431. *Studies of Electrolytic Polarisation. Part X. Ammines of Copper, Silver, Zinc, and Cadmium.*

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THE object of the present work was to apply the methods used in the study of the complex cyanide ions (J., 1929, 690, 702; 1930, 1237) to the investigation of the rates of dissociation of complex metal-ammine kations.

The discharge of a positive metal-ammine ion at a cathode may take place in one or both of two ways: either (*a*) the complex ion may be directly discharged with the formation of an unstable intermediate molecule which decomposes immediately into a metal atom and ammonia molecules,

$$M(NH_3)_x^+ + \ominus \longrightarrow M(NH_3)_x \longrightarrow M + xNH_3,$$

or (*b*) only simple ions, produced by the dissociation of the complex, are capable of being discharged, thus

$$M(NH_3)_x^+ \longrightarrow M^+ + xNH_3,$$

and

$$M^+ + \ominus \longrightarrow M.$$

If the first mechanism only is operative, the question of the rate of dissociation of the complex ion does not arise; if, however, the second mechanism occurs, either partly or exclusively, the problem is of importance in connexion with certain theories, proposed to account for the irreversibility of deposition of the iron-group metals, which will be discussed in a future paper. There seems to be no method available for distinguishing between the two alternative mechanisms for metal deposition, and since it is probable that dissociation of the complex ion is the first stage in the process, it is necessary to know if the reaction, should it occur, is fast or slow.

Two important factors which did not enter into the work on the complex cyanides have now to be taken into consideration: (1) Whereas sodium and potassium cyanides may be regarded as almost completely dissociated, the degree of dissociation of an aqueous solution of ammonia varies, and so there is an uncertainty as to the concentration of free ammonia concerned in the formation of the metal-ammine ions in any particular solution. This fact is responsible for the somewhat abnormal shape of the curve obtained by Britton (J., 1925, **127**, 2956) during the electrometric titration of silver nitrate solution with aqueous ammonia using a silver indicator electrode. In the present work an excess of ammonium sulphate was added to all solutions, thereby depressing the dissociation of the ammonium hydroxide so that all the ammonia in solution could be regarded as being in the form of NH_3 molecules. The electrometric titration curves thus obtained were much more of the normal type. (2) Allowance had to be made for the possibility of the migration of kations to the electrode under the influence of the applied potential, in addition to those diffusing to the cathode in the ordinary manner. This difficulty does not apply to the complex cyanide solutions, since there was always a sufficiently large concentration of cyanide ions near the cathode to carry almost the whole of the current passing. In ammoniacal silver nitrate solution, however, the small concentration of ammonium hydroxide is unable to supply sufficient ammonium ions for this purpose. The ammonium sulphate which was added provides such a large concentration of ammonium ions that no appreciable proportion of the ammine ions was involved in electrolytic transport; all the complex ions reaching the cathode may be regarded, therefore, as arriving as a result of natural diffusion only.

If it is assumed, as previously, that the diffusion coefficients of all ions, other than hydrogen and hydroxyl ions, are almost the same, it can be calculated (J., 1929, 690; *Trans. Amer. Electrochem. Soc.*, 1931, **59**, 277) that the maximum rate of diffusion of metal-ammine ions is equivalent to a *C.D.* of $0{\cdot}027n$ amp. per sq. cm., where n is the concentration of the complex ion in g.-equiv. per litre. If the complex ion dissociates rapidly and no hydrogen evolution occurs during the course of metal deposition, then this *C.D.* represents the maximum at which the metal can be deposited with an efficiency of 100%; if this *C.D.* is exceeded, the cathode potential should rise rapidly and the liberation of hydrogen gas should commence.

