

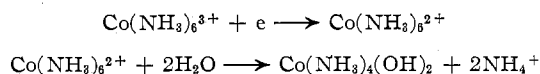
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## The Composition and Reactivity of the Precipitate Formed at the Dropping Mercury Electrode upon One-Electron Reduction of Hexaamminecobalt(III)

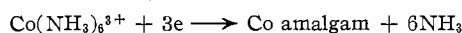
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In the one-electron reduction of hexaamminecobalt(III) chloride a precipitate of  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  is formed at the surface of the electrode



The initial precipitate formed in an air-free mixture which is 0.06 *M* in ammonia and 0.01 *M* in cobalt(II) has the composition  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ . A precipitate of the same composition was found when the molar ratio of cobalt to ammonia was 2 or 3 to 6. As the mixtures stand the precipitate is transformed into hydrous cobalt(II) hydroxide. At a potential of -1.6 volts, hexaamminecobalt(III) yields a three-electron reduction



At this potential added cobalt(II) reacts with ammonia in a molar ratio of 1 to 6. The reactivity of the precipitate formed in the one-electron reduction of hexaamminecobalt(III) and of ammonia formed in its three-electron reduction with cadmium perchlorate and mercuric chloride has been determined. No precipitation equilibrium with mercuric chloride is attained during the growth of the mercury drop. In mixtures of hexaamminecobalt(III) and aluminum perchlorate 2 moles of aluminum were found to react at the electrode with 1 mole of  $\text{Co}(\text{NH}_3)_6^{2+}$  or  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ . This was confirmed by chemical tests. Bound ammonia in hexaamminecobalt(III) has been determined and found to be equal to 6 in amperometric titrations with hydrochloric acid at a potential where the three-electron reduction of hexaamminecobalt(III) occurs and in the presence of iodate at a potential where a one-electron reduction occurs.

The polarography of the hexaamminecobalt(III) complex, denoted as I, has been studied by several authors. Willis, *et al.*,<sup>1</sup> found that upon reduction of cobalt(III) complex with non-reducible ligands two waves are observed, the first one being a one-electron and the second a three-electron reduction to cobalt amalgam. Extensive studies on the polarographic behavior of I have been carried out by Laitinen, *et al.*<sup>2-4</sup>

In the present paper we have tried to establish the composition of the precipitate which is formed on the surface of the dropping mercury electrode upon the reduction of Co(III) to Co(II) in neutral unbuffered medium



and also the extent and kind of interaction of this precipitate with cobalt(II), cadmium ions, mercuric chloride, and aluminum ions. It is to be expected that the ammonia formed in reaction 1—in whatever form it is present—will react readily and quantitatively with a strong acid. This has been shown to be true and it has been found possible to determine bound ammonia in I by titrating amperometrically with a strong acid in the presence of an excess of iodate. The reduction of iodate in the presence of hydrogen ions supplied by a strong acid occurs at such positive potentials that only the first reduction wave of I is observed. After the hydrogen ions have been consumed no further reduction of

iodate is observed until at much more negative potentials. The reduction of hydrogen ions to hydrogen occurs at potentials where I is reduced to cobalt amalgam. Amperometric titrations with a strong acid also have been carried out at potentials where hydrogen ions are reduced to hydrogen. Both in the presence and in the absence of iodate no current due to free hydrogen ions is observed until all the ammonia formed at the surface of the electrode has reacted quantitatively with the hydrogen ions diffusing to the electrode. Both diffusion currents of cobalt(III) (to cobalt(II) and (0)) are proportional to the flux of I to the electrode, which is proportional to the bulk concentration of I. The concentration of ammonia formed at the surface of the electrode therefore also is proportional to the flux of I to the electrode. Considering that the Ilkovic equation is only an approximate expression, the flux is not simply proportional to  $c_I D_I^{1/2}$ ,<sup>5</sup> but rather to  $(i_d)_I$ . It is easily derived<sup>5</sup> that the hydrogen ion concentration  $c_{\text{H}^+}$  in the bulk of the solution required to neutralize the six ammonia molecules formed at the surface of the electrode is given by the equation

$$(i_d)_{\text{H}^+} c_{\text{H}^+} = 6 \frac{(i_d)_I}{n} c_I \quad (2)$$

in which  $(i_d)_{\text{H}^+}$  and  $(i_d)_I$  are diffusion currents of equimolar solutions of hydrogen ions and of I, while *n* is the number of electrons involved in the reduction of I.

The reactivity of the products formed at the surface of the electrode in the one- and three-electron reductions of I with cobalt, cadmium, and aluminum per-

(1) J. W. Willis, J. A. Friend, and D. P. Mellor, *J. Am. Chem. Soc.*, **67**, 1680 (1945).

