[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarographic Reduction of Hexamminecobalt(III) Ion. II. The Effect of Complexing Agents

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The polarographic reduction of hexamminecobalt(III) ion to the divalent state has been studied in the presence of various concentrations of ammonia. Comparison of half-wave potentials with equilibrium potential measurements indicates that the first step in the reduction process is an electron transfer to form hexamminecobalt(II) ion. The irreversibility of the process may be attributed to a slow step, namely, the transformation of the hexamminecobalt(II) ion from the initial d^2sp^3 hybridization structure to the stable sp^3d^2 structure. This mechanism is supported by the observation that the anodic current due to oxidation of hexamminecobalt(II) ion at the rotating platinum electrode is only of the order of 1% of the diffusion-controlled value, and must be limited by the rate of the reverse transformation. In the presence of ethylenediamine, the reduction of hexamminecobalt(III) occurs at the reversible reduction potential of the trisethylenediaminecobalt(III) ion, although this species of ion is not present in solution. A mechanism for this process is suggested. In concentrated chloride solution, the second step of the reduction was observed to be shifted 0.4 v. to a more positive potential, because of the formation of a chloro complex of cobalt(II) by rapid exchange of ligands by the hexamminecobalt(II) ion. In concentrated hydroxide medium, a similar effect was observed, but with the shift of the second reduction step to a more negative potential.

The polarography of hexamminecobalt(III) ion has been previously discussed by Brdicka,[1] Willis, Friend and Mellor[2] and in a first paper on the subject from this Laboratory.[3] The product of the first step of reduction has been regarded as being the aquated cobalt(II) ion.[2,3] The present investigation was undertaken to determine the effect of various substances which form complexes with cobalt(II), in the hope of gaining further insight into the mechanism of electro-reduction of the hexamminecobalt(III) ion.

Experimental

Materials.—Hexamminecobalt(III) chloride was prepared according to Bjerrum and McReynolds[4] and was recrystallized twice from alcohol and hydrochloric acid. The salt was dried at 90° for 8 hours.

Apparatus.—Current–voltage curves were determined with a Leeds and Northrup Type E Electro-Chemograph, except for one series of experiments (Table II) in which a Sargent Polarograph, Model XXI, using 0.5-v. span was employed. To avoid traces of agar an H-cell having a 20-mm. fine sintered glass plug separating the two compartments was used. The solution for analysis was placed in both compartments so that the liquid level was about 1 cm. higher in the cathode compartment than in the anode compartment. The reference electrode was a saturated calomel electrode connected to the anode compartment by means of a salt bridge containing saturated potassium chloride solution. The a.c. resistance of this type of cell was 680 ohms (minimal value at instant of drop fall), using 0.1 *N* potassium chloride solution with the dropping mercury electrode as one electrode and the saturated calomel electrode as the other electrode. Oxygen was removed from the solutions with oxygen-free nitrogen. The cell and the reference electrode were kept in a water thermostat having a temperature of 25 ± 0.1°. Two dropping mercury electrodes were used: electrode I, m = 1.746 mg./sec., t = 4.68 sec.; electrode II, m = 1.538 mg./sec., t = 4.72 sec. (open circuit) using a mercury column height of 60.0 cm.

For some experiments a rotating platinum electrode was used. The electrode was rotated with a small induction motor at about 500 r.p.m. The microelectrode, which was 1.5 mm. long and 0.2 mm. in diameter, protruded at an angle of 45° from the side of a piece of glass tubing. The distance between the tip of the electrode and rotation center was 5 mm. The rotating electrode was inserted in the H-cell, described above, through which nitrogen was bubbled continuously during the experiment. The cell was covered with a round rotating rubber disc, which was fastened to the electrode shaft through a hole in its center and which rotated barely above the edge of the cell.

