

metal ketyl anion as a result of their wandering around in the benzene rings.<sup>11b</sup> This coulomb interaction would tend to localize the charge electron in the vicinity of the sodium ion so that the ion pair would be formed at the expense of some of the resonance energy of the anion, and the resulting instability of the ion pair would be revealed by an increase in the values of  $K$  and  $a$ . The difference between the  $a$  values of the metal ketyl and of sodium benzohydroxide corresponds to an energy difference of 0.55 kcal., which could be considered as an approximate measure of the *minimum*<sup>16</sup> contribution of the charge electron to the resonance energy of the free anion. The conductance data furnish no basis for a decision between these two interpretations, but the evidence advanced by Bent<sup>11b</sup> establishes a presumption in favor of the second hypothesis. It should be noted, however, that these alternative hypotheses are merely limiting cases since the two factors suggested as possible causes of the increased  $a$  value are not, necessarily, mutually exclusive.

**The Association of Ion Pairs.**—The mass action constants  $k$  and  $k_4$  are much more sensitive than  $K$  to errors<sup>17</sup> in the approximations introduced in applying the conductance equation and are, perhaps, reliable only as to order of magnitude. The independent evidence regarding association to the pinacolate in 0.3 normal solution, presented in the second paper of this series,<sup>1b</sup> in-

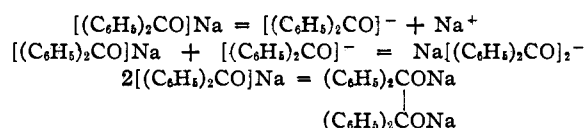
(16) The coulomb interaction may cancel only a fraction of the contribution of the charge electron to the resonance energy.

(17) It seems likely that such errors can be reduced by using a solvent of lower dielectric constant. Accordingly, an attempt will be made to measure the conductance of metal ketyls in pyridine.

indicated a much lower degree of association than is obtained by extrapolation to that concentration using these observed values of the mass action constants. Although such extrapolation is justified only as a crude approximation, it is unlikely that the discrepancy is due entirely to the uncertainties in the constants or in the extrapolation. It is probable that the actual proportion of pinacolate in such concentrated solutions is higher than was indicated by the application of a modification of Bachmann's method<sup>9</sup> to liquid ammonia solutions, and that a considerable fraction of the pinacolate dissociated during the decomposition with ammonium chloride.

### Summary

1. It has been shown that the conductance of sodium benzophenone in liquid ammonia may be described quantitatively by assuming the presence of the following equilibria



2. The structure of the ion pair has been discussed. The available evidence is consistent with the hypothesis that the sodium ion is located in the vicinity of the oxygen in the ion pair, provided it is further assumed that this ion pair is formed at the expense of some of the resonance energy of the free anion and that the charge electron participates in the resonance phenomenon in this anion.

PROVIDENCE, R. I.

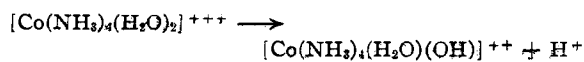
RECEIVED DECEMBER 4, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

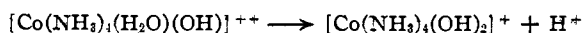
## The Dissociation Constants of Diaquotetrammine Cobaltic Cation as an Acid

BY ARTHUR B. LAMB AND EDWIN B. DAMON

Diaquotetrammine cobaltic ion may be regarded, in accordance with Brønsted's definition, as a cation acid which dissociates in two steps as follows



and



Brønsted and his collaborators<sup>1</sup> have measured

(1) J. N. Brønsted and C. V. King, *Z. physik. Chem.*, **130**, 699 (1927); J. N. Brønsted and K. Volqvartz, *ibid.*, **134**, 97 (1928).

the primary dissociation constants of this and of a number of similar aquo ion acids and have found interesting differences among them. Their measurements, in the case of the diaquotetrammine cation, were carried out by two independent methods. In the first method, the solubility of the slightly soluble diaquotetrammine salt of the oxalodinitrodiammine cobaltic anion was measured in solutions of varying known acidity; this was compared with the solubility of the luteo salt under similar conditions. In the

second method, the concentration of hydrogen ion in a solution containing this cation was ascertained from the rate of aquation of added nitratotetrammine cobaltic nitrate (as shown by measurements of the electrical conductance of the solution).

These methods are ingenious and elegant and have evidently been applied with skill. Nevertheless there appear to be difficulties inherent in them, since successive determinations by both methods under substantially identical conditions showed variations of 20% and more in the dissociation constants obtained.

In this situation it has seemed to us worth while to ascertain whether the glass electrode, thanks to its rapidity of response and its indifference to the presence of oxidizing substances, could not be used to measure these constants with greater precision and certainty. We have, therefore, applied this instrument to solutions of diaquotetrammine cobaltic chloride containing known, varying amounts of sodium hydroxide. In other words, we have carried out a non-cumulative electrometric titration of the cation acid.

