# PHILOSOPHICAL TRANSACTIONS.

## I. The Bakerian Lecture.—*Researches on Vanadium.*

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### I. INTRODUCTION.

Amongst the physical properties which point out the general relationship and classification of chemical substances, none has so deservedly obtained the confidence of chemists as isomorphism. The vanadium compounds have, however, proved a remarkable and unexplained exception to the conclusions which generally follow from well-ascertained identity of crystalline form.

Rammelsberg[*], and afterwards, more completely, Schabus[†], pointed out the fact that the mineral vanadinite from several localities (a compound of lead vanadate and lead chloride) is isomorphous with apatite, pyromorphite, and mimetesite, minerals consisting of calcium phosphato-fluoride, lead phosphato-chloride, and lead arsenato-chloride, having the formulæ $3(Ca_3 P_2 O_8).Ca Fl_2$; $3(Pb_3 P_2 O_8).Pb Cl_2$, and $3(Pb_3 As_2 O_8).Pb Cl_2$. The crystalline form of all these minerals is an hexagonal prism, terminated by 6-sided pyramids. The angle P: P (terminal) found by Rammelsberg for vanadinite, and by different observers for the other minerals, is as follows:—

| | | | |
|---|---|---|---|
| (1) Vanadinite | 142° 30′; | (3) Pyromorphite | 142° 15′; |
| (2) Apatite | 142° 20′; | (4) Mimetesite | 142° 7′; |

and the relation of the axes

(1) 1:0·727;
(2) 1:0·732;
(3) 1:0·736;
(4) 1:0·739.

So far, indeed, has the isomorphism of these compounds been traced, that in many specimens these minerals have been found to crystallize together in all proportions; and Heddle[‡] describes a crystal in his possession the upper half of which consists of vanadinite and the lower half of pyromorphite.

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[*] Pogg. Ann. Bd. xcviii. p. 249 (1856).

[†] Ibid. Bd. c. p. 297.

[‡] Greg and Lettsom's British Mineralogy, pp. 409–410 (1858).

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We are indebted to the researches of BERZELIUS for almost all we know concerning the chemical relations and composition of vanadium and its compounds. From his celebrated investigation on Vanadium* (1831), the results of which have since been more or less completely confirmed by SCHAFARIK† and CZUDNOWICZ‡, it appears that the formula of vanadic acid is $V O_3$. Hence it is evident that we have here to do with either a case of dissimilarly constituted substances acting as isomorphous bodies and crystallizing together, or else the conclusions of BERZELIUS are erroneous, and the true formula of vanadic acid is $V_2 O_5$, corresponding to the pentoxides of phosphorus and arsenic. The first of these alternatives has been properly accepted by most chemists as the only present solution of the difficulty, inasmuch as the definite experimental data given by BERZELIUS render the assumption of any other formula but $V O_3$ for vanadic acid perfectly gratuitous in the absence of experiments proving these data to be erroneous.

BERZELIUS based his conclusions on the following experiments, viz. (1) the constant loss of weight which vanadic acid undergoes on reduction in hydrogen at a red heat; (2) the action of chlorine on this reduced oxide, when a volatile chloride is formed and a residue of vanadic acid remains, which is found to be exactly one-third of the quantity originally taken for reduction in hydrogen. Hence BERZELIUS concludes that the number of atoms of oxygen in the oxide is to that in the acid in the proportion of 1 to 3; so that (assuming the lowest oxide to contain one atom of oxygen) the acid contains three atoms, a result which BERZELIUS finds borne out by its capacity of saturation. The question whether the acid contains one or two atoms of metal BERZELIUS decides in favour of the former view, by finding that no compound corresponding to the alums is formed when vanadic acid is brought together with sulphuric acid and potash. The analyses of the volatile chloride made both by BERZELIUS and SCHAFARIK confirm this conclusion, and place beyond all doubt the fact that, if the atomic weight of vanadium be taken to be 68·5 and $O=8$, the formula of vanadic acid is $V O_3$, that of the oxide prepared by reduction $V O$, and that of the chloride $V Cl_3$.

In the present communication I shall show that, whilst confirming these fundamental results in every particular, I still arrive at a totally different conclusion from BERZELIUS respecting the constitution of vanadic acid, and all the other vanadium compounds; for I shall prove that the true formula of vanadic acid is $V_2 O_5$ (when $O=16$), and the true atomic weight of vanadium 51·3, inasmuch as the substance supposed by BERZELIUS to be vanadium is not the metal but an oxide with an atomic weight of 67·3, nearly that of BERZELIUS's metal, whilst the supposed terchloride is an oxychloride.

The following are the grounds upon which I base my conclusions; the experimental proofs are contained in the sequel:—

(1) An oxide of vanadium exists which unites with three atoms of oxygen to form vanadic acid. Hence this latter substance must contain more than three atoms of oxygen.

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* POGG. Ann. Bd. xxii. p. 1 (1831).

† Ann. Ch. Pharm. cix. p. 84 (1859).

‡ POGG. Ann. Bd. cxx. p. 33 (1863).

(2) The following vanadium oxides have been obtained both in the dry and wet way, and their compositions determined:—

*(1) $V_2O_2$, vanadium dioxide, or divanadyl . . . . = 134·6
(2) $V_2O_3$, vanadium trioxide (Berzelius's suboxide) = 150·6
(3) $V_2O_4$, vanadium tetroxide . . . . . . . . = 166·6
(4) $V_2O_5$, vanadium pentoxide (vanadic acid) . . . = 182·6

(3) The so-called terchloride of vanadium ($VCl_3 . V=67·3$) contains oxygen; it is an oxychloride having the formula $VOCl_3$ ($V=51·3$); it may be called vanadyl trichloride, or vanadium oxytrichloride, and corresponds to $POCl_3$, phosphorus oxychloride.

(4) Three other solid oxychlorides exist, having the composition

(1) $VOCl_2$, vanadyl dichloride, or vanadium oxydichloride.
(2) $VOCl$, vanadyl monochloride, or vanadium oxymonochloride.
(3) $V_2O_2Cl$, divanadyl monochloride.

(5) All the native vanadates are tribasic:—

(*a*) Vanadinite from Zimapan, analyzed by Berzelius (Pogg. Ann. Bd. xxii. p. 63), contains nearly three equivalents of lead oxide to one of vanadium pentoxide.

(*b*) Eusynchnite, analyzed by Czudnowicz (Pogg. Ann. Bd. cxx. p. 27), contains three equivalents of a mixture of lead and zinc oxides to one of vanadium pentoxide.

