The
Atomic Weight
of
VANADIUM

THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

BY

D. J. McADAM, JR.

WASHINGTON, PA.

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INTRODUCTORY.

In this laboratory, use has frequently been made of dry hydrochloric acid gas in making various separations, and in several atomic weight determinations.

Smith and Hibbs (J. Am. Ch. S. 16, 578; Zeit. Anorg. Ch. 7, 41) found that vanadium as well as a number of other substances could be completely volatilized from their alkali salts by heating in a current of dry hydrochloric acid gas. It therefore seemed probable that this method might be used in determining the atomic weight of vanadium.

A new determination of the atomic weight of this element would be particularly desirable since the results obtained by previous investigators differ widely.

Historical.

Berzelius, in 1831 (Köngl. Vet. Acad, Handl. 1-65; Ann. Phys. 22, 1-67), made four determinations of the atomic weight of vanadium. In three of these, he reduced V_2O_5 to V_2O_3 by heating in a stream of hydrogen; in the fourth, he reoxidized the V_2O_3 to V_2O_5. As the average of four fairly concordant results he obtained a value which corresponds to 52.46, referred to oxygen as 16. As Roscoe pointed out later, Berzelius' material undoubtedly contained phosphorus, a small trace of which interferes greatly with the reduction of V_2O_5 to V_2O_3. The ammonium molybdate test for phosphoric acid was unknown in Berzelius' time.

Roscoe, in 1867 (Phil. Trans. R. S. 158, 1-27), made four determinations by the method of Berzelius, using material carefully purified in several different ways. The average of the four results was 51.371, but the maximum and minimum differed by nearly one-half of one per cent.

He also obtained a series of nine values by determining the amount of silver required to precipitate the chlorine from vanadium oxychloride, $VOCl_3$. He did not use the proper end point for this reaction, but the final results would not be affected very much by this error; loss of chlorine on the treatment of the $VOCl_3$ with water was probably a more serious source of error.

In still another series of eight experiments, Roscoe weighed the silver chloride obtained from a known weight of vanadium oxychloride. He does not mention any correction for the solubility of the silver chloride in the wash water. If this was neglected, his value for the percentage of the chlorine is too low, and consequently his value for the atomic weight is too high. The variation in the percentage of chlorine in these seventeen experiments is from 60.86 to 61.55, or about 1.13 per cent. This, of course, means a variation of 1.13 per cent. in the calculated molecular weight of $VOCl_3$; and, since the atomic weights of oxygen and chlorine are assumed to be known, all this variation would apply to the vanadium alone, and would amount to about 3.4 times 1.13 or 3.84 per cent. For example, the maximum calculated value for the atomic weight would be 52.39, and the minimum, 50.44. The average of his results by both methods is 51.24.

For over forty years, our knowledge of the atomic weight of this element rested entirely on the work of Roscoe. Within the last year, however, two articles on the atomic weight of vanadium by Wilhelm Prandtl and Benno Bleyer have appeared. (Zeit. Anorg. Chem. 65, 152 and 67, 257.) These authors have used the same methods that were used by Roscoe, but have used great care in avoiding the sources of error in the work of the earlier author.

The vanadium oxychloride was carefully purified, and kept out of contact with air until it had been weighed.

Moreover, on treatment of the oxychloride with water, they reduced the vanadium to the valence of four by means of pure zinc, and thus avoided loss of chlorine.

In order to make allowance for the solubility of silver chloride in water, they prepared twelve wash waters and used them in regular order. These were prepared by washing the silver chloride precipitated in the first experiment in each series, the twelve filtrates being preserved in the same order in which they were obtained.

In the first article published by Prandtl and Bleyer are given the results of two series of experiments by this method. In series I, consisting of five determinations (the first one being, of course, rejected), the average percentage of chlorine obtained from the oxychloride was 61.3095 ± 0.0158; the maximum was 61.352 and the minimum 61.284, a variation of 0.11 per cent. This variation when applied to the vanadium content would be multiplied by 3.4, making 0.37 per cent. variation in the calculated values for the atomic weight. The average value for the atomic weight in this series is given as 51.133 ± 0.013. The authors, however, have overlooked the fact that the probable error in the percentage of chlorine must be multiplied by 3.4 to give the probable error in the atomic weight of vanadium. So it should be ± 0.044 instead of ± 0.013.

In series II, consisting of six determinations, the average percentage of chlorine was 61.3696 ± 0.0098, the extremes being 61.405 and 61.348, a variation of 0.093 per cent.; this would correspond to a variation of 0.316 per cent. in the atomic weight. The average value for the atomic weight in the series is 50.963, and the probable error, as before, should be multiplied by 3.4, giving ± 0.027 instead of 0.008. As a mean of the two series they get 51.048 ± 0.010, but it should be ± 0.034.