This procedure has the advantage that minute impurities, which might seriously alter the hydrogen ion concentration if the salt were merely dissolved in pure water, have a decidedly smaller effect in the presence of the added alkali. Also, measurements in the more alkaline solutions permit the determination of the secondary as well as the primary dissociation constant.

From numerous points on the titration curve thus obtained, we have computed a series of values for the primary and also for the secondary dissociation constant of the diaquotetrammine ion.

In carrying out this titration it was important to recognize that this ammine is by no means a stable substance under these conditions. In the first place, it changes into the acido salt to at least a limited extent; Stevens<sup>2</sup> found in the case of the chloride that in a 0.005 *M* solution at 25° an equilibrium was reached in about 200 minutes, at which analyses indicated the presence of 12% of the chloroaquoammine. In the second place, this ammine suffers an irreversible decomposition in which ammonia is liberated and an oxide or hydroxide of cobalt ultimately is precipitated. While in acid solution this decomposition is relatively slow, the rate increases

rapidly as the solution becomes more alkaline and this decomposition sets an upper limit to the pH value at which useful measurements can be made.

#### Apparatus

The glass electrode assembly used in these measurements was of the convenient, durable type described by MacInnes and Belcher.<sup>3</sup>

Measurements of e. m. f. were made with a Compton quadrant electrometer and a Leeds and Northrup type K potentiometer, standardized against an Eppley standard cadmium cell. With this arrangement it proved more rapid and convenient not to balance the potentiometer exactly, but rather to set the slide wire within one or two millivolts of the unknown e. m. f., and then determine the difference from the electrometer deflection. The total deflection on reversing the connections to the electrometer amounted to not less than 10 mm. per millivolt, so that the e. m. f. could be measured to 0.1 mv.

For this use with an electrometer the series of tapping keys provided in the potentiometer for use with a galvanometer were disconnected by detaching the movable part of the switch marked "STD. CELL-E.M.F.," leaving the center posts of the switch open. The end posts of the switch were then bridged across by U-shaped brass strips, which served to connect the "E.M.F.-" and the "STD. CELL-" binding posts directly to the potentiometer circuit. An external switchboard could then be connected to the potentiometer through the "E.M.F." and "STD. CELL" binding posts, without making any internal changes.

The glass electrode assembly, potentiometer and auxiliary apparatus were surrounded by appropriate electrostatic shields of copper sheet or gauze, which were interconnected and earthed. The potentiometer and its accessories were kept dry by trays of calcium chloride, and were operated from outside the shield by means of suitably insulated, earthed metal rods.

The glass electrode and the solutions were contained in a large air thermostat which, undisturbed, maintained a temperature of 25.00 ± 0.02°. However, opening the door to operate the glass electrode caused fluctuations of temperature which were best corrected by a manual readjustment. Readings of the temperature made at the time of every measurement with the glass electrode showed, however, that the temperature of the cell could hardly have varied more than about 0.1° from 25.0° during these measurements.

#### Materials

Diaquotetrammine cobaltic chloride was prepared from pure carbonatotetrammine chloride (described below) by the method of Jörgensen.<sup>4</sup> The crystals thus obtained were washed 3-5 times with ice-cold concentrated hydrochloric acid, then 3-5 times with cold 95% alcohol, a motor-driven centrifuge being used to settle the wash liquors before decantation. They were then transferred to a platinum Gooch crucible, washed 5 times with absolute alcohol and drained in the centrifuge. After a final centrifuging

(3) Duncan A. MacInnes and Donald Belcher, *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1930).

(4) S. M. Jörgensen, *Z. anorg. Chem.*, **2**, 294 (1894).

(2) R. G. Stevens, Thesis, Harvard University, 1927.

for twenty to fifty minutes, the apparently dry crystals were exposed in the open air for one to two hours before weighing. The product was in all cases used on the day it was prepared.

Analyses of the six different preparations used in these measurements gave the following percentages of cobalt: 21.93, 21.93, 21.96, 21.92, 21.94, 21.96; average, 21.94. Analysis of a seventh sample, prepared in the same way, gave the following additional data.

	I	II	Average	Calculated for $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_2$
Cobalt, %	21.93	21.92	21.93	21.87
Total chlorine, %	39.39	39.40	39.39	39.47 <sub>4</sub>
Complexly bound chlorine, %	0.236	0.230	0.233	0.000

The high value found for cobalt probably indicates the presence of a small amount of cobalt oxide, formed by decomposition of the complex. The 0.233 g. of complexly bound chlorine found in 100 g. of sample is equivalent to 1.650 g. of chloroaquotetrammine chloride, containing 0.699 g. of chlorine all told. This leaves 38.69 g. of chlorine, equivalent to 98.02 g. of diaquotetrammine chloride, in 100 g. of sample. The cobalt analyses show an excess of cobalt over that contained in these amines equivalent to 0.19 g. of cobaltic hydroxide. The analysis of this sample thus corresponds to that of such a mixture as

Diaquotetrammine chloride	98.02%
Chloroaquotetrammine chloride	1.65%
Cobalt hydroxide, $\text{Co}(\text{OH})_2$	0.19%
Moisture, etc., by difference	0.14%

Previous investigators who have analyzed this salt have obtained low values for chlorine and high values for cobalt. Thus for total chlorine Jørgensen<sup>4</sup> found 39.17 *versus* 39.475%, and for cobalt Birk<sup>5</sup> found 21.95 *versus* 21.87%.