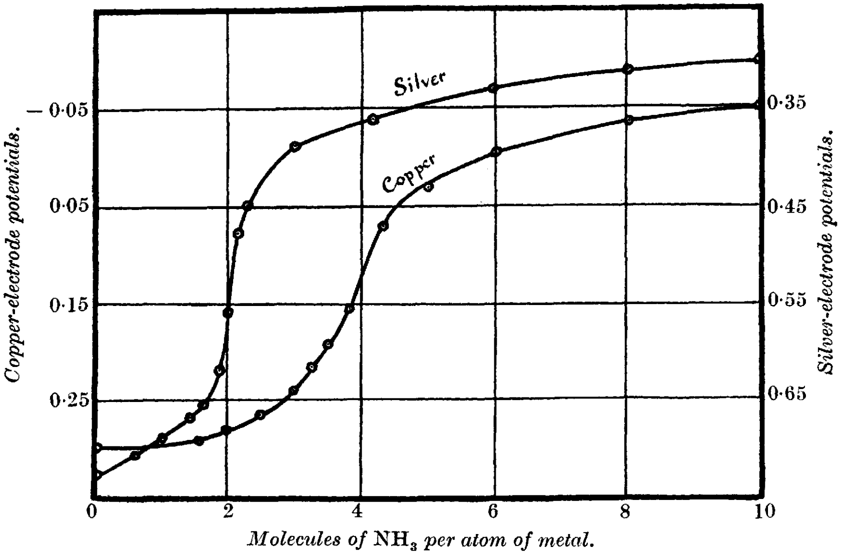
Electrometric titrations of copper, silver, zinc, and cadmium salts with ammonia solution, using the appropriate metal as indicator electrode, have been carried out; the results, as with the cyanide titrations (*loc. cit.*), can be readily correlated with the curves obtained by plotting cathode potential against *C.D.* for solutions containing various ratios of metal to ammonia. Owing to experimental difficulties only a limited number of observations of current efficiency for metal depositions were made; copper and zinc dissolve spontaneously in ammoniacal solutions, the latter with the evolution of hydrogen, and all the metals studied tend to give non-adherent deposits, especially at the higher *C.D.*'s. The limiting *C.D.* for 100% efficiency of metal deposition can, however, be inferred in all cases studied, except that of zinc, from the sudden rise in the cathode potential which occurs when this limit is passed.

EXPERIMENTAL.

The procedure was similar to that used for the complex cyanides (*loc. cit.*). For the electrometric titration, 5 c.c. of a N-solution of a salt of the metal, to which had been added about 2 g. of $(NH_4)_2SO_4$, were titrated with N-NH_4OH. A thick wire of the metal (Ag or Cu) or a thick Cu wire coated with the metal (Zn or Cd) by electrodeposition was used as indicator electrode. In order to diminish the possibility of dissolution of the metal, a current of H was passed through the solution during the titration. Under the conditions of the experiments no ppt. of hydroxide or basic salt occurred on addition of NH_4OH; the decreased OH' concn. caused by the excess of $(NH_4)_2SO_4$, together with the removal of simple kations to form metal-ammine complexes, prevented the solubility product of any of the hydroxides being attained. The titration curves, therefore, show no breaks at points corresponding to hydroxides.

Cathode-potential measurements were made by the commutator–extrapolation method used in previous work. All the electrode potentials are expressed on the normal hydrogen scale, and unless otherwise stated, experiments were carried out at room temp. (about 15°) in unstirred solutions.

FIG. 1.



RESULTS.

Copper.—The results of the titration of N-$CuSO_4$ solution, containing $(NH_4)_2SO_4$, by N-NH_4OH are shown in Fig. 1. The marked inflexion in the potential–composition curve occurs in the region corresponding to $Cu(NH_3)_4^{\cdot\cdot}$; this conclusion is in agreement with that reached by Dawson (J., 1906, **89**, 1666), Hantzsch and Robertson (*Ber.*, 1908, **41**, 4328), and others from different methods. In the absence of added $(NH_4)_2SO_4$ the inflexion in the curve is barely noticeable, for under these conditions the amount of NH_3 added is not proportional to the volume of NH_4OH solution used; there is no doubt, however, that the same complex ion is formed.

