[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE VOLUMETRIC DETERMINATION OF CERIUM BY MEANS OF POTASSIUM PERMANGANATE.

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The permanganate separation of cerium from the other rare earths is based on the principle that cerium forms compounds having the valence of four in addition to the trivalent type ordinarily exhibited in the rare earths.

$$6Ce(NO_3)_3 + K_2Mn_2O_8 + 4H_2O = 4Ce(NO_3)_4 + 2Ce(OH)_4 + 2KNO_3 + 2MnO_2.$$

In addition to the formation in this first reaction of ceric hydroxide, the tetranitrate undergoes hydrolysis with the further formation of more ceric hydroxide.

$$Ce(NO_3)_4 + 4H_2O = Ce(OH)_4 + 4HNO_3.$$

The nitric acid thus liberated tends to make the reaction reversible; hence, in order to obtain complete reaction and subsequent precipitation of the cerium, this free acid must be neutralized in the proper manner.

This general reaction doubtless originated with Winkler,[1] and has been studied by a number of chemists[2] since that time. It has been repeatedly suggested that this principle could be applied to the determination of cerium, but few results have been published, and the conditions under which this reaction takes place have not been sufficiently emphasized. Brauner[3] has stated that the method gives excellent results for the determination of trivalent cerium in the presence of tetravalent cerium.

Experimental.

Materials Employed.—For our experiments standard solutions of cerium nitrate[4] were prepared of convenient strength, and the cerium in them was accurately determined by gravimetric means, being finally weighed in all cases as CeO_2. The potassium permanganate solutions used were standardized against ferrous-ammonium sulfate and sodium oxalate.

Sources of Error.—If a cerous solution is rendered distinctly alkaline and the solution either heated or allowed to stand for some time, atmos-

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[1] *J. prakt. Chem.*, **95**, 410 (1865).

[2] Stolba, *Chem. Zentr.*, 10 (3 Folge), 595 (1879); Brauner, *Chem. News*, **71**, 285 (1895); Drossbach, *Ber.*, **29**, 3, 2453 (1896); **35**, 2830 (1902); Muthmann and Rolig, *Ber.*, **31**, 1719 (1898); Böhm, *Z. angew. Chem.*, **1903**, 1130; Muthmann and Weiss, *Ann.*, **331**, 9 (1904) ; Meyer and Schweitzer, *Z. anorg. Chem.*, **54**, 104 (1907); James, THIS JOURNAL, **30**, 985 (1908); Roberts, *Z. anorg. Chem.*, **71**, 305 (1911).

[3] *Chem. News*, **71**, 285 (1895).

[4] The cerium nitrate used was courteously furnished by H. S. Miner, of the Welsbach Co.

pheric oxygen is absorbed to such an extent that the subsequent titration with potassium permanganate necessarily yields low results. This absorption of the oxygen of the air is, however, so slow that by immediately titrating, even in the cold, or by adding the most of the permanganate solution before the neutralizing agent is added, no appreciable error is introduced.

Low results may be due to occlusion. When the entire amount of neutralizing agent required is added all at once, and the cerous hydroxide precipitated before titration with the permanganate, the particles of the gelatinous precipitate are first superficially coated with the ceric hydroxide and hydrated manganese dioxide formed in the reaction, and on account of this protective coating of oxidized material, small amounts of the cerous hydroxide may escape oxidation. Low results produced in this manner may be obviated in large part by greater dilution or, still better, by adding the most of the permanganate before the neutralizing agent is introduced. A far more satisfactory procedure consists in the use of such a substance as zinc oxide, which neutralizes the free acid but does not immediately precipitate the cerous hydroxide.

In all cases it is recommended that the titration be finished hot, and that the permanency of the end point be insured by finally boiling the solution for an instant. Unless these conditions are fulfilled low results are not infrequently obtained.

The authors have not obtained results which are high, doubtless because the solutions worked with did not contain other rare earths. Others have reported high results under such conditions.

Zinc Oxide Series.—The results reported in Tables I and II were obtained by using zinc oxide as the neutralizing agent.