Results and Discussion

The Effect of Ammonia Concentration.—In 1941, Bjerrum[5] showed by potentiometric titration that the oxidation–reduction reaction of the hexamminecobalt(III, II) system is reversible. The titrations were made in media where the divalent hexamminecobalt complex is stable, *i.e.*, in solutions containing ammonium salt and an excess of the complexing agent. In a 2 *M* ammonium nitrate solution the standard potential at 30° for this couple appeared to be −0.211 v.[6] *vs.* the saturated calomel electrode (S.C.E.). Curve 1 in Fig. 1 represents the oxidation–reduction potential for the system in question as a function of the activity of ammonia as obtained by Bjerrum. The standard potential for the system is represented by the straight line of −0.211 v. *vs.* S.C.E. and is obtained by the relationship

$$E^0 = E_{\mathrm{redox}} + 0.0601 \log \alpha_6 \ (30°) \qquad (1)$$

where α_6, the fraction of the total divalent cobalt being in the hexammine form, is a function of the activity of ammonia.

The polarographic reduction of hexamminecobalt(III) ion to the divalent form appears to proceed irreversibly in most media. Table I gives half-wave potentials and reciprocal slopes of the plots of E *vs.* log $(i_d - i)/i$ obtained with non-

TABLE I

Concn., *M*	Supporting electrolyte	$E_{1/2}$, v. *vs.* S.C.E.	Reciprocal slope of log plot
1.0	$NaNO_3$	−0.245	0.090
1.0	HNO_3	− .280	.076
0.2	$Ba(NO_3)_2$	− .246	.086
0.1	$NaClO_4$	− .245	.105
1.0	NaCl	− .200	.105
1.0	HCl	− .216	.116

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(1) R. Brdicka, *Coll. Czechoslov. Chem. Communs.*, **2**, 112 (1933).

(2) J. B. Willis, J. A. Friend and D. P. Mellor, THIS JOURNAL, **67**, 1680 (1945).

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

(4) J. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 216.

(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 250.

(6) W. M. Latimer has calculated the standard potential of the couple to be +0.1 v. *vs.* hydrogen electrode, which is about −0.14 v. *vs.* S.C.E. using the polarographic sign convention. "Oxidation Potentials," Second Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 214.

TABLE II

$[NH_3]$	pa-$[NH_3]^a$	$\alpha_6{}^a$	$E_{1/2}$, v. *vs.* S.C.E.	0.059 log α_6	$E_{1/2}$, cor.	Reciprocal slope of log plot
0.71	+0.148	0.081	−0.2702	−0.0645	−0.3347	0.073
1.42	− .175	.212	− .2754	− .0397	− .3151	.072
2.13	− .385	.330	− .2785	− .0284	− .3069	.074
3.55	− .655	.503	− .2812	− .0175	− .2987	.073
5.69	− .95	.684	− .2842	− .0098	− .2940	.075
7.11	−1.11	.760	− .2912	− .0071	− .2982	.075
9.25	−1.34	.847	− .2985	− .0043	− .3028	.077
11.10	−1.53	.90	− .3040	− .0027	− .3067	.078

[a] The activity of ammonia calculated on the basis of Bjerrum's data[5] as well as the value of α_6 which is the fraction of the total Co(II) in hexamminecobalt(II) form.

complexing supporting electrolytes. Table II shows the results of a study of this reduction in the presence of various concentrations of ammonia. In order to be able to compare the results with Bjerrum's, the supporting electrolyte used was 2 *M* ammonium nitrate. The activity of ammonia was calculated on the basis of Bjerrum's experiments, which were run at 22–23°. The temperature in the present experiment was 25°, but the error due to the temperature difference is considered negligible. The α_6-values were calculated for 25° and the corrected half-wave potentials were calculated by an equation similar to equation (1) but using the slope 0.0591 corresponding to 25°. As can be seen, the half-wave potential becomes more negative with increasing ammonia concentration. The reciprocal slopes of the logarithmic plots seem to be closer to the reversible values. Curves 2 and 3 in Fig. 1 represent the plot of the half-wave potential and the corrected half-wave potential, respectively, *vs.* the negative logarithm of the ammonia activity. A plausible explanation of the results of these experiments seems to be as follows:

