To Mr. C. H. Meyers of the Bureau of Standards, especial credit is due for placing at the writer's disposal his specialized knowledge of critical temperature determinations, and for assistance freely given in cases where two observers were required.

Summary

The critical temperature of carbon dioxide has been measured in glass tubes ranging from 2 mm. to 0.004 mm. in diameter. The critical temperature was found to be independent of the size of the tube and 30.96° was taken as the most probable value. Large differences in critical point were found for different methods of illumination and depending on whether a sharp meniscus or diffuse band is taken as a criterion.

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VOLUMETRIC DETERMINATION OF VANADIUM BY MEANS OF POTASSIUM IODATE

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Introduction

The advantages of the iodate method of volumetric analysis have been pointed out by Andrews[1] and Jamieson,[2] and more recently reviewed by Heisig.[3] Among these advantages are the ease with which a standard solution of potassium iodate is prepared and the stability of its solution. Not only can substances which reduce iodate in hydrochloric acid solution be titrated, but it has been shown by Andrews[1] that oxidizing agents, such as chromates and chlorates, which oxidize iodide and are not re-oxidized by iodine monochloride, can be determined by adding an excess of a standard solution of potassium iodide and then converting the iodine liberated and the excess of iodide to iodine monochloride by titration with iodate solution. It was to be expected that a similar determination of vanadium as vanadate could be made, provided a sufficiently high concentration of hydrochloric acid could be maintained during the titration with the iodate to prevent re-oxidation of the quadrivalent vanadium formed. The chemical reactions involved in such a process can be represented as follows

$$H_3VO_4 + HI + 2HCl = VOCl_2 + \tfrac{1}{2}I_2 + 3H_2O$$
$$2I_2 + HIO_3 + 5HCl = 5ICl + 3H_2O \text{ and}$$
$$2HI + HIO_3 + 3HCl = 3ICl + 3H_2O$$

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[1] Andrews, *Z. anorg. Chem.*, **36**, 83 (1903); THIS JOURNAL, **25**, 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, **1926**, p. 9.

[3] Heisig, THIS JOURNAL, **50**, 1687 (1928).

Such a method would offer the advantages of not requiring a previous reduction of the vanadate, which is the most commonly occurring form of vanadium, and of determining vanadium in the presence of iron, arsenic and phosphate, substances commonly occurring with vanadium in its natural sources.

Preliminary determinations which gave promising results were carried out by Mr. T. G. Bernhardi in this Laboratory. A more detailed study of the method was then undertaken by the authors.

Substances and Solutions.—All chemicals used were of "analytical chemical" grade.

Ammonium metavanadate was used as the source of the vanadium. The solution was prepared by weighing out the solid, dissolving it in an equivalent amount of sodium carbonate solution and expelling the ammonia by boiling. The vanadate solution was then standardized by the iodimetric method, using the procedure recommended by Ramsey.[4] Three determinations gave the values 0.05215, 0.05217 and 0.05215 for the molal concentration of the solution.

The potassium iodate was tested for iodide with negative results. The solutions were prepared by weighing out the dried salt and dissolving it in the proper volume of water to make the resulting solutions 0.025 molal.

The potassium iodide solution was prepared from the same grade of salt and proved to be iodate-free. The salt was weighed out and dissolved, and the concentration was determined by titration with the iodate solution under the conditions of the method being used.

The Method of Analysis.—The general procedure was to pipet the vanadate solution into a 200-ml. or 400-ml. conical flask with a ground-glass stopper and then to add slowly to this, while cooling the flask with tap water, the volume of 12 molal hydrochloric acid necessary to give the final concentration of the acid which was desired. The hydrochloric acid used in most cases had previously had a slow current of carbon dioxide passed through it for fifteen to twenty minutes in order to remove most of the dissolved oxygen. Through the flask containing the acid and the vanadate was then passed over the solution for two to three minutes a vigorous current of carbon dioxide. Then 3 to 5 ml. of carbon tetrachloride and a measured excess of the standard potassium iodide solution were added, the flask was closed and allowed to stand for one to two minutes; the solution was titrated as rapidly as possible with the iodate solution until no more iodine color could be detected in the carbon tetrachloride.

Test Analyses: Effect of Acid Concentration and Presence of Air.—In Table I are shown the results obtained in titrating known quantities of vanadium in the presence of hydrochloric acid at different concentrations and under certain other variations of the conditions.

In each case 25 ml. of the standard potassium iodide solution was added, except in Expt. 18, where 50 ml. was taken. Two standard solutions of potassium iodide were used in the experiments, one solution being 0.05414 molal and the other 0.05404 molal. The volume of potassium iodate used in the titrations varied from 13.46 ml. in Expt. 1 to 28.08 ml. in Expt. 18.

