$= \frac{-L}{4.58}$. The values of L calculated from this expression are, in calories per mole: near the melting point, in benzene 4770, in toluene 4630; from 25° to 80°, in benzene 6900, in toluene 6760; and as an average for both systems over the entire range, 6360. The marked discrepancy between these values might be thought to indicate a transition point in the vicinity of 95°, and attempts were made to detect this point by cooling curves. No transition point was observed. Moreover the solubility data in both solvents indicate a gradual rather than an abrupt change in the slope of the curve.

Summary

The solubility of benzoic acid in benzene and in toluene has been determined. These solubilities, expressed as mole fractions are practically identical above 30°.

A labor-saving device for evaluating solubility data has been described.

The latent heats of solution of benzoic acid in the two solvents have been calculated.

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THE IODIMETRIC DETERMINATION OF VANADIUM

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Several investigators have attempted the iodimetric determination of vanadium, by titrating with sodium thiosulfate the iodine liberated by pentavalent vanadium in acid solution. A comprehensive review of the literature of this method has been given by Ditz and Bardach.[1] The conditions under which the different investigators worked varied considerably, as did also their results. In some instances nearly correct results could be obtained by basing the calculation on a reduction to the vanadyl state, while in others the assumption of a reduction to the trivalent stage was necessary for even approximately correct results.

Other investigators[2] have claimed that under proper conditions the reduction goes definitely to the vanadyl stage, but there is lack of agreement as to what these proper conditions are.

The statement of Ditz and Bardach that vanadic acid passes by reduction with hydriodic acid directly from the pentavalent to the trivalent state without formation of any vanadyl compound as an intermediate

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[1] Ditz and Bardach, *Z. anorg. Chem.*, **93**, 97 (1915).

[2] Rosenheim, *Dissertation*, Berlin, **1888**. Browning, *Am. J. Sci.*, [4] **2**, 185 (1896). Warynski and Mdivani, *Mon. Sci.*, **22**, 11, 527 (1898). Perkins, *Am. J. Sci.*, [4] **29**, 540 (1910).

stage has been disputed by Edgar[3] who shows, on the basis of experiments by Rutter,[4] that even if trivalent vanadium were formed it should immediately react with vanadic acid to form a vanadyl compound, the latter being quite stable toward dil. hydriodic acid. Edgar repeated the work of Ditz and Bardach with special precautions to eliminate atmospheric oxygen during the reduction and his results indicate that the reduction under his conditions of operation does not go beyond the vanadyl state. He concluded that the excessive amounts of iodine liberated in the experiments of Ditz and Bardach and others were due at least in part to the catalytic effect of vanadic acid in accelerating the oxidation of hydriodic acid by atmospheric oxygen. But the effect of varying concentrations of hydrogen ion and iodide ion must not be lost sight of, as it has been shown by Gooch and Curtis[5] that with sufficiently high acid concentration and by long boiling a complete reduction to trivalent vanadium is possible.

It seemed possible that even though the catalytic effect of vanadium pentoxide were operative under some circumstances, yet under other conditions this might be eliminated, and a satisfactory determination of vanadium by this method might be obtained. In this paper are recorded the results of an investigation of the proper conditions for the iodimetric determination of vanadium.

Experimental Part

Vanadium pentoxide of high purity was prepared by recrystallizing ammonium metavanadate several times from boiling water containing a little ammonium hydroxide, igniting the crystals in a porcelain dish at about 400°, moistening the oxide with redistilled nitric acid, and again heating to 400°. This gave a powder of uniform orange-yellow color

TABLE I

WEIGHTS OF VANADIUM PENTOXIDE FOUND

							Av.
By zinc reduction,[6] g.	0.0857	0.0855	0.0855	0.0854	0.0855	0.0852	0.0855
By KBr distillation,[7] g.	.0850	.0849	.0856	.0851	.0849	...	.0851
By mercury reduction,[8] g.	.0858	.0852	.0856	.0858	.0860	...	.0857

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

[4] Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

[5] Gooch and Curtis, *Am. J. Sci.*, [4] **17**, 41 (1904).

[6] Gooch and Edgar, *ibid.*, [4] **25**, 233 (1908); reduction to the divalent state by passing through a zinc column in a Jones reductor, into ferric alum solution and titration with permanganate.

[7] Holverscheidt, *Dissertation*, Berlin, **1890**; distilling with conc. hydrochloric acid and potassium bromide, catching the liberated iodine in potassium iodide and titrating with thiosulfate.

[8] McCay and Anderson, THIS JOURNAL, **44**, 1018 (1922); reduction by metallic mercury in the presence of sodium chloride and titration with permanganate.

with no dark spots of lower oxide. A standard vanadium solution was prepared by adding the oxide in small quantities at a time to a hot solution of sodium bicarbonate. The pentoxide dissolved rapidly and completely, giving a permanent solution which after six months showed no signs of turbidity.

In standardizing, 10cc. portions were pipetted out and the vanadium content was determined by three methods. In Table I the weights of pentoxide found in 10 cc. are shown.

When potassium iodide is added to a very dilute acid solution of a vanadate, and the liberated iodine is immediately titrated with standard sodium thiosulfate solution, an end-point is reached before the reduction has gone as far as tetravalent vanadium for all the vanadium present. This end-point is fleeting, however, and the blue iodine-starch color soon returns. This can be kept up for a long time. The apparent degree of reduction depends upon the dilution, the amounts of acid and iodide present, and the time of standing before titration, as is shown by the following preliminary tests.

Three aliquot portions of an ammonium vanadate solution, each containing 0.0650 g. of vanadium pentoxide, were diluted to initial volumes of 40, 70 and 90 cc., respectively. To each was added 5 cc. of concd. hydrochloric acid and 3 g. of potassium iodide. After one minute each solution was diluted to a volume of 300 cc. and titrated with thiosulfate solution. The amounts of vanadium pentoxide found were 0.0638, 0.0377 and 0.0132 g., respectively.

When the amounts of acid and iodide are unduly increased, high results are always obtained. For example, a solution containing 0.0650 g. of vanadium pentoxide was diluted to 200 cc., 25 cc. of concd. hydrochloric acid and 5 g. of potassium iodide were added, and the solution was immediately titrated with thiosulfate; 0.0815 g. of vanadium pentoxide was indicated by the titration—an excess of nearly 25%.

When, however, to a concentrated neutral solution of a vanadate (about 10 cc.) 5 or 10 cc. of 6 *N* mineral acid and a few grams of potassium iodide are added, iodine is immediately and quantitatively liberated in amount equivalent to the reduction of the vanadium to the tetravalent vanadyl condition. The iodine can be estimated very accurately by diluting the solution to 200 or 300 cc., adding standard thiosulfate solution until most of the yellow color has disappeared, then adding starch and titrating to the appearance of the characteristic pale blue of a pure vanadyl solution. The color change from the dark blue of the starch-iodine complex to the pale blue of the vanadyl solution is very sharp; so sharp, in fact, that a fraction of a drop of 0.05 *N* thiosulfate will give an unmistakable end-point. This end-point is much more sensitive than the permanganate end-point with vanadium, as the reddish-yellow color of the hexavanadate ion is a serious hindrance to some persons in the detection of the permanganate pink.

In Table II are shown the results obtained by taking standard sodium vanadate solution in the volumes shown in the columns marked "Initial volume," and acid and iodide in amounts shown in the second and third columns. After the addition of the acid and iodide the solutions were diluted to about 300 cc. without delay and titrated. There was no special haste in any of the operations, but also there was no unusual delay.

Accepting the figures for standardization by the Gooch and Edgar, and by the McCay and Anderson methods as more trustworthy than those by Holverscheidt's distillation method, we may assume that the weight of vanadium pentoxide in 10 cc. is 0.0856 g.

TABLE II

EFFECT OF VARIATION IN THE INITIAL VOLUMES AND IN THE QUANTITIES OF REAGENTS USED

5 cc. of 6 *N* HCl used				10 cc. of 6 *N* HCl taken			
Initial volume Cc.	KI G.	V_2O_5 found G.	V_2O_5/10 cc. G.	Initial volume Cc.	KI G.	V_2O_5 found G.	V_2O_5/10 cc. G.
30	3	0.2563	0.0854	10	2	0.0860	0.0860
20	3	.1710	.0855	10	2	.0860	.0860
20	3	.1714	.0857	20	4	.1719	.0859
10	3	.0854	.0854	20	4	.1716	.0858
10	3	.0857	.0857	20	4	.1721	.0860
10	2	.0856	.0856	30	4	.2579	.0860
10	2	.0860	.0860	30	4	.2577	.0859
10	2	.0858	.0858	40	4	.3432	.0858
10	4	.0859	.0859	..	.	....	.....
10	4	.0859	.0859	...	.	....	....
10	4	.0860	.0860	..	.	....	.....
						Av.	0.08575

From the above values it is seen that with 5 to 10 cc. of 6 *N* hydrochloric acid, and with 2 to 4 g. of potassium iodide the method is satisfactory for quite large amounts of vanadium. However, in the presence of over 0.2 g. of vanadium pentoxide the end-point is not quite so sharp owing to the more intense blue of the vanadyl solution. It is still sensitive to one drop of 0.1 *N* thiosulfate, however.

TABLE III

EFFECT OF VARYING THE TIME OF STANDING AND KINDS OF ACID USED

Time of standing Min.	6 *N* acid Cc.	KI G.	V_2O_5 found G.	Time of standing Min.	6 *N* acid Cc.	KI G.	V_2O_5 found G.
5	5[a]	2	0.0854	1	2	2	0.0824
5	5	2	.0853	5	1	2	.0851
5	5	2	.0856	5	1	4	.0855
5	5	4	.0857	5	5[b]	4	.0858
5	5	4	.0857	5	10	4	.0858
1	2	4	.0856	1	5[c]	2	.0057
1	2	2	.0819				

[a] HCl. [b] H_2SO_4. [c] $HC_2H_3O_2$.

In Table III, all samples had an initial volume of 10 cc. (0.0856 g. of vanadium pentoxide). The additional variables of time of standing after the addition of acid and iodide before diluting and kinds of acid are also shown.

From this it is seen that with 5 cc. of 6 N mineral acid, standing does no harm, but it is not necessary. With smaller amounts of acid, a little time must be allowed for the completion of the reaction, but with comparatively larger amounts of potassium iodide it is not so necessary to wait before dilution. Sulfuric acid works as well as hydrochloric acid. Acetic acid cannot be used.

To obtain satisfactory results with this iodimetric method the vanadium must be wholly in the pentavalent form. In view of the susceptibility of vanadium solutions to reduction[9] it often becomes necessary to oxidize the vanadium as a preliminary step. Boiling the acid solution with bromine water will not cause complete oxidation owing to the reversible nature of the reaction. A mixture of nitric and sulfuric acids cannot be used. Substituting phosphoric acid for sulfuric gives somewhat better results, but still they are not entirely satisfactory. The most satisfactory method of oxidation is the use of hydrogen peroxide in alkaline solution. The fact that the excess of hydrogen peroxide can be readily expelled in alkaline solution is attested by the following experiments. Samples of a pure vanadium pentoxide which had suffered slight reduction were weighed out and dissolved in sodium hydroxide solution. A little hydrogen peroxide was added and the solutions were boiled for a few minutes longer than was necessary to cause the disappearance of the yellow color of the pervanadate solution. The cooled solutions were acidified with hydrochloric acid, potassium iodide was added and the titration with thiosulfate was carried out as usual.

Calc.: g. of V_2O_5	0.0117	0.0335	0.0458	0.0856	0.1735
Found	.0118	.0336	.0461	.0854	.1740

The effects of molybdenum, tungsten and uranium on the determination were tried. A blank experiment showed that molybdenum trioxide had no very appreciable effect on potassium iodide when alone, but in the presence of vanadium the results were irregular. When, however, phosphoric acid is substituted for hydrochloric acid, the results for vanadium in the presence of molybdenum are satisfactory. Weighed amounts of

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[9] It was found that evaporation of a standard solution of vanadium pentoxide, which had been made by just neutralizing the sodium bicarbonate solution with a very little hydrochloric acid, caused sufficient reduction to affect the results materially. Even with sulfuric acid in the absence of hydrochloric acid, the danger of reduction is not entirely eliminated. Cain and Hostetter [*J. Ind. Eng. Chem.*, **4**, 252 (1912)] have recorded a similar experience. We have found a slight reduction even by evaporation with a mixture of sulfuric and nitric acids.

pure vanadium pentoxide were dissolved in sodium bicarbonate solution, and these solutions were mixed with various volumes of standard ammonium molybdate solution. The mixed solutions were evaporated to small volume on the steam-bath, small amounts of sodium peroxide were added, and the solutions were boiled to decompose the excess of peroxide. The determinations were then finished in the regular way, except that phosphoric acid was used instead of hydrochloric acid, and a few minutes were allowed for the completion of the reaction after the addition of the iodide before diluting. The results are shown in Table IV.

TABLE IV

MoO_3 taken, g.	0.0457	0.0925	0.1925	0.2050	0.2324	0.4021
V_2O_5 taken, g.	.0832	.0295	.0594	.0402	.1579	.1259
V_2O_5 found, g.	.0831	.0296	.0590	.0400	.1574	.1245

With amounts of molybdic oxide up to 0.02 g. the results are good; above that the error is slight, but noticeable, becoming quite appreciable with 0.4 g. These results indicate that vanadium may be determined iodimetrically in the presence of moderate amounts of molybdenum, when phosphoric acid is used.

In the presence of tungsten the results are slightly low, due probably to occlusion of vanadium by the precipitated tungstic acid. The loss of vanadium pentoxide runs from 0.5 to 1.5 mg.

Uranium interferes seriously with this determination of vanadium. While uranyl salt does not itself oxidize potassium iodide, it interferes with the oxidation of vanadium in alkaline solution with hydrogen peroxide. When the acid solution is made alkaline with sodium peroxide a precipitate of uranyl vanadate is formed, and at the same time a higher oxide of uranium may be formed which is hard to decompose by boiling. When the solution is acidified with hydrochloric acid and boiled to decompose the excess of peroxide, the vanadium is partially reduced.

Summary

The conditions have been established under which vanadium can be conveniently and accurately determined iodimetrically.

The necessity for a preliminary oxidation has been pointed out, and the most reliable method for this oxidation has been given.

It has been shown that moderate amounts of molybdenum do not interfere when proper precautions are taken. Tungsten renders the results somewhat low, and uranium interferes decidedly with the method.

MINNEAPOLIS, MINNESOTA