The primary step in the reduction of hexamminecobalt(III) ion is the electron transfer giving the divalent complex

$$Co(NH_3)_6{}^{+++} + e^- \rightleftharpoons Co(NH_3)_6{}^{++} \qquad (2)$$

Consider the expression

$$E_{d.e.} = E^0 - \frac{RT}{nF} \ln \frac{a^0{}_{Co(NH_3)_6{}^{++}}}{a^0{}_{Co(NH_3)_6{}^{+++}}} \qquad (3)$$

where a^0 refers to activities at the surface of the dropping mercury electrode and E^0 is the standard potential of reaction 2. Assuming the activity coefficients and diffusion coefficients of the two forms to be equal, E^0 is identical with the corrected half-wave potential. Realizing that the concentration of the divalent hexammine complex at the half-wave potential is not equal to half of the bulk concentration of trivalent complex, but a fraction, α_6, of the total divalent cobalt produced by the reduction, one can see from equation (3), that the half-wave potential should become more negative with increasing hexamminecobalt(II) concentration. At low concentrations of ammonia, where only a small fraction of the total divalent cobalt is stable in the hexammine form, the kinetics of the decomposition of the hexamminecobalt(II) ion affects the potential. Curve 3 in Fig. 1 shows this effect. Instead of being constant, the corrected half-wave potential becomes more negative with decreasing ammonia concentration thus indicating that the concentration of hexamminecobalt(II) ion is higher than predicted, *i.e.*, the time has not been long enough to attain equilibrium between the different divalent cobalt amines.

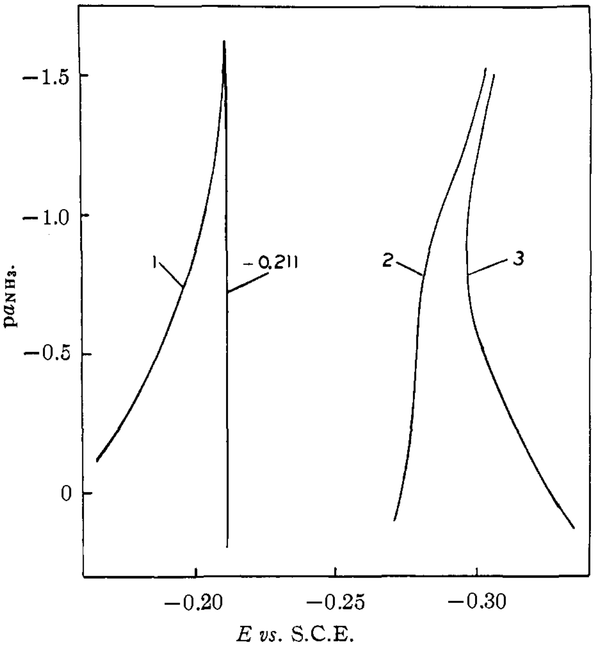

Fig. 1.—Curve 1, oxidation–reduction potential for hexamminecobalt(III, II) couple acc. to Bjerrum obtained at 30° in 2 *M* ammonium nitrate; curve 2, $E_{1/2}$ for the same couple at 25° in 2 *M* ammonium nitrate; curve 3, $E_{1/2}$ corrected for α_6.