It will be seen that when the final concentration of the hydrochloric acid is 6 molal or 7 molal the results are satisfactory. The average of the fifteen

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

TABLE I

TITRATION OF VANADIUM WITH IODATE AT VARIOUS ACID CONCENTRATIONS

Expt.	Vanadium taken, mg.	Final concn. of HCl, *M*	Vanadium found, mg.
1[a]	66.44	3.8	69.36
2[a]	66.44	3.8	66.91
3[a]	66.44	3.8	63.45
4[a]	66.44	3.8	65.99
5	66.44	3.7	63.60
6	66.44	3.8	65.99
7	66.44	3.9	66.61
8	66.44	3.8	65.08
9	66.44	3.8	64.72
10[a]	66.44	5.0	66.61
11[a]	66.44	5.0	66.81
12	66.44	5.0	66.10
13	66.44	5.0	66.20
14[b]	66.44	6.0	66.45
15	66.44	6.0	66.30
16	66.44	6.0	66.16
17[b]	66.44	6.0	66.30
18	132.88	6.0	132.32
19	26.58	6.0	26.66
20	66.44	6.0	66.41
21	66.44	6.0	66.36
22	66.44	6.0	66.16
23	66.44	6.0	66.21
24	26.58	6.0	26.71
25	26.58	6.0	26.66
26	26.58	6.0	25.74
27	26.58	6.0	26.61
28	26.58	6.0	26.25
29	26.58	6.0	26.10
30[c]	26.58	6.0	26.71
31[c]	26.58	6.0	26.66
32[c]	66.44	7.0	66.47
33[c]	66.44	7.0	66.41
34[c]	66.44	7.0	66.41

[a] Neither the hydrochloric acid nor the flask was swept out with carbon dioxide.

[b] The flask was not swept out with carbon dioxide.

[c] Carbon dioxide was passed through the flask with vanadate before adding hydrochloric acid.

analyses at 6.0 *M* (excluding Expts. 26–29 for the reasons given below) is 0.08% low, and the greatest deviation from the correct value is 0.43%.

When the hydrochloric acid is 5 molal the results are not so good; they are low where the air is excluded and high when it is present, the latter probably being due to slight re-oxidation of the quadrivalent vanadium. It will be noted that a difference of about 1% is caused by not excluding the oxygen of the air. This effect (of not excluding the air) is apparently larger than with the 6 molal acid. It seems remarkable that this effect is not greater, considering the larger deviation obtained by Ramsey[4] when he allowed vanadate and iodine to react without excluding the oxygen of the air at much lower concentration of acid than was present in these experiments, but the smaller excess of iodide here present probably decreases the oxygen error.

At the lowest concentration of the hydrochloric acid the results show still more variability. This may be attributed to two factors: partial re-oxidation of the vanadium to vanadate and insufficient concentration of the hydrochloric acid to prevent hydrolysis of the iodine monochloride; this concentration is at the minimum of 12% which Jamieson[2] states is necessary in order to eliminate this hydrolysis.

It may be mentioned that the acid concentration during the vanadate–iodide reaction varies from 7 to 10 molal, and that under these conditions the vanadium may be reduced below the quadrivalent state; but, so long as oxygen is excluded, this causes no error, since it is immediately re-oxidized upon addition of the iodate.

In Expts. 26–29 the solution of the vanadate was 10 molal in hydrochloric acid while being swept with carbon dioxide; subsequent tests above the surface of the solution with paper strips moistened with a solution of starch and potassium iodide showed that a slight amount of chlorine was formed even in a cold solution, thus accounting for the low results obtained. Under the same conditions when the hydrochloric acid was added after sweeping out the flask with carbon dioxide and the iodide was immediately added, the error was eliminated. The results with 7 molal hydrochloric acid are consistent, but, owing to the large amounts of acid required, it is desirable to work at the lowest possible concentration. In Expt. 34 only half of the hydrochloric acid was added before adding the potassium iodide, making the hydrochloric acid slightly less than 6 molal during the vanadate–iodide reaction. The remainder of the acid was added when the titration was half finished.

Test Analyses: Effect of Presence of Other Constituents.—In Table II are shown the results obtained when vanadium was present with various other substances. Here the final concentration of the hydrochloric acid was always approximately 6 molal. The amount of vanadium taken was 66.4 mg. in all cases (except in Expts. 6 and 9), and in every case 25 ml. of potassium iodide of the concentration shown in the table was used.

TABLE II

TITRATION OF VANADIUM WITH IODATE IN THE PRESENCE OF OTHER SUBSTANCES

Expt.	Subs. present, mg.	Concn. of KI soln., mole/liter	KIO_3 used, ml.	Vanadium found, mg.
1	7350 H_3PO_4 (75 millimoles)	0.05414	14.06	66.30
2	1000 Fe (as $FeCl_3$)	.05404	14.12	65.74
3	500 Fe	.05404	14.13	65.68
4	100 Fe	.05404	14.09	65.90
5	50 Fe	.05404	14.08	65.95
6	40 Fe[a]	.05414	21.89	26.41
7	1030 Fe, 75 millimoles of H_3PO_4	.05414	14.11	66.06
8	220 As (as As_2O_5)	.05414	14.08	66.21
9	266 As[a]	.05404	21.80	26.61
10	300 W,[b] 75 millimoles of H_3PO_4	.05414	14.11	66.06
11	1000 W,[c] 75 millimoles of H_3PO_4	.05414	14.12	66.01

[a] 26.58 mg. of vanadium taken.

