[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S UNIVERSITY]

Quantitative Determination of Cobaltammine Ammonia. Application to the Determination of Ferrocyanide Ion

BY HAROLD A. HORAN AND HENRY J. EPPIG[1]

A modification of the analytical method ingeniously employed by Brönsted[2] for solubility measurements with the cobaltic ammines, can be adapted advantageously to the volumetric determination of anionic constituents which form quantitatively insoluble, filterable precipitates with common ammines such as hexammine cobalt (III) chloride. The determination of ferrocyanide ion by this adaptation is presented in the experimental part of this paper. Although the cobaltic ammines have been used for the gravimetric determination of anions,[3] the thermal instability of the precipitated ammines generally precludes weighing of the compounds as such. The necessary conversion to a suitable weighing form sacrifices time and an advantageous ratio of compound weight found per unit weight of constituent sought. The proposed volumetric procedure has the advantages of speed and accuracy. In essence the method is that commonly used for the determination of combined ammonia in ammonium salts, the presence of the many ammonia groups in the ammine compound serving to increase the accuracy of the calculated anion. The latter is simply precipitated with a cobaltic ammine cation. After filtering and washing, the precipitated ammine is decomposed with alkali under conditions such that its ammonia is quantitatively evolved and determined by the standard alkalimetric procedure. The anion is then calculated from the known ratio of ammonia to anion in the compound. As pointed out by Horan,[3d] the hexammines are more reliable as precipitants than the substituted complex ions such as $Co(NH_3)_nX_m$, $X = Cl$, NO_3, etc., and $n + m = 6$. The proposed methods are accordingly limited to hexammine precipitants.

In the initial stages of this work the quantitative evolution and determination of cobaltammine ammonia presented a problem which has been recognized by many, including those who first investigated the compounds nearly a century ago. Although Genth[4] originally employed simple alkaline decomposition of the ammine and absorption of the evolved ammonia in hydrochloric acid, Gibbs and Genth[5] later reported difficulty with this method. They indicated a loss of ammonia in the course of the decomposition, due to oxidation by tervalent cobalt. Even after prior reduction by agents such as sulfurous acid, this method was found to be unsatisfactory. Krok[6] and Jörgensen[7] experienced low ammonia analyses by this method, and Jörgensen showed that alkaline decomposition in the presence of the reducing agent stannous chloride did not obviate the difficulty; nitrogen results were at best 1% low. It seems paradoxical that Brönsted in his earlier works[2,8] used simple alkaline decomposition for the evolution of ammonia, and without a reducing agent. Later, Brönsted[9] claimed, contrary to Jörgensen,[7] that "accurate ammonia determinations for all compounds of this type can be carried out by decomposing with alkali, with or without addition of reducing agents such as stannous chloride." Neusser[10] referred to "incomplete decomposition" into ammonia when certain cobaltic ammines were decomposed by means of alkali. Recently Lamb and Mysels[11] mentioned a method developed by Lamb and Damon.[12] It involves a preliminary reduction of the cobalt in hot acid solution by means of stannous chloride, after which the solution is made alkaline and the ammonia quantitatively evolved. This modification, however, requires an extra step as compared with the direct alkaline decomposition which is the basis of the methods suggested in the present paper.

Repeated experiments in this Laboratory with several types of carefully purified cobaltic ammines, using varied concentrations of alkali and observing proper experimental and mechanical precautions,[13] confirm the conclusions of Gibbs and Genth,[5] namely, that accurate and precise ammonia values cannot be obtained when the compounds are decomposed by means of alkali alone. This is the case with solid samples or solutions of the compounds; it is characteristic of the cobaltic ammines in general, and can be ascribed to oxidation of ammonia by tervalent cobalt.[14] We have found, however, that alkaline

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(1) Present address: Picatinny Arsenal, Dover, New Jersey.

(2) Brönsted, *K. Vetenskaps Akad. Nobelinstitut*, **5**, 25, 10 (1919).

(3) (a) Parks, Dissertation, Columbia University, 1930; (b) Hynes, Malko and Yanowski, *Ind. Eng. Chem., Anal. Ed.*, **8**, 356 (1936); (c) Furman and State, *ibid.*, **8**, 420 (1936); (d) Horan, THIS JOURNAL, **61**, 2022 (1939); (e) Spacu and Pop, *Z. anal. Chem.*, **120**, 322 (1940).

(4) Genth, *Nordamerika Monatsvericht*, **II**, **8** (1851).

(5) Gibbs and Genth, *Am. J. Sci.*, [2] **23**, 240 (1857).