(*c*) Arœoxene, analyzed by V. Kobell (Journ. für. Chem. Bd. l. p. 496), was found to have a similar composition to eusynchnite.

(*d*) An American vanadinite, analyzed by Smith (Journ. Pr. Chem. Bd. lxvi. p. 433), is a tribasic compound.

(*e*) Dechenite from the Pfalz is, according to Brush (Sill. Am. Journ. series 2, vol. xxxiv. p. 116), identical with Arœoxene, and therefore a tribasic compound.

(*f*) Volborthite, according to Credner's analysis (Pogg. Ann. Bd. lxxiv. p. 546), also contains one of vanadic acid to three of basic oxide.

(6) Vanadic acid fused with sodium carbonate displaces three molecules of carbon dioxide, showing that normal or ortho-sodium vanadate is tribasic, the formula of this salt being $Na_3VO_4$.

(7) The so-called monovanadates are salts corresponding to the monobasic phosphates, and may be termed metavanadates; thus, $NaVO_3$, $NH_4VO_3$, $Ba2VO_3$. The so-called bivanadates are anhydro-salts, similar in constitution to the anhydro-salts of chromic and boric acids.

* [I had originally intended to call the first and third oxides vanadium monoxide and dioxide respectively, giving to these substances the simplest empirical formulæ $VO=67·3$ and $VO_2=83·3$, as it is as yet uncertain whether the molecular weights of these oxides, in accordance with the law of even atomicities, are multiples of the above, or whether, as in the only similar case, that of the nitrogen oxides, they are represented by the above numbers themselves. Acquiescing in the opinion expressed by several chemists that the former alternative is the most probable, I have now adopted the names as they stand in the text.—Jan. 20, 1868.]

(8) Vanadium nitride has been prepared, which, on analysis, was shown to contain 51·3 parts by weight of vanadium to 14 parts of nitrogen.

All the reactions according to which vanadic acid was supposed (BERZELIUS, RAMMELSBERG, SCHAFARIK, &c.) to contain three atoms of oxygen with an atomic weight $V=67·3$ can equally well be explained when $V_2O_5$ ($V=51·3$) is taken to represent the composition of this substance. That this is the case is seen from the following:—

| | Berzelius's formulæ.<br>($V=68·5$. $O=8$.) | New formulæ.<br>($V=51·3$. $O=16$.) |
|---|---|---|
| (1) | $VO_3+H_2=VO+H_2O_2$ | $V_2O_5+2H_2=V_2O_3+2(H_2O)$ |
| (2) | $3(VO)+Cl_6=VO_3+2(VCl_3)$ | $3(V_2O_3)+6Cl_2=V_2O_5+4(VOCl_3)$ |

## II. OCCURRENCE AND PREPARATION OF THE VANADIUM COMPOUNDS.

1. The sources of vanadium, although numerous, have up to the present time yielded the compounds of this metal in such extremely small quantities that vanadium salts may still be counted amongst the greatest of chemical rarities; and consequently the satisfactory investigation of their properties has proved so difficult that contradictory statements, concerning even fundamental points, are made by recent experimenters. My attention was directed some time ago to the occurrence of vanadium in some of the copper-bearing beds of the Lower Keuper Sandstone of the Trias, worked at Alderley Edge and Mottram St. Andrews, in Cheshire; and I was fortunate enough to secure a plentiful supply of this rare metal by the purchase of a lime precipitate containing vanadium which had been obtained as a residue in the extraction of cobalt from the cobalt-bed sandstone at Mottram, by the Alderley Edge Copper Mining Company. The geological features of the remarkable deposit of metallic salts which occurs in this Keuper Sandstone have been well described by Mr. HULL*. The horizontal beds of sandstone contain copper as blue and green carbonates, lead both as carbonate and as galena, cobalt as black cobalt-ochre, and iron oxides, all in workable quantities, together with arsenic, silver, manganese as dioxide, and barium as heavy spar. The sandstone is of a soft and uniform texture, and is metalliferous to a depth of at least 60 feet; it is coloured variously from green and brown to black, according to the nature of the covering of metallic ore which surrounds the grains of sand. The following arrangement of the beds is given by Mr. HULL:—

| | ft. | in. |
|---|---|---|
| 1. Yellowish sandstone | 4 | 0 |
| 2. Shaly clay with a band of copper-sand at the bottom | 2 | 6 |
| 3. Ferruginous sandstone, with large nodules containing carbonate of lead | 6 | 0 |
| 4. Cobalt bed, laminated sandstone containing earthy cobalt | 4 | 6 |
| 5. White compact sandstone, with carbonate of lead | 5 | 0 |
| 6. Iron-stained sandstone, with cobalt, manganese, and iron | 12 | 0 |

The copper is disseminated throughout the sand in quantities on an average of not

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[*] Geological Magazine, vol. i. p. 65 (1864).

more than from 0·5 to 2·5 per cent.; it is dissolved out by hydrochloric acid, and the metal precipitated from the solution by scrap iron. The lead is contained in small crystals throughout the mass, and is separated from the sand by maceration and washing; some of the rock contains as much as from 30 to 40 per cent. of the ore.

The sandstone from which the vanadium precipitate was prepared possesses a light colour, and contains from 0·1 to 0·3 per cent. of the oxides of cobalt, nickel, and copper disseminated as small black, green, and red specks throughout the mass. After crushing, the metals were dissolved out by hydrochloric acid; bleaching liquor and milk of lime were then added to alkaline reaction; a portion of the copper, together with the whole of the nickel and cobalt, remained in solution, whilst the lead, iron, arsenic (partly derived from the acid used), a little copper, and the vanadium were precipitated. As the Mottram mine is now closed I have been unable to obtain a sample of the above-mentioned sandstone for examination, and therefore I cannot state positively whether the vanadium occurs as vanadinite, although for other reasons I am inclined to think that it does.

The above-mentioned lime precipitate was believed by the manager of the mines to contain about 10 per cent. of copper; but when it was dissolved in acid and the copper thrown down by zinc, the solution still retained a bright blue colour, which I soon recognized as being due to vanadium. A rough analysis of the crude lime precipitate shows that it contains about 2 per cent. of vanadium, together with lead, arsenic, iron, lime, and sulphuric and phosphoric acids.