In the second article, by the same authors, they have a third series of four accepted values varying from 61.301

to 61.333 for percentage of chlorine. As an average for the thirteen accepted values in the three series, they obtain 51.061 for the atomic weight.

In the same article, these authors have recorded the results of four determinations by the method of Berzelius. In this series, they obtained results that are considerably higher, giving an average of 51.374 ± 0.033. But they found that the V_2O_3 takes up oxygen so rapidly that the weight of the compound cannot be obtained with any certainty. It is, therefore, probable that the observed weights of V_2O_3 are too great, and consequently the calculated values for the atomic weight of vanadium are too high.

The discrepancies in the results of their careful investigation have thus made more evident the need for a redetermination of the atomic weight of vanadium by a new method.

Method and Apparatus.

The salt of vanadium used in these experiments was sodium meta-vanadate ($NaVO_3$), the most stable of the vanadates of sodium. Some attempts were made to use other vanadates of sodium, but all except the meta-vanadate were found to be unstable or indefinite.

The meta-vanadate was heated in hydrochloric acid gas in order to drive out the vanadium and leave sodium chloride. Since hydrochloric acid has a tendency to reduce vanadates, it seemed probable that a mixture of hydrochloric acid and chlorine would drive out the vanadium more readily than the hydrochloric acid alone. Experiments proved that the presence of a small proportion of chlorine had a good effect.

The apparatus was constructed entirely of glass, with connections of ground glass or sealed by sulphuric acid. The arrangement of the gas generators and drying apparatus is shown in Fig. 1.

In the vessel A, the hydrochloric acid gas is generated by allowing concentrated sulphuric acid to drop into strong hydrochloric acid solution. In B, the chlorine is generated by allowing hydrochloric acid to drop into the flask containing pure potassium permanganate moistened with water. C, C, are drying vessels containing sulphuric acid.

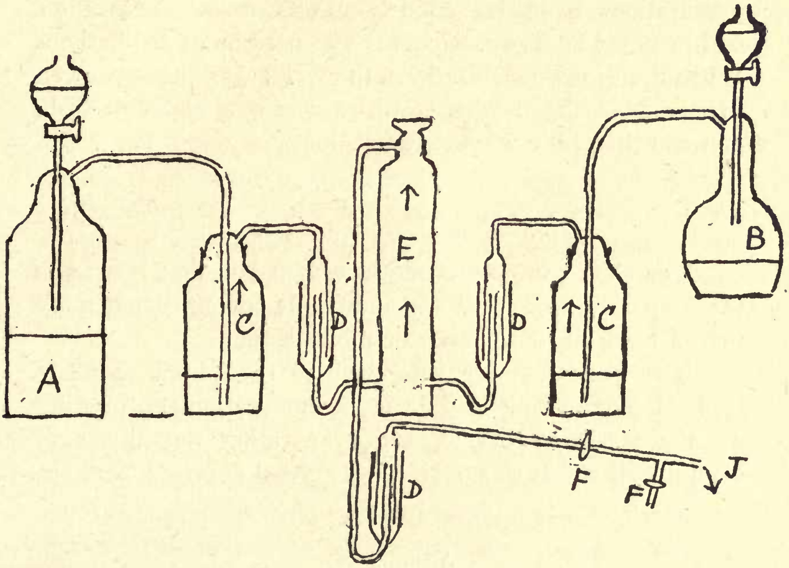

FIG. 1

D, D, D are connectors in which sulphuric acid is placed so as to make the connection air tight. E is a drying tower containing glass beads moistened with sulphuric acid. F, F are stop-cocks so arranged that the gas from the generators can be shut off and a current of pure air substituted.

Several modifications were made in the apparatus containing the sodium vanadate, before the best form was obtained. These are shown in Figs. 2 and 3.

PREPARATION OF PURE MATERIAL.

Water.

The distilled water of the laboratory was redistilled once from alkaline permanganate, rejecting the first fourth of the distillate. It was then redistilled twice more, the last time with a block tin condenser; in some of the later preparations a quartz condenser was used. The water seal invented by T. W. Richards was used in all distillations. When used for crystallizations, the water was either allowed to run from the condenser directly into a platinum dish, or was collected in a quartz flask.

Sodium Meta-Vanadate.

The chief source was the iron vanadate that is used in the preparation of ferro-vanadium. It contained not more than a trace of phosphorus or molybdenum.

The iron vanadate was changed to sodium vanadate by boiling with caustic soda or sodium carbonate, filtering off the ferric hydroxide, and evaporating the filtrate to crystallization. It was purified by several different methods.

Sample A.