(6) Krok, *Lunds Univ., Arsskrift*, **VII**, **3** (1870).

(7) Jörgensen, *J. prakt. Chem.*, [2] nf, **18**, 246 (1878); *Z. anorg. Chem.*, **5**, 160 (1894).

(8) Brönsted, *D. kgl. Danske Vedersk Selsk, Math-fysike Meddel* **II** [10], 21 (1919); **IV** [4], 23 (1921).

(9) Brönsted and Peterson, THIS JOURNAL, **43**, 2266 (1922).

(10) Neusser, *Z. anorg. Chem.*, **207**, 386 (1932).

(11) Lamb and Mysels, THIS JOURNAL, **67**, 470 (1945).

(12) Unpublished work, privately communicated by Dr. A. B. Lamb.

(13) (a) Davisson, *Ind. Eng. Chem.*, **11**, 465 (1919); (b) Moose, Dissertation, Columbia University, 1935; (c) Miller, *Ind. Eng. Chem., Anal. Ed.*, **8**, 50 (1936).

(14) This effect of tervalent cobalt on ammonia in alkaline solution can be readily observed by treating a solution of an ammonium salt and a tervalent cobalt compound, for instance potassium cobalt (III) oxalate $[K_3Co(C_2O_4)_3]$, with sodium hydroxide.

decomposition of stable hexammine and pentammine cobaltic salts in the presence of the soluble, alkaline-stable reductant, arsenious oxide, proceeds with the quantitative evolution of ammonia. Volumetric determinations of the latter, when the compounds are decomposed in this manner, are highly accurate and reproducible. The adaptation to determinations of cobaltammine precipitated anions is simple and direct, and the results obtained are excellent. The procedure is presently described for the determination of ferrocyanide. The precipitate which forms upon addition of hexammine cobalt (III) ion to ferrocyanide ion has the composition indicated by the formula $[Co(NH_3)_6]_4[Fe(CN)_6]_3 \cdot H_2O$.[15] Eight moles of ammonia are equivalent to one of ferrocyanide.

Experimental

Materials.—The following ammines were prepared and carefully purified: hexammine cobalt(III) chloride,[16] hexammine cobalt(III) nitrate,[17] bromopentammine cobalt(III) bromide,[18] chloropentammine cobalt(III) chloride[19] and carbonatotetrammine cobalt(III) chloride.[20] The compounds were analyzed for cobalt and anion. *Anal.* Calcd. for $Co(NH_3)_6Cl_3$: Co, 22.03; Cl, 39.78. Found: Co, 22.05, 22.05; Cl, 39.74, 39.77. Calcd. for $Co(NH_3)_6(NO_3)_3$: Co, 16.98; $NH_3 + NO_3$ as N, 36.32. Found: Co, 16.98, 17.00; N, 36.23, 36.28. Calcd. for $[Co(NH_3)_5Br]Br_2$: Co, 15.36; Br (total), 62.46. Found: Co, 15.39, 15.37; Br (total), 62.42, 62.49. Calcd. for $[Co(NH_3)_5Cl]Cl_2$: Co, 23.53; Cl (ionized), 42.47. Found: Co, 23.59, 23.52; Cl (ionized), 42.42, 42.43. Calcd. for $[Co(NH_3)_4CO_3]Cl$: Co, 26.49; Cl, 15.93. Found: Co, 26.53, 26.44; Cl, 15.88, 15.89.

An aqueous solution of hexammine cobalt(III) chloride, containing 4.0 g. of the solid in 96 ml. of water, was prepared for use in the determination of ferrocyanide.

Apparatus.—For determination of ammonia, weighed samples were decomposed with sodium hydroxide solution in a 500-ml. Kjeldahl flask which was connected through a Davisson scrubber trap[13a] to a water condenser; the latter was fitted with an improved adapter[13c] at its outlet. The entire apparatus was made of Pyrex glass, in order to avoid rubber connections: 250 ml. of redistilled water, free of ammonia and ammonium salts, together with a suitable amount of sodium hydroxide was present in the flask at the outset. Most of the air within the apparatus was expelled[13c] before the sample was allowed to enter the alkaline solution. The distillate was received under standard sulfuric acid.

Typical results which were obtained with hexammine cobalt(III) chloride, when the decomposition was effected with different amounts of sodium hydroxide, are given in Table I. Similar results were obtained with other hexammines and also with the substituted ammines listed above.