In order to prepare pure vanadium compounds in quantity from this material, I was glad to avail myself of the kindness of my friends Messrs. ROBERTS, DALE, and Co., who were good enough to place their works at my disposal for this purpose. Three cwt. of the crude material was dried, and then finely ground with four times its weight of coal, and the mixture well furnaced with closed doors for several days until the greatest part of the arsenic had been driven off. The coal having been thus burnt off, the mass was then ground up with one quarter of its weight of soda-ash, and well roasted in a reverberatory furnace with open doors for two days, to oxidize the vanadium to a soluble vanadate; the mass was next lixiviated, and the solution drawn off from insoluble matters: the liquid was acidified with hydrochloric acid, and sulphurous acid was then passed into the solution to reduce the arsenates, when the remaining arsenic was precipitated by sulphuretted hydrogen.

The deep-blue solution thus obtained was carefully neutralized by ammonia (an excess causes much of the vanadium to pass into solution), the precipitated vanadium oxide washed on cloth filters, oxidized by nitric acid, and evaporated to dryness. The well-dried crude vanadic acid was then boiled out with a saturated solution of ammonium carbonate, which left iron oxide and calcium sulphate, alumina, &c. insoluble, and the filtrate evaporated until the insoluble ammonium vanadate separated out. This crude vanadate was then washed with sal-ammoniac solution to free it from soda-salt, and recrystallized. In order to prepare from this salt pure vanadic acid, it was roasted in the air and the powdery acid obtained was suspended in water, into which ammonia gas was passed; the dissolved ammonium vanadate was separated by filtration from a residue containing silica, phosphates, &c., and was crystallized by evaporation in platinum; the pentoxide obtained from this salt was free from phosphorus. Another mode, which was adopted in order to obtain perfectly pure vanadium pentoxide, was to prepare the pure oxychloride, and this, on being decomposed by water, yielded the acid as a fine orange-coloured powder. In order to free this powder from any trace of obstinately adhering silica, it was moistened with sulphuric acid and exposed in a platinum vessel for some days to hydrofluoric-acid gas; after expelling the sulphuric acid and on fusion, a mass of large transparent crystals of chemically pure vanadic acid was obtained.

The vanadium minerals appear invariably to contain more or less phosphorus, and this fact in itself serves to establish the close relationship which exists between these two elements. The complete separation of this substance from vanadium is attended with great difficulty: if much phosphorus is contained with the vanadium, the method which has proved most effectual for its removal is to deflagrate the finely divided impure acid with its own weight of sodium in a well-covered wrought-iron crucible, and wash the resulting mixture of vanadium oxides by decantation until the wash-water ceases to give an alkaline reaction; frequently this operation had to be repeated three times before the molybdenum test ceased to indicate phosphorus. In other preparations, in which the phosphorus had been more completely removed by previous operations, the process described above, of repeated crystallization of the ammonium salt, was found capable of furnishing a product in which no trace of yellow precipitate was produced by molybdenum.

The action of even traces of phosphoric acid on vanadic acid is most remarkable; if present in quantities exceeding 1 per cent. of the weight of the vanadium, phosphoric acid altogether prevents the crystallization of the vanadic acid, and the fused mass possesses a glassy fracture, and a black vitreous lustre; this effect is not produced by the presence of either silica, arsenic, or the lower oxides of vanadium. Still more singular is the protective influence which even traces of phosphoric acid exert upon the reducing action of hydrogen on vanadic acid at a red heat. Thus a mixture of pure vanadic acid with 1 per cent. of phosphorus pentoxide weighing 1·5888 grm., on ignition in a current of hydrogen lost only 0·0007 grm.; if no phosphorus had been present it must have lost 0·2784 grm.

## III. ATOMIC WEIGHT DETERMINATION OF VANADIUM BY REDUCTION OF VANADIUM PENTOXIDE IN HYDROGEN.

The method originally adopted by BERZELIUS for the determination of the atomic weight of vanadium, viz. the reduction of vanadic acid in a current of hydrogen, is perfectly reliable, inasmuch as the reduced trioxide (the suboxide of BERZELIUS) does not undergo any further change when the temperature is raised to a bright-red heat, and the reduction of the pentoxide to trioxide at temperatures much below this is perfectly definite. The number obtained by BERZELIUS according to this method was $V=68·5$; the exact number which the following experiments yield, when calculated on BERZELIUS'S hypothesis, is 67·3.

In the following determinations of atomic weights the quantity of powdered pentoxide employed was always more than 5 grms.* It was placed either in a bent tube of hard glass, which when heated in a magnesia bath was found not to lose more than 0·0001 grm. after repeated ignition and cooling, or in a platinum boat placed in a glass tube.

Before reduction the powdered vanadium pentoxide was gently heated in a current of dry air until the weighings, after two successive operations, were found to be constant. After the reduction, the tube was allowed to cool completely in a current of hydrogen, and this gas was then displaced by a stream of dry air. If the reduced oxide be even slightly warm when it is exposed to the air it absorbs oxygen, suddenly glows, and is superficially converted into a blue oxide; if, however, the oxide be cold, it may be exposed to dry air for some time without change of weight, an experiment in which nitrogen was substituted for air giving results identical with those in which air was used.

In the experiments in which the oxide was contained in the glass tube the latter was carefully stoppered, and allowed to remain for half an hour in the balance-case before weighing; when the platinum boat was used it was carefully withdrawn, with the reduced oxide, from the combustion-tube and placed in a stoppered test-tube for weighing. These precautions are absolutely necessary in order to ensure accuracy, owing to the hygroscopic nature of the trioxide.

The hydrogen employed was most carefully purified and dried; all joints and stoppers in the apparatus were well secured by copper wire and paraffin. The gas passed through solutions of silver nitrate, sodium pyrogallate, caustic soda, and sulphuric acid, and a tube filled with metallic copper kept red-hot during the experiment was placed before the final drying-tube to ensure absence of oxygen. In order to ascertain whether atmospheric oxygen diffused into the apparatus, a weighed tube containing phosphorus pentoxide was attached to the further end of the combustion-tube during an experiment, and allowed to remain for four hours whilst hydrogen was passing through the heated tube; at the end of the operation the drying-tube had gained only 0·0002 grm., proving the absence of diffused oxygen. For the purpose of drying the hydrogen, boiled sulphuric acid alone can be used. In many of the preliminary experiments phosphorus pentoxide was used in the last drying-tube, and in all these cases the reducing action of the hydrogen was not complete, the numbers thus obtained for the atomic weight being all too high. After much labour this was found to be entirely caused by small traces of the light particles of the phosphorus pentoxide, which were invariably carried over, in spite of stoppers of cotton-wool, with the air and hydrogen into the vanadic acid,

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* In order to ensure accuracy, it is absolutely necessary to employ a larger quantity of material than was taken by BERZELIUS. The largest amount which he used was 2·2585 grms. vanadic acid, and the smallest 0·6499 grm. An error of one milligramme on the first weight will produce a variation of ±0·2 in the atomic weight, whilst a similar error on the smaller quantity would throw out the result by ±0·7. If 5 grms. of substance are operated upon the variation arising from a milligramme error is ±0·086.

the presence of the smallest quantity of phosphorus pentoxide rendering, as has been shown, the complete reduction of the vanadic acid impossible. Thus, for example, in two determinations it was found that

(1) 2·9232 grms. vanadium pentoxide yielded 2·4840 grms. trioxide, or V=65·4.
(2) 4·2826 grms. yielded 3·5649 grms. trioxide, or V=55·4.