From Fig. 1 it can be seen that the polarographic reduction proceeds with an overpotential of about 0.1 v. Part of this may be due to the temperature difference (Bjerrum's potentials obtained at 30°) and the difference in the diffusion coefficients of the trivalent and the divalent forms of the complex, but the main part must be due to the slowness of the reaction. It was also found that, in accordance with Bjerrum's results, the half-wave potential became more positive with decreasing ammonium ion concentration. For example, in 7.1 *M* ammonia the half-wave potentials in 2, 1 and 0.5 *M* ammonium nitrate were −0.291, −0.275 and −0.271 v. *vs.* S.C.E., respectively. The postulation that the reduction of hexamminecobalt(III) ion consists of the electron transfer to form the divalent hexamminecobalt ion, which in turn decomposes more or less depending upon the medium, is supported by some recent radioactive tracer investigations on the rate of electron exchange between complex ions by Hoshowsky, Holmes and McCallum[7] as well as by Lewis, Coryell and Irvine.[8] These authors reported a noticeable but slow rate of exchange of electron between hexamminecobalt(III) and hexamminecobalt(II), thus indicating a certain degree of reversibility. It is of interest to note that the trisethylenediaminecobalt(III, II) couple which has a much higher rate of electron exchange than the hexammine system, was shown

[7] S. A. Hoshowsky, O. G. Holmes and K. J. McCallum, *Can. J. Research*, **27B**, 258 (1949).

[8] W. Lewis, C. D. Coryell and J. W. Irvine, Jr., *J. Chem. Soc.* (Suppl. Issue, No. 2), S386 (1949).

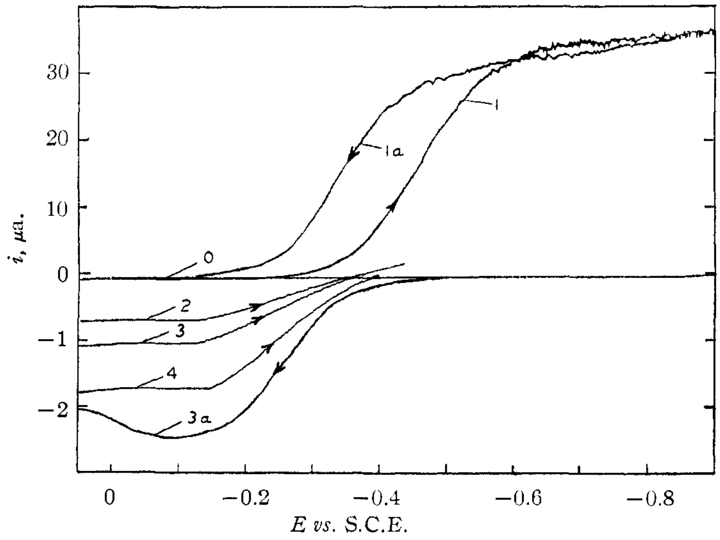

Fig. 2.—Polarograms obtained with the rotating platinum electrode in 1 *M* ammonium nitrate and 12.7 *M* ammonia: curve 0, residual current; curves 1 and 1a, 1 millimolar hexamminecobalt(III); curve 2, *ca.* 2 millimolar; curves 3 and 3a, *ca.* 3 millimolar; curve 4, *ca.* 4 millimolar Co(II) total. The arrow shows the direction of polarization. The sensitivity setting, when recording the anodic currents, was ten times higher than when recording the cathodic currents.

by Bjerrum[5] to be reversible. However, both of the above mentioned systems have very slow rates of exchange compared to the rates of such reversible systems as Ce(IV, III) and MnO_4^-, $MnO_4^=$. In this Laboratory, M. W. Grieb (unpublished investigations) has studied the polarographic reduction of the trisethylenediamine couple and found that the half-wave potential is nearly identical with Bjerrum's oxidation–reduction potential for this system and that the reduction proceeds reversibly.