(2) H. A. Laitinen, J. C. Bailor, Jr., H. F. Holtzclaw, and J. V. Quagliano, *ibid.*, **70**, 2999 (1948).

(3) H. A. Laitinen and P. Kivalo, *ibid.*, **75**, 2198 (1953).

(4) H. A. Laitinen, J. A. Frank, and P. Kivalo, *ibid.*, **75**, 2865 (1953).

(5) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, p. 105.

chlorates and with mercuric chloride also has been determined either from complete polarograms of mixtures or from amperometric titrations with these metal salts at potentials where I is reduced to cobalt(II) or to cobalt amalgam. Again, the stoichiometry at the end point is related to the diffusion currents of I and that of the titrant ions. An expression similar to that in the titration with hydrogen ions (eq. 2) is easily derived.

In order to get further insight in the composition of the reaction product formed in the one-electron reduction of I (eq. 1), analyses have been carried out of air-free mixtures containing cobalt(II) perchlorate and ammonia in a molar ratio of 1 to 6 and a few other ratios. Moreover, mixtures containing equimolar amounts of cobalt(II) perchlorate and mercuric chloride, or cadmium perchlorate or aluminum perchlorate with ammonia in a molar concentration six times that of cobalt(II), have been analyzed.

In a subsequent paper a detailed study will be presented of the effect of the precipitate formed in the one-electron reduction of I on the polarographic current-potential curves.

### Experimental

**Materials.**—Hexaamminecobalt(III) chloride was prepared and recrystallized according to Bjerrum's<sup>6</sup> method as described by Walton.<sup>7</sup> Other salts were C.P. products. Stock solutions of cadmium, cobalt, and aluminum perchlorates were analyzed for metal content by standard methods.

**Polarography.**—All experiments were carried out at  $25 \pm 0.1^\circ$ . Polarograms were run in the absence of oxygen in an atmosphere of high purity Linde nitrogen which had been passed through acidified vanadous chloride solution.<sup>8</sup> The dropping mercury electrode had the following characteristics at open circuit in 0.1 *M* sodium perchlorate:  $m = 1.09$  mg./sec.,  $t = 6.40$  sec. Potentials refer to the saturated calomel electrode (s.c.e.). Polarograms were recorded using a Sargent Model XXI polarograph. The instrument always was used in damping position 2.

**Determination of the composition of the precipitate** formed under various conditions in mixtures of cobalt(II) and ammonia, in the absence or presence of mercuric chloride or cadmium or aluminum perchlorates.—Mixtures of solutions of cobalt(II) perchlorate and ammonium perchlorate in the desired molar ratio were prepared in a suitable container in the absence or presence of mercury(II) or cadmium or aluminum. The volume was adjusted to  $(50 - x)$  ml. and the mixture made oxygen- and carbon dioxide-free with nitrogen. Then  $x$  ml. of relatively concentrated sodium hydroxide solution was injected in an amount equivalent to the amount of ammonium in the solution. The mixture was shaken, centrifuged for a few minutes, and then filtered. An aliquot part of the filtrate was analyzed for free ammonia by potentiometric titration with standard hydrochloric acid using a glass electrode as indicator electrode. In another aliquot ammonium was determined by titration with standard base using the formaldehyde method.<sup>9</sup> Dissolved cobalt(II) (and mercury(II) and cadmium(II) or aluminum(III) when added to the original mixture) in the filtrate was determined polarographically. Several experiments were carried out in which mixtures were prepared in the polarographic cell. The concen-

tration of dissolved metal then was determined immediately after addition of sodium hydroxide.

### Results

**Determination of Bound Ammonia in Hexaamminecobalt(III) Chloride (I).** (a) **Titration with Hydrochloric Acid in Absence of Iodate.**—Polarograms of mixtures of 1 *mM* solutions of I with hydrochloric acid were run in a supporting electrolyte 0.5 *M* in sodium perchlorate and the current was measured at  $-1.8$  volts. At this potential I yields a diffusion current corresponding to a three-electron reduction. The diffusion current of hydrogen ions does not appear until the flux of these ions from the bulk of the solution to the electrode becomes greater than that required to neutralize the ammonia liberated at the surface of the electrode. The diffusion current of I at  $-1.8$  volts was subtracted from the total current at this potential. After correction for dilution the hydrogen ion diffusion current was plotted *vs.* the volume of hydrochloric acid added. From several experiments an average value of 1.90 mmoles of hydrochloric was found to be required to neutralize the ammonia liberated in the reduction of 1.00 mmole of I. The same result was obtained in direct amperometric titrations at  $-1.8$  volts. The average value of the diffusion current of hydrogen ions at  $-1.8$  volts was found to be  $7.45 \mu\text{a./mM}$ , while that of I was  $6.95/3 = 2.32 \mu\text{a./mM}$  referred to a one-electron reduction. Denoting  $x$  as the number of molecules of ammonia formed per mole of I we can write the relation

$$1.90 \times 7.45 = 2.32x \quad (3)$$

This yields a value of  $x$  of 6.1.