The most negative potential reached was about – 0·05 volt ($Cu : NH_3 = 1 : 10$); even in conc. aq. NH_3 (d 0·88), in which the concn. of $Cu^{\cdot\cdot}$ ions is as low as it can be in a cupriammine solution, the potential of the Cu electrode was − 0·4 volt, whereas the potential for the reversible evolution of H in such a solution is in the vicinity of − 0·6 volt. There appears to be no danger, therefore, that the evolution of H will interfere with the deposition of Cu from the cupriammine solutions. The cathodic potential in such electrolytes should rise rapidly from about 0·25 to ± 0·0 volt, and then slowly to more negative values, approaching − 0·4 volt when the limiting current is reached. If the H overvoltage at a Cu cathode is about 0·15, then gas evolution in the solutions under examination should commence at about − 0·75 volt, and so a sudden rise of cathode potential should occur when the limiting *C.D.* is exceeded.

The actual cathode potentials measured at various *C.D.*'s are given in Table I; each solution, unless diluted, was 0·1*M* with respect to Cu, and about *M* in $(NH_4)_2SO_4$. The ratio of Cu : NH_3 was 1 : 4 in solution I, 1 : 5 in II, and 1 : 7 in III.

TABLE I.

Copper cathode potentials.

C.D. × 10^4 (amps./cm.^{2}).	Solution I.		Solution II.		Solution III.	
	I.	Diluted 10-fold.	II.	Diluted 10-fold.	III.	Diluted 10-fold.
—	0·11	0·19	0·03	0·15	−0·02	0·01
1	—	0·15	—	0·12*	—	−0·02*
2	—	0·09*	—	0·02	—	−0·09
3	—	−0·03	—	−0·05	—	−0·14
5	0·09	−0·11	0·01	−0·12	−0·03	−0·21
6	—	−0·18	—	−0·15*	—	−0·30*
7	—	−0·25*	—	−0·85	—	−0·88
10	—	−0·90	−0·02	−0·92	—	−0·92
15	0·07*	−0·95	−0·05*	−0·97	−0·06*	−0·97
20	−0·10	—	−0·19	—	−0·17	—
30	−0·12	—	−0·22	—	−0·20	—
40	−0·14	—	−0·25	—	−0·23	—
50	−0·18	—	−0·28	—	−0·24	—
60	−0·24	—	−0·32	—	−0·27	—
65	−0·35*	—	−0·39*	—	−0·34*	—
70	−0·81	—	−0·90	—	−0·65	—
90	−0·94	—	−0·97	—	−0·98	—

These results show that the expected rapid rise of cathode potential from 0·25 to ± 0·0 volt, which should have been observed at the lowest *C.D.*'s in solution I, does not occur. Further, in each solution there are two *C.D.*'s, marked with an asterisk, at which there is a sudden rise of cathode potential, whereas in the electrolysis of the complex cyanides only one such *C.D.* is observed. If the $Cu(NH_3)_4^{\cdot\cdot}$ ion may be supposed to dissociate very rapidly, then the limiting *C.D.* for 100% Cu deposition should be about 0·0054 amp./cm.^{2} (see p. 2850) in the 0·1*M*-solutions, but the two observed limiting *C.D.*'s are 0·0015 and 0·0065 amp./cm.^{2} in each case. When attempting to determine the current efficiencies for Cu deposition in these solutions, the probable cause of the two discontinuities became evident, for the Cu cathode dissolved spontaneously in the solutions at a rate equiv. to a *C.D.* of about 0·0015 amp./cm.^{2}. There is no simultaneous evolution of H, but the Cu probably dissolves to form $Cu(NH_3)_x^{\cdot}$ ions which may subsequently become oxidised to $Cu(NH_3)_4^{\cdot\cdot}$ ions. As the *C.D.* at the cathode is increased, therefore, the