[b] WO_3 was dissolved in the H_3PO_4.

[c] WO_3 was partly dissolved in the H_3PO_4.

Experiments 1, 6, 10 and 11 in Table II show that even a large excess of phosphoric acid has very little effect on the determination. This shows that any phosphate–vanadate complex molecule that is formed is not so stable as to prevent reduction of the vanadate. The presence of ferric ion, even in very large quantities, seems to cause only a slight, though apparently definite, decrease in the amount of vanadium found. The reason for this is not clear. The ferric chloride used was proved to contain no appreciable quantity of ferrous salt; moreover, the work of Heisig[3] shows the tendency of ferrous chloride solutions to oxidize rapidly in the presence of air under the conditions of this procedure; this would cause an effect opposite to that observed. Expts. 8 and 9 show that although arsenic acid oxidizes iodide, it is re-oxidized by iodine monochloride when titrated with iodate and does not interfere with this determination of vanadium. Expts. 10 and 11 show that tungstic acid can be held in solution with phosphoric acid and the titration made in its presence.

Final Analytical Procedure.—Upon the basis of the above experiments the following procedure is suggested. Bring the vanadium as vanadate into as small a volume of solution as possible, preferably not over 25 ml., in order to avoid the use of an excessive quantity of hydrochloric acid. Transfer the solution to a 200–400-ml. conical flask with a ground-glass stopper and pass for two to three minutes a rapid current of carbon dioxide into the flask, but not through the solution. Gently swirl the solution in the flask during this time. Add through a funnel to the solution in the flask such a volume of 12 molal hydrochloric acid as will make the solution 6–8 molal in acid during the vanadate–iodide reaction. Cool the flask with tap water during the addition of the acid. Add to the solution from a pipet or buret an excess (as small as practicable) of standard potassium iodide solution. Mix the solutions, let the flask stand for one to two minutes, add to it 5 ml. of carbon tetrachloride and then titrate with standard iodate solution, adding 12 molal hydrochloric acid as needed so that its concentration may never fall below 6 molal in the solution being titrated. Where the approximate amount of vanadium present is known, the calculated volume of hydrochloric acid can be added before the titration. When approaching the end-point shake the solution vigorously so that equilibrium of the iodine between the carbon tetrachloride and water layers is attained. Cool the solution with tap water during this shaking to prevent drops of the solution from blowing out around the stopper when the flask is opened.

As a direct test of this procedure some ammonium metavanadate from the same source as that used in preparing the vanadate solution was recrystallized, then ignited to the oxide at 400–500°. This product was moistened with nitric acid and again heated at the same temperature. Of this 1.4174 g. was weighed out, dissolved in sodium carbonate solution, the solution diluted to 100 ml., four 10-ml. portions were pipetted out and treated by the above procedure. The results obtained are shown below. The iodide solution was 0.05404 molal.

Table III

Test Analyses for Final Procedure

No.	1	2	3	4
Iodine added, ml.	35	35	35	35
Iodate used, ml.	22.25	22.27	38.47	38.50
Vanadium found, mg.	79.40	79.29	79.34	79.19

The calculated weight of vanadium present was 79.41 milligrams.

In No. 1 half of the hydrochloric acid was added before adding the potassium iodide and the remainder during the titration. In No. 2 all of the acid was added before the iodide, while in Nos. 3 and 4 half of the acid was added before the iodide and half just before beginning the titration.

Summary

A method for the volumetric determination of vanadium by means of standard solutions of potassium iodide and potassium iodate has been developed. The method depends upon the reduction of vanadate by a known amount of iodide in hydrochloric acid solution and conversion of the iodine formed and of the excess of iodide into iodine monochloride by titration with iodate.

It is shown that when the concentration of the hydrochloric acid is 6 molal or more, quadrivalent vanadium is not oxidized by the iodine monochloride and the reactions are quantitative.

Tests analyses proved that vanadate can be determined by this method in the presence of phosphate, arsenate or ferric iron, and also in the presence of tungstic acid, which may be held in solution by adding phosphoric acid.

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THE ABSORPTION SPECTRUM AND DECOMPOSITION OF HYDROGEN PEROXIDE BY LIGHT

By H. C. Urey, L. H. Dawsey and F. O. Rice

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Very extensive studies have been made on hydrogen peroxide in dilute and concentrated solutions and recently in the pure liquid state.[1] These studies have dealt particularly with its thermal, photochemical and catalytic decomposition in solution.[2] No work has been done on its decomposition in the gaseous state other than that of Elder and Rideal,[3] showing that the thermal decomposition is predominantly a surface reaction.

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[1] (a) Maass and Hatcher, This Journal, **42**, 2548 (1920); (b) Maass and Hiebert, *ibid.*, **46**, 2693 (1924).

[2] For a complete review of this work, see Kistiakowsky, "Photochemical Processes," McGraw-Hill Book Co., Inc., New York, **1928**, pp. 173–177.

[3] Elder and Rideal, *Trans. Faraday Soc.*, **23**, 545 (1927).