A mixture of vanadic acid and acid vanadates of sodium was boiled with a slight excess of C. P. sodium carbonate. It was then recrystallized five times in glass from ordinary distilled water, and twice in platinum from twice distilled water. The crystallization was carried on in a room free from acid fumes, so no special precautions were taken to keep the material out of contact with the air of the room. The sample was dried and preserved in porcelain dishes in a desiccator, over sulphuric acid that had been boiled with ammonium sulphate.

Sample B.

Some meta-vanadate containing phosphates was recrystallized a few times, rejecting the first crop of crystals each time. The phosphate was thus almost completely removed. The partially purified meta-vanadate was now recrystallized six times in glass and once in platinum from twice distilled water, being drained by suction each time.

It was next crystallized six times more in platinum by dissolving in hot water, cooling, and distilling into the dish some twice distilled alcohol. The substance separated out in small crystals and settled rapidly, leaving a large volume of liquid, which was poured off. It was then recrystallized twice from water by allowing the crystals to form slowly without stirring; for each crystallization several weeks were required, and considerable liquid was left, which was poured off. The substance was dried and kept for about two years in a desiccator over caustic soda.

Sample C.

Some sodium vanadate, which had been crystallized several times, was recrystallized twice more in porcelain, from ordinary distilled water. It was then recrystallized in platinum three times from ordinary distilled water and three times from thrice distilled water. It was kept in a desiccator over caustic soda during crystallization.

Centrifugal drainage was used in the last five crystallizations. The centrifugal machine had an arrangement by which the material could be placed in a perforated platinum cone. Not enough time was allowed to each crystallization, consequently the crystals formed in a pasty mass, which did not drain well. This error was avoided in later preparations.

The crystals were now dissolved in hot water and allowed to stand in a desiccator over caustic soda; crystals formed slowly and the remaining liquid was poured off.

The solution was yellow at first, but as crystallization proceeded it became colorless.

The fused material was quite hygroscopic, indicating that it still contained an excess of alkali.

Sample D.

The mother liquor from sample C was put in a desiccator over caustic soda and allowed to evaporate to dryness. A little over two grams were obtained, and this was used later as a test of the neutrality of sample C.

It showed some excess of alkali.

Sample E.

Since sample C still contained excess of alkali, a portion of it was recrytallized twice more with centrifugal drainage, and was washed each time with a little distilled water. The crystallization was allowed to take place slowly, so that the substance was not pasty as in sample C; consequently it drained readily, giving a light yellow filtrate. Contact with the air of the room was prevented as much as possible by keeping it in a desiccator over caustic soda during crystallization.

The material had now been put through eleven crystallizations altogether, and was apparently free from excess of alkali.

While the fused material of sample C was so hygroscopic that it could hardly be weighed to 0.0001 gm. the weight of sample E could be obtained without difficulty to 0.00001 gm.

Sample F.

Crude sodium vanadate was acidified with sulphuric acid, and the precipitated vanadic acid washed repeatedly with distilled water, but it still gave a test for sulphuric acid.

It was then treated with a large quantity of water, and reduced to vandyl oxalate by heating with oxalic acid. A slight excess of ammonium oxalate was added and the double ammonium oxalate crystallized out on evaporation and cooling. After three crystallizations, with drainage by suction, no trace of sulphate could be detected, and the material was probably free from phosphoric and molybdic acids.

By addition of excess of ammonia, a brown precipitate of ammonium vanadate was obtained which was filtered and washed several times. It was then heated to get rid of ammonia, and fused with sodium carbonate. Since the water solution was still greenish, the oxidation was completed by addition of a little sodium peroxide. The analyses of the sodium carbonate and sodium peroxide, according to J. T. Baker, showed the following:

	Na_2CO_3		Na_2O_2
Fe	0.0005%	Fe	0.003 %
Al_2O_3	0.0002%	Al_2O_3	0.001 %
CaO	0.008 %	Cl	0.007 %
SiO_2	0.001 %	SO_3	0.001 %
Cl	0.085 %	Na_2O_2	83.1 %
SO_3	0.001 %	CO_2	0.32 %
H_2O	0.95 %		

The sodium vanadate was now crystallized eight times in porcelain and three times in platinum, from ordinary distilled water, suction being used after each crystallization. It was now practically neutral to phenol-phthalein.

It was next crystallized four times more from thrice distilled water, each time with centrifugal drainage and washing. The last three times the water came in contact with nothing but quartz and platinum. Special precautions were taken to avoid contact with carbon dioxide of the air during the last few crystallizations.

The effect of carbon dioxide of the air could be only slight, but experiments showed that it affects the equilibrium to a certain extent. The gas prepared by the action of dilute sulphuric acid on sodium bicarbonate, washed in a sodium bicarbonate solution, was passed through a vessel containing glass beads moistened with water, and introduced into a nearly colorless solution of meta-vanadate, which it soon turned to a deep orange red. The equation might be represented as follows:

$$4NaVO_3 + H_2O + 2CO_2 = Na_2V_4O_{11} + 2NaHCO_3.$$

On boiling this orange colored solution, or putting it in a desiccator over caustic soda, the reverse reaction takes place, CO_2 is given off and the solution becomes colorless. If the meta-vanadate contains excess of alkali or sodium carbonate, only a faint yellow color appears on passing in CO_2, since the increased mass of bicarbonate favors the reverse reaction.

