[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE REACTION OF IODATE AND TETRAVALENT VANADIUM IN ALKALINE SOLUTIONS

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Whether or not a reaction occurs between iodate and tetravalent vanadium in alkaline solutions has apparently not been determined. That no reaction takes place in hydrochloric acid solutions of moderate concentrations (6 *N* or above) is evident from the results recently obtained by Swift and Hoeppel.[1] The accepted molal electrode potentials of the half-reactions involved, as given by Latimer and Hildebrand,[2] indicate that a measurable equilibrium may exist in dilute acid solutions.

The present work was initiated with the hope of making use of the reaction in alkaline solution, if such occurs, in the determination of tetravalent vanadium. The results obtained show that a reaction does take place in a conveniently short time in hot alkaline solutions, the equation of which may be written

$$6VOSO_4 + KIO_3 + 18KOH = 6KVO_3 + 6K_2SO_4 + KI + 9H_2O$$

A method of determining tetravalent vanadium by means of this reaction has been developed.

Reagents Used.—The solutions of potassium permanganate and sodium thiosulfate were prepared and standardized by the methods previously used.[3] The tetravalent vanadium solutions were prepared from ammonium metavanadate, by converting to sodium vanadate, acidifying with sulfuric acid and reducing with sulfur dioxide. After the excess sulfur dioxide had been removed by sufficient boiling in a rapid stream of air, the concentration of vanadium was determined by oxidation with a known permanganate solution.[3,4] The potassium iodate solutions were prepared from pure potassium iodate and standardized against known thiosulfate solutions. The potassium iodide was tested for iodate with negative results. All other reagents were of standard c. p. quality.

Preliminary Experiments and Results

1. Evidence of Reaction and Probable Use in Analysis.—In solutions from 0.02 to 0.2 *N* in alkali, nearly 0.025 *N* in tetravalent vanadium and from 0.03 to 0.05 *N* in iodate, the brown color due to tetravalent vanadium is not changed appreciably after standing for several hours at room tem-

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[1] Swift and Hoeppel, THIS JOURNAL, **51**, 1366 (1929).

[2] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, **1929**, pp. 367 and 368.

[3] Ramsey, THIS JOURNAL, **49**, 1138 (1927).

[4] Lundell and Knowles, *ibid.*, **43**, 1560 (1921).

perature. (Pentavalent vanadium is colorless in alkaline solutions.) If these brown solutions are heated, they become colorless after boiling for a short time (not longer than twenty minutes in the case of any solution used). The time required is appreciably decreased by a relatively small increase in the concentration of the iodate but is not noticeably changed by a considerable change in the alkali concentration. These results indicate the possibility of determining tetravalent vanadium by oxidation with an excess of iodate in boiling alkaline solutions provided the excess iodate may be determined in the resulting solution. An obvious method of finding the quantity of excess iodate consists of adding potassium iodide, acidifying and determining the iodine formed with known thiosulfate solution.

2. **Acidity Tests in Determination of Excess Iodate.**—Since vanadic acid and oxygen will be present during the determinations of the excess iodate by the method proposed, it is necessary to have a concentration of acid sufficient to cause rapid reduction of iodate but not so great as to cause formation of iodine due to either the vanadic acid or oxygen during the titration with thiosulfate solution. Experiments show that if the acid concentration is 0.02 *N* or less in solutions containing vanadic acid, oxygen and iodide at concentrations used in obtaining the results given in the table, the quantity of iodine formed in the time required for titration is not measurable. In acidifying the alkaline iodate solution it is found that sulfuric acid having a concentration as high as 1.2 *N* may be used without causing the liberation of iodine by vanadic acid or oxygen due to the momentary production of high acidity. Since the volume (10 to 20 ml.) of this acid required is conveniently small, no experiments were conducted with greater acid concentration. The acid is introduced as rapidly as it will flow from a buret against the side of the reaction flask, which is kept moving in such a way as to give the solution a swirling motion.

3. **Effect of Oxygen during Iodate–Vanadium Reaction.**—It is well known that tetravalent vanadium is slowly oxidized by oxygen in alkaline solutions. That a large effect is produced by oxygen during the iodate–vanadium reaction is shown by the fact that if solutions of the reactants are prepared without previously excluding oxygen, as much as 20% of the tetravalent vanadium may be oxidized by the oxygen present. Results given in the table show the effect of oxygen present in the vanadium solution alone.

