2. The volume functions used for the constants of the various isometrics are those suggested by Keyes and Phillips which are found to be suitable down to volumes of 10 cc. per gram.

3. The resultant equation as based on Amagat's data between 0 and 100° is $P = [RT(1 - y/2)]/(V - \delta) - \phi$, where $y = g\cdot e^{a/T}/V$; $\log_{10} y = -3.7267 + 928.44/T - \log_{10} V$; $y = (1.8764 \times 10^{-4}/V) e^{2137.8/T}$; $\delta = \beta\, e^{-\alpha/V}$; $\log_{10} \delta = 0.430719 - 1.2860/V$; $\delta = 2.6960\, e^{-2.9701/V}$; and $\phi = (A/V^2)e^{l/v}$; $\log_{10} \phi V^2 = 3.48539 - 0.46108/V$; $\phi V^2 = 3057.7\, e^{-1.0617/V}$; and a comparison is given between the observed values and those calculated from this equation for various isometrics down to 10 cc. per gram, the average deviation being ±0.02 atm., or 0.07%.

4. All of Andrews' data have been recomputed by the author and the agreement between his low-pressure values and those calculated from the above equation is fair. The recent data of Maass and Mennie at pressures around 1 atm. and below have been transformed into isometrics, and over the temperature range from 0 to 100° throughout which the proposed equation of state holds, the agreement between calculated and observed values is good.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE IODIMETRIC DETERMINATION OF VANADIUM

BY J. B. RAMSEY

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In an alkaline solution or in a neutral buffer solution, tetravalent vanadium is oxidized by iodine to the pentavalent condition,[1] while in acid solution pentavalent vanadium is reduced by iodide ion. At very high concentrations of acid and iodide the reduction may be made to proceed to the trivalent condition,[2] but over a wide range of acid and iodide concentrations at ordinary room temperatures, it stops at the tetravalent state. The effect of the concentration of the acid and iodide on the extent of the reduction has been discussed by Edgar.[3]

Methods of determining vanadium based on the determination of the iodine formed in the reduction of pentavalent vanadium to the tetravalent condition by iodide ion have been described by Perkins[4] and Edgar.[3] The iodine formed is determined in the one case[4] by converting it into silver iodide and weighing as such; in the other[3] by removing it from the vana-

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[1] Browning, *Am. J. Sci.*, [4] **2**, 185 (1896).

[2] Friedheim and Euler, *Ber.*, **28**, 2067 (1895). Edgar, *Am. J. Sci.*, [4] **26**, 333 (1908); [4] **27**, 174 (1908).

[3] Edgar, THIS JOURNAL, **38**, 2369 (1916).

[4] Perkins, *Am. J. Sci.*, [4] **29**, 540 (1910).

dium solution with carbon disulfide and reducing with a known solution of sodium thiosulfate. Various other investigators,[5] who have studied the reduction of pentavalent vanadium in concentrations of acid and iodide in which the vanadium is reduced to the tetravalent condition, have invariably obtained more iodine than that equivalent to the vanadium used. The simplest explanation for this, as pointed out by Edgar,[3] is that oxygen of the air had not been excluded and that the oxidation of iodide ion by oxygen is catalyzed by pentavalent vanadium. In the two analytical methods referred to above, oxygen is excluded by means of hydrogen. The time required, however, to complete a determination by either of these methods is greater than desirable for many purposes (not less than one hour and a half by the simpler method[3] of the two). Recently Stoppel, Sidener and Brinton[6] have described a more rapid and direct iodimetric method, in which no precaution was taken to exclude oxygen. Under the conditions of acid and iodide concentrations used by these investigators, the reduction of the pentavalent vanadium by the iodide is complete within one or two minutes. The iodine formed is determined by direct titration with a known solution of sodium thiosulfate in the presence of the tetravalent vanadium. They conclude that they have "established the conditions under which the catalytic effect of pentavalent vanadium is not operative" and that under these conditions "vanadium can be conveniently and accurately determined iodimetrically." Other investigators[3,5b,d,f,g] who have studied this more rapid and direct method without excluding oxygen, have in every case obtained more iodine than that equivalent to the vanadium present. The excess of iodine found varied from 1 to as much as 20% in some cases.

It seems worth while to record the results of our experience with this more direct and rapid iodimetric method. These results show that over a wide range of acid and iodide concentrations, including those used by previous investigators, this method gives quite accurate results when oxygen is excluded from the solutions used, but that more iodine is always formed than that equivalent to the vanadium present, if oxygen is not excluded.

Materials Used

Ammonium metavanadate, containing only a very small percentage of ammonium chloride as impurity, was used without further purification. The potassium iodide used was free from alkali and iodate.