(b) **Titration in the Presence of Iodate.**—In a supporting electrolyte 0.5 *M* in sodium perchlorate and 0.01 *M* in potassium iodate, reduction of iodate starts at a potential slightly more negative than  $-1.0$  volt. In the presence of hydrogen ions, a diffusion current corresponding to that of hydrogen ions is found between  $-0.2$  and  $-1.0$  volt. In the above supporting electrolyte I yields a diffusion current corresponding to a one-electron reduction at potentials between  $-0.45$  and  $-0.75$  volt. Polarograms were run in mixtures 0.5 *M* in sodium perchlorate, 0.01 *M* in potassium iodate, and 0.5 *mM* in I in the presence of varying concentrations of hydrochloric acid, and the current was measured at  $-0.5$  volt. The current remains equal to the first diffusion current of I until the flux of hydrogen ions from the bulk of the solution to the electrode becomes greater than that required to neutralize the ammonia at the electrode in the reduction product of I. From the experimental data an average value of  $x$  (eq. 3) of 6.1 was found. The over-all average of 6.1 is in satisfactory agreement with the theoretical number of six coördinated ammonia molecules in I.

In the above experiments in the presence of 0.01 *M* iodate a precipitate of I with iodate was formed when the concentration of I was 1 *mM*.

**Reactivity of Reduction Products of I with Cobalt(II).**

(6) J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 216 (1946).

(7) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 88.

(8) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, p. 34.

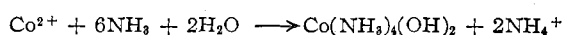
(9) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 158.

—Polarograms in 0.1 *M* sodium perchlorate of mixtures 0.001 *M* in I and containing varying concentrations of cobalt(II) perchlorate are presented in Fig. 1. In agreement with the observations by Laitinen, *et al.*,<sup>4</sup> the first reduction step of I has a constant diffusion current between about  $-0.45$  and  $-0.75$  volt, then the current decreases to attain a minimum value at  $-0.85$  to  $-0.90$  volt, whereupon it increases to the value of the diffusion current, just before the second reduction wave appears, which corresponds to the reduction of I to cobalt amalgam. As stated by Laitinen, *et al.*,<sup>4</sup> the dip at  $-0.85$  volt is due to the formation of a film adherent to the surface of the mercury drop of a precipitate formed in the first reduction step of I. In a subsequent paper a detailed study will be reported of the characteristics of the current at the minimum under varying experimental conditions in the presence and absence of surface active substances. As is observed in Fig. 1, addition of cobalt(II) to I hardly affects the characteristics of the polarogram of the first reduction wave, except that the minimum value of the current becomes more accentuated (at  $-0.85$  volt) with increasing concentration of cobalt(II).

At a potential of  $-1.6$  volts the diffusion current corresponds to the sum of that of I (three-electron reduction) and of cobalt(II) which has not reacted at the surface of the electrode with the six ammonia molecules produced in the reduction of I. The difference between the total diffusion current calculated from the over-all composition of the mixture and the experimental value corresponds to the diffusion current of the cobalt(II) which has reacted with ammonia at the surface of the electrode. These values are plotted in curve a, Fig. 2, vs. the analytical concentration of cobalt(II) added. It is clear that the reaction between cobalt(II) and ammonia at the surface of the electrode is not instantaneous. The amount of reacted cobalt(II) increases with increasing concentration of cobalt(II) in the solution and reaches a limiting value corresponding to  $4.80 \mu\text{a}$ . in a 1 *mM* solution of I. Considering that the diffusion current of a 1 *mM* cobalt(II) solution was found equal to  $5.00 \mu\text{a}$ . (two-electron reduction) and of a 1 *mM* solution of I,  $6.95 \mu\text{a}$ . (three-electron reduction), the relation

$$x = \frac{4.80}{5.00} \times \frac{2.50}{2.35} = 1.0$$

can be written, in which  $x$  is the number of millimoles of cobalt(II) reacting with 6 ammonia molecules at the surface of the electrode. The value for  $x = 1$  corresponds to the reaction



In order to verify the conclusion that the primary precipitate has the composition  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  an oxygen-free mixture initially 0.01 *M* in cobalt(II) perchlorate and 0.06 *M* in ammonia was centrifuged and filtered. The filtrate was analyzed for ammonia, ammonium, and cobalt 5 min. after preparation of the original mixture. Upon addition of the cobalt to the air-free ammonia solution a bluish green precipitate is formed. Polar-

