41
30	−0·06		−0·16	−0·33		−0·42
50	−0·19		−0·21	−0·34		—
60	−0·32		−0·32	−0·35		−0·43

These results are in harmony with the anticipations based on the general principles applicable to the electrolysis of complex cyanide solutions. As in previous cases, dilution decreases the limiting *C.D.* to an extent proportional to the reduction of concentration, whereas raising the temperature (and stirring) increases this *C.D.* The extent of cathodic polarisation is a function of the variation of the mercury potential with changes in the Hg : CN ratio; although the mercuricyanide ion probably dissociates rapidly into its constituents, there must be some polarisation in Solution II, but less in Solution III.

Summary.

(1) Cathode-potential and current-efficiency measurements have been made in solutions containing complex cyanides of zinc, cadmium, and mercury.

(2) The main factors influencing the results are (*a*) the variation of electrode potential with increasing ratio of cyanide to metal, (*b*) the potential for hydrogen evolution at the given metal, and (*c*) the concentration of the electrolyte.

(3) There is no reason to believe that any of the complex cyanides studied hitherto dissociate slowly.

(4) Electrometric-titration curves indicate the presence of $Zn(CN)_4''$ ions in zinc solutions, $Cd(CN)_3'$ and $Cd(CN)_4''$ ions in cadmium solutions, and $Hg(CN)_3'$ and $Hg(CN)_4''$ ions in mercuric solutions.

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