[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.[1]]

THE ATOMIC WEIGHT OF VANADIUM.

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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[2] 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,[3] 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,[4] 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 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 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,

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[1] From the author's doctoral thesis.

[2] THIS JOURNAL, **16**, 578; *Z. anorg. Chem.*, **7**, 41.

[3] *Kgl. Vet. Acad. Handl.*, 1–65 (o); *Ann. Physik*, **22**, 1–67.

[4] *Phil. Trans.*, *R. S.* **158**, 1–27 (o).

of course, means a variation in the calculated molecular weight of $VOCl_3$ of 1.13 per cent.; 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.[1] 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 by washing the silver chloride precipitated in the first experiment in each series; the twelve filtrates, in the same order, were used to wash the silver chloride in the remaining experiments of the series.

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 value 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 this 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 51.048 ± 0.034.

In the second article by the same authors, they have a third series of

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[1] *Z. anorg. Chem.*, 65, 152; and 67, 257.

four accepted values, varying from 61.301 to 61.333 for percentage of chlorine. As an average for the thirteen accepted values of all three series, they obtain 51.061.

In the same article are 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 are too high.

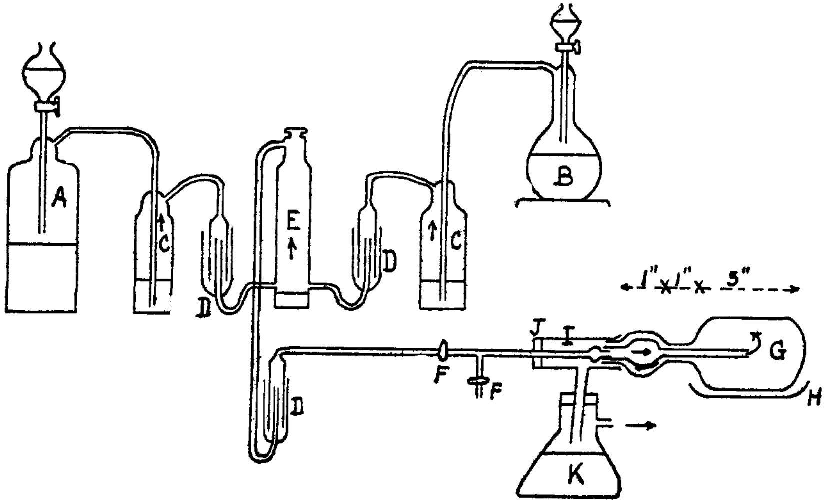
The discrepancies in the results of this careful investigation have thus made more evident the need for a redetermination for the atomic weight of vanadium by a new method.

Method and Apparatus.

The salt of vanadium used in these experiments was sodium metavanadate ($NaVO_3$), the most stable of the vanadates of sodium. Some attempts were made to use other vanadates of sodium, but they were found to be unstable or indefinit.

The metavanadate was heated in hydrochloric acid gas in order to drive out the vanadium and leave sodium chloride. Since the hydrochloric acid has a tendency to reduce vanadates, it seemed probable that a mixture of hydrochloric acid gas 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 gas generators and drying apparatus were constructed entirely



of glass, with connections of ground glass or sealed by sulphuric acid; the vessel in which the sodium vanadate was heated was of quartz.

The arrangement of the apparatus is shown in the figure.

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. 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 stopcocks so arranged that the gas from the generators can be shut off and a current of pure air substituted. G is the flask containing the sodium vanadate; it is supported by the quartz dish H. I is a tube of hard glass. J is a rubber stopper through which the tube from the gas generator passes. K is a flask containing water, through which the acid fumes from the generator are drawn by suction.

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 the platinum dish, or was collected in a quartz flask.

Sodium Metavanadate.—The chief source was 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, and its freedom from phosphorus and molybdenum was tested and proved.

Sample A.—A mixture of vanadic acid and acid vanadate 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 in this sample 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 metavanadate containing phosphate, was recrystallized a few times, rejecting the first crop of crystals each time. The phosphate was thus almost completely removed. The partially purified metavanadate 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 next 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 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 during the last five crystallizations, the material being rotated 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.

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 for the neutrality of sample C.