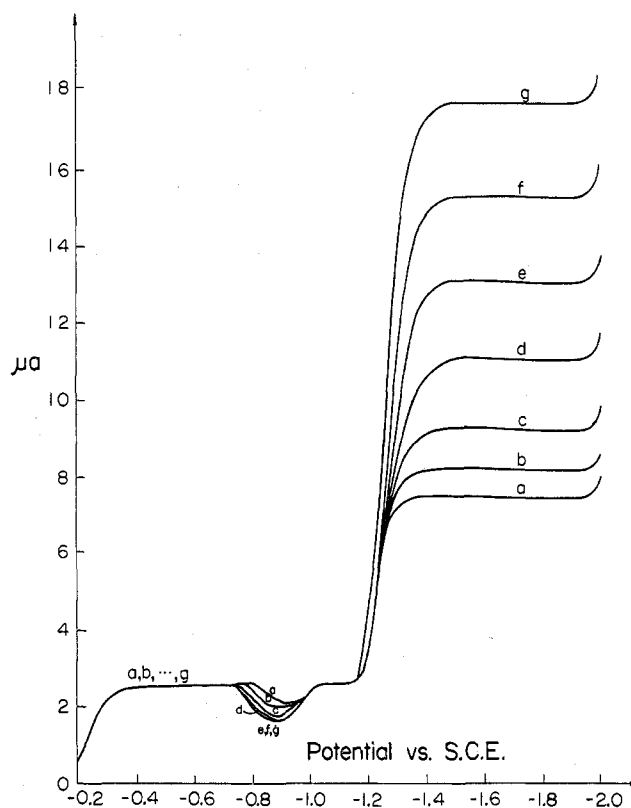


Fig. 1.—Polarograms of mixtures of 1 *mM* I and cobalt(II) in 0.1 *M* sodium perchlorate. *mM* concentration of Co(II): a = 0; b = 0.5; c = 1.0; d = 1.5; e = 2; f = 2.5; g = 3.

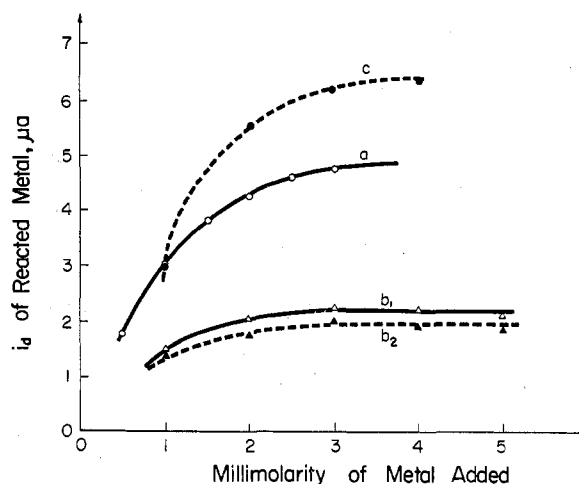


Fig. 2.—Decrease in current in mixtures 1 *mM* in I and 0.1 *M* in sodium perchlorate with a, cobalt(II) perchlorate at  $-1.6$  v.; b<sub>1</sub>, cadmium perchlorate at  $-0.7$  v.; b<sub>2</sub>, at  $-1.6$  v.; c, mercuric chloride at  $-0.4$  v.

ographically the filtrate was found to be free of dissolved cobalt, the ammonia concentration was 0.006 *M*, and the ammonium concentration 0.020 *M*. The composition of the filtrate corresponds closely to the above reaction equation, according to which the ammonia concentration should be zero. The precipitate is not stable and the ammonia concentration in the supernatant liquid increases on standing of the original suspension. After 24 hr. the ammonium concentration in the filtrate was still 0.02 *M* but the ammonia concentration had