NH_3 : Cu ratio does not increase at first as rapidly as would have been the case if the electrode had not been attacked; the cathode potential at low *C.D.*'s consequently changes only slowly as the *C.D.* is increased. When the latter exceeds 0·0015 amp./cm.^{2}, the rate of deposition of Cu exceeds the rate of dissolution and further increase of *C.D.* causes a marked increase in the NH_3 : Cu ratio and the cathode potential rises rapidly. This potential subsequently increases, with increasing *C.D.*, to about − 0·35 volt, as anticipated, when the second limiting current at 0·0065 amp./cm.^{2} is reached; beyond this point there is another rapid rise of potential accompanied by H evolution. The *C.D.* of 0·0065 amp./cm.^{2} may be regarded as equiv. to the sum of the rate of diffusion of the $Cu(NH_3)_4^{\cdot\cdot}$ ions to the cathode and the rate of dissolution of the Cu from the electrode, since this represents the max. rate of deposition of the metal under the experimental conditions. As the rate of dissolution is equiv. to 0·0015 amp./cm.^{2}, the rate of diffusion is equiv. to a *C.D.* of 0·0050 amp./cm.^{2}, which agrees with the value of 0·0054 amp./cm.^{2}, calc. on the assumption that the $Cu(NH_3)_4^{\cdot\cdot}$ ion dissociates rapidly and that its diffusion coefficient is 1·2.

In the solutions which have been diluted 10-fold, *i.e.*, 0·01*M*-Cu, the two limiting *C.D.*'s are at about 0·0001 and 0·0006 amp./cm.^{2}, and the difference (0·0005 amp./cm.^{2}) corresponds, according to the views given here, to the max. rate of diffusion of the $Cu(NH_3)_4^{\cdot\cdot}$ ions in the 0·01*M*-solution; the calc. value is 0·00054 amp./cm.^{2}. The results obtained in the present work indicate, therefore, that if dissociation of the $Cu(NH_3)_4^{\cdot\cdot}$ ions is a necessary preliminary to the deposition of Cu on a cathode, then this dissociation occurs very rapidly.

Silver.—The curve similarly obtained in the electrometric titration of *N*-$AgNO_3$ (Fig. 1) indicates that $Ag(NH_3)_2^{\cdot}$ is the main complex ion formed; this formula is the one generally accepted (see Britton, *loc. cit.*). The most negative potential reached, with Ag : NH_3 = 1 : 10, is 0·20 volt, and consequently there is no likelihood that H will be evolved at a Ag cathode in $Ag(NH_3)_2^{\cdot}$ solution until the *C.D.* exceeds that at which diffusion of kations can keep pace with the rate of deposition of Ag. From the titration curve it appears that with a solution containing 1Ag to $2NH_3$ the cathode potential

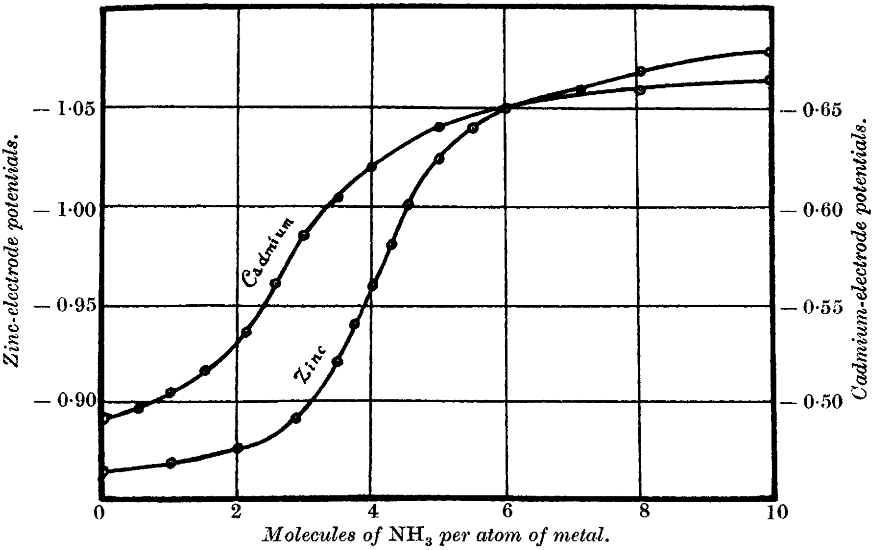
TABLE II.