4. **Catalysis of the Iodate–Vanadium Reaction.**—Failure to remove the dissolved oxygen completely in the earlier attempts gave results which were then assumed to be due to the incompleteness of the reaction. Various substances were introduced which might remove the vanadate more completely from the assumed equilibrium. None of the substances tried eliminated the error. However, disodium acid phosphate, one of those used, was found to catalyze the reaction appreciably. With phosphate

present, the solution became colorless after boiling four or five minutes while without it, ten to twelve minutes were required in solutions otherwise the same. At present we are unable to give a probable explanation of this catalytic effect.

General Analytical Procedure

On the basis of these experiments, the following procedure is the one finally adopted. Measured volumes of known solutions of alkali, iodate and phosphate are mixed in a 400-ml. Florence flask. The resulting solution is boiled for about four minutes to remove oxygen. During this time a measured volume of acid vanadyl sulfate solution is treated for removal of oxygen in one of two ways, either by boiling or by addition, in the cold, of a small volume of saturated sodium bicarbonate solution. About five minutes after adding the bicarbonate, the vanadium solution is added dropwise from a dropping funnel to the boiling iodate solution. When the vanadium solution is boiled to remove the oxygen, it is added while still hot to the boiling iodate solution. After the reaction is completed, as shown by the disappearance of the brown color, the solution is cooled in tap water and diluted to approximately 250 ml. About two grams of potassium iodide is then added and the solution is acidified. To determine the quantity of acid needed, one run is made in which the acid is added slowly until iodine is formed. Starch solution is added and the iodine reduced carefully with thiosulfate. With addition of more acid, iodine is liberated and again reduced. This is continued until no iodine is formed on addition of more acid. The last portion of acid is added dropwise. The quantity of acid found necessary is introduced in all other runs in the manner previously described. The titration with thiosulfate solution is made immediately after acidification. The starch solution is added after almost all of the iodine has been reduced.

Results

In obtaining the results given in the following table, the volumes and approximate concentrations of the solutions used were as follows: 50 ml.

TABLE I

OXIDATION OF TETRAVALENT VANADIUM BY IODATE IN ALKALINE SOLUTION

Expt.	Vanadium taken, millieq.	Iodate reduced, millieq.	Diff., millieq.	Treatment of vanadium solution
1	2.027	2.033	+0.006	Boiled for three to five minutes
2	2.027	2.027	.000	
3	2.027	2.031	+ .004	
4	2.027	2.026	− .001	
5	2.027	2.028	+ .001	
6	2.027	2.028	+ .001	
7	2.027	2.025	− .002	
8	2.027	2.009	− .018	Oxygen not removed
9	2.027	2.001	− .026	
10	2.990	2.989	− .001	Treated with sodium bicarbonate solution
11	2.990	2.986	− .004	
12	2.990	2.988	− .002	
13	2.990	2.991	+ .001	
14	2.990	2.986	− .004	
15	2.990	2.986	− .004	
16	2.990	2.987	− .003	

of standard potassium iodate solution (approximately 0.1 N); such a volume (between 10 and 20 ml.) of approximately 4.0 N potassium hydroxide that the solution remains alkaline after completion of the reaction; 10 ml. of approximately 0.25 F disodium hydrogen phosphate; 25 ml. of standard vanadyl sulfate solution, approximately 0.1 N in vanadium and 1.5 N in sulfuric acid; the required volume of approximately 1.2 N sulfuric acid, which is usually between 10 and 20 ml. The volume of standard thiosulfate solution (approximately 0.1 N) is in every case between 20 and 30 ml.

From the results of Expts. 8 and 9 it is seen that, on the average, approximately 1% of the tetravalent vanadium used is oxidized by the oxygen present in the vanadium solution alone. If oxygen is excluded from all solutions, the results obtained are, on the average, within 0.1% of those calculated.

Summary

It has been shown that iodate and tetravalent vanadium react completely in hot alkaline solutions. Phosphate has been found to catalyze this reaction.

A method of determining vanadium by means of this reaction has been described. The results check on the average within 0.1% of the calculated if oxygen is excluded during the reaction.

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THE DIELECTRIC CONSTANTS OF WATER AT VARIOUS TEMPERATURES

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As a step in the measurement of the dielectric constant of hydrogen peroxide it was found necessary to use water for purposes of comparison. A large divergence exists in the values of the dielectric constant given for water and little attention has been paid to the measurement of the temperature coefficient over a wide range. This led to the development of the method described below in which measurements were carried out between 0 and 75°. This method offers no originality in its main principles but in the details of procedure improvements have been made which lead to consistent results.

Experimental

General Outline.—The method employed involves the resonance principle for the measurement of capacity in the ingenious set-up described by Williams and Krchma.[1] The distinguishing feature from that used

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[1] Williams and Krchma, This Journal, **48**, 1892 (1926).