On testing the residual oxide for phosphorus, the top layer of trioxide in the boat was found to contain phosphorus pentoxide, whereas the lower layers were free from it. In order to show that the reduction in these cases was incomplete, 3·4886 grms. of the reduced oxide from an experiment of the kind was treated in a tube with dry chlorine; when all the chloride had volatilized, the residual vanadic acid was fused and found to weigh 2·165 grms.; if the oxide had been completely reduced, the residual vanadic acid would have weighed 1·407 grm.

No less than nine determinations of atomic weight were made with every possible precaution, in which the results varied from 52·2 to 65·4, owing solely to the employment of drying-tubes containing phosphoric anhydride. As soon as this source of error was removed and a sulphuric-acid tube substituted, the pentoxide was completely reduced to trioxide and the numbers became constant.

The formula of vanadic acid being $V_2O_5$, and that of the oxide obtained by reduction $V_2O_3$, the atomic weight of vanadium is found from the equation

$$x=\frac{8(5b-3a)}{a-b},$$

where $a=$ the weight of vanadic acid taken, and $b=$ the weight of reduced oxide obtained.

*Determination* No. 1.—The vanadic acid used in this and the following determinations was prepared from ammonium vanadate by roasting; the acid thus obtained was found to contain traces of phosphorus and silica. To free it from these substances it was treated as follows: the powdered acid was first deflagrated with its own weight of metallic sodium in an iron crucible, the reduced oxide completely washed by decantation, treated with hydrochloric acid to free it from iron, and oxidized with nitric acid. This vanadic acid was then reduced in a current of hydrogen and converted into the oxychloride by heating in a current of chlorine; after rectification the chloride was decomposed by water, and the resulting powdery acid dried and afterwards moistened with pure sulphuric acid and exposed in a platinum vessel for ten days to the action of hydrofluoric-acid gas. On fusing and cooling this purified acid, dark red transparent crystals, five to six centimetres in length, were obtained, stretching across the bottom of the basin.

| | |
|---|---|
| Platinum boat after first heating in air + tube* | 19·6287 grms. |
| ,, ,, second ,, ,, | 19·6287 ,, |

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* The glass tube and stopper were frequently reweighed to ascertain if the friction of the stopper produced any appreciable diminution of weight. At the end of the series of determinations they were found to have

| | |
|---|---|
| Boat, tube, and vanadic acid after first heating in air 1 hour . . . | 27·368 grms. |
| „ „ „ „ second „ 2 hours . . . | 27·3684 „ |
| „ „ „ „ third „ 2 hours . . . | 27·3684 „ |

Hence weight of vanadium pentoxide taken =7·7397 grms.

After the reduction the weighings were not begun until every trace of water had disappeared; two weighings serve, therefore, to show that a constant weight has been reached.

| | |
|---|---|
| Boat, tube, and reduced oxide after first heating in hydrogen 5 hours . . | 26·0120 grms. |
| „ „ „ „ second „ 3½ hours . . | 26·0114 grms. |

The atomic weight calculated from these numbers, according to the above formula, is V=51·257.

| | |
|---|---|
| *Determination* No. 2.—Platinum boat after first heating in air + tube | 19·6258 grms. |
| „ „ second „ „ | 19·6259 grms. |
| Boat, tube, and vanadic acid after first heating in air 2¼ hours . . | 26·2074 grms. |
| „ „ „ „ second „ 2½ hours . . | 26·2079 grms. |

Hence weight of vanadium pentoxide taken =6·5819 grms.

| | |
|---|---|
| Boat, tube, and reduced oxide after first heating in hydrogen for 3½ hours . | 25·058 grms. |
| „ „ „ „ second „ „ 3 „ . | 25·0569 „ |
| „ „ „ „ third „ „ 3 „ . | 25·0560 „ |
| „ „ „ „ fourth „ „ 3 „ . | 25·0555 „ |

The atomic weight calculated from these numbers is V=51·391

In order to confirm this result, the reduced oxide was roasted in a current of dry air until it again attained a constant weight. The powdery acid obtained was of a very brilliant orange-colour; the following numbers show that the original weight was regained to within 0·0004:—

| | |
|---|---|
| Platinum boat, tube, and vanadic acid after gently heating in a current of air for 14 hours . . . . . . . . . . . . . . . . . . | 26·2075 grms. |
| Ditto, after heating for 3 hours longer . . . . . . . . . . . | 26·2073 grms. |

*Determination* No. 3.—The pentoxide employed for this determination was prepared by the decomposition of another portion of rectified oxychloride by water. It was free from phosphorus, but was not treated with hydrofluoric acid. A hard glass tube heated in a magnesia bath was used in this experiment.

| | |
|---|---|
| Tube after first heating and cooling . . . . . . . . | 38·4666 grms. |
| „ second „ . . . . . . . . . | 38·4667 „ |
| Tube and vanadic acid after heating 1 hour in dry air . | 43·6562 „ |

Hence the weight of vanadium pentoxide taken =5·1895 grms.

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lost 0·0004 grm., a weight perfectly appreciable with the balance employed, but without influence on the results. STAS likewise noticed a regular decrease of weight in a stoppered tube owing to the same cause.

Tube and reduced oxide after heating in hydrogen over three BUNSEN'S lamps 42·7689 grms.

| | | | | | |
|---|---|---|---|---|---|
| First heating in hydrogen gas in combustion-furnace | | | | 42·7678 | grms. |
| Second | „ | „ | „ | „ 42·7511 | „ |
| Third | „ | „ | „ | „ 42·7486 | „ |

The atomic weight calculated from these numbers is V=51·485.