Sample E.—Since later results indicated that sample C still contained excess of alkali, a portion of it was recrystallized twice more, with centrifugal drainage, and was washed each time with a little distilled water. The crystallization was allowed to take place slowly; so the substance was not pasty as in sample C, and 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 later results indicated that it was free from excess of alkali.

Sample F.—Crude sodium vanadate was acidified with sulphuric acid and the precipitated vanadic acid washed repeatedly with distilled water; it still gave a test for sulphuric acid.

It was then treated with a large quantity of water and reduced to vanadyl 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 vanadite was obtained, which was filtered and washed several times. It was then heated to get rid of ammonia, and fused with sodium carbonate. The water solution was still greenish, so 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 th following:

	Na_2CO_3 Per cent.		Na_2O_2. Per cent.
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
A	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 phenolphthalein. It was next crystallized four times more from thrice distilled water, each time with centrifugal drainage and washing. The last three times the distilled 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. To show the effect of carbon dioxide, the gas was prepared by the action of dilute sulphuric acid on sodium bicarbonate, and passed through two bottles of sodium bicarbonate solution, and thence through a vessel containing glass beads moistened with water. The purified gas was then passed into some of the nearly colorless solution of metavanadate, and soon turned the solution deep orange-red. The equation might be epresented 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, carbon dioxide is given off, and the solution becomes colorless. If the metavanadate contains excess of alkali or sodium carbonate, only a faint yellow color appears on passing in carbon dioxide, since the increased mass of bicarbonate favors the reverse reaction.

Metavanadate 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 carbon dioxide of the air. A solution of the metavanadate, which was light yellow in color, was heated to boiling in a glass flask. On cooling in contact with the 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 carbon dioxide of the air can have no effect on the solutions when they are hot; and therefore its effect would be negligible in preparing sodium metavanadate, 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, litmus or phenolphthalein. The fused substance was colorless and transparent.

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 hydrochlroic 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 gram, 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 Metavanadate.—The powdered substance, when heated for several hours at 385°, still retains about 0.05 per cent. of moisture. It 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 Anhydrous Sodium Vanadate.—The specific gravity of the fused salt was determind by putting a known weight of the substance into a pycnometer, filling the pycnometer with alcohol and weighing it.

The weight of alcohol required to fill the pycnometer was 14.593; the weight of sodium vanadate used was 5.4375, and 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 $5.437/1.600 \times 0.82 = 2.79$.

Corrections for Buoyancy of the Air.

The correction for the weight of one gram of sodium vanadate is equal to the weight of 1 cc. of air multiplied by the difference between the volume of 1 gram of vanadate and 1 gram of weights. The temperature varied from 20 to 30° in the progress of the experiments, but the pressure did not vary much from 750 mm., so the correction was calculated for 25° and 750 mm. The weight of 1 cc. of air under these 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 $0.00117 (0.468 - 0.119) = +0.00041$.

Experiments and Results.

Several modifications of the vessel used to contain the sodium vanadate were tried before a satisfactory form was found.

It was found impossible to remove all vanadium from the vessel unless a fresh surface of material was frequently exposed to the action of the gases. This could be done only by moistening the substance and again drying it. To admit of this treatment, a flask, G, of the form shown in the figure, was designed; the flask and inner tube were made of quartz. The small bulbs prevent loss of sodium chloride by decrepitation.

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 weighed quartz flask, which was held vertically. After again heating the capsule and rod, the loss in weight indicated the amount of sodium vanadate transferred to the flask.

The apparatus was now adjusted and hydrochloric acid and chlorine were passed through the quartz vessel while it was heated. The quartz dish H was heated by a Bunsen burner, and two other burners were arranged above the vessel, so as to radiate sufficient heat downward; a small flame was also placed under the exit tube and thus any crawling of material was prevented.

When as much as possible of the vanadium had been removed, a little water was added to the substance in the flask, and it was again dried in the stream of gas, being rotated at the last in order 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 hydrochloric acid was passed in, the vanadium dissolved and the sodium chloride crystallized out. As the liquid evaporated, the vanadium compound was left on the surface, where it could be attacked by the gases.

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

The aniline test was worked out by Witz and Osmond,[1] 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 hydrochloride, 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 hydrochloric acid, 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 gram V_2O_5 to 1 cc.; this was used for color comparison as in the Nessler test for ammonia, and in neutral solution was about as delicate.