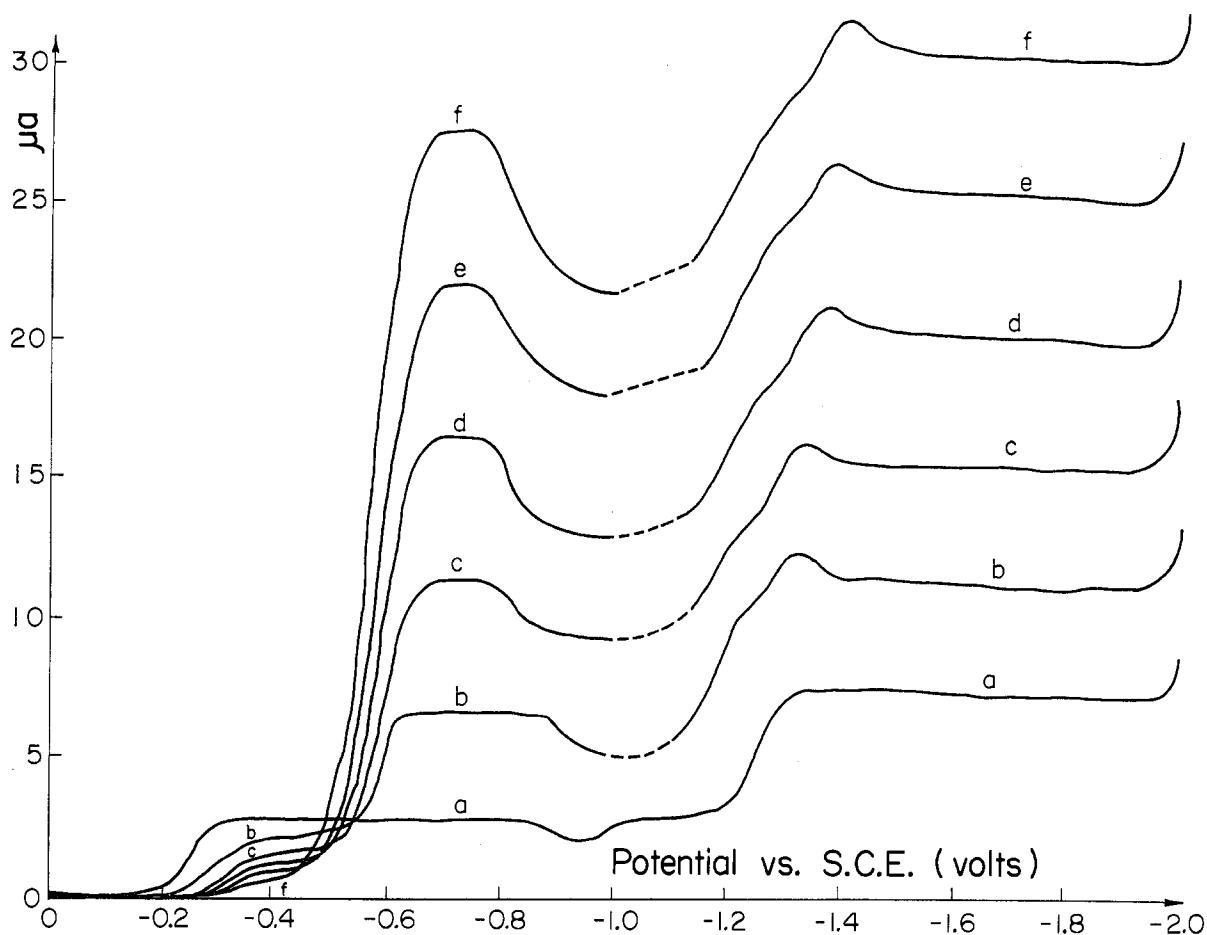


Fig. 3.—Polarograms of 1 mM I and cadmium perchlorate in 0.1 M sodium perchlorate. mM concentration of cadmium: a = 0; b = 1; c = 2; d = 3; e = 4; f = 5; . . . denotes abnormal current-time curves.

increased to 0.04 M, indicating that the primary precipitate had been transformed into hydrous cobalt(II) hydroxide. In the polarographic experiments (see Fig. 1) the maximum concentration of cobalt(II) added gave a flux to the surface of 3 moles of cobalt(II) per 6 moles of ammonia formed at the surface in the reduction of cobalt(III). Therefore, it was considered desirable to test whether the primary precipitate formed on mixing cobalt(II) and ammonia in a mole ratio of 1 to 3 still had the composition  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ . In the polarographic cell an oxygen-free mixture was prepared which was 0.1 M in sodium perchlorate, 0.001 M in cobalt(II) perchlorate, 0.003 M in ammonium perchlorate, and 0.003 M in sodium hydroxide. Immediately after the mixing the diffusion current of cobalt(II) was measured at -1.8 volts, at which potential the preceding maximum in the cobalt current no longer interfered. The concentration of dissolved cobalt(II) left in the solution was  $5.3 \times 10^{-4}$  M, again indicating a molar reaction ratio of cobalt(II) to ammonia of 1 to 6. The concentration of cobalt(II) remained unchanged for 10 min., and then started to decrease. After 1 hr. it had become less than  $10^{-4}$  M, and after several hours equal to zero. Again, the primary precipitate is  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ , which is unstable and transformed into hydrous cobalt(II) hydroxide. Experiments in which the molar ratio of cobalt(II) and ammonia in the reaction mixture

was 1 to 2 allowed the same conclusion to be drawn. On the basis of these results it is fair to conclude that the precipitate formed in the one-electron reduction of I has the composition  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  and is not cobaltous hydroxide.

