considered the series $M_2Ru^{iii}Cl_5$ containing trivalent ruthenium, in reality contains quadrivalent ruthenium, of formula $M_2Ru^{iv}Cl_5OH$; that what has been considered an "aquo" series is actually the ordinary series of trivalent ruthenium, but always crystallizing as a monohydrate of formula $M_2Ru^{iii}Cl_5.H_2O$. In all of these salts the coördination number of ruthenium is *six*. Also Claus' view that the blue solution of reduced ruthenium contains the metal in bivalent form is again confirmed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM. XI
A VOLUMETRIC ESTIMATION OF RUTHENIUM

BY JAS. LEWIS HOWE

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The estimation of ruthenium, except in crystallized compounds, has always been difficult. Neither hydrogen sulfide nor metals, as zinc or magnesium, precipitate ruthenium completely from any of its solutions, and while it can be precipitated by caustic alkalies, it is impossible to wash the gelatinous precipitate free from salts. Somewhat more than a year ago it was found in this Laboratory[1] that ruthenium in a finely divided form could be completely dissolved in alkaline sodium hypochlorite solution and the ruthenium distilled quantitatively from this solution as ruthenium tetroxide after treatment with a stream of chlorine; but no simple method was found by which the ruthenium in the distillate could be estimated.

The reduction of quadrivalent ruthenium by stannous chloride, as described in the preceding paper, affords a solution of the problem. The volatile ruthenium tetroxide is condensed in concentrated hydrochloric acid, preferably in a small Erlenmeyer flask surrounded by ice. A two-necked Wolff bottle with ground-glass joints may be used if the amount of ruthenium is considerable, but with small quantities (as is usual in the analysis of alloys) we have found no difficulty in condensing all the RuO_4 in an Erlenmeyer flask. After all the ruthenium tetroxide has been reduced by the hydrochloric acid, which is apparent by the disappearance of any drops of liquid ruthenium tetroxide, the solution is boiled until all absorbed chlorine has been eliminated. It is then titrated with a solution of stannous chloride of about 0.05 N strength. The stannous chloride solution is standardized immediately before using against 0.1 N iodine solution with starch indicator.

In titrating the ruthenium solution, the stannous chloride can be added until the dark, brownish-red solution of quadrivalent ruthenium changes to the light red or rose of trivalent ruthenium. As this end-point is often

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[1] Howe and Mercer, THIS JOURNAL, **47**, 2926 (1925).

not sharp, it is better to use a slight excess of stannous choloride, add starch paste and titrate back with iodine solution. Since the ruthenium of ruthenium tetroxide is reduced only four units by hydrochloric acid, it does not matter whether the hexa- or the pentachloro salt is formed, as both contain quadrivalent ruthenium.[2] This titration was carried out in concentrated hydrochloric acid, as well as in quite dilute solutions; in hot solutions and in cold solutions; by adding only just sufficient excess of stannous chloride to make an iodine-starch reaction visible, and by adding a large excess of stannous chloride; in no case was there any evidence of conditions of titration making any difference in the results. Titrations of K_2RuCl_6 and of K_2RuCl_5OH gave the same results, as described in the previous paper. Reduction does not go beyond the rose trivalent ruthenium, as was shown by adding a large excess of stannous chloride solution and allowing it to stand for several days. No change was apparent in the solution, nor in any case was there any sign of blue or green, which would have indicated the presence of bivalent ruthenium.

It should be noted that in almost every case the amount of stannous chloride required for reduction was somewhat lower than that called for by theory. Just why this is, is not apparent.[3] For this reason, the method cannot be recommended for accurate determination of ruthenium, but it affords a ready method for the approximate evaluation of ruthenium solutions, and also for the determination of ruthenium where only a small amount is present.

Experimental Work

A solution of ruthenium tetroxide in hydrochloric acid was prepared, containing 4.91 mg. of ruthenium per cc., as determined by the evaporation of 10 cc. in a quartz boat, heating in the air and reducing in hydrogen. The ruthenium was reoxidized and reduced without change in weight. Two cc. portions of this solution were then titrated with stannous chloride solutions, varying from 0.08 to 0.03 *N*. As this solution was used as a check in titrating the chlororuthenate salts, it was actually titrated many times. The results, omitting only three which were manifestly in error, are as follows.

TABLE I

RUTHENIUM FOUND, MG. PER CC. IN TEST SOLUTION CONTAINING 4.91 MG.

4.81, 4.58, 4.60, 4.93, 4.98 (excess $SnCl_2$), 4.72, 4.62, 4.81 (in concd. HCl), 4.60, 4.82, 4.82 (very dilute HCl), 5.05, 4.65, 4.94 (warm), 4.75, 4.68, 4.85, 4.62, 4.74 (excess $SnCl_2$ in concd. HCl, hot); average of 19 titrations, 4.766.

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[2] Howe, THIS JOURNAL, 49, 2381 (1927).

[3] It is possible that it may have been due to the small quantities used, and that the results might have been made to approach the theoretical more closely by using large amounts, or by titrating with more dilute solutions. A more probable explanation is that there was a small quantity of trivalent ruthenium present, which would not be recognized as such by gravimetric analysis, but would affect the volumetric analysis.

TABLE I (*Concluded*)

RUTHENIUM FOUND IN K_2RuCl_6;[4] THEORETICAL, 25.89%

22.65, 23.91, 23.03, 24.10, 22.11, 24.64, 24.39, 24.64, 25.31, 24.69, 23.42, 24.47, 24.07, 24.27; average of 14 determinations, 23.99.

RUTHENIUM FOUND IN K_2RuCl_5OH; THEORETICAL, 27.18%

24.675, 25.68, 26.64, 24.05, 25.68, 20.12, 25.54, 19.89, 24.84; average of 9 determinations 24.124.

Summary

This paper presents a simple method of determining ruthenium volumetrically, when present in small amounts, and of evaluating ruthenium solutions approximately.

LEXINGTON, VIRGINIA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 41]

AN INVESTIGATION OF THE REACTION OF ALUMINUM WITH THE AMMONIUM SALT OF AURINTRICARBOXYLIC ACID UNDER DIFFERENT EXPERIMENTAL CONDITIONS, AND ITS APPLICATION TO THE COLORIMETRIC DETERMINATION OF ALUMINUM IN WATER

BY JOHN H. YOE AND WILLIAM L. HILL

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Recently Hammett and Sottery[1] described a new qualitative test for aluminum in which the principal reagent is the ammonium salt of aurintricarboxylic acid, now sold under the trade name, "Aluminon." These authors studied the behavior of several of the elements and ions commonly dealt with in qualitative analysis which would be likely to interfere with the test. Middleton[2] and later Corey and Rogers[3] have studied the behavior of several of the less common elements with "Aluminon." A brief summary of the results with respect to the final solution follows.

1. Silicic acid, salts of antimony, bismuth, lead, mercuric mercury, stannic tin and titanium give white precipitates. The qualitative test may be made without a separation.

2. Salts of cadmium, chromium, cobalt, germanium, indium, manganese, nickel, rare earths, thallium, thorium, zinc and zirconium give no precipitates.

3. Ferric salts produce a reddish-brown precipitate which is stable under the same conditions as the aluminum lake. Beryllium gives a lake which cannot be distinguished from aluminum. The gallium lake

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[4] For details see ref. 2.

[1] Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

[2] Middleton, *ibid.*, **48**, 2125 (1926).

[3] Corey and Rogers, *ibid.*, **49**, 216 (1927).