The electron exchange and thus the reversibility of both hexammine and trisethylenediamine systems is, however, difficult to understand from the following point of view. Libby[9] has postulated that electron exchange occurs only between symmetrical complexes. In the case of the cobalt complexes, the trivalent forms, as is well known, have covalent bonds (d^2sp^3-hybridization) and are distinctively inert (Taube's[10] terminology) and the divalent forms are labile, having ionic bonds (sp^3d^2-hybridization). The electron configuration is too different to allow a reversible electron transfer. In order to satisfy Libby's symmetry principle, the following mechanism may be postulated for the hexammine cobalt couple

$$Co(NH_3)_6^{+++}\ (d^2sp^3\text{-hybridization}) + e^- \longrightarrow Co(NH_3)_6^{++}\ (d^2sp^3\text{-hybridization}) \quad (4)$$

$$Co(NH_3)_6^{++}\ (d^2sp^3\text{-hybridization}) \longrightarrow Co(NH_3)_6^{++}\ (sp^3d^2\text{-hybridization}) \quad (5)$$

Equations (4) and (5) are written in an irreversible manner. Actually both of these reactions are capable of being reversed, although with some overvoltage, as is shown by the following experiments with alternating current polarography and with the rotating platinum electrode.

Alternating current polarography using a technique similar to that described by Müller, Garman, Droz and Petra[11] and by Breyer and Guttman[12] was employed in order to investigate the reversibility of certain electrode reactions (unpublished investigations). In a solution containing 1 *M* sodium nitrate and 3 millimolar hexamminecobalt(III) and using a 60 cycle a.c. with a voltage amplitude of 50–100 mv. it was found by comparison with well-known reversible (Cd^{++}) and irreversible (H^+) systems that oxidation of the hexamminecobalt(II) complex formed during reduction actually takes place during the second half of the a.c. cycle, thus indicating a certain degree of reversibility.

The oxidation of hexamminecobalt(II) ion was studied by using the rotating platinum electrode. Figure 2 shows current–voltage curves obtained in 12.7 *M* ammonia and 1 *M* ammonium nitrate. The reduction of hexamminecobalt(III) ion gives a well defined diffusion current. $E_{1/2}$ is about −0.47 v. *vs.* S.C.E. However, by reversing the polarization from an increasingly cathodic to a decreasingly cathodic, the $E_{1/2}$ has changed to −0.36 v. *vs.* S.C.E. The hysteresis effect can be explained by the fact that with increasingly negative polarization the concentration of the hexamminecobalt(II) complex product actually will stay higher than the equilibrium concentration and thus shift the wave to more negative potential. When the polarization is decreasingly negative equilibrium conditions should be more closely approached. The oxidation experiments were conducted in the following manner: The supporting electrolyte containing the ammonia was first deaerated and then a few drops of a 2 *M* cobalt sulfate solution were added, preventing thus any air oxidation of the divalent ammine complex. In Fig. 2, a few current–voltage curves of the oxidation of divalent complex are presented. At this ammonia activity about 90% of the total divalent cobalt present is in the hexammine form. The results are somewhat surprising. The half-wave potential seems to be roughly right (−0.260 v. *vs.* S.C.E.) regardless of whether the polarization is increasingly or decreasingly cathodic. The current, is, however, only of the order of 1% of the expected value. The limiting current is proportional to concentration of cobalt(II) up to 3 millimolar, but tends to become concentration independent above that. For instance 3 millimolar total cobalt(II) gave a current of about 1 μa., while 15 millimolar gave only 2 μa. It might be mentioned that, as expected, the oxidation current decreases with decreasing ammonia concentration.

The results indicate that the oxidation proceeds very slowly and that probably the surface area of the electrode is one of the rate-determining factors, approaching a zero-order of reaction with increasing

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(9) W. F. Libby, *J. Phys. Chem.*, **56**, 39 (1952).

(10) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(11) R. H. Müller, R. L. Garman, M. E. Droz and J. Petra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).

(12) B. Breyer and F. Guttman, *Faraday Soc. Discussion*, **1**, 19 (1947).

concentration. A plausible mechanism for the slow rate would be represented by equations (5) and (4) reversed. Why the current is higher using decreasingly negative polarization than with the opposite polarization cannot be explained.