#### Reactivity of Reaction Products of I with Cadmium.—

Laitinen, *et al.*,<sup>4</sup> state that the first diffusion current of I is almost completely suppressed in the presence of cadmium. They attribute this to the formation of an insoluble film of basic cadmium salt. We also observed that the first reduction current of I is decreased in the presence of cadmium (Fig. 3), the suppression increasing with increasing cadmium concentration in the solution. Contrary to the statement of Laitinen we do not find the wave height at -0.75 volt equal to the sum of diffusion currents of I and of cadmium, but smaller. The same is true at -1.5 volts. The difference between calculated and experimental diffusion currents in Fig. 3 corresponds to the diffusion current of cadmium which has reacted at the surface of the electrode. The values at -0.7 and at -1.6 volts are plotted in curves  $b_1$  and  $b_2$  in Fig. 2. It is seen that slightly more cadmium reacts at -0.7 than at -1.6 volts, even though at -0.7 volt cadmium reacts with  $\text{Co}(\text{NH}_3)_6^{2+}$  or  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  at the surface of the drop, while at -1.6 volts it reacts with the six ammonia molecules liberated in the reduction of 1 mole of I to cobalt amalgam. In a similar

way as has been done in the interpretation of the polarograms of mixtures of I and cobalt(II) it is found for the mixtures of I with cadmium that 0.5 mole of cadmium ion reacts with 1 mole of  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  or 6 moles of ammonia at the surface of the mercury drop. This does not correspond to a simple stoichiometric reaction. In a supporting electrolyte 0.20 *M* in sodium perchlorate which was  $5 \times 10^{-3}$  *M* in cadmium perchlorate and to which I was added in increasing concentration the diffusion current at  $-0.7$  volt decreased from 34.80  $\mu\text{A}$ . in the absence of I to 27.6  $\mu\text{A}$ . when the concentration of I was  $10^{-3}$  *M* and 27.25  $\mu\text{A}$ . when it was  $3 \times 10^{-3}$  *M*. The results clearly indicate that some cadmium was precipitated. The great suppressive effect of the precipitated cadmium on the diffusion current of I on the positive side of the isoelectric point of mercury ( $-0.5$  volt) and the disappearance of this effect on the negative side suggests that the film of the cadmium precipitate (basic salt?) is negatively charged and strongly adheres to the mercury surface at the positive side of the isoelectric point.

In separate experiments it was shown that cadmium can react with  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ . An air-free suspension of this precipitate was prepared to which cadmium perchlorate was added. The over-all composition of the mixture was 0.01 *M* in cobalt, 0.01 *M* in cadmium, 0.06 *M* in ammonium (all three as perchlorates), and 0.06 *M* in sodium hydroxide. After shaking, centrifuging, and filtering, the solution was analyzed polarographically for cadmium and cobalt. No cobalt was in the solution, and 50% of the cadmium was found to be precipitated. This happens to agree with the reaction ratio of 0.5 cadmium to 1  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  which had been derived from the polarographic experiments in Fig. 3.

The incomplete precipitation of one cadmium with six ammonias was verified in the following experiment. An air-free mixture which was 0.001 *M* in cadmium and 0.006 *M* in ammonia was prepared in the polarographic cell and the diffusion current of cadmium measured within 2 min. The concentration of residual cadmium corresponded to 85% cadmium precipitated. This is more than was derived from the decrease in the diffusion current at  $-1.6$  volts in mixtures of I and cadmium. Apparently, no precipitation equilibrium is attained under polarographic conditions.

**Reactivity of Reduction Products of I with Mercuric Chloride.**—Polarograms were run of mixtures of I and mercuric chloride of varying composition in 0.08 and 0.5 *M* sodium perchlorate as supporting electrolyte. Figure 4 illustrates polarograms in 0.08 *M* sodium perchlorate. The mercuric chloride waves appear before the first reduction wave of I. They are not shown in Fig. 4, because of the large maxima in these waves. It is clear from Fig. 4 that the diffusion currents at  $-0.4$  and  $-1.4$  volts are smaller than the sum of the diffusion currents of I and mercuric chloride. The difference was plotted *vs.* the bulk concentration of mercuric chloride. One example at  $-0.4$  volt is given in Fig. 2. The difference is slightly greater at  $-1.4$  than at  $-0.4$  volt. At both potentials the lines are

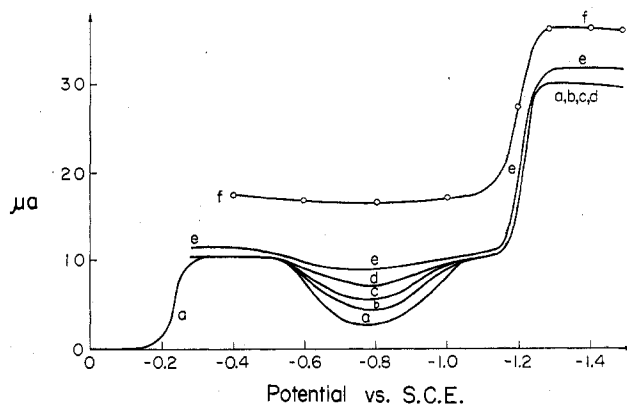


Fig. 4.—Polarograms of mixtures of 4 *mM* I and  $\text{HgCl}_2$  in 0.08 *M* sodium perchlorate. *mM* concentration of  $\text{HgCl}_2$ : a = 0; b = 1; c = 2; d = 3; e = 4; f = 5.