**Carbonatetetrammine Cobaltic Chloride.**—This ammine prepared by following the directions of Jørgensen<sup>6</sup> proved on analysis to have a low and variable content of chlorine. This presumably was caused by the presence therein of carbonato bicarbonate and by the separation of a part of the product as an oil, rather than as crystals, on precipitation with alcohol.

We found that these difficulties could be remedied by a more careful regulation of the concentration of ammonium carbonate and ammonium chloride, and, after careful precipitation with alcohol, by recrystallizing the product first from a solution of ammonium chloride and finally from water. Our procedure with these supplementary details was as follows.

Twenty grams of cobalt carbonate was dissolved, with warming, in 56 ml. of 1:1 hydrochloric acid. The clear solution, diluted to 100 ml., was poured into 800 ml. of a solution containing 100 g. of ammonium carbonate and 250 ml. of concentrated ammonium hydroxide (sp. gr., 0.90). After oxidation by a vigorous current of air for three hours, the solution was transferred to a porcelain dish (diameter, 30 cm.) and evaporated on a steam-bath for two hours, with the addition of small (2.5 to 3 g.)

lumps of ammonium carbonate at five-minute intervals. The solution, now concentrated to a volume not greater than 250 ml., was filtered while warm, cooled in an ice-bath and diluted to 300 ml. with a solution containing 18 g. of ammonium chloride in the required amount of distilled water. The solution, cooled in ice, was treated with 750 ml. of cold 95% alcohol, added in 50-ml. portions at ten-minute intervals. The product, which usually separated in good crystalline form, was collected on a suction filter, washed with cold 70% alcohol and dried in the open air; yield, about 24 g.

The crude material from ten such batches was combined for purification. To convert into chloride any carbonato bicarbonate that might be present, it was dissolved at room temperature in the required amount of a 15% solution of ammonium chloride, which had been made neutral to litmus with ammonium hydroxide; the resulting solution was cooled in ice and treated with cold 95% alcohol added in 150-ml. portions at ten-minute intervals. The crystals thus formed were collected and washed as before.

After two such recrystallizations, the product was crystallized once from water without the addition of alcohol. In this process, the salt was divided in several portions, and the mother liquor from the crystallization of the first portion used over and over again. (At the end, a small amount of less pure material was precipitated by adding alcohol to the mother liquor.) The crystals were collected in a platinum Gooch crucible, washed once with cold water and drained in the centrifuge; yield, 101 g. of good crystals, plus 18 g. of less pure material.

The crystals obtained in this way were clear, garnet-red 4- and 6-sided prisms, mostly small, but a few as long as 1 mm. On standing, the crystals became less transparent, while the color changed toward purple. After being ground and exposed over calcium chloride for forty-eight hours they were analyzed with the following results.

	I	II	Average	Calculated for $\text{Co}(\text{NH}_3)_4(\text{CO}_3)\text{Cl}$
Cobalt, %	26.56	26.54	26.55	26.49
Chlorine, %	15.94	15.91	15.92 <sub>4</sub>	15.93

**Standard Solution of Sodium Hydroxide, 0.1 M.**—A solution sufficiently free from carbonate for our purposes was prepared by the method of Sørensen<sup>7</sup> and Cowles.<sup>8</sup> After dilution with boiled distilled water, the solution was standardized first against potassium biphthalate and found to be 0.0999, 0.1001 and 0.1001 M; and second, against oxalic acid and found to be 0.1001, 0.1001 and 0.1000 M; average, 0.1000<sub>4</sub> M; temperature, 23–24°. The solution was kept in a Pyrex bottle, protected by soda-lime tubes.

#### Analytical Methods

Cobalt was determined as usual by conversion to cobaltous sulfate. A porcelain crucible was employed with the serrated, clear quartz lid described by J. D. Main Smith<sup>9</sup> for prevention of loss by spattering.

In determining the complexly bound chlorine in the diaquotetrammine chloride (presumably present as chloroaquo chloride) every precaution was taken to prevent loss

(5) E. Birk, *Z. anorg. Chem.*, **153**, 114 (1927).

(6) S. M. Jørgensen, *ibid.*, **2**, 281 (1892).

(7) S. P. L. Sørensen, *Biochem. Z.*, **21**, 186 (1909).