[5] (a) Rosenheim, *Inaug. Dissertation*, Berlin, **1888**. (b) Holverscheit, *Inaug. Dissertation*, Berlin, **1890**. (c) Gooch and Curtis, *Am. J. Sci.*, [4] **17**, 41 (1904). (d) Hett and Gilbert, *Z. öffentl. Chem.*, **12**, 265 (1906). (e) Warynski and Mdivani, *Mon. sci.*, [4] **22** [II], 527 (1908). (f) Müller and Diefenthäler, *Z. anal. Chem.*, **51**, 21 (1912). (g) Wegelin, *ibid.*, **53**, 81 (1914). (h) Ditz and Bardach, *Z. anorg. Chem.*, **93**, 97 (1915).

[6] Stoppel, Sidener and Brinton, This Journal, **46**, 2448 (1924).

The sodium vanadate solutions were prepared by dissolving the desired quantity of ammonium metavanadate and slightly more than an equivalent quantity of c. p. sodium carbonate in about 200 cc. of water. This solution was boiled until ammonia was no longer evolved, and then filtered and diluted to the desired volume.

The solutions of potassium permanganate were prepared and standardized by the method recommended by McBride.[7] Each standardization consisted of not less than three determinations. The average deviation of each determination from the mean did not exceed, in any case, 0.1%.

The permanganate-iodide (Volhard) method was used in standardizing the solutions of sodium thiosulfate. This method has been shown by Bray and Miller[8] to give results accurate to within 0.1%. The standardizations were made at intervals of two weeks and the average deviation of each determination from the mean in any standardization did not exceed 0.1%.

Method and Results

Weight burets were used throughout this investigation. The buret containing the solution to be weighed was partly counterbalanced with a buret of approximately the same size. Weighings were made to the nearest centigram.

The concentration of the sodium vanadate solutions was determined by two standard methods: (1) by reduction to the tetravalent state with bromide ion in a solution approximately 8 N in hydrochloric acid by absorption of the bromine formed in potassium iodide solution and by determination of the resulting free iodine with a known sodium thiosulfate solution (the Holverscheit process[5b,9]); (2) by reduction to the tetravalent state with sulfur dioxide in a solution acid with sulfuric acid, and by oxidation of the resulting tetravalent vanadium with a known solution of potassium permanganate. In the use of the latter method the directions given by Lundell and Knowles[10] were in general observed. Since, however, the conditions used in making a determination by the sulfur dioxide-potassium permanganate method vary considerably with the individual investigator, a statement of those adopted in this work is given. The reduction by sulfur dioxide is carried out in solution made by mixing a weighed portion (between 10 and 20 g.) of vanadate solution (approximately 0.1 N) with 5 cc. of 6 N sulfuric acid. With this small volume, it is possible to reduce the vanadium and remove the excess of sulfur dioxide in a relatively short time (about 20 minutes). Be-

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[7] McBride, This Journal, **34**, 393 (1912).

[8] Bray and Miller, *ibid.*, **46**, 2204 (1924).

[9] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1924**, vol. 2, p. 566.

[10] Lundell and Knowles, This Journal, **43**, 1560 (1921).

fore adding the known potassium permanganate solution, the vanadium solution is diluted to 200 cc. Although the temperature of the solution is above 70° during the addition of the major portion of the potassium permanganate, it is always raised to 90–100° just before the titration is completed. The end-point of this reaction is ascertained most satisfactorily by making a direct comparison of the color of the titrated solution with that of a sodium vanadate solution of equal volume, and of approximately the same concentration of acid and vanadium. This acidified vanadate solution is heated to boiling in order that the vanadium shall be in the same ionic or molecular condition that it is in the titrated solution. However, it is not necessary to have this solution hot when in use. The addition of less than one drop (0.03 g.) of approximately 0.1 N potassium permanganate to one of two such acidified solutions of sodium vanadate produces an easily distinguishable difference in color. The solution containing the permanganate has a distinctly reddish tint. The time required to complete a determination by this procedure is approximately 30 minutes.[11]

The procedure given by Stoppel, Sidener and Brinton[6] was followed in making a determination by the direct iodimetric method without excluding oxygen. This consisted of the following steps: (a) the addition of the desired quantity of sulfuric acid and potassium iodide to a weighed quantity of the sodium vanadate solution in a 400cc. flask; (b) the dilution of this solution to 200–300 cc. within three minutes after the addition of the last reagent (the time usually allowed for complete reduction under the conditions used); (c) the titration of the free iodine with a known solution of sodium thiosulfate. The effects of varying this procedure and the conditions are discussed in connection with the results.