curved; the difference continues to increase with increasing concentration of mercuric chloride. Extrapolated values roughly correspond to a reaction of 2 moles of mercuric chloride with the reduction products of I. Evidently, there is no precipitation equilibrium at the surface of the electrode. In separate experiments with mixtures of mercuric chloride and ammonia it was shown that the molar reaction ratio was 1 to 2, corresponding to the formation of  $\text{NH}_2\text{HgCl}$ . Of greater interest are experiments with mixtures of mercuric chloride, cobalt(II) perchlorate, and ammonia. The initial composition of one such mixture was 0.01 *M* in  $\text{HgCl}_2$ , 0.01 *M* in  $\text{Co}(\text{ClO}_4)_2$ , 0.06 *M* in  $\text{NH}_4\text{ClO}_4$ , and 0.06 *M* in  $\text{NaOH}$ . After centrifuging and filtering no mercury was found in the filtrate, while all the cobalt was recovered. Also, when the mercuric chloride in the original mixture was 0.02 *M* no precipitation of cobalt occurred.

An experiment was conducted in which a 0.01 *M* suspension of  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  was prepared; immediately after its preparation the mixture was made 0.01 *M* in mercuric chloride, shaken, centrifuged, and filtered. No mercury was found in the filtrate and all the cobalt was recovered. From the above it may be concluded that mercuric chloride solubilizes the precipitate formed in the first reduction step of I. The minimum at  $-0.8$  volt in the reduction of I (curve a, Fig. 4), which is due to the precipitate of  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ , disappears when the concentration of mercuric chloride becomes large enough to solubilize the precipitate (curve f, Fig. 4).

**Reactivity of Reduction Products of I with Aluminum Ions.**—Curves a, b, c, and d in Fig. 5 are polarograms of 1 to 3.7 *mM* aluminum perchlorate in 0.1 *M* sodium perchlorate. A reduction current starts at  $-1.4$  volts; it increases gradually with increasing negative voltage, but very steeply when the potential becomes more negative than  $-1.75$  volts. It is beyond the scope of this paper to present a detailed discussion of the polarography of the hexaquo aluminum ion. Suffice it to state that the diffusion current at  $-1.85$  volts was proportional to the aluminum concentration up to 2 *mM* and corresponded to a three-electron reduction. At higher concentrations than 2 *mM* the migra-

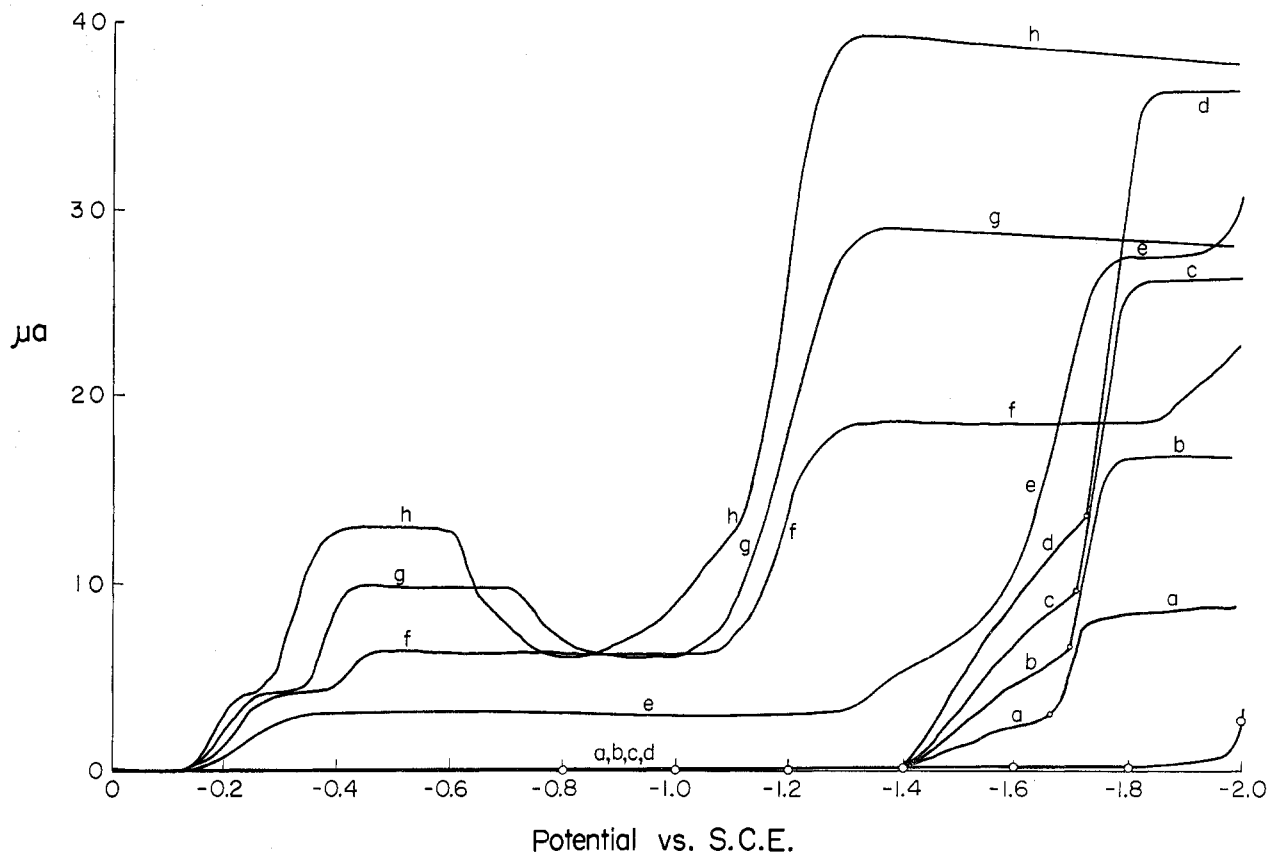
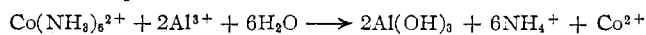