Silver cathode potentials.

	Solution I.		Solution II.		Solution III.	
C.D. × 10^4 (amps./cm.^{2}).	I.	Diluted 5-fold.	II.	Diluted 5-fold.	III.	Diluted 5-fold.
—	0·56	0·54	0·36	0·40	0·32	0·37
1	—	0·48	—	0·39	—	0·35
2	—	0·44	—	0·38	—	0·33
4	—	0·38	—	0·36	—	0·32
5	0·47	0·36	0·33	0·35	0·30	0·31
6	—	0·30*	—	0·32*	—	0·29*
7	—	0·10	—	0·12	—	0·19
10	0·39	−0·15	0·32	−0·43	0·28	−0·22
15	0·36	−0·40	0·30	—	0·27	−0·45
25	0·32	—	—	—	—	—
30	0·28*	—	0·28*	—	0·26*	—
40	−0·15	—	−0·08	—	−0·05	—
50	−0·40	—	−0·42	—	−0·43	—
60	−0·46	—	−0·50	—	−0·52	—

during polarisation should rise rapidly from 0·55 volt to about 0·40, and then more slowly to 0·3 volt, which should be attained in the vicinity of the limiting *C.D.*; when the latter is exceeded, a sudden rise of potential to that of H evolution, about — 0·6 volt, should ensue. If the ratio NH_3 : Ag in the original solution is greater than 3 : 1, it is evident from the titration curve that the cathode polarisation should be small as the *C.D.* is increased, the potential changing from about 0·4 to 0·3 volt; at the limiting *C.D.* the sudden change of potential to — 0·6 volt, accompanied by H evolution, should occur. If the $Ag(NH_3)_2^{\cdot}$ complex dissociates rapidly, this limiting *C.D.* in a 0·1*N*-solution of Ag should be 0·0027 amp./cm.^{2}, and in a 0·02*N*-solution 0·00054 amp./cm.^{2}, irrespective of the Ag : NH_3 ratio in the original electrolyte.

FIG. 2.



The cathode-potential measurements are given in Table II; unless diluted, the solutions were 0·1*N* with respect to Ag, and *M* with respect to $(NH_4)_2SO_4$. The ratio Ag : NH_3 was 1 : 2 in solution I, 1 : 4 in II, and 1 : 6 in III.

These results are in excellent agreement with anticipation; the obs. limiting *C.D.*'s (potentials marked with asterisks in Table II) are 0·0030 and 0·0006 amp./cm.^{2} in 0·1 and 0·02*N*-solutions of Ag, respectively. It is evident, therefore, that the $Ag(NH_3)_2^{\cdot}$ ion does not dissociate slowly.

Zinc.—The shape of the electrometric titration curve for zinc (Fig. 2) indicates that $Zn(NH_3)_4^{\cdot\cdot}$ is the chief complex ion formed. This formula is in agreement with the one proposed by Euler (*Ber.*, 1903, **36**, 3400), although Bonsdorff (*ibid.*, p. 2322; *Z. anorg. Chem.*, 1904, **41**, 132), from *E.M.F.* measurements, suggested $Zn(NH_3)_3^{\cdot\cdot}$. The titration curve does not indicate that such an ion is formed to any appreciable extent, and Bonsdorff's results are probably due to the fact that he calculated the formula of the complex from $Zn^{\cdot\cdot}$ concns. obtained by measuring the potential of a Zn electrode in solutions containing a large excess of NH_3; such measurements are vitiated by the spontaneous dissolution of Zn in these solutions (see p. 2850). It is owing to this behaviour that the cathode-potential measurements in $Zn(NH_3)_4^{\cdot\cdot}$ solutions do not afford any information concerning the rate of dissociation of the complex ion. Some of the results obtained with electrolytes containing 0·1*M*-Zn, and having Zn : NH_3 ratios of 1 : 4 (solution I), 1 : 5 (II), and 1 : 8 (III), are given in Table III; in each case H was evolved even before the current was applied.