Meta-vanadate solutions are usually colorless when hot, and yellow when cold, but an experiment tried on some of the pure material seems to indicate that the yellow color is due to traces of acid vanadate caused by CO_2 of the air. A solution of the meta-vanadate, which was light yellow in color, was heated to boiling in a glass flask. On cooling in contact with air, a yellow color appeared; but, if the flask was stoppered while the liquid was boiling, no color appeared on cooling.

These experiments prove that CO_2 of the air can have no effect on the solutions when they are hot; therefore, its effect would be negligible in preparing sodium meta-vanadate, if the material is kept in a desiccator over caustic soda.

The substance which had thus been put through fifteen crystallizations was cream colored. It was neutral in hot or cold solution to methyl orange, litimus or phenolphthalein. The fused substance was colorless and transparent.

Samples G, H and I have not been finished, but are to be used in later work.

Sample G.

Iron vanadate was boiled with caustic soda, filtered and acidified with sulphuric acid. The preciptated vanadic acid was washed twice with water and then heated with sulphuric and oxalic acids; by this process the vanadium was reduced from the valence five to the valence four, and with the sulphuric acid formed vanadyl sulphate, $V_2O_4\ 3SO_3$. On evaporation, small blue deliquescent crystals were formed, which were filtered from the syrupy liquid with suction. It was crytallized five times in this way.

After the third crystallization, it was tested for phosphoric acid by adding ammonium molybdate and nitric acid, dissolving the reddish brown precipitate in ammonia and adding magnesia mixture, and alternating with ammonium molybdate and magnesia mixture until a yellow precipitate of phospho-molybdate was obtained. The amount was quite small, and a comparison test showed it to be less than 0.1 per cent.

After the fifth crystallization of the vanadyl sulphate, it was dissolved in a large quantity of distilled water, and an excess of sodium carbonate of especial purity, according to J. T. Baker, was added. The brownish precipitate was washed fourteen times with water (in which its solubility is considerable), but it still showed traces of sulphates.

In order to convert it into sodium vanadate, it was now treated with sodium peroxide having the following anaysis, according to J. T. Baker:

Fe..0.005% Al_2O_3..0.001% Cl..0.002% SO_3..none, insoluble matter —— trace, phosphates —— none.

To combine with the excess of alkali, CO_2 was passed into the liquid. The CO_2 was generated by action of sulphuric acid on C. P. sodium bicarbonate, and was washed by passing through three bottles of distilled water. The solution was now evaporated to crystallization and it was necessary to leave it at this point.

Sample H.

The preparation of this sample was begun before any of the others; but, since it was not possible to work at it continuously, the process has extended over several years.

Some C. P. ammonium vanadate from Kahlbaum was treated with ammonium sulpho-cyanide acidified with hydrochloric acid and shaken with ether. A slight pink color appeared in the ether, and became deeper when the solution was reduced by zinc, thus indicating traces of iron and molybdenum.

In order to remove molybdenum, the ammonium vanadate was ignited to drive off ammonia and ammonium chloride, and was dissolved in strong HCl; the excess of the latter was removed by evaporation and the residue dissolved in water and filtered. The liquid was now saturated with H_2S and heated in a 2½ liter pressure flask at 85°C. for several hours. A brown precipitate appeared, which was principally V_2S_5 and should contain all the molybdenum.

The next process was to remove traces of arsenic. The blue filtrate from the molybdenum sulphide was evaporated and oxidized with nitric acid. It was then saturated with ammonia, diluted to four or five liters, and saturated with H_2S; then, from the ammonium sulpho-vanadate thus formed, the vanadium sulphide was precipitated by HCl. The sulphide was washed several times by decantation, dried, and gently heated in a hard glass tube in a current of dry HCl gas. This should remove the arsenic, according to Smith and Hibbs.

The remaining V_2S_5 now gave no test for molybdenum in several grams of material, although the test was delicate enough to show a color with less than 0.0001 gm. of MoO_3.

The vanadium sulphide was next oxidized with redistilled nitric acid and heated to form V_2O_5. In order to volatilize the vanadium and leave behind various impurities, the V_2O_5 was then heated in a hard glass tube in dry HCl gas. (Smith and Hibbs, Jr. Am. Ch. S. 17, 682-686.) The volatile portion was collected in distilled water, evaporated, oxidized with redistilled nitric acid, and heated to form V_2O_5.