Reduction in Ethylenediamine.—Lewis, *et al.*,[8] in their studies on the rates of electron exchange, found a remarkably fast rate for the reaction

$$\mathrm{Co(NH_3)_6^{+++} + Co(en)_3^{++} \rightleftarrows Co(en)_3^{+++} + Co(NH_3)_6^{++}} \quad (6)$$

It was of interest to try the polarographic reduction of hexamminecobalt(III) ion in the presence of ethylenediamine.

It was first ascertained that the hexammine ion was stable in 0.1 *M* ethylenediamine. A millimolar solution of hexamminecobalt(III) chloride stood for 48 hours in 0.1 *M* ethylenediamine. The amine was then neutralized with acid and a polarogram recorded, showing that the original ion still was present. A different type of experiment led to the same conclusion: a 0.08 *M* ethylenediamine solution containing 0.012 *M* of the hexamminecobalt(III) chloride was allowed to stand for 48 hours. The hexamminecobalt(III) chloride was then precipitated using concentrated hydrochloric acid and alcohol. The dried product dissolved in water gave the same polarograms as the original material.

Figure 3 shows a family of polarograms obtained in a supporting electrolyte containing 0.1 *M* potassium nitrate and 0.1 *M* ethylenediamine. The reduction of the hexamminecobalt(III) ion proceeds apparently reversibly, the reciprocal slope of the logarithmic plot having a value of 0.064. The half-wave potential for this reduction was -0.465 v. *vs.* S.C.E. W. M. Grieb (unpublished investigations) has determined the half-wave potential for the reduction of trisethylenediaminecobalt(III) ion to be -0.451 v. *vs.* S.C.E. in this medium. Curve 2 in Fig. 3 was obtained by having both hexamminecobalt(III) and trisethylenediaminecobalt(II) in solution and curve 3 represents the oxidation of the latter only. The procedure of forming the divalent complex in the solution was the same as described above in connection with the oxidation of hexamminecobalt(II) complex. As can be seen, the couple

$$\mathrm{Co(NH_3)_6^{+++} + e^- \rightleftarrows Co(en)_3^{++}} \quad (7)$$

apparently represents a reversible system.

It is, however, clear that the hexamminecobalt(III) ion is reduced at the usual potential of about -0.250 v. *vs.* S.C.E. and the product, the divalent hexammine complex, being a labile complex[10] will rapidly come into equilibrium with the complexing agent in the solution

$$\mathrm{Co(NH_3)_6^{++} + 3en \rightleftarrows Co(en)_3^{++} + 6NH_3} \quad (8)$$

Because of the excess of ethylenediamine and the relative stability of the complexes, the equilibrium is shifted to the right. As long as the potential is more positive than required for the reduction of trisethylenediaminecobalt(III), an oxidation of the divalent ethylenediamine complex occurs, thus resulting in a net current equal to zero. When the potential of the electrode is made increasingly negative, the oxidation will cease, with the half-wave potential equal to that of the trisethylenediamine system, and with the reversible slope, thus giving the impression that the system represented by equation (7) is a reversible one.