TABLE I

AMMONIA ANALYSES; SAMPLES DECOMPOSED WITH ALKALI ALONE

Calcd. for $Co(NH_3)_6Cl_3$: NH_3, 38.20

Sodium hydroxide present in flask	NH_3, found, %	
5 ml. of 50% NaOH solution	37.50	37.66
10 ml. of 50% NaOH solution	37.85	37.78
25 ml. of 50% NaOH solution	37.84	37.90
200 g. NaOH, solid	37.95	37.90

Potassium Ferrocyanide.—Merck reagent potassium ferrocyanide was first purified by recrystallization from water between 25 and 0°, and then treated according to Loftfield and Swift[21] for final purification. The salt was dried to constant weight at 95° in an atmosphere of pure dry nitrogen. An exact weight of the salt was dissolved in sufficient water to make a solution of known total weight. The solution was measured from a weight buret, and the weight of potassium ferrocyanide taken was then calculated. Several different solutions were used in the course of this work; a typical composition was 1.3900 g. of the salt in 98.0355 g. of aqueous solution.

Arsenious Oxide.—Merck reagent was used without further purification.

Blanks containing the redistilled water, sodium hydroxide and arsenious oxide (7.0 g.) were distilled into standard acid, and the amounts of the latter which were consumed were estimated by back titration. These were less than 0.03 ml. of 0.1 *N* acid.

Standard Sulfuric Acid and Sodium Hydroxide Solutions.—Solutions of these were prepared in 0.1 *N* and in 0.05 *N* concentrations, and were standardized by the usual methods. Methyl red was used as the indicator in ammonia determinations.

Accurate Ammonia Analyses of the Cobaltic Ammines. The failure to recover completely the ammonia of these compounds when the decomposition was effected by alkali alone (Table I), was the result of a reaction between tervalent cobalt and ammonia; no detectable nitrogen remained in the residues from such decompositions.

Preliminary experiments demonstrated that the stable, alkaline soluble reductant, arsenious oxide, reacted with many of the cobaltic ammines forming a clear, deep-purple colored solution. The evolution of ammonia in these cases was quantitative. The following procedure was finally adopted for accurate ammonia analyses. The Kjeldahl flask of the previously described apparatus was charged with 250 ml. of redistilled water, 15 g. of sodium hydroxide and 7 g. of arsenious oxide. A weighed sample (*ca.* 0.2 g.) of the ammine was suspended in the neck of the flask while most of the air within the apparatus was displaced[13c] by rapidly bringing the solution to the boiling point. The sample was released; reduction took place rapidly. Distillation was continued until about 80% of the solution was distilled over into the standard acid. The condenser was briefly steamed, rinsed and the titration of the remaining acid performed. Results are given in Table II.

TABLE II

ACCURATE COBALTAMMINE AMMONIA ANALYSES IN THE PRESENCE OF ARSENIOUS OXIDE

Ammine used	NH_3, % Calcd.	Found	
$Co(NH_3)_6Cl_3$	38.20	38.17	38.21
$Co(NH_3)_6(NO_3)_3$	29.44	29.45	29.47
$[Co(NH_3)_5Br]Br_2$	22.19	22.18	22.20
$[Co(NH_3)_5Cl]Cl_2$	33.99	33.93	33.95
$[Co(NH_3)_4CO_3]Cl$[a]	30.61	30.43	30.48

[a] In connection with the low results obtained with this relatively unstable tetrammine, it should be noted that decomposition proceeded with the immediate formation of a small amount of dark brown precipitate, instead of the immediate formation of a homogeneous purple mixture.

Determination of Ferrocyanide by the Cobaltammine-Ammonia Method.—A suitable amount of potassium ferrocyanide solution (containing no more than 0.2 g. of the

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[15] (a) Gibbs and Genth, *J. prakt. Chem.*, **72**, 161 (1857); (b) Braun, *Ann.*, **125**, 182 (1863); (c) Ephraim and Mosimann, *Ber.*, **54**, 396 (1921); (d) Steinmetz, *Z. Kryst.*, **57**, 233 (1922).

[16] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Hasse and Son, Copenhagen, 1941, p. 241.

[17] Jörgensen, *J. prakt. Chem.*, 2, **23**, 227 (1881).

[18] Booth, "Inorganic Synthesis," McGraw-Hill Book Co., New York, N. Y., 1939, Vol. I, p. 186.

[19] Hynes, Yanowski and Schiller, THIS JOURNAL, **60**, 3053 (1938).

[20] Lamb and Damon, *ibid.*, **59**, 385 (1937).