The purified substance was now dissolved in redistilled ammonia in platinum vessels and the excess of ammonia boiled off. Acetic acid (which gave no precipitate with H_2S, NH_4OH, $(NH_4)_2\ C_2O_4$ or $(NH_4)_2S$) was added to form the tetra-vanadate, which was precipitated by redistilled alcohol, and the supernatant liquid poured off.

After standing in this way for about two years, it was recrystallized from redistilled water and the liquid removed by centrifugal drainage. It was then boiled with a slight excess of especially pure sodium carbonate until no more ammonia fumes were given off, and evaporated to crystallization.

Sample I.

An acid vanadate of magnesium was prepared by boiling vanadic acid with excess of magnesia, filtering, concentrating the filtrate and adding acetic acid. An orange colored crystalline precipitate was formed, which could be recrystallized by using a very large quantity of water; only a few grams would be obtained from several liters of water. With each crystallization, some of the salt was decomposed into an insoluble acid vanadate, nevertheless, about eighty grams passed through the sixth crystallization.

Owing to the large amount of water used, this ought to be free from impurities. Even after the third crystallization, it gave no test for molybdenum or phosphoric acid, although the original material contained traces. It is intended to convert this magnesium salt into sodium vanadate and use it later.

Hydrochloric and Sulphuric Acids.

For all but the last two experiments, ordinary C. P. acids were used. Since the method of generating the hydrochloric acid gas was a purification in itself, it was thought that the ordinary acids would be sufficiently pure.

If the hydrochloric acid contained any hydrobromic acid, the bromine would be set free and driven out by the action of the chlorine. No arsenic would remain with the sodium chloride in the final weighing, since it is easily volatilized by heating in contact with hydrochloric acid gas. Any sulphur dioxide in the sulphuric acid would be oxidized by chlorine, and remain in the drying vessels.

Nevertheless, in the last two experiments, special hydrochloric and sulphuric acids were used, containing no arsenic, nitric acid, or sulphurous acid, and only a trace of iron, according to the analysis of J. T. Baker.

Balance and Weights.

A Staudinger balance sensitive to 0.00001 gm., was used in these experiments. It was kept in the basement, in a room that was used for no other work. The balance rested on a brick and stone support that was sunk directly into the ground.

The weights were kindly loaned by Professor Franklin, of the Physics Department of Lehigh University. The larger weights were of brass, gold plated, and the smaller weights were of platinum. They were carefully standardized and allowance was made for the buoyancy of the air;

the standardization was repeated several times in the course of the experiments.

All weighings were by substitution, and were corrected for the buoyancy of the air. A counterpoise was always used, of the same size and material as the vessel to be weighed, and the vessel was always left near the balance for several hours before weighing.

Dehydration of the Sodium Meta-Vanadate.

A portion was heated for several hours at 385°C. in a Caries furnace in a current of dry air, and weighed. After being fused and again weighed, a further loss of 0.05 per cent was observed.

The substance melts at a dull red heat and on cooling forms white radiating crystals, slightly hygroscopic. If heated for a time at bright redness, it appears to lose weight continuously, although very slowly. By fusion at dull redness, however, it is easy to get a constant weight.

Specific Gravity of Anyhydrous Sodium Vanadate.

The specific gravity of the fused salt was determined by putting a known weight of the substance into a pyknometer, filling the latter with alcohol, and weighing it.

The weight of alcohol required to fill the pyknometer was 14.593, the weight of sodium vanadate used was 5.4375, the weight of the sodium vanadate and alcohol required to fill the vessel was 18.4335. Therefore the weight of alcohol displaced by the vanadate was $14.593-(18.4335-5.4375)=1.600$. Since the specific gravity of the alcohol was 0.82, the specific gravity of the sodium vanadate is

$$\frac{5.437}{1.600}\times 0.82=2.79.$$

Corrections for Buoyancy of the Air.

The correction for the weight of one gram of sodium vanadate is equal to the weight of 1 c. c. of air multiplied by the difference between the volume of one gram of vanadate and 1 gram of weights.

The temperature varied from 20°C. to 30°C. in the progress of the experiments, but the pressure did not vary much from 750 mm.; the average correction was, therefore, calculated for 25° C. and 750 mm. The weight of 1 c. c. of air under those conditions is 0.00117, the volume of 1 gram of vanadate is 0.358, and of 1 gram of brass, 0.119; therefore the correction for 1 gram of vanadate is $0.00117 \times (0.358 - 0.119) = +0.00028$. For 1 gram of sodium chloride, using the accepted value 2.14 for the specific gravity, the correction is $0.00117\ (0.468 - 0.119) = +0.00041$.