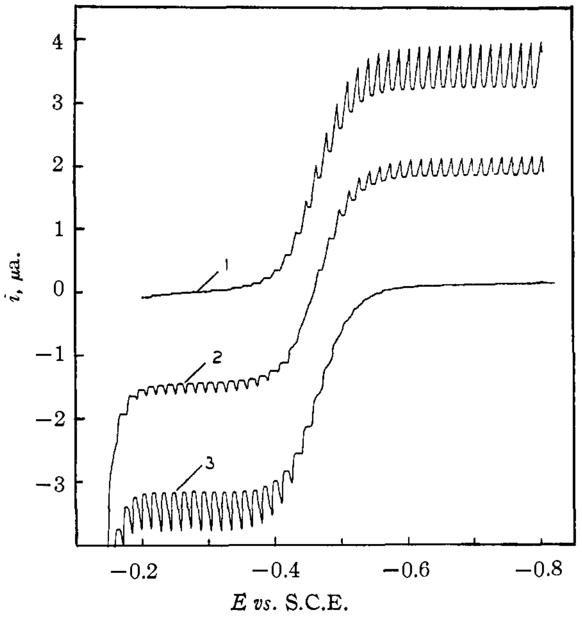

Fig. 3.—Polarograms obtained in 0.1 *M* potassium nitrate containing 0.1 *M* ethylenediamine, electrode II, damping 1: curve 1, 1 millimolar hexamminecobalt(III); curve 2, *ca.* 0.55 millimolar hexamminecobalt(III) and *ca.* 0.44 millimolar trisethylenediaminecobalt(II); curve 3, *ca.* 1 millimolar trisethylenediaminecobalt(II).

Reduction in High Chloride Concentration.—Brdicka[13] found in 1930, that the reduction of the blue chloro complex of divalent cobalt is more nearly reversible and occurs at 0.4 v. more positive potential than the reduction of the hexaaquo ion. The polarogram of hexamminecobalt(III) was recorded in 5 *M* calcium chloride solution. The first wave was drawn out, but $E_{1/2}$ was roughly normal at -0.260 v. *vs.* S.C.E. The second wave, the reduction of the divalent cobalt to metal, had a half-wave potential of -0.876 v. *vs.* S.C.E. and a logarithmic reciprocal slope of about 0.060. In the reduction of the divalent chloro complex of cobalt in the same medium, $E_{1/2}$ was -0.822 v. *vs.* S.C.E. and the reciprocal slope was 0.042. From the large shift of the second reduction wave of hexamminecobalt(III) it is obvious that a chloro complex of cobalt(II) must be formed by a rapid exchange of ligands by the hexamminecobalt(II) ion. Since the second wave of cobalt(III) is not identical in potential or shape with the cobalt(II) wave, it is probable that the species involved in the two cases are not identical, *i.e.*, that the exchange is not complete.

Reduction in High Hydroxide Concentration.—Although it has been long known that cobalt(II) hydroxide will dissolve in concentrated alkali solution to form a blue solution,[14] very little is

[13] R. Brdicka, *Coll. Czechoslov. Chem. Communs.*, **2**, 489, 545 (1930).

[14] Gmelin, "Handbuch der Anorganischen Chemie," Verlag Chemie G. M. B. H., Berlin, 1932 (8th Ed.), Vol. 58, Teil A, p. 208.

known about the actual species formed. Scholder[15] reports preparing well crystallized compounds like $Ba_2[Co(OH)_6]$ and $Na_2[Co(OH)_4]$. More recently Gordon and Schreyer[16] have studied spectrophotometrically the species of cobalt(II) in strongly alkaline solutions and report results indicating that a blue trihydroxocobalt(II) exists in solutions containing 3 to 12 *M* potassium hydroxide.

Some experiments were carried out in order to find out whether the blue complex of cobalt(II) is reducible at the dropping mercury electrode. The supporting electrolyte (10 *M* sodium hydroxide) was deaerated and then a few drops of a 2 *M* cobaltous sulfate solution were added to it. A pink to blue precipitate was at first formed, but after 15 minutes' stirring (nitrogen bubbling) a deep blue solution was obtained, containing about 2 millimolar of cobalt(II) as the hydroxo complex. Most of the precipitated cobaltous hydroxide remained undissolved. The reduction proceeded irreversibly, the half-wave potential being −1.54 v. *vs.* S.C.E.

The reduction of the hexamminecobalt(III) complex in 10 *M* sodium hydroxide was also studied. The first step comes at around −0.35 v. *vs.* S.C.E. and the second step has a half-wave potential of −1.54 v. *vs.* S.C.E. It seems obvious that the mechanism is similar to that described in the case of the chloro complex.

Whether the exchange here is complete or not cannot be said on the basis of this experiment.