TABLE III.

Zinc cathode potentials.

C.D. × 10^4 (amps./cm.^{2}).	Solution I.	Solution II.	Solution III.
—	−0·94	−1·02	−1·05
5	−1·02	−1·06	−1·07
10	−1·06	−1·08	−1·09
25	−1·10	−1·11	−1·12
60	−1·14	−1·17	−1·19
100	−1·19	−1·21	−1·23

In each solution the cathode potential rises steadily; there is no limiting *C.D.*, since the current efficiency for metal deposition is always below 100%.

Cadmium.—From the titration curve (Fig. 2) of *N*-$CdSO_4$, containing $(NH_4)_2SO_4$, it appears that the main complex ion is $Cd(NH_3)_3^{\cdot\cdot}$, or $Cd[(NH_3)_3(H_2O)]^{\cdot\cdot}$, although this is not very stable. Both Euler and Bonsdorff (*locc. cit.*) considered that the Cd–NH_3 complex was $Cd(NH_3)_4^{\cdot\cdot}$, but these authors used solutions containing a much higher ratio of NH_3 to Cd than those used here; under such conditions it is not improbable that the tetrammine ion exists.

The most negative potential of the Cd electrode observed in the Cd–NH_3 solutions is about − 0·7 volt, but owing to the high overvoltage at a Cd cathode ($>$0·4 volt) evolution of H does not commence until potentials in the vicinity of − 1·0 volt are attained in the NH_3 solutions. Since the whole range of Cd potentials, from a solution containing no NH_3 to one having an NH_3 : Cd ratio of 10 : 1, is only − 0·49 to − 0·64 (see Fig. 2), polarisation

TABLE IV.

Cadmium cathode potentials.

	Solution I.		Solution II.		Solution III.	
C.D. × 10^4 (amps./cm.^{2}).	I.	Diluted 10-fold.	II.	Diluted 10-fold.	III.	Diluted 10-fold.
—	−0·55	−0·54	−0·62	−0·58	−0·65	−0·60
2	—	−0·59	—	−0·63	—	−0·65
4	—	−0·62	—	−0·66	—	−0·68
5	−0·57	−0·66*	−0·65	−0·71*	−0·66	−0·70*
6	—	−1·02	—	−1·13	—	−1·15
7	—	−1·10	—	−1·18	—	−1·22
10	−0·59	−1·20	−0·66	−1·25	−0·67	−1·28
25	−0·62	—	−0·68	—	−0·68	—
40	−0·65	—	−0·69	—	−0·70	—
50	−0·67	—	−0·71	—	−0·72	—
55	−0·71*	—	−0·73*	—	−0·76*	—
60	−0·98	—	−0·99	—	−1·03	—
80	−1·03	—	−1·05	—	−1·08	—
100	−1·10	—	−1·13	—	−1·15	—

should never be appreciable in the electrolysis of any Cd–NH_3 solution, provided the *C.D.* is below the limiting value for 100% deposition of Cd. When this *C.D.* is exceeded, a marked rise of cathode potential, from about − 0·7 to − 1·0 volt, should occur accompanied by H evolution. If the complex ions dissociate rapidly, the limiting *C.D.* should be at 0·0054 amp./cm.^{2} in a 0·1*M*-Cd solution.