(8) H. W. Cowles, Jr., *This Journal*, **30**, 1192 (1908).

(9) J. D. M. Smith, *Chem. Ind.*, **44**, 839T (1925).

of complex chlorine by aquation. A 1-g. sample was dissolved rapidly in 175 ml. of 0.33 *M* nitric acid, containing 100 g. of clear cracked ice in a 500-ml. glass stoppered Erlenmeyer flask; and then 25 ml. of 0.5 *M* silver nitrate was run in from a pipet, with shaking. The flask was stoppered and shaken vigorously for two minutes; the solution was then filtered rapidly with suction through two sheets of Whatman No. 42 filter paper supported on the sintered Jena glass disk of a suction funnel, care being taken to avoid transferring ice, which might contain unprecipitated chloride, to the funnel. Filtration was completed ten minutes after starting to dissolve the sample. After 6 to 10 washings with 0.001 *M* silver nitrate, the first silver chloride precipitate was discarded. The filtrate and washings, which appeared perfectly clear, were treated with 3 ml. of 30% hydrogen peroxide, heated to boiling, and boiled gently for fifteen minutes. This brought about complete decomposition of the complex ion. After standing overnight in a dark place, the second precipitate of silver chloride was collected and weighed.

### Measurements with the Glass Electrode

For standardizing the glass electrode assembly, 0.05 *M* potassium biphthalate was used as our standard buffer. We have assumed that the *pH* of this solution at 25.0° is 3.983, as determined by MacInnes and Belcher.<sup>10</sup> To detect possible changes in the asymmetry potential of the glass membrane, standardizations were carried out at the beginning and end of each day's series of measurements (and in some cases more frequently).

The above-mentioned instability of the tetrammine ion made it necessary not only to determine the hydrogen ion concentration on a series of independent solutions, each with its quota of sodium hydroxide, but also to follow in each solution the change in potential of the glass electrode with time and to extrapolate these potentials back to the moment at which the solid ammine was added to the solution. It was assumed that the salt dissolved instantaneously, and that the relative amounts of diaquo and chloroquo salts in the solution at that moment were the same as in the solid sample. In performing the extrapolation, it was necessary to take into

(10) Duncan A. MacInnes and Donald Belcher, *THIS JOURNAL*, **53**, 3326 (1931). This value conforms to the widely used, arbitrary *pH* scale defined by the specifications of W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins Co., Baltimore, 1928, p. 480. Dr. MacInnes has kindly pointed out (private communication, also *Cold Spring Harbor Symposia on Quantitative Biology*, **1**, 190 (1933)) that in accordance with his present point of view an agreement between *pH* measurement and thermodynamic ionization constants, etc., is best attained by shifting the scale by about 0.03 unit; the *pH* of the phthalate buffer is then 4.015. Adoption of this *pH* scale would result in raising the *pH* values reported in this paper by 0.032. When the individual dissociation constants in Table I are recalculated on this basis, the average values become  $k_1 = 4.42 \times 10^{-7}$ ,  $k_2 = 4.7 \times 10^{-8}$ .

account that in the large Pyrex container the ammine might decompose at a rate different from the rate in the glass electrode vessel, where the solution is exposed to a relatively large surface of soft, alkaline glass.

Details of a typical experiment are given in the following. Four buffer solutions (*i. e.*, mixtures of the diaquo chloride and sodium hydroxide) were generally prepared and measured on the same day. Approximately 1-liter samples of distilled water, contained in 2-liter Pyrex Erlenmeyer flasks, were boiled to remove carbon dioxide, cooled to room temperature under the protection of soda-lime tubes, weighed, and brought to 25.0° by standing overnight in the air thermostat. Measured volumes of standard 0.1 *M* sodium hydroxide were added from a re-calibrated buret. Samples of diaquotetrammine chloride, which had been prepared on the same day, were weighed on watch glasses small enough to enter the necks of the 2-liter flasks. At the same time, samples were weighed for the determination of the percentage of cobalt.

At a suitable moment a stop-watch was started and the sample of ammine was dropped into the dilute alkali solution. This was immediately shaken very vigorously for sixty to ninety seconds. The glass electrode vessel was then rinsed three times and filled with the buffer solution; the time when the solution entered the glass spiral was noted. The first measurement of e. m. f. was in most cases made at four minutes by the stop-watch, but with the least stable buffers this time was reduced to two and one-half minutes. Measurements of e. m. f. were repeated at one and one-half to two and one-half minute intervals. At about ten minutes, and again at about twenty minutes, the buffer solution in the glass spiral was replaced by a fresh sample.

The observed values of e. m. f. were then graphically extrapolated in two steps: first, the values observed with each sample of the buffer were extrapolated to find the e. m. f. at the moment when this sample was run into the glass electrode; then these corrected values were extrapolated to zero time.