With oxygen excluded, the following procedure was the one finally adopted for making a determination by this direct method.

Between 10 and 20 g. of the vanadate solution and 5 cc. of a sulfuric acid solution are added to a 400cc. flask. The flask is closed with a rubber stopper, fitted with an inlet and an outlet tube for carbon dioxide. The end of the inlet tube reaches to within 1 cm. of the surface of the solution. A current of carbon dioxide is passed through the flask while the solution is heated just to boiling. A trap containing water is then attached to the outlet tube and the solution is cooled with water at such a rate that the carbon dioxide continues to bubble through the water in the trap. This precaution is taken to prevent air from being sucked back into the flask during the cooling. After the solution has been cooled to room temperature, and while passing a moderate current of carbon dioxide through the flask, the stopper is removed for just sufficient time to add the desired quantity of solid potassium iodide from a test tube. The rate of flow of the carbon dioxide is then diminished until the pressure in the flask is only slightly greater than that of the atmosphere, as shown by the water in the trap. This precaution

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[11] Using this procedure, the sulfur dioxide-potassium permanganate method is somewhat simpler and more accurate than the mercury-potassium permanganate method developed by McCay and Anderson, [This Journal, **44**, 1018 (1922)].

is taken to prevent the loss of iodine. The solution is then shaken in order to dissolve the potassium iodide. The time required for complete reduction of the vanadium depends chiefly on the concentration of the sulfuric acid. When using 5 cc. of 6 *N* sulfuric acid (the resulting solution approximately 2 *N*) and from 2 to 4 g. of potassium iodide, the reaction is complete in any case within two minutes after the addition of the latter. Usually one minute is sufficient. After complete reduction the stopper is removed and the solution is diluted to approximately 300 cc. This dilution is necessary partly to prevent the slow oxidation of iodide ion by oxygen of the air in solutions having the concentrations of acid and iodide used in these experiments, and partly to decrease the concentration of vanadium so that the blue color of tetravalent vanadium will not obscure the end-point which occurs at the disappearance of the deep blue of starch-iodine. To the diluted solution is added the known solution of sodium thiosulfate until reduction is almost complete. The starch solution is then added and the titration completed. The end-point is determinable to within a fraction of a drop of 0.05 *N* sodium thiosulfate. After a little practice, a determination can be completed in approximately 15 minutes.

In obtaining the results given in Table I, the following solutions were used: potassium permanganate solution, 0.1079 equivalent in 1000 g. of solution; sodium thiosulfate solution, 0.04430 equivalent in 1000 g. of solution.

Table I

Analysis of Sodium Vanadate Solution

By SO_2-$KMnO_4$ method			By Holverscheit process		
Vanadate soln. used, g.	$KMnO_4$ soln. used, g.	Vanadate found, equiv./1000 g. of soln.	Vanadate soln. used, g.	$Na_2S_2O_3$ soln. used, g.	Vanadate found, equiv./1000 g. of soln.
16.20	12.72	0.08472	13.06	24.99	0.08477
13.03	10.24	.08480	10.55	20.22	.08490
15.76	12.39	.08483	11.11	21.28	.08485
16.99	13.37	.08492	12.50	23.92	.08477
13.17	10.36	.08488	14.27	27.29	.08472
17.88	14.05	.08479	13.31	25.47	.08477
19.89	15.62	.08474	16.14	30.83	.08461
14.67	11.53	.08480	17.84	34.06	.08457
16.97	13.33	.08476	11.96	22.92	.08489
19.89	15.64	.08485	12.85	24.60	.08481
			12.84	24.62	.08494
	Av.	0.08481	14.09	26.99	.08486
	Av. deviation	0.000049			
				Av.	0.08479
				Av. deviation	0.000088

In order to determine whether or not the small amount of chloride ion present in the vanadate solution had any effect on the results obtained by the sulfur dioxide-potassium permanganate method, different portions of the vanadate solution were reduced a second time with sulfur dioxide and reoxidized with permanganate without producing any measurable difference in the results.

From these results, the concentration of the sodium vanadate solution is taken as 0.08480 ± 0.00008 equivalent in 1000 g. of solution. This is equivalent to 7.717 g. of vanadium pentoxide, V_2O_5, in 1000 g. of solution.

The results given in Table II were obtained by the use of 5 cc. of 6 *N* sulfuric acid and approximately 3 g. of potassium iodide. The thiosulfate solution used in the first series of experiments contained 0.04430 equivalent in 1000 g. of solution, and that used in the second series, 0.04490 equivalent in 1000 g. of solution.