Preliminary Experiments on the Action of Hydrochloric Acid Gas on Sodium Vanadate

Some sodium vanadate of sample A was placed in a porcelain boat, in a glass tube, through which a mixture of hydrochloric acid gas and chlorine was passed. The tube was heated to 385° C. in a Caries furnace, but after several hours the material still showed by its color the presence of vanadium. It was then heated in a combustion furnace for an hour and a half, but still showed a yellow tinge. Nevertheless, it was weighed and the amount of vanadium estimated by the aniline test described later. It was found by this test that 0.0013 gm. of V_2O_5 remained. The corrected weights were:

Wt. of $Na V O_3$	0.8843
" " $Na Cl$	0.4241

Assuming the atomic weights of sodium and chlorine to be 23.00 and 35.46, respectively, this would give 50.90 for the atomic weight of vanadium.

To see if it would be possible to remove all the vanadium by means of HCl gas and chlorine, a still smaller weight of sodium vanadate was used; yet after several hours' heating, the residue still showed a yellow color and the aniline test showed 0.003 gm. V_2O_5. The corrected weights were:

$Na\,V\,O_3$	0.4538
Na Cl	0.2175

This would give 50.97 for the atomic weight.

No importance is attached to these values, for the quantities used were too small.

The aniline test was worked out by Witz and Osmond (Bull. Soc. Chim. (2) 45,309), and is of value in estimating very small quantities of vanadium. It depends on the fact that vanadium salts are easily oxidized and reduced, and therefore can act as oxygen carriers.

If a solution of potassium chlorate is added to a solution of aniline hydro-chloride, heated to boiling and allowed to stand at room temperature, no coloration appears. If, however, a trace of vanadium is present, a color appears, varying from light yellow to black, according to the amount of vanadium present; more than a trace of vanadium will cause a precipitate of aniline black. The sensitiveness is increased by the presence of a small quantity of dilute HCl, but a larger quantity will cause a precipitation of aniline black, even when no vanadium is present

In making this test, a standard vanadium solution was used, containing about 0.0001 gm. V_2O_5 to 1 c. c.; this was used for color comparison, as in the Nessler test for ammonia, and in neutral solution was about as delicate.

Since the vanadium could not all be removed by treatment in a porcelain boat, some trials were made with a Jena glass bulb of the form shown in Fig. 2, a form used by T. W. Richards in some of his work.

G is the bulb containing the vanadium. H, H are extra bulbs to catch any material that may spatter out of G. I, I are flasks containing water, through which the acid fumes and volatile vanadium compounds are drawn by suction. At J the apparatus is connected to the generator at the point marked J in Fig 1. A counterpoise of the same size and shape as the bulb G was used, and the difference in weight was determined by substitution.

The sodium vanadate was fused in a platinum capsule, then powdered and transferred to the bulb, which was held slightly inclined. After weighing the bulb and vanadate, it was heated in a current of hydrochloric acid gas and chlorine. The heat was furnished by Bunsen burners placed the proper distance above and below the bulb; a small flame was also placed under the exit tube and thus any crawling of material prevented.

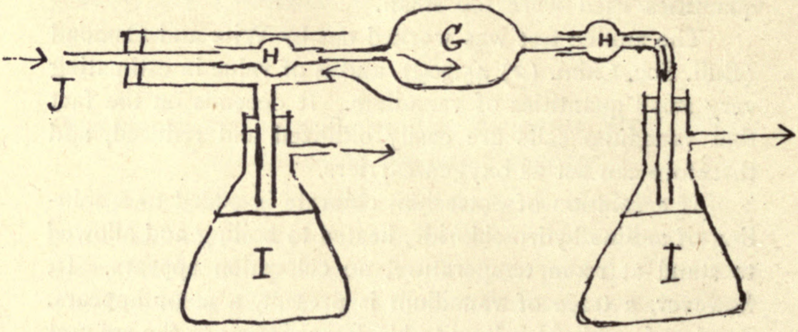

FIG. 2

When as much as possible of the vanadium had been removed, a little water was added to the substance in the bulb and it was again dried in the stream of gas, being rotated at the last, so as to spread the material over the inner surface of the vessel. In this process the sodium chloride first dissolved in the water, leaving the vanadium;

then, as the HCl was passed in, the vanadium dissolved and the sodium chloride crystallized out. As the liquid evaporated the vanadium compound was left at the surface, where it could be attacked by the gases. The process was thus a combination of crystallization and distillation.

After three or four of these treatments, the vanadium could all be driven out of more than five grams of vanadate, leaving a perfectly white residue, which gave no indication of vanadium by the aniline test.

After displacing the hydrochloric acid gas by air, the sodium chloride was heated nearly to fusion, and this was repeated until the weight was constant.

It was found, however, that there are two disadvantages to this form of apparatus. The fused sodium vanadate, which is slightly hygroscopic, takes up a little moisture while it is being pulverized and transferred to the bulb. It does not give up all of this moisture even after standing over night in a desiccator; experiment showed that seven grams of vanadate retained 0.0025 gram of moisture or 0.035 per cent. But the most serious disadvantage was that the sodium chloride decrepitated, when heated, and a small quantity was thrown out of the vessel into the extra bulbs H.