The results of measurements of cathodic potential at various *C.D.*'s in solutions 0·1*M* with respect to Cd, and these diluted 10-fold, in which the Cd : NH_3 ratios were 1 : 2 (solution I), 1 : 4 (II), and 1 : 6 (III), are given in Table IV. Each solution was about *M* with respect to $(NH_4)_2SO_4$.

Current-efficiency determinations in the NH_3 solutions were not reliable because of the non-adherent nature of the Cd deposited, but the results indicated that the *C.D.*'s above which the cathode potentials (marked with asterisk) rise to that of H evolution are actually the highest at which Cd can be deposited at 100% efficiency; the values are 0·0055 and 0·0006 amp./cm.^{2} for the 0·1*M* and 0·01*M*-solutions of Cd, respectively. These results are in agreement with the values calculated on the assumption that the Cd–NH_3 complexes dissociate rapidly, and that the max. *C.D.* which can be applied before H commences to be evolved is equiv. to the rate of diffusion of the Cd-containing ions to the cathode.

DISCUSSION.

If the deposition of metal from ammine solutions requires the prior dissociation of the complex ions, then it seems definitely established, at least for the ammines of copper, silver, and cadmium, that this dissociation does not occur slowly. Apart, however, from any particular mechanism which may be involved, the results of the present work can be interpreted as implying that none of the stages in the process $M(NH_3)_x^+ \longrightarrow M$ is slow. For the zinc-ammine ions it is not possible by the methods at present available to obtain any indication concerning the speeds at which the intermediate stages occur; the low current efficiencies for metal deposition are partly due to the spontaneous dissolution of the zinc and partly to the direct liberation of hydrogen by the current. There is no reason to believe, however, that there is a retardation of any intermediate stage of the metal deposition process.

It must be emphasised (see J., 1929, 690) that appreciable cathodic polarisation with increasing *C.D.* does not necessarily indicate that the complex ion in solution dissociates slowly. The cathode potentials, *e.g.*, in Table II, show that there is appreciable polarisation in the silver solution I, but very little in solutions II and III, yet each probably contains the same complex ions which dissociate rapidly; at least, it can be stated with certainty that the same process is involved in the deposition of silver from each solution. The change of potential with *C.D.* depends on the variation of the potential of the electrode as the ratio of ammonia to metal in the solution is increased, and alone throws no light on the rate of dissociation of the complex ions present.

It is of interest to compare the formulæ of the ammines of silver, zinc, and cadmium with those of the complex cyanides of the same metals; silver forms $Ag(NH_3)_2^{\cdot}$ and $Ag(CN)_2'$ only, zinc forms $Zn(NH_3)_4^{\cdot\cdot}$ and $Zn(CN)_4''$, whereas cadmium yields both $Cd(NH_3)_3^{\cdot\cdot}$ and $Cd(NH_3)_4^{\cdot\cdot}$, and $Cd(CN)_3'$ and $Cd(CN)_4''$.

SUMMARY.

(1) Solutions of copper, silver, zinc, and cadmium salts, to which an excess of ammonium sulphate had been added, were titrated electrometrically with ammonia solution, the appropriate metal being used as indicator electrode; from the results the existence of the ions $Cu(NH_3)_4^{\cdot\cdot}$, $Ag(NH_3)_2^{\cdot}$, $Zn(NH_3)_4^{\cdot\cdot}$, and $Cd(NH_3)_3^{\cdot\cdot}$ or $Cd[(NH_3)_3(H_2O)]^{\cdot\cdot}$ is inferred.

(2) Cathode-potential measurements have been made in solutions containing these ammines and the results have been interpreted by means of the titration curves and by the theory of the limiting current.

(3) There is no reason to believe that any of the intermediate processes, *e.g.*, the dissociation of the ammine ions, involved in the discharge of a metal-ammine kation and the separation of the metal on the cathode occurs slowly.

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