A measured volume of the standard cerium nitrate solutions was diluted to about 110 cc. and an excess of zinc oxide paste added. The most of the permanganate was then added in the cold, after which the solution was brought to boiling and the titration finished hot. The permanency of the end point was tested by boiling for a moment. Under these conditions a dense, granular precipitate was obtained which settled readily. The end point was sharp.

TABLE I.

Data showing the effect of zinc oxide added in the cold. 0.3026 g. Ce taken.

Ce found, g.: 0.3031; 0.3028; 0.3031; 0.3033; 0.3028.

The results shown in Table II were obtained by heating the solution to boiling before any permanganate was added.

TABLE II.[1]

Data showing the effect of zinc oxide in a solution titrated at boiling temperature. 0.1630 g. Ce taken.

Ce found, g.: 0.1633: 0.1633; 0.1633, 0.1632; 0.1637; 0.1632; 0.1626; 0.1632; 0.1629; 0.1624; 0.1633; 0.1633.

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[1] Results obtained by Miss Grace Van Natta.

Calcium Carbonate Series.—In the next series of experiments precipitated calcium carbonate was used as the neutralizing agent. An excess of the solid reagent was added in the form of a dry powder. The reaction in this case does not proceed with sufficient rapidity either in the cold or hot. Calcium carbonate is not as satisfactory a neutralizing agent in this titration as a number of other substances. If, however, the solution is boiled for a short time, accurate results are obtained.

TABLE III.

Data showing the influence of calcium carbonate. 0.3026 g. Ce taken.

Ce found, g.: 0.3024; 0.3035; 0.3029; 0.3026; 0.3036.

TABLE IV.

Data showing the results obtained by adding most of the permanganate before calcium carbonate was added. 0.3260 g. Ce taken.

Ce found, g.: 0.3259; 0.3258; 0.3261; 0.3258; 0.3260; 0.3254; 0.3260; 0.3261.

Magnesium Oxide Series.—Milk of magnesia was found to be one of the best neutralizing agents available for this titration. In the presence of this reagent the oxidation of the cerium by means of potassium permanganate takes place readily, even in the cold. In order to avoid the error of air oxidation, preliminary titrations were made to ascertain the approximate amount of permanganate consumed. In the titration proper, most of the permanganate is added before the magnesia is introduced. By finishing the titration hot and at the end bringing to boiling for an instant, a very sharp and satisfactory end point is obtained.

TABLE V.

Data showing the results obtained by the use of magnesia. 0.3026 g. Ce taken.

Found: 0.3024; 0.3024; 0.3022; 0.3017; 0.3024.

0.3260 g. Ce taken.

Found: 0.3262; 0.3261; 0.3261; 0.3266; 0.3265; 0.3265; 0.3260; 0.3266; 0.3263; 0.3259.

Soluble Neutralizing Agents.—When soluble compounds, such as borax, sodium carbonate, or sodium bicarbonate, were employed as the neutralizing agent, the substance was dissolved in water and a solution used. In general it may be said that a large excess of such reagents yields low results, but a slight excess does no harm. The hydrolysis taking place in the reaction itself produces potassium hydroxide from the potassium permanganate in sufficient quantity to precipitate one-third of the cerium; consequently it is only necessary to add sufficient alkali to precipitate a little more than two-thirds of the cerium. This is not the case, however, if the neutralizing agent contains a nonvolatile radical.

Borax Series.—A satisfactory neutralizing agent was found in a saturated solution of borax. This reagent possesses the added advantage that when it is used in excess no serious low errors are produced, such as invariably result when a large excess of sodium carbonate is added.

The procedure in case of soluble neutralizing agents was as follows:

30 cc. of the standard cerium solution were measured into an Erlenmeyer flask and diluted. A saturated solution of borax was gradually added with stirring until all of the cerium had been precipitated and the solution was alkaline to litmus. The solution, which then had a volume of about 110 cc., was titrated with the standard potassium permanganate. Most of the permanganate was added in the cold. The titration was finished hot, and the permanency of the end point was assured by boiling for a moment.

TABLE VI.

Data showing the results of adding borax before permangantate. 0.3026 g. Ce taken.