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 vana-

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[1] *Bull. soc. chim.*, (2) **45**, 309.

date used. The white color of the sodium chloride proved to be a very good indication of its freedom from vanadium.

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. The material used was Sample A.

It was necessary to send to Germany and have two quartz flasks made of the form shown in the figure.

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 definit 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. After complete fusion, there was a loss of 0.0012 gram. After again fusing it for several minutes to the highest temperature of the blast lamp, there was a further loss of 0.0001, or sometimes 0.0002 gram. 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 opposit 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 flasks seemed to lose about 0.001 gram in weight in the first 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."

On the second experiment, there was a slight increase in weight of the flask, and at the same time a slight greenish yellow coloration appeared in the neck. The yellow color remained through all the experiments; and the weight of the flask remained practically constant except in experiment IV.

In experiment IV there was a considerable gain in weight of the flask and an increase in the yellowish color on the neck. The increased color persisted until the inner surface of the neck of the vessel had been rubbed with a cloth moistened with various reagents, such as acids, ammonia and caustic potash. This treatment caused the yellow color to fade somewhat and the weight of the flask to become normal.

On heating the neck of the flask with the blast lamp, the 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.

By taking the loss of 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 five experiments were filtered through a small filter whose ash weighed 0.00003 gram; 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 material absorbed; for the weight of the vessel did not decrease, and yet in one case a slight corrosion of its walls was visible. It was finally decided to assume that the silica came from the flask, 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 are given in the table in the order in which they were obtained.

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 of 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.

Number. Date. Sample.	I. 1909. A.	II. 1910. B.	III. 1910. B.	IV. 1910. E.	V. 1910. 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	—0.8609	2.1286	2.1282	2.1283	2.1283
Excess wt. of counterpoise over flask—after	....	2.1282	2.1283	2.1257	2.1282
Excess of wt. of flask, and NaCl 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 $NaVO_3$	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 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 in each experiment.

Conclusion.

This series of fairly concordant results, obtained with material prepared in several different ways, proves that sodium metavanadate is a definit 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 values 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 remaining 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.

The writer wishes to express his thanks to Prof. W. B. Schober, of Lehigh University, for the use of the laboratory and valuable apparatus in part of this work. The valuable assistance of Mr. F. B. Kingsbury and Mr. C. A. Pierle is hereby acknowledged.

PHILADELPHIA, PA.

[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES BY MEASUREMENT OF LOWERING OF VAPOR PRESSURE.[1]

BY ALAN W. C. MENZIES.

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Among the methods available for measuring the molecular weights of substances in solution, the cryoscopic and the ebullioscopic methods are most commonly used. The method of directly measuring the lowering of vapor pressure due to the dissolved substance has not been commonly applied for molecular weight determination owing, perhaps, to the difficulty of obtaining trustworthy values of vapor pressure by the static method, even when elaborate apparatus is employed. It is proposed in the present paper to describe an apparatus and procedure by means of which, without any thermometer, molecular weights may be simply determind in the laboratory by static measurement of vapor pressure, with an accuracy at least equal to that obtained by the ebullioscopic method.

In 1858 Wüllner,[2] working with aqueous solutions, found the lowering of vapor pressure roughly proportional to the concentration of the dissolved substance. The fact that workers[3] in this field confined their observations to aqueous solution of salts, which are abnormal, prevented the recognition of the underlying regularities until as late as 1886–7. Raoult's work[4] of that epoch is the basis of the present-day cryoscopic and ebullioscopic methods.

Raoult used a barometer tube, static method for measuring vapor pressures of solvent and solution. As with all static methods, chief among the sources of error are (1) the difficulty of completely eliminating gaseous and volatil impurities, and (2) the variation of the superficial concentrations of solutions due to evaporation and condensation. Even were it sufficiently accurate, Raoult's apparatus is too cumbrous for every-day use in molecular weight determination.

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[1] Read before the American Chemical Society, Dec. 31, 1909.

[2] *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[3] For example, Pauchon, *Compt. rend.*, **89**, 752 (1879); Tammann, *Wied. Ann.*, **24**, 523 (1885); Emden, *Wied. Ann.*, **31**, 145 (1887).

[4] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353 (1888); *Ann. chim. phys.*, [6] **15**, 375 (1888).