The slope of the extrapolation curve at zero time,  $(dE/dt)_0$ , may be taken as a measure of the instability of the buffer solution. In Fig. 1, values of  $(dE/dt)_0$  (as read from the extrapolation curves) are plotted as a function of *pH*. It will be seen that the more acid solutions changed

very slowly; with these, the change may have been due to a shift in the relative proportions of diaquo and chloroquo ions. In solutions of higher  $pH$ , the more rapid changes were caused principally by decomposition of the complex ion; in such solutions a precipitate of cobalt hydroxide was formed on standing. The most alkaline buffer of this series,  $pH = 6.066$ , became perceptibly cloudy within thirteen minutes. This appeared to be the most alkaline buffer with which useful measurements could be made.

The  $pH$  values of the freshly prepared buffer solutions were finally calculated from the extrapolated values of e. m. f. In these calculations, the diffusion potential at the junction between buffer solution and saturated potassium chloride was neglected. The data which we have obtained are collected in Table I.

The first column of this table gives the volume of exactly tenth molar sodium hydroxide used in preparing a volume of buffer solution containing 0.004 mole of pure diaquo chloride; the second column gives the volume of this buffer solution; the third column gives the  $pH$  of the freshly prepared buffer solutions. (In correcting for the presence of chloroquo chloride and other impurities, it is assumed that all samples of diaquo chloride crystals had the composition stated on page 385.)

TABLE I  
BUFFER SOLUTIONS CONTAINING 0.004 MOLE OF  
[Co(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>

Volume 0.1 M NaOH, ml.	Volume buffer soln., ml.	$pH$	$A$	$10^4 k_1$	$10^4 k_2$
36.17	1067	6.066	2.095	4.78	5.4
20.64	1050	5.335	2.483	4.79	4.6
33.49	1069	5.925	2.162	4.71	6.2
12.84	1050	4.995	2.676	4.71	4.3
30.41	1046	5.756	2.239	4.78	4.7
15.14	1019	5.105	2.620	5.00	(1.)
28.51	1066	5.684	2.287	4.8	(4.)
7.64	1038	4.712	2.804	4.82	(4.)
28.09	1048	5.656	2.297	4.82	(4.)
7.53	1021	4.697	2.807	4.8	(4.)
25.78	1059	5.553	2.355	4.8	(4.)
10.22	1042	4.844	2.741	4.8	(4.)
23.01	1038	5.436	2.424	4.8	(4.)
2.03	1026	4.183	2.932	4.8	(4.)
17.94	1052	5.223	2.550	4.82	(4.)
5.12	1039	4.513	2.864	4.82	(4.)
0.00	1034	3.915	2.969	(3.9)	...
.00	1011	3.866	2.966	(4.8)	...
.00	948	3.865	2.968	(4.5)	...
Average of accepted values.....		4.80	5.0		

By plotting the  $pH$  values of these buffers as a function of the volume of tenth molar sodium hydroxide solution we obtain the titration curve shown in Fig. 2. This curve represents the titration of 0.004 mole of diaquotetrammine chloride

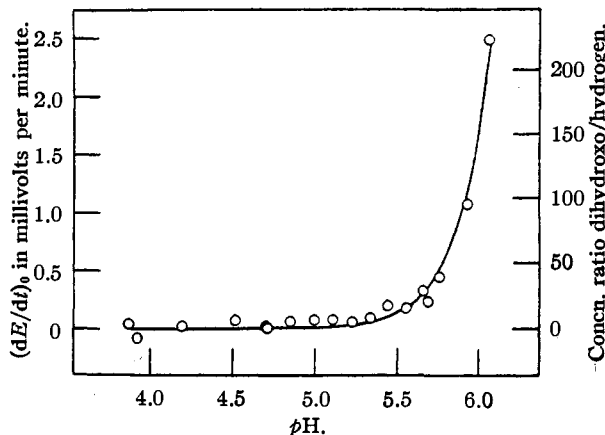


Fig. 1.

in an average volume of solution of 1020 ml. (plus or minus about 2%).

### Calculation of Dissociation Constants

The primary and secondary dissociation constants of the cation acid,  $Co(NH_3)_4(H_2O)_2^{+++}$ , have been calculated from the data for titration with sodium hydroxide given in Table I. The method of calculation is similar to that outlined by Britton.<sup>11</sup> In these calculations, we have assumed the relation

$$pH = -\log h$$

(where  $h$  represents the concentration of hydrogen ions) as a sufficiently good approximation for our present purposes. As a result, the constants which we obtain are neither thermodynamic dissociation constants in terms of activities, nor classical dissociation constants in terms of true concentrations; they are approximately the same as the "acidity constants" defined by Brønsted.<sup>12</sup>

In the following discussion, brackets are used to denote concentrations; other symbols are tabulated below.