*Determination* No. 4.—The acid used in this experiment was prepared by roasting, and afterwards completely oxidizing with nitric acid, pure ammonium vanadate which had been recrystallized four times, and had been prepared from acid obtained by the decomposition of the rectified oxychloride in water. The acid was free from phosphorus and silica, having been exposed, moistened with pure sulphuric acid*, for several days to the action of hydrofluoric-acid gas in a platinum vessel. Platinum boat and tube (constant weight) 25·2630 grms.

| | | | | | | |
|---|---|---|---|---|---|---|
| Boat, tube, and vanadic acid after | | | first heating in air | | 30·3109 | grms. |
| „ | „ | „ | second | „ | 30·3074 | „ |
| „ | „ | „ | third | „ | 30·3083 | „ |
| „ | „ | „ | fourth | „ | 30·3080 | „ |

Hence the weight of vanadium pentoxide taken =5·0450 grms.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Boat, tube, and reduced oxide after | | | | first heating with hydrogen . | | | 29·4290 | grms. |
| „ | „ | „ | „ | second | „ | „ | 29·4252 | „ |
| „ | „ | „ | „ | third | „ | „ | 29·4244 | „ |
| „ | „ | „ | „ | fourth | „ | „ | 29·4244 | „ |

The atomic weight calculated from these numbers is V=51·353.

On gently roasting the reduced oxide in a current of air, the constant weight 30·3074 grms. was attained; this is within 0·0006 grm. of the original weight of boat, tube, and vanadic acid taken.

The mean of these four determinations is 51·371; hence we may assume the atomic weight of vanadium, as obtained from the reduction of pentoxide to trioxide, to be 51·4 as probably true to within ±0·07.

| | | | | | | |
|---|---|---|---|---|---|---|
| *Determination* | No. 1. | 51·257, | difference | from | mean | −0·114 |
| „ | No. 2. | 51·391 | „ | „ | „ | +0·020 |
| „ | No. 3. | 51·485 | „ | „ | „ | +0·114 |
| „ | No. 4. | 51·353 | „ | „ | „ | −0·018 |
| Mean . . . | | 51·371 | | Mean error | | ±0·066 |

BERZELIUS'S mean number, calculated for $V_2 O_5$, is found to be 52·55 with a mean error of 0·12, whilst the subsequent estimations of CZUDNOWICZ serve only as an approximate control of BERZELIUS'S number, giving a mean of 55·35 with a mean error of 2·33.

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* A special experiment proved that every trace of sulphuric acid is easily expelled from vanadium pentoxide on ignition.

The fact that these older determinations all give a higher number than the above experiments, shows either that the acid was not fully oxidized, or, more probably, that the oxide was not completely reduced. It has already been stated (1) that the presence of the slightest trace of phosphorus prevents the complete reduction of the pentoxide to trioxide in hydrogen, (2) that all the naturally occurring vanadium ores contain phosphorus which can only be detected, when present in small traces, by molybdic acid, a test unknown in BERZELIUS'S time, and (3) that the complete separation of phosphorus from vanadium is attended with great difficulty. Hence we may fairly conclude that the difference of 1·15 in the atomic weight between the above experiments and those of BERZELIUS is due to the presence of small traces of phosphorus in the vanadic acid used by the great Swede.

## IV. THE VANADIUM OXIDES.

The oxides of vanadium of which BERZELIUS determined the composition were three in number:—

1. The suboxide, or lowest oxide, obtained by reducing vanadic acid in hydrogen. This oxide BERZELIUS supposed to contain one atom of oxygen, and gave to it the formula $VO=76{\cdot}5$.

2. Vanadic oxide, to which BERZELIUS gave the formula $VO_2=84{\cdot}5$, founding his view upon the analysis of a hydrated sulphate as well as on that of the precipitated oxide dried *in vacuo.*

3. Vanadic acid, $VO_3=92{\cdot}5$, was shown to contain three times as much oxygen as the suboxide.

BERZELIUS describes several other intermediate oxides, but he did not isolate or analyze any of them.

All these three oxides exist and possess in the main the properties which BERZELIUS assigns to them; they all, however, contain for every one atom of BERZELIUS'S vanadium (68·5) one additional atom of oxygen ($O=16$), with the existence of which he was unacquainted. Besides these oxides, a still lower one has been found containing one atom less oxygen than BERZELIUS'S suboxide, and therefore having the atomic weight of BERZELIUS'S metal; this oxide acts as a radical; it may be termed vanadyl, VO, and may be supposed to exist in the higher oxides.

Thus we have ($V=51{\cdot}3$):—

1. Vanadium dioxide, or vanadyl, $V_2O_2$.
2. Vanadium trioxide (BERZELIUS'S suboxide), $V_2O_3$, or $V_2O_2+O$.
3. Vanadium tetroxide (BERZELIUS'S vanadic oxide), $V_2O_4$, or $V_2O_2+O_2$.
4. Vanadium pentoxide (vanadic acid), $V_2O_5$, or $V_2O_2+O_3$.

1. *Vanadium Dioxide* (*or Vanadyl*), $V_2O_2=134{\cdot}6$.—In its power of uniting with oxygen vanadium surpasses even uranium, as observed by PELIGOT*. Like uranium, the

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* Ann. de Ch. et de Phys. 3 sér. tomes v. & xii.

metal vanadium can be separated from its last atom of oxygen with such extreme difficulty, and the lowest oxide is found to enter as a radical into so many compounds, that to this oxide the name vanadyl (VO) may appropriately be given.

Vanadium dioxide can be obtained in the dry state, as a grey powder possessing a metallic lustre, by passing the vapour of vanadyl trichloride ($VO\,Cl_3$), mixed with excess of hydrogen, through a combustion-tube containing red-hot carbon. Lower solid oxychlorides (see page 25) are found to be deposited in the further portions of the tube, whilst vanadium dioxide remains as a bright grey metallic powder mixed with the charcoal. On strongly igniting this mixture in a current of hydrogen, every trace of chlorine is removed, and a pure mixture of charcoal and dioxide remains.

Vanadium dioxide possesses a grey metallic lustre, dissolves in acids without evolution of hydrogen, and yields a lavender-coloured solution which bleaches strongly. Vanadium dioxide is insoluble in water.

*Preparation* 1. *Analysis* 1.—0·8650 grm. of a mixture of vanadium dioxide and carbon, prepared as described, and freed from chlorine by heating in hydrogen, was treated with hydrochloric acid: the carbon, collected on a tared filter and dried at 120° C., weighed 0·6126 grm.; the filtrate, evaporated to dryness with nitric acid, the residue fused and weighed, yielded 0·3605 grm. of vanadium pentoxide.

*Analysis* 2.—Another portion of the same substance free from chlorine was burned in a platinum boat in a current of oxygen. The carbon dioxide formed was weighed, and the residual vanadium estimated as pentoxide: 0·0996 grm. substance yielded 0·2482 grm. $CO_2$, and 0·0416 grm. $V_2\,O_5$. Therefore the percentage of vanadium dioxide contained in the grey powder is as follows:—No. 1, 105·3; No. 2, 96·1.