Ce found, g.: 0.3020; 0.3016; 0.3014; 0.3014; 0.3016.

TABLE VII.

Data showing the effect of adding most of the permanganate before adding borax and finishing hot. 0.1630 g. Ce taken.

Ce found, g.: 0.1628; 0.1626; 0.1626; 0.1626; 0.1624; 0.1626; 0.1626; 0.1624; 0.1627.

Sodium Bicarbonate Series.—With sodium bicarbonate as a neutralizing agent the best results are obtained when a sufficient quantity is added to precipitate at least two-thirds of the cerium. It is not necessary to render the solution alkaline to litmus at the beginning of the titration. In other respects the procedure is the same as when borax is added.

TABLE VIII.

Data showing the results obtained by adding sodium bicarbonate before permanganate. 0.3026 g. Ce taken.

Ce found, g.: 0.3013; 0.3015; 0.3009; 0.3019; 0.3010.

TABLE IX.

Data showing results obtained by the addition of most of the permanganate before the sodium bicarbonate. 0.3260 g. Ce taken.

Ce found, g.: 0.3263; 0.3262; 0.3260; 0.3261; 0.3261; 0.3261; 0.3263; 0.3265.

Sodium Carbonate Series.—A number of determinations were also made, using a 10% solution of sodium carbonate as a neutralizing agent. In this case, as with sodium bicarbonate, an excess of the reagent should be avoided. The amount required to precipitate about two-thirds of the cerium gives the best results. The solution will then be slightly alkaline to litmus at the end of the titration.

TABLE X.

Data showing the results obtained by the use of sodium carbonate. 0.3026 g. Ce taken.

Ce found, g.: 0.3014; 0.3016; 0.3016; 0.3014; 0.3010.

Alkaline Hydroxides.—When the fixed alkali hydroxides, sodium hydroxide and potassium hydroxide, or barium hydroxide, were introduced as neutralizing agents, low results and indistinct end points were invariably obtained.

Addition of Other Substances.—The following reagents were also tried and found to be unsuitable in this titration: sodium acetate, sodium silicate, sodium phosphate (tribasic), disodium phosphate, sodium tungstate, and sodium arsenate.

Conclusions.

It has been shown that when cerium is titrated by means of potassium permanganate, zinc oxide or magnesium oxide are the best neutralizing agents. Fairly good results may also be obtained by using borax or sodium bicarbonate, while sodium carbonate, though yielding fair results, is still less satisfactory. The other reagents worked with are unsatisfactory so far as accurate results are concerned.

It has been shown that under proper conditions, the method is capable of giving very accurate results.

The method is also suitable for the determination of trivalent cerium in the presence of tetravalent cerium.

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CHANGES IN VOLUME UPON SOLUTION IN WATER OF THE HALOGEN SALTS OF THE ALKALI METALS. II.

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In earlier papers[1] data were given for the changes in volume upon solution in water of the chlorides, bromides and iodides of lithium, sodium and potassium at various concentrations, and by the use of these data, together with a few observations upon rubidium and caesium halides by Buchanan, a tentative hypothesis was proposed as to the reasons for the direction and magnitude of the observed effects. At the time when the earlier paper was published the desirability was evident of additional data covering wider ranges of concentration and different temperatures, as well as the examination of other salts and other solvents. In the present paper are presented new data for the halogen salts of all five alkali metals, covering nearly all concentrations from saturation down, for temperatures between 0° and either 50°, 70° or 100°.

The experimental method was in outline as follows: A weighed amount of salt was dissolved in nearly a minimum quantity of water and the volume of the solution was adjusted to a mark in a 50 cc. flask at the highest temperature employed. The flask was then cooled to room temperature and weighed. The adjusting of the volume and weighing were then carried out at several lower temperatures. Next the solution was transferred quantitatively to a 100 cc. flask and the operations were repeated at the same temperatures, beginning with the highest. Then 250 cc., 500 cc.

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[1] Baxter, Boylston, Mueller, Black and Goode, THIS JOURNAL, 23, 901 (1911); Baxter, *Ibid*, 23, 922 (1911).