- [+++] concentration of  $Co(NH_3)_4(H_2O)_2^{+++}$
- [++] concentration of  $Co(NH_3)_4(H_2O)OH^{++}$
- [+] concentration of  $Co(NH_3)_4(OH)_2^+$
- $b$  concentration of added sodium hydroxide
- $c$  total concentration of diaquotetrammine chloride
- $h$  concentration of hydrogen ion

(11) H. T. S. Britton, "Hydrogen Ions," Chapman and Hall, Ltd., London, 1929, page 150.

(12) J. N. Brønsted and Cecil V. King, *Z. physik. Chem.*, **130**, 700 (1927).

The primary and secondary dissociation constants,  $k_1$  and  $k_2$ , are defined by the equations

$$k_1 = [++]/[+++]h \quad (1)$$

$$k_2 = [^+]/[++]h \quad (2)$$

Since the total concentration of diaquotetrammine chloride is known, we may write

$$[+++] + [++] + [^+] = c \quad (3)$$

From the law of electroneutrality we obtain the relation

$$3[+++] + 2[++] + [^+] + [H^+] + [Na^+] = [Cl^-] + [OH^-]$$

In the buffers included in these measurements, the concentration of hydroxyl ion is very small and may be neglected. The concentrations of  $Cl^-$  and  $Na^+$  are known from the concentrations of the ammine and of the added hydroxide; the concentration of  $H^+$  from the measurements of  $pH$

$$[H^+] = h \quad [Na^+] = b \quad [Cl^-] = 3c$$

Substitution of these values in the above equation gives

$$3[+++] + 2[++] + [^+] = 3c - b - h \quad (4)$$

By eliminating the unknown concentrations  $[+++]$ ,  $[++]$  and  $[^+]$  from equations 1, 2, 3 and 4 we obtain the expression

$$\frac{3h^2 + 2k_1h + k_1k_2}{h^2 + k_1h + k_1k_2} = \frac{3c - b - h}{c} = A \quad (5)$$

which defines the convenient function,  $A$ . Values of  $A$ , calculated from known values of  $b$ ,  $c$  and  $h$  for the various buffer solutions, are listed in Table I.

By substituting in equation 5 values of  $h$  and  $A$  for two different buffer solutions in which these values are  $h_1$ ,  $A_1$  and  $h_2$ ,  $A_2$ , we obtain a pair of simultaneous equations, from which, by elimination of  $k_2$  or  $k_1$ , we obtain finally

$$k_1 = \frac{(A_1 - 1)(3 - A_2)h_2^2 - (A_2 - 1)(3 - A_1)h_1^2}{(A_1 - 1)(A_2 - 2)h_2 - (A_2 - 1)(A_1 - 2)h_1} \quad (6)$$

and

$$k_2 = \frac{(A_2 - 2)(3 - A_1)h_1^2h_2 - (A_1 - 2)(3 - A_2)h_1h_2^2}{(A_1 - 1)(3 - A_2)h_2^2 - (A_2 - 1)(3 - A_1)h_1^2} \quad (7)$$

The dissociation constants  $k_1$  and  $k_2$  may now be calculated by substituting numerical values in equations 6 and 7. The results of such calculations are presented in the last two columns of Table I. In selecting the different pairs of buffers to be used in these calculations, we have combined, wherever possible, measurements made on the same day using the same sample of ammine.

### Correction for Chloroaquotetrammine Chloride

In the preceding calculations, chloroaquotetrammine chloride has been treated as an inert impurity. The chloroaquotetrammine ion, however, is presumably an acid of about the same strength as the hydroxo-aquotetrammine ion, that is, an acid with a dissociation constant of the same magnitude as  $k_2$ . It is accordingly worth while to investigate how large an error in the values of  $k_1$  and  $k_2$  might have been caused by the presence of 1.65% of chloroaquo chloride in the samples of diaquo chloride.

Calling  $c'$  the total concentration of chloroaquotetrammine chloride and  $k'$  the dissociation constant of the chloroaquotetrammine ion as an acid, and inserting them in equations 3-5 above, we obtain as a corrected value of  $A$

$$A' = \frac{3c - b - h}{c} + \frac{k'c'}{(k' + k)c} \quad (8)$$

In the buffers of Table I the value of  $c'$  is  $7 \times 10^{-6}$ . If it is assumed that  $k'$  has the same value as  $k_2$ , we find that the maximum value of the correction to be applied to  $A$  (*i. e.*, in the case of the most alkaline buffer) amounts to 0.001. It is evident that in the present measurements this correction may be neglected.

### Calculation of the Theoretical Titration Curve

To test the agreement between the individual measurements and the average calculated values of  $k_1$  and  $k_2$ , we have computed the volumes of 0.1  $M$  alkali which must be added to 0.004 mole of diaquo chloride in 1020 ml. of solution in order to produce buffer solutions having predetermined  $pH$  values. These are shown as small shaded circles in Fig. 2 and through them we have drawn the theoretical titration curve shown as a solid line. It can be seen that the observed values, shown as open circles, lie within 0.015 of a  $pH$  unit from this curve except in the case of those for solutions in pure water where in one instance the discrepancy is three times this amount.