*Vanadium Dioxide in solution.*—If the dark-red solution obtained by dissolving finely powdered vanadium pentoxide in strong boiling sulphuric acid be diluted with fifty times its bulk of water and then digested with metallic zinc, the liquid rapidly changes colour under the influence of the nascent hydrogen, passing through all shades of blue and green until, after lapse of some time, it assumes a permanent lavender or violet tint. The vanadium is then contained in solution in the lowest degree of oxidation ($V_2\,O_2=134{\cdot}6$) as sulphate, and this compound absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring-matters as quickly as chlorine itself, and acts far more powerfully than any other known reducing agent. In order to estimate the degree of oxidation of the dissolved vanadium, a standard solution of potassium permanganate was added to the reduced liquid until a permanent pink colour was produced, experiments with vanadium trioxide of known composition (given on page 15) having proved that this point is that of maximum oxidation ($V_2\,O_5$), and that it can be accurately reached provided an excess of sulphuric acid be present*.

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* This method of estimation was proposed and used by CZUDNOWICZ (POGG. Ann. Bd. cxx. p. 37); the results described by him differ, however, altogether from my own. He did not obtain the lavender-coloured solution by the action of zinc, and it is clear that in his experiments the reducing action of the hydrogen was not complete.

The strength of the permanganate solution, prepared from the pure crystals, was accurately estimated by iron and oxalic acid; 1 cub. centim. of standard solution was found to be equal to 0·001413 grm. oxygen as a mean of three well-agreeing experiments; the strength of this solution, as tested from time to time, was found not to vary during the course of the determinations.

*Reduction with Zinc.*—

| | Exp. 1. | Exp. 2. | Exp. 3. |
|---|---|---|---|
| Weight of $V_2O_5$ taken . . . . . . . | 0·1038 | 0·0963 | 0·1672 |
| Cub. centims. permanganate required . | 19·4 | 18·2 | 31·6 |
| Loss of oxygen on 100 $V_2O_5$ . . . . | 26·4 | 26·6 | 26·6 |

The calculated loss of oxygen on 100 vanadium pentoxide, when reduced to the dioxide $V_2O_2$, is 26·3; the mean experimental number is 26·53.

In order to control the foregoing results, a fresh solution of permanganate was prepared; 1 cub. centim. represented 0·001301 grm. oxygen; 0·1397 grm. vanadium pentoxide dissolved in sulphuric acid and completely reduced by zinc required 27·7 cub. centims. of this solution for complete oxidation, corresponding to a loss of 25·8 on 100 parts. In ascertaining the reliability of this method, it was further found that a solution containing 0·1 grm. of vanadium pentoxide dissolved in sulphuric acid became of a permanent pink colour on the addition of 0·3 cub. centim. of permanganate solution; also that 5 grms. of zinc dissolved in sulphuric acid and diluted to the same strength as in the determinations, required only one drop of permanganate solution to produce the permanent pink tint.

*Reduction with Cadmium and Sodium Amalgam.*—If solutions of vanadium pentoxide in sulphuric acid be reduced by cadmium (platinum scraps being added to facilitate the evolution of hydrogen), or by an amalgam of sodium, the ultimate result is the formation of the lavender-coloured solution of the dioxide. Thus:

| | Reduction by cadmium. | Reduction by sodium amalgam. |
|---|---|---|
| Weight of $V_2O_5$ taken . . . . . . . . . . . | 0·0897 | 0·0681 |
| Cub. centims. permanganate required (1=·001413) | 16·4 | 12·8 |
| Loss of oxygen on 100 $V_2O_5$ . . . . . . . . . | 25·8 | 26·6 |

The mean of these six determinations gives 26·3 as the loss on 100 parts of vanadium pentoxide, exactly corresponding to the calculated numbers.

The salt formed by the reducing action of hydrogen in presence of the above metals and sulphuric acid is doubtless a vanadium sulphate, that is, sulphuric acid in which the equivalent quantity of hydrogen is replaced by the metal. I have yet to determine the composition of these salts. When ammonia or caustic potash is added to the lavender solution, a brown-coloured precipitate, probably of vanadium hydroxide, is formed, and this instantaneously absorbs oxygen.

On allowing the neutralized lavender solution to stand exposed to air for a few seconds the colour changes to a deep chocolate-brown; so rapid, indeed, is this change of colour, when nearly the whole of the free acid is neutralized by zinc, that such a lavender solution may serve as a reagent for the detection of free oxygen not inferior in delicacy to an alkaline pyrogallate. When a current of air is passed through the lavender solution of sulphate in presence of excess of acid, oxygen is absorbed, the colour of the liquid gradually changes to a bright and permanent blue, and the vanadium is contained in solution as tetroxide, two atoms of oxygen having been taken up (see tetroxide, page 16). If the free acid contained in the lavender solution of vanadium sulphate be completely neutralized by zinc and air passed through, the liquid assumes a permanent brown colour, which on addition of acids turns green, and the vanadium is contained in solution as trioxide (see trioxide, page 15). The point of the reduction at which the bleaching action commences is easily ascertained by testing the liquid from time to time with litmus paper. The changes in colour which the sulphuric-acid solution of vanadium pentoxide undergoes when treated with zinc may be divided into seven stages.

| Stage. | Colour. | Reaction. | State of oxidation of the metal. |
|---|---|---|---|
| 1 | Green ............ | Acid ............ | Vanadium pentoxide to tetroxide. |
| 2 | Bluish green ...... | Acid ............ | Vanadium pentoxide to tetroxide. |
| 3 | Blue ............ | Acid ............ | Vanadium tetroxide. |
| 4 | Greenish blue ...... | Acid ............ | Vanadium tetroxide to trioxide. |
| 5 | Green ............ | Bleaches slightly .. | Vanadium trioxide to dioxide. |
| 6 | Bluish violet ...... | Bleaches strongly .. | Vanadium trioxide to dioxide. |
| 7 | Lavender or violet .. | Bleaches strongly .. | Vanadium dioxide. |

This shows that the bleaching action commences in stage 5 with the formation of the dioxide. A quantitative experiment made in the same way showed that the bleaching action of the reduced solution ceased when to 100 parts of the dioxide 9·5 parts of oxygen had been added; in order to pass completely into trioxide, 11·9 parts of oxygen would have been needed.