Fig. 5.—Polarograms of aluminum perchlorate and its mixture with I in 0.1 *M* sodium perchlorate. *mM* concentration of Al: a = 0.93; b = 1.87; c = 2.80; d, e, f, g, h = 3.74; *mM* concentration of I: e = 1; f = 2; g = 3; h = 4.

tion current started to contribute to the limiting current.

The diffusion current constant was found to be 3% greater than that of cobalt(III) (three-electron reduction). It is to be expected that the diffusion coefficients of the hexaquo aluminum and hexaamminecobalt(III) ions are of the same order of magnitude. In a mixture which was 3.74 *mM* in aluminum and 1 *mM* in I (curve e, Fig. 5) the first reduction of cobalt(III) was not affected by the presence of aluminum. The second wave (reduction to cobalt amalgam) was displaced to more negative potentials and did not yield a well defined diffusion current as it started to coalesce with the aluminum wave. The height of the aluminum wave was greatly reduced. When the concentration of I in the mixture was made 2 *mM* or greater (curves f, g, and h in Fig. 5) the first reduction wave of I became split in two waves, the first one starting at more positive potentials the greater the concentration of I. In the absence of aluminum the first reduction wave of I also is displaced to more positive potentials with increasing concentration of I. In mixtures in which the concentration of I was 2 *mM* or greater no aluminum wave was observed. From the experiments in Fig. 5 and from polarograms of several other mixtures it could be concluded that 2 moles of aluminum are precipitated by the reduction products of I



At -1.6 volts 6 moles of ammonia liberated at the electrode react with 2 moles of aluminum. It is of interest

to note that in the mixtures which were 3.74 *mM* in aluminum and 1 and 2 *mM*, respectively, in I no dip was observed in the first diffusion current of I (curves e and f, Fig. 5). When the concentration of I was greater than 2 *mM* (curves g and h) typical dips were found as in the absence of aluminum. At these higher concentrations of I the aluminum concentration becomes too small to decompose all  $\text{Co}(\text{NH}_3)_6^{2+}$  and a precipitate of  $\text{Co}(\text{NH}_3)_4(\text{OH})_2$  is formed at the surface of the electrode. Experiments with mixtures of cobalt(II), aluminum, and ammonia substantiated the above conclusions. For example, a mixture which was 1 *mM* in cobalt(II) and 2 *mM* in aluminum was made 6 *mM* in ammonia. A white, gelatinous precipitate was formed. After centrifuging and filtering, no aluminum was found in the filtrate, while 86% of the original amount of cobalt was present. Apparently some cobalt was coprecipitated with the hydrous aluminum oxide. In another experiment the cobalt was precipitated first with the ammonia and then the aluminum was added. The bluish green precipitate disappeared after 1 min. of shaking and the white, gelatinous aluminum precipitate was formed instead. Analysis of the filtrate revealed that 20% of the cobalt had remained in the precipitate. When the cobalt was added to the mixture after precipitation of the aluminum all the cobalt was found back in the filtrate.

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