To test this concordance still further we have constructed similar curves based on  $k_1 = 4.3 \times 10^{-6}$  and  $5.3 \times 10^{-6}$  and  $k_2 = 10^{-7}$  and  $10^{-8}$  instead of our calculated values of  $4.80 \times 10^{-6}$  and  $5 \times 10^{-8}$ , respectively. These curves are shown as broken lines in the inserts in Fig. 2. Their distance from the curve through the observed points is several times the experimental error and justifies an estimate of the precision of

our calculated values of  $k_1$  and  $k_2$  as about 2 and 20%, respectively.

this decrease in acidity undoubtedly reflects the liberation of ammonia from the ammine. From

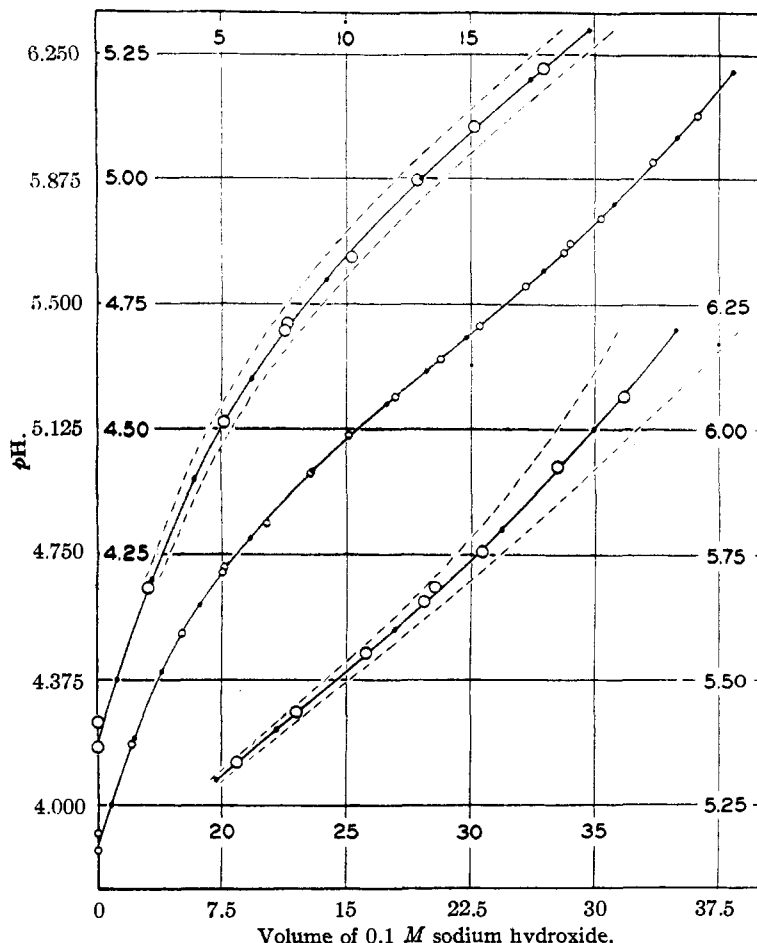


Fig. 2.—Titration curve of diaquotetrammine cobaltic ion: open circles, observed points; small shaded circles, points calculated for  $k_1 = 4.8 \times 10^{-6}$ ,  $k_2 = 5 \times 10^{-8}$ . Inserts show same curve on 50% larger scale, with broken lines showing (upper insert) effect of varying  $k_1$  between  $4.3$  and  $5.3 \times 10^{-6}$  and (lower insert) effect of varying  $k_2$  between  $10^{-7}$  and  $10^{-8}$ .

**Velocity of Decomposition**

In conclusion, it should be pointed out that the data on the change in the potential of the glass electrode with time (used above in extrapolating to zero time) permit some interesting inferences regarding the decomposition of this ammine. The observed values of  $(dE/dt)_0$  are a measure of the fraction of the hydrogen ions present in the solution which are neutralized in unit time;

$$\frac{dE}{dt} = -\frac{RT}{F} \frac{d \ln h}{dt} = -\frac{RT}{F} \frac{1}{h} \frac{dh}{dt} \quad (9)$$

Except for small changes resulting from shifts in the relative proportions of aquo and acido ions,

it is evident that the rate of this reaction, starting from approximately zero, begins to increase very rapidly at the pH value where  $k_2$  first becomes important in determining the shape of the titration curve. This suggests that it is the dihydroxo ion which undergoes decomposition, and hence that the rate at which hydrogen ions are used up is proportional to the concentration of the dihydroxo ion;

$$-dh/dt = K[+] \quad (10)$$

Combination of equations 9 and 10 leads to

$$\frac{dE}{dt} = \frac{RT}{F} K \frac{[+]}{h} \quad (11)$$

This relation is tested by the solid curve shown in Fig. 1, which represents the variation with pH of the concentration ratio  $[+]/h$ , as calculated for the average concentration of diaquotetrammine chloride in our solutions, using our values of  $k_1$  and  $k_2$ . It can be seen that this curve runs very exactly through the observed values of  $(dE/dt)_0$ .