Nevertheless, three experiments were made with this form of apparatus, using material of sample A. In each case 0.035 per cent. was subtracted from the observed weight of sodium vanadate to make allowance for moisture, and any sodium chloride thrown out by decrepitation was weighed and its weight added to that of the main quantity. The results are given in the following table:

	Weight, $NaVO_3$.	Weight, NaCl.	Molec. Wt. $NaVO_3$.	Atomic Wt., Vanadium.
(1)	4.8850	2.3393	122.08	51.08
(2)	5.5793	2.6691	122.20	51.20
(3)	5.6975	2.7244	122.23	51.23
		Average		51.17

Not much importance, however, is attached to this value on account of the uncertainty of the corrections. So, in order to avoid these sources of error, an apparatus of the form shown in Fig. 3 was devised, and it finally proved satisfactory.

K is the flask containing the sodium vanadate. The small bulbs on the inner and outer vessels prevent loss by decrepitation; and, by means of a platinum wire fastened around it at L, the flask may be suspended vertically for weighing. M is a quartz dish to support the flask while being heated. N is a hard glass tube used as a connector.

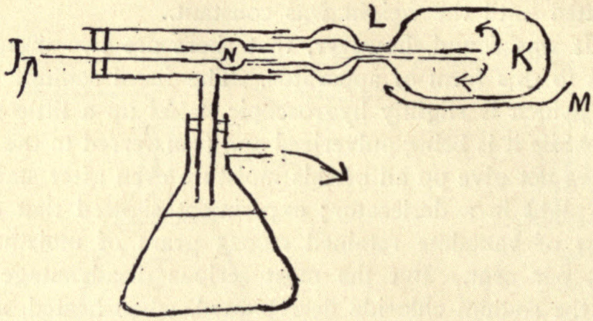

FIG. 3.

In order to get the weight of the sodium vanadate, it was fused in a platinum capsule and rotated just before solidifying, so as to spread the substance in a thin layer. The total weight of capsule, vanadate and a platinum rod was then taken. By means of the platinum rod, the vanadate was then broken up and as much as possible transferred to the flask, which was held vertically. After again heating the capsule and rod, the loss of weight was obtained, which was the weight of the sodium vanadate transferred to the flask.

The heating with hydrochloric acid gas and chlorine was the same as in the experiments with the glass bulb. The quartz dish, M, was heated gently by a Bunsen burner, and two other burners were arranged above the vessel, so as to radiate sufficient heat downward. After about four treatments with the gas, followed each time by adding a little water and again drying in the gas, pure sodium chloride was left. The white color of this substance proved to be a very good indication of its freedom from vanadium. The time required to get all the vanadium out was about thirty hours of actual heating, and seemed to be independent of the quantity of vanadate used.

An attempt was made to use a Jena glass flask, but it cracked at a critical moment, so a quartz flask with straight neck and Jena glass inner tube was next tried. Only one experiment was completed, because the inner tube fused in contact with the quartz, when the sodium chloride was finally heated to fusion. The results of this experiment are recorded under (1) in the Table on page (26). The material used was sample A.

It was necessary to send to Germany and have two quartz flasks made of the form shown in Fig. 3, with both inner and outer tubes of quartz. For this reason the work had to be left for a year.

An advantage of the use of the quartz apparatus is that the sodium chloride could be heated to complete fusion in the vessel and all moisture thus removed. It was found that the fusion caused practically no loss by volatilization, and a quite definite weight for the salt could be obtained. The losses on heating were about as follows: The flask and salt were weighed after fusion of the salt on the edges, then after complete fusion, there would be a loss of 0.0012 gm.

After again fusing it for several minutes to the highest temperature of the blast lamp, there would be a further loss of 0.0001, or sometimes 0.0002 gm. The last weight was taken as correct. The bulb on the inner tube nearly closes the outlet to the flask, when it is held vertically, and this evidently prevents loss by volatilization.

Another quartz apparatus of the same size and shape was used as a counterpoise, the difference in weight by substitution of the flask and counterpoise being taken. On the opposite pan of the balance a quartz dish of the same weight was used as a tare. It was necessary to leave the apparatus in the balance case for several hours before the final weighing was taken. On being transferred from desiccator to balance case, the flask seemed to lose about 0.001 gm. in weight in about an hour; after that the weight would be practically constant. The loss was undoubtedly due to the fact that the flasks were filled first with the dry air of the desiccator and then with the moister air of the balance case.

After getting the final weight of the flask and fused sodium chloride, the flask was rinsed out with distilled water, heated with a blast lamp and again weighed. The difference in weight is recorded in the Table as "loss on rinsing."