TABLE II

ANALYSIS OF SODIUM VANADATE SOLUTION BY DIRECT IODIMETRIC METHOD

Series I, with exclusion of O_2			Series II, without exclusion of O_2			
Vanadate soln. used, g.	$Na_2S_2O_3$ soln. used, g.	I_2 formed per 1000 g. of $NaVO_3$ soln., equiv.	Expt. no.	Vanadate soln. used, g.	$Na_2S_2O_3$ soln. used, g.	I_2 formed per 1000 g. of $NaVO_3$ soln., equiv.
10.71	20.48	0.08471	1	12.31	23.67	0.08634
12.70	24.30	.08476	2	14.43	27.79	.08647
11.07	21.17	.08472	3	12.02	23.17	.08655
10.40	19.90	.08477	4	16.53	31.82	.08644
12.00	22.95	.08472	5	16.25	31.23	.08629
10.21	19.51	.08465	6	13.35	25.61	.08614
11.60	22.18	.08470	7	12.31	23.58	.08601
12.32	23.56	.08472	8	10.23	19.64	.08620
12.90	24.70	.08482	9	12.87	24.67	.08607
12.73	24.34	.08470	10	10.79	20.80	.08655
11.06	21.17	.08479	11	12.19	23.37	.08608
			12	11.14	21.37	.08613
	Av.	.08473	13	11.16	21.49	.08646
Av. deviation		.000038	14	12.24	23.58	.08650
			15	12.47	24.02	.08650
					Av.	.08632
				Av. deviation		0.000172

In each of the experiments of Series II, the solution containing the acid, iodide and vanadium was diluted within three minutes after the addition of the last reagent (potassium iodide or sulfuric acid). That the reaction was completed in this time was indicated by the permanence of the end-point. These results show that the direct iodimetric method, when carried out with the exclusion of oxygen under the conditions used, gives results which check the results obtained by the two standard methods within less than 0.1%, but that if oxygen is not excluded, approximately 1.8% more iodine is formed, on the average, than that equivalent to the vanadium present. The concentrations of acid, iodide and vanadium used in these experiments are approximately those recommended by Stoppel, Sidener and Brinton.[6] In the experiments carried out by the procedure recommended by these investigators (Series II), the effect of varying the order of addition of the acid and iodide, as well as the extent of shaking the solution after all reagents were present, was considered. In Expts.

1, 2, 3, 4, 5, 14 and 15 the solid potassium iodide was added last. Except in Expt. 15, the solution was then shaken for sufficient time to dissolve the potassium iodide. This required between 20 and 30 seconds. In Expt. 15, the solution was shaken continuously for three minutes after the addition of the potassium iodide. From these results it seems that the reduction is practically completed during the time required to dissolve the potassium iodide. In Expts. 9, 10, 11, 12 and 13, the potassium iodide was dissolved in the vanadate solution before adding the sulfuric acid. In Expts. 9, 11 and 12, the solution was shaken for five seconds after addition of the acid, and in Expts. 10 and 13 for 45 seconds. These results as well as others not given show that remarkably constant results may be obtained without excluding oxygen, if care is taken to carry out the different determinations in as nearly the same manner as possible.

That light has no measurable effect upon the excess of iodine formed has been shown by results obtained in the dark, in the diffuse light of the laboratory and within about 100 cm. of three 150-watt Mazda lamps. The effect of temperature and the concentration of dissolved oxygen has not been considered in this investigation. That other factors are effective is indicated by the fact that the excess of iodine formed in different sets of experiments has been found to vary from 1 to 2.5%, although the results of any one set carried out with the same solutions and within a relatively short time check as well as those given in Series II.

In order to determine the effect of varying the concentrations of acid and iodide on the excess of iodine formed, a series of experiments was performed in which these concentrations were varied over a range including that used above while the concentration and quantity of the vanadate solution were practically the same. The acid concentrations studied were obtained by the use of 5 cc. of the following solutions, respectively: 3 *N*, 6 *N* and 12 *N* sulfuric acid. At each acid concentration, 2, 4 and 6 g. of potassium iodide were used. These quantities gave a variation of approximately 1 to 4 *N* in sulfuric acid and 0.6 to 2 *N* in iodide. The average deviation of each determination from the mean of twenty-two results obtained over this range was 0.12%, and this average was 1.2% greater than that obtained with oxygen excluded, using 5 cc. of 6 *N* sulfuric acid and 3 g. of potassium iodide as in Series I, Table II.

That no error is produced by the reduction of pentavalent vanadium to the trivalent condition over a wide range of acid and iodide concentrations, is shown by the results given in Table III.