The reduction of vanadium to dioxide by means of nascent hydrogen in presence of zinc serves as an easy and accurate method of estimating vanadium when mixed with certain other metals.

2. *Vanadium Trioxide* (the suboxide of BERZELIUS), $V_2 O_3 = 150·6$.—The anhydrous trioxide is obtained, as is well known, by reducing vanadium pentoxide in a current of hydrogen at a red heat. It is perfectly stable up to temperatures approaching a white heat; and even when heated in a current of hydrogen to this temperature the trioxide does not lose weight. 0·411 grm. vanadium pentoxide, when reduced in hydrogen and heated for two hours to whiteness in a wind furnace, yielded 0·366 grm. of black trioxide, the theoretical quantity being 0·368 grm.

In addition to the complete description of the properties of the oxide given by BERZELIUS, I have only to add that it undergoes oxidation, not only rapidly glowing when exposed whilst warm to the air, but likewise slowly when exposed to the air at ordinary temperatures. Black amorphous trioxide, when allowed to stand exposed to the air for some months, undergoes a remarkable change; it takes up an atom of oxygen, and is transformed to small dark indigo-coloured crystals of tetroxide (see page 16).

*Vanadium Trioxide in solution.*—The trioxide is insoluble in acids, but it may be obtained in solution as follows:—If solutions of vanadium pentoxide in sulphuric acid are diluted and treated with excess of metallic magnesium, the changes of colour which are observed when zinc, cadmium, or sodium amalgam are used do not continue beyond the green, and the liquid contains vanadium trioxide in solution.

In order to ascertain the reliability of the method of analysis described, viz. oxidation by means of a standard permanganate solution, a known weight of vanadium trioxide was prepared by reducing vanadium pentoxide in a current of dry hydrogen with the precautions which will be found described under the atomic weights determinations.

The resulting trioxide was placed in a flask containing dilute sulphuric acid and filled with carbonic acid; on the addition of permanganate the black finely divided oxide is rapidly oxidized, dissolving in the acid, and the point of complete oxidation can thus be accurately attained. 0·4043 grm. of vanadium pentoxide thus reduced required 50·4 cub. centims. of permanganate solution (1 cub. centim. = 0·001413 grm. oxygen) for complete oxidation; this corresponds to a gain of 21·35 on 100 parts of trioxide; the theoretical gain in passing from trioxide to pentoxide is 21·24.

The following numbers were obtained by the action of magnesium on the solution of vanadium pentoxide in sulphuric acid (1 cub. centim. standard solution represents 0·001413 grm. oxygen):—

*Reduction with Magnesium.*—

| | Exp. 1. | Exp. 2. | Exp. 3. | Exp. 4. |
|---|---|---|---|---|
| Weight of $V_2O_5$ taken . . . . . . . | 0·0759 | 0·1593 | 0·1025 | 0·1187 |
| Cub. centims. permanganate required . | 9·4 | 19·6 | 13·0 | 15·0 |
| Observed loss of oxygen on 100 $V_2O_5$ . | 17·5 | 17·38 | 17·9 | 17·9 |
| Ditto, calculated . . . . . . . . . | 17·5 | 17·5 | 17·5 | 17·5 |

Solutions of vanadium trioxide can also be obtained by partial oxidation of the lavender-coloured solution of dioxide. If a current of air be passed through a reduced solution in which the free acid has been neutralized by excess of zinc, and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which, on the addition of a few drops of acid, turns to green. Both the brown and green liquids contain trioxide in solution, the dioxide having taken up one atom of oxygen, as the following analyses show:—

(1) 0·1672 $V_2O_5$, reduced by zinc and oxidized by air passing through for one hour, required 21·9 cub. centims. of the foregoing permanganate solution for complete oxidation.

(2) 0·1652 $V_2O_5$, treated in the same way, but exposed for four hours to a current of air, required 21·0 cub. centims. permanganate (1 cub. centim. = 0·001320 grm. oxygen).

Hence 100 parts of vanadium dioxide have absorbed (1) 13·05 and (2) 12·96 parts of oxygen; to pass to trioxide, 11·9 parts are required.

If a few drops of acid are added to the brown solution, which does not undergo change even when air is passed through for several days, it immediately turns green, but does not undergo any alteration as regards its oxygen; thus a brown solution was divided into two equal parts, the one which was oxidized whilst neutral and brown required 12·13 per cent. of oxygen, the other, to which a few drops of hydrochloric acid were added, became at once green and required 10·82 per cent. of oxygen to raise it to $V_2O_5$.

*Action of Chlorine upon Vanadium Trioxide.*—The action of chlorine upon this oxide led **Berzelius** to give to it the formula VO, (V=68·5); but, as has already been stated, the fact that one-third of the vanadium remains in combination with oxygen in the residual vanadic acid follows equally from the formula $V_2O_3$ when V=51·3.

Thus $$3(V_2O_3)+6Cl_2=V_2O_5+4VOCl_3.$$

Two experiments made in order to test the purity of the trioxide prepared by reduction of vanadic acid in hydrogen gave the following results:—

(1) 4·6004 grms. $V_2O_3$, treated with dry chlorine, gave a residue of 1·8307 grm. $V_2O_5$; theoretically it should yield 1·8597 grm.

(2) 0·2686 grm. $V_2O_3$ yielded 0·992 $V_2O_5$, instead of 1·0858 grm.

The composition and constitution of the salts forming the green solution still remain to be ascertained.

3. *Vanadium Tetroxide*, $V_2O_4$=166·6 (the vanadic oxide of **Berzelius**).—The anhydrous tetroxide was obtained by **Berzelius** (Pogg. Ann. Bd. xxii. p. 19) by precipitating the hydrated oxide from a sulphate by sodium carbonate, washing, and igniting *in vacuo* to free it from water. On reducing in hydrogen **Berzelius** found that 0·762 grm. yielded 0·691 grm., or 90·67 per cent. of his "suboxide" ($V_2O_3$, V=51·2); and hence he legitimately concludes that "vanadic oxide has lost as much oxygen as the suboxide contains,—that is, as much as he thought it contained, for $V_2O_4$ yields 90·36 per cent. of $V_2O_3$:

$$V_2O_2+O=V_2O_3,$$
$$V_2O_2+O_2=V_2O_4.$$

The anhydrous tetroxide can also be prepared by the slow oxidation of the black trioxide at the ordinary atmospheric temperature. It possesses an indigo-blue colour, and under the microscope is seen to consist of brilliant blue shining crystals. This remarkable change occurs when the black trioxide is exposed for several weeks to the air, and it has been repeatedly observed. 1·1686 grm. of the blue crystals thus obtained were dried completely under the air-pump, yielded 1·2688 grm. vanadium pentoxide, corresponding to a percentage increase of 8·57: 100 parts of the tetroxide require 9·59 parts of oxygen for conversion into the pentoxide. These blue crystals are anhydrous. A weighed portion of trioxide was exposed to the air and from time to time dried *in vacuo* and weighed. On November 13th, 1866, the weight of the black trioxide was 0·7507; on February 4th, 1867, the colour had changed to a bluish black, and the weight was

0·8112; on March 25th the colour had become blue and the weight of the oxide was 0·8267, showing a percentage increase of 10·13, or an absorption of nearly one atom of oxygen, as 100 of trioxide require 11·87 of oxygen for conversion into the pentoxide. On further exposure the blue oxide increases in weight, again changes colour to a dark olive-green, and a hydrated oxide is formed.