As a more explicit test of equation 10, we have computed from  $(dE/dt)_0$  the actual change in hydrogen ion concentration in the nine least acid solutions, namely, in those solutions where the arith-

metical change is not swamped by the experi-

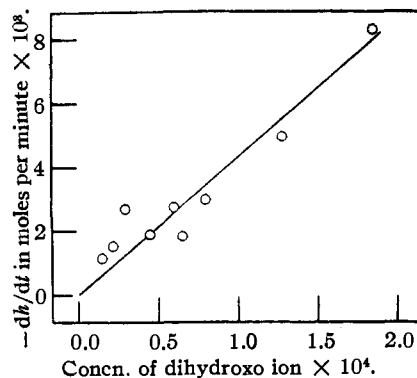


Fig. 3.

mental error. The resulting values are shown in Fig. 3, the straight line there drawn through the points being the best one as determined by the method of least squares. Its equation is

$$-dh/dt = 4.3 \times 10^{-4} [+]$$
 (12)

The concordance of these points with a straight line indicates that the reaction of decomposition is unimolecular with respect to the dihydroxotetrammine ion.

#### Summary

It has been shown:

1. That concordant values of the dissociation

constants of diaquotetrammine cobaltic ion as an acid can be obtained by measuring with the glass electrode the concentration of hydrogen ion in solutions of this ammine ion to which various amounts of sodium hydroxide have been added.

2. That the velocity of decomposition of this ion in these solutions is proportional to the first power of the concentration of the dihydroxotetrammine ion in equilibrium with it, as computed from these values of the dissociation constants.

CAMBRIDGE, MASS.

RECEIVED DECEMBER 12, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

## The Lead-Uranium-Thorium Ratio of a Single Crystal of Wilberforce Uraninite

BY CHESTER M. ALTER AND LAURA A. YUILL

It has been shown recently<sup>1</sup> that the composition of a single crystal of uraninite from near Wilberforce, Cardiff Township, Ontario, may not be uniform throughout the crystal. Ellsworth<sup>2</sup> has found the same phenomenon in the case of Villeneuve uraninite. It is interesting to note that in both cases the percentage of thorium is highest in the outer portion of the crystal, decreases toward the interior and then increases again in the core. The variation in thorium content was not great in the case of the Villeneuve crystal but was very noticeable in the Wilberforce crystal. The lead and thorium contents showed certain irregularities which were also difficult to explain, especially by any process of leaching.

Alter and Kipp removed succeeding layers of the crystal by dissolving in nitric acid. In spite of the fact that this dissolution was done very rapidly, it was thought possible that there may have been preferential leaching throughout the crystal while any one layer was being dissolved. In that case the results would be meaningless, as definite layers of the crystal would not have been removed for analysis. In order to preclude such a possibility it was decided to repeat the work by analyzing various layers which had been mechanically removed from a single crystal rather than by acid dissolution.

For this purpose a rather well-developed crystal, a part of a large collection of material from the

Wilberforce locality,<sup>3</sup> weighing approximately 42 g., was obtained from Professor Alfred C. Lane. According to Dr. H. V. Ellsworth<sup>4</sup> this material was collected from Pit 4<sup>5</sup> where the uraninite occurs in a gangue of fluorite and calcite. He further reports that the uraninite from this pit is considerably altered. This specimen, however, apparently carried very little of the usual surface alteration products and exhibited very distinct crystal faces and angles. A spot of apparently foreign material appeared on one face, and this proved to penetrate well into the core of the crystal.

The crystal was divided into three parts—outer, middle, and core—by carefully removing successive parts by means of a steel file. Each face was filed down an equal amount, great effort being taken to maintain the original form of the crystal during the process of filing off the outer portions. The outside, middle, and core portions weighed, respectively, 12.7 g., 15.2 g., and 13.5 g.

The particles of steel introduced in the samples were removed by very thorough magnetic separation.

The analytical procedures for the determination of lead, thorium, and uranium were in general those described in detail by Alter and Kipp.<sup>1</sup> Approximately one-gram samples were dissolved

(3) Report of Committee on Measurement of Geologic Time by Atomic Disintegration, National Research Council, Division of Geology and Geography, May 3, 1930.

(4) Private communication.

(5) Ellsworth, Canadian Geological Survey, Econ.-Geol. Series, No. 11, pp. 214, 221 (1932).

(1) Alter and Kipp, *Am. J. Sci.*, **32**, 120 (1936).

(2) Ellsworth, *Am. Mineral.*, **15**, 455 (1930).