The last column of this table contains the number of grams of the thiosulfate solution used per gram of the vanadate solution. The first three results were obtained with the concentrations of acid and iodide the same as used in obtaining the results given in Series I of Table II. It is evident that no error is made due to the reduction of the vanadium

TABLE III

EFFECT OF ACID AND IODIDE CONCENTRATIONS; OXYGEN EXCLUDED

H_2SO_4 soln. Cc.	N	KI, g.	Vanadate soln., g.	$Na_2S_2O_3$ soln., g.	Ratio, T/V
5	6	3	15.43	29.19	1.892
5	6	3	14.66	27.73	1.892
5	6	3	10.13	19.19	1.894
5	18	6	10.36	19.62	1.894
5	18	6	10.64	20.14	1.893
5	18	10	14.08	26.66	1.893
5	18	6	9.93	18.80	1.893

to the trivalent condition in solutions having a concentration of iodide as great as 2 N and of sulfuric acid as great as 6 N. It may be noted that these results do not show whether vanadium is so reduced or not, but do show that if it is so reduced in the solution before dilution, it must be immediately and completely oxidized by the iodine to the tetravalent condition when the solution is diluted.

A solution of ammonium vanadate, free from ammonium chloride, was prepared and analyzed by determining the weight of vanadium pentoxide, V_2O_5, obtained from a known weight of the solution by careful evaporation and ignition in the presence of oxygen. In no case did the color of the resulting oxide indicate reduction below the pentavalent condition. Nevertheless, in each case the solid was treated with a few drops of concd. nitric acid and the mixture evaporated to dryness as recommended by Browning.[1] In no case was there a measurable change in weight produced by this treatment. This solution was also analyzed by the direct iodimetric method, with and without the exclusion of oxygen. The average of sixteen results obtained with oxygen excluded check within 0.1% of those obtained gravimetrically, whereas the average of twenty results obtained without excluding oxygen is 2.5% greater than the gravimetric result. The average deviation of each determination from the mean obtained with oxygen excluded is 0.06%; not excluding oxygen 0.21%. The concentration of vanadium in this ammonium vanadate solution was approximately two-thirds of that in the sodium vanadate solutions used, due to the limited solubility of ammonium vanadate at room temperatures. Otherwise the concentrations of reagents were the same as those used in obtaining the results given in Table II. These results are given merely to show that the catalytic effect of pentavalent vanadium is as evident under these conditions in solutions of ammonium vanadate as in those of sodium vanadate.

Additional facts are needed in order to develop a probable explanation of this catalysis. Further work is in progress with this end in view.

The author wishes to express his indebtedness to Professor W. C. Bray for his suggestions and advice in connection with this work.

Summary

The excess of iodine formed when pentavalent vanadium is reduced by iodide ion to the tetravalent state in the presence of oxygen of the air, has been shown to be appreciable (from 1.0 to 2.5%) in solutions having approximately the following concentrations: of iodide, from 0.6 to 2.0 *N;* sulfuric acid, from 1 to 4 *N;* vanadate, from 0.053 to 0.062 *N* (corresponding to 0.0772 to 0.136 g. of vanadium pentoxide used in these experiments).

From these results, and those obtained by others who have studied the iodimetric method for determining vanadium, it is concluded that under no conditions of acid, iodide and vanadium concentrations so far studied is the catalytic effect of pentavalent vanadium on the oxidation of iodide ion by oxygen negligible, and that therefore the iodimetric method of determining vanadium will not give accurate results under these conditions, when carried out in the presence of oxygen.

A simple and rapid method for carrying out the iodimetric determination of vanadium with oxygen excluded has been developed. The results obtained by this method have been shown to agree within 0.1% of those given by recognized standard methods for determining vanadium. The time required for a complete determination by this method is approximately 15 minutes.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 190]

EQUILIBRIUM PRESSURES OF A GAS IN A MIXTURE, ESPECIALLY OF AMMONIA MIXED WITH NITROGEN

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Introduction

A knowledge of the equilibrium pressures of individual gases in mixtures of gases and a method for the calculation of these pressures from the composition, pressure and temperature of the mixture are of theoretical and practical importance, the term equilibrium pressure of a gas in a mixture being defined as the pressure of the pure gas in equilibrium with the mixture through a semi-permeable membrane, the entire system being at constant temperature.

In Fig. 1, the pressure, p_1, of pure ammonia in Compartment I, when equilibrium subsists, is the equilibrium pressure of ammonia in the mixture. If we had a real membrane semi-permeable to ammonia we could easily determine by means of this apparatus the composition of different mix-