[21] Loftfield and Swift, *ibid.*, **60**, 3083 (1938).

salt) was discharged from a weight buret into a 50-ml. beaker and this solution, which contained a known amount of the salt, was diluted to 20 ml. with water. Hexammine cobalt(III) chloride solution was added dropwise with stirring, sufficient to provide an excess of 20–30% over that required to form $[Co(NH_3)_6]_4[Fe(CN)_6]_3$. The beaker was placed in cold water (about 4°) for twenty minutes, and the precipitate allowed to settle. The latter was quantitatively filtered on a dense filter paper (Whatman No. 5) and washed thoroughly with approximately 45 ml. of cold water. The filter paper containing the precipitate was folded carefully, tied with a thin wire and suspended in the neck of the Kjeldahl flask of the apparatus described above. The flask contained 250 ml. of redistilled water, 15 g. of sodium hydroxide and 7 g. of arsenious oxide. After rapidly bringing the contents of the flask to the boiling point in order to expel most of the air,[13c] the filter paper was released. The liberated ammonia was distilled rapidly into the standard acid in the receiver. The final steps were as described above under accurate ammonia analyses: 0.1 *N* acid was used for the larger amounts of ferrocyanide; 0.05 *N* acid was used for amounts less than 0.1 g.

Blank determinations with ferrocyanide included were not measurably different from those mentioned above under arsenious oxide. Results are given in Table III. They were calculated from the ammonia analyses found, on the basis of eight moles of ammonia equivalent to one mole of potassium ferrocyanide.

TABLE III

DETERMINATION OF FERROCYANIDE BY THE COBALTAMMINE–AMMONIA METHOD

$K_4Fe(CN)_6$ taken, g.	$K_4Fe(CN)_6$ found, g.	$K_4Fe(CN)_6$ taken, g.	$K_4Fe(CN)_6$ found, g.
0.1914	0.1916	0.0532	0.0532
.1845	.1847	.0528	.0527
.1782	.1781	.0539	.0540
.1609	.1609	.0186	.0187
.1048	.1045	.0174	.0173
.1125	.1125	.0185	.0183

Discussion

The results in Table III show that the proposed method for the determination of ferrocyanide is very reliable even when semi-micro quantities of this anion are under consideration. In such instances no special equipment is required, and it is unnecessary to use standard solutions of extreme dilution. These are decided advantages over the usual oxidation–reduction methods generally used for this constituent, since the oxidimetric gram-equivalent weight of potassium ferrocyanide is very high, 368.34; in determinations of quantities of the order of 0.025 g. one must use 0.01 *N* oxidizing agent and a micro buret. Furthermore, the cobaltammine–ammonia method permits results of higher precision and accuracy than the corresponding gravimetric method[3b] which uses hexammine cobalt(III) ion as the precipitant for ferrocyanide. This follows since the present method takes advantage of a found/sought mole ratio of $8NH_3/1K_4Fe(CN)_6$, in comparison to the unfavorable 0.503/1.00 (wt. ignited oxides found/wt. potassium ferrocyanide taken) factor of the gravimetric procedure. An additional disadvantage of the latter is the adverse influence caused by small, uncontrollable variations in the composition of the ignited residues.

The reliability of the weighing forms used in most gravimetric cobaltammine methods is questionable. Since the precipitates are generally unstable on drying at 100° the compounds are either dried at room temperature after the final removal of the aqueous phase with volatile organic solvents, or they are converted to mixed oxides of cobalt by ignition. In the first instance loosely bound or lattice water[22] may be removed to an indefinite degree; in the second, the existence of several oxides of cobalt, *viz.*, CoO, Co_2O_3, Co_3O_4, with uncertain ranges of thermal stability[23] is a source of indeterminate error.

In view of the large number of ammonia groups present, it is suggested that adaptations similar to that suggested for ferrocyanide ion should make it possible to determine accurately several other anions, which are quantitatively precipitated by hexammine cobalt(III) chloride.

Summary

A direct, accurate, volumetric method for the quantitative evolution and determination of ammonia in the stabile hexammine and pentammine cobalt(III) salts is presented.

Use of this method for ammonia present in hexammine cobalt(III) ferrocyanide which has been quantitatively precipitated from a solution containing ferrocyanide ion, serves as a convenient and accurate means of estimating this anion.

Suggestions are made relative to similar modifications of cobaltammine methods for the determination of other anions.

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[22] Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., New York, N. Y., 1938, p. 163.

[23] Ephraim-Thorne, "Inorganic Chemistry," Nordeman Publishing Co., Inc., New York, N. Y., 1939, p. 439.