Acknowledgment.—This investigation has been supported by the Office of Naval Research under Contract No. N6 ori-07136.

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[15] R. Scholder, *Z. angew. Chem.*, **46**, 509 (1933).

[16] S. Gordon and J. M. Schreyer, THIS JOURNAL, **74**, 3169 (1952).

[CONTRIBUTED FROM THE ROSS CHEMISTRY LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

The Thermodynamics of Aqueous 2-Propanol–Sulfuric Acid Solutions from Electromotive Force Measurements[1]

BY WILLIAM N. WHITTEN AND JAMES E. LAND

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Electromotive force measurements have been made at 5, 10, 15 and 20° with cells consisting of a hydrogen electrode and a mercury–mercurous sulfate electrode in aqueous 2-propanol–sulfuric acid solutions. The solutions contained 5 and 10% by weight 2-propanol and the acid molalities varied from 0.05 to 1.0. From these electromotive force values the mean ionic activity coefficients of the acid have been calculated. The relative partial molal heat contents of the sulfuric acid in these solutions have been computed for the temperature range 5 to 25°.

The mean ionic activity coefficients of sulfuric acid in aqueous 2-propanol solutions at 25° have been determined by Land and Crockford.[2]

The purpose of the investigation reported on in this paper was, first, to determine the mean ionic activity coefficients of sulfuric acid in the same solvent media at 5, 10, 15 and 20°. Then, these values and the mean ionic activity coefficients previously measured at 25° permitted the variation of the mean ionic activity coefficients with temperature to be found, so that the relative partial molal heat content of the sulfuric acid in aqueous 2-propanol mixtures could be calculated for the temperature range 5 to 25°.

The cell used in these studies was

$$H_2(g)/H_2SO_4(m),\ \text{2-propanol}\ (x\%),\ \text{water}\ (100 - x\%)/Hg_2SO_4(s)/Hg(l)$$

5 and 10% by weight aqueous solutions of 2-propanol were studied. The molalities of the sulfuric acid employed ranged from 0.05 to 1.0 molal. Readings below 0.05 molal and above 1.0 molal were not attempted for reasons previously reported.[2]

Experimental Procedure.—The methods of purification of chemicals, experimental techniques and equipment employed were the same as those used by Land and Crockford.[2] Density measurements were made on all solutions at 5, 10, 15 and 20°.

In order that all electromotive force measurements could be corrected to one atmosphere pressure of dry hydrogen, the vapor pressures of all solutions over the entire range of temperatures studied were determined by the method used by Crockford, Bailey and Land.[3] The vapor pressure results for solutions not exceeding one molal of sulfuric acid in 5 and 10% by weight 2-propanol–water solutions can be expressed by the equation

$$\text{v.p.} = \alpha - \beta(m)$$

in which α and β are constants. These constants are given in Table I.

TABLE I

CONSTANTS OF THE EQUATION V.P. = $\alpha - \beta(m)$

Temp., °C.	α: 5% 2-propanol–water soln.	α: 10% 2-propanol–water soln.	β: 5% 2-propanol–water soln.	β: 10% 2-propanol–water soln.
5	7.9	8.6	0.40	0.13
10	10.7	11.7	.31	.20
15	14.6	16.2	.51	.42
20	20.1	22.4	.71	.22

Data and Results.—Tables II and III give a summary of the mean ionic activity coefficients determined. The values of *E* recorded were ascertained from very large scale curves obtained by plotting the experimentally determined electromotive force values against the square root of the molality. The density values were also obtained

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[1] Based partly upon William N. Whitten's M.S. thesis. Presented at the Southeastern Regional Meeting of the American Chemical Society, October 23–25, 1952.

[2] J. E. Land and H. D. Crockford, THIS JOURNAL, **72**, 1895 (1950).

[3] H. D. Crockford, W. Bailey and J. E. Land, *J. Alabama Acad. of Science*, **21**, 12 (1952).