*Vanadium Tetroxide in solution.*—Solutions of the salts of vanadium tetroxide are bright blue as described by BERZELIUS. They may be obtained (1) by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen (probably also oxalic acid, sugar, alcohol, &c.) upon solutions of vanadium pentoxide in sulphuric acid, (2) by the action of a current of air upon the acid solution of vanadium sulphate.

(1) If sulphur dioxide or sulphuretted hydrogen be passed into the yellow solution of vanadium pentoxide in dilute sulphuric acid, the liquid becomes permanently blue, no green or violet colour being obtained by the continued action of these reducing agents. In order to determine the state of oxidation of the metal, these blue solutions were boiled in an atmosphere of carbonic acid until every trace of the reducing agent was expelled, and on cooling standard permanganate was added until the pink tint was noticed.

| | Reduced by $SO_2$. | | Reduced by $SH_2$. | | | |
|---|---|---|---|---|---|---|
| | (1) | (2) | (3) | (4) | (5) | (6) |
| Weight of $V_2O_5$ taken . . | 0·1062 | 0·1106 | 0·1060 | 0·1248 | 0·1489 | 0·1239 |
| Cub. centim. permanganate required (1 cub. centim. =0·0014130) . . . . | 6·7 | 7·0 | 6·8 | 8·3 | 9·5 | 7·9 |
| Loss of oxygen on 100 pentoxide . . . . . . | 8·91 | 8·94 | 8·97 | 9·39 | 9·01 | 9·00 |

Giving a mean loss of 9·03, whereas theory requires a loss of 8·75.

(2) When a current of air is passed through acid solutions of the dioxide a permanent blue colour is attained, two atoms of oxygen have been absorbed, and the solution contains tetroxide.

(1) 0·1149 grm. vanadium pentoxide completely reduced by zinc, and the acid solution oxidized by a current of air passing through for fifteen hours, required 9·5 cub. centims. of permanganate solution (1 cub. centim.=0·001320 grm. oxygen) for complete oxidation.

(2) 0·0919 grm. vanadium pentoxide, treated in the same way, required 6·3 cub. centims. of the permanganate solution for complete oxidation.

Hence 100 of vanadium dioxide has absorbed (1) 20·9 and (2) 23·4 parts of oxygen; in order to pass from the dioxide to the tetroxide 23·78 per cent. is needed. The sulphate obtained by evaporating the blue solution containing this oxide was analyzed by BERZELIUS (*loc. cit.* p. 18), and it may be regarded as a vanadyl sulphate, or sulphuric acid in which hydrogen is replaced by vanadyl.

4. *Vanadium Pentoxide* (Vanadic acid, $V_2O_5$, molec. weight 182·6).—The properties

of vanadic acid have been fully described by BERZELIUS; the only important addition to our knowledge of this oxide made since his time is the determination of the crystalline form (rhombic prisms) made by NORDENSKJÖLD*. In the present communication I propose to discuss the properties and composition of vanadic acid and the vanadates only so far as is necessary for the purpose of elucidating the true atomic weight of the metal.

*Constitution of the so-called Monovanadates.*—The analyses made by BERZELIUS of the ammonium and barium vanadates† suffice to point out the true character of these salts. The formulæ which he there gives, assuming the atomic weight of the metal to be 68·5, show that these compounds must be considered as metavanadates when the atomic weight of the metal is taken to be 51·3.

BERZELIUS'S formulæ. $V=68{\cdot}5,\ O=8$.

Vanadiate of ammonia, $NH_3\,VO_3+HO$.

Vanadiate of baryta, $BaO\,VO_3$.

New formulæ. $V=51{\cdot}3,\ O=16$.

$$NH_4\,VO_3\text{, ammonium metavanadate, or }\left.\begin{matrix}NH_4\\VO\end{matrix}\right\}O_2.$$

$$Ba\,V_2O_6\text{, barium metavanadate, or }\left.\begin{matrix}Ba\\2VO\end{matrix}\right\}O_4.$$

In order to confirm BERZELIUS'S analysis of the ammonium salts, the following analyses were made of the white anhydrous salt obtained by blowing ammonia gas into water containing suspended vanadic acid, and repeatedly crystallizing. The ammonium salt, on careful roasting in a platinum boat in a current of oxygen gas, yielded vanadium pentoxide, which was fused and weighed.

| Nos. | Weight of ammonium salt taken. | Weight of pentoxide obtained. | Percentage of pentoxide found. | Calculated percentage. |
|---|---|---|---|---|
| 1. | 6·8531 | 5·3263 | 77·72 | 77·82 |
| 2. | 2·0445 | 1·5902 | 77·78 | |
| 3. | 2·6129 | 2·0314 | 77·75 | |

BERZELIUS found 77·59 per cent. of vanadic acid. The analysis of the ammonium metavanadate, if accurately made, serves likewise as a check on the atomic weight determinations. If $a$ represent the weight of the salt taken, and $b$ that of the vanadium pentoxide obtained, the atomic weight of vanadium is found from the equation

$$V=\frac{66b-40a}{a-b}.$$

From No. 1. $V=50{\cdot}65$.

From No. 2. $V=51{\cdot}06$.

From No. 3. $V=50{\cdot}82$. Mean result 50·84.

*Constitution of the so-called Bivanadates.*—The bivanadates obtained by the cautious addition of acetic acid to the monovanadates, according to BERZELIUS'S directions, have

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* POGG. Ann. Bd. cxii. p. 160.

† Ibid. Bd. xxii. p. 49.

been analyzed by Von HAUER*. The ammonium and sodium bivanadates were found to correspond with the formulæ $NH_4O.2VO_3$ and $NaO\,2VO_3$, where $V=68\cdot5$ and $O=8$. If we