In experiment II, there was a slight increase in weight of the flask, and at the same time a slight greenish yellow coloration appeared in the neck of the flask. The yellow color then remained through all the experiments, and the weight of the flask was practically constant, except in experiment IV, where there was a considerable gain in weight of the flask, and an increase in the yellowish color on the neck. The deeper color persisted until the inner surface had been rubbed with a cloth moistened with various reagents, such as acids, ammonia and caustic potash; this treatment caused the color to become lighter and brought the weight back to normal. On heating the neck of the flask with the blast lamp, the yellow color would travel around to the opposite side from the flame, but could not be driven away. Our explanation is that some vanadium vapors were taken up by the quartz in the neck of the apparatus, where the heat was much less than in the body of the flask. By taking the loss in weight on rinsing, this would not cause any error in the results.

The solution obtained by rinsing out the vessel showed a very slight turbidity which looked like silica. In one case, a few shining scales could be noticed, which evidently came from the quartz flask. This was undoubtedly due to the contraction of the fused sodium chloride on cooling; although it was spread as thin as possible, it always broke apart with considerable crackling. The solutions obtained in the last four experiments were filtered through a small filter whose ash weighed 0.00003 gm. After ignition in a platinum crucible, the weight of the silica was obtained.

Just how to apply this correction was somewhat of a puzzle. If the silica came from the quartz vessel, its loss was evidently balanced by other materials absorbed; for the weight of the vessel did not decrease, and yet in one case the corrosion of its walls was observed after rinsing. It was finally decided to assume that the silica came from the vessel, and subtract its weight from the "loss on rinsing." If part of it came from the sodium vanadate, our method of correction would not be far wrong, since the silica would affect the observed weight of sodium chloride over twice as much as that of the vanadate.

In practically all cases the filtrate from the silica was tested for vanadium by the aniline test, and any trace thus indicated was subtracted from the loss on rinsing.

The results of five experiments with quartz apparatus are given in the Table in the order in which they were obtained.

Number		I	II	III	IV	V
Date		1909	1910	1910	1910	1910
Sample		A	B	B	E	F
Color of fused vanadate		Colorless	Nearly colorless	Nearly colorless	Nearly colorless	Colorless
Wt. of $NaVO_3$ in air		4.8550	5.6388	4.4251	5.7789	9.4875
Correction for buoyancy of air		0.0014	0.0016	0.0012	0.0016	0.0027
Wt. of $NaVO_3$ in vacuum		4.8564	5.6404	4.4263	5.7805	9.4902
Excess wt. of counterpoise over flask	before	0.8690	2.1286	2.1282	2.1283	2.1283
	after		2.1282	2.1283	2.1257	2.1282
Excess wt. of flask and Na Cl over counterpoise		3.1876	0.5746	—0.0062	0.6450	2.4187
Loss of Wt. on rinsing		......	2.7028	2.1221	2.7707	4.5469
Wt. of silica		......	0.0006	0.00094	0.0008	0.0009
Wt. of vanadium left		None.	None.	0.00006	0.00005	0.00005
Wt. of NaCl in air		2.3267	2.7022	2.1211	2.7699	4.5460
Correction for buoyancy of air		0.0010	0.0011	0.0009	0.0011	0.0018
Wt. of NaCl in vacuum		2.3277	2.7033	2.1220	2.7710	4.5478
Mol. Wt. of Na VO_3		121.966	121.976	121.946	121.952	121.997
Atomic Wt. of vanadium		50.966	50.976	50.946	50.952	50.997

The average is 50.967 ± 0.006. The atomic weights of sodium and chlorine were assumed to be 23.00 and 35.46, respectively.

The sample used in V had been the most carefully prepared of any in the series, and the amount of material used was so large that the percentage error in the weighing of the sodium chloride would be considerably diminished. So, perhaps, this should be given more weight in making up the average.

The experiments had to be interrupted at this point, but it is intended to make another series at some future time, using from seven to ten grams of vanadate to each experiment.

CONCLUSION.

This series of fairly concordant results, obtained with material prepared in several different ways, proves that sodium meta-vanadate is a definite and stable compound and that it can be prepared free from excess of alkali and from acid vanadates.

The errors which would make our calculated value for the atomic weight too high are: Presence of acid vanadate, silica or moisture in the fused sodium vanadate, and loss of sodium chloride by decrepitation or volatilization.

The errors which would make the calculated value too low are: Presence of excess of alkali in the fused vanadate, and presence of moisture in the sodium chloride.

It is hard to see how our calculated value can be too low, since correction has been applied for silica, and for any vanadium left in the sodium chloride, and the moisture must have been completely removed.

This work in connection with that of Prandtl and Bleyer therefore indicates that the value for the atomic weight of vanadium is about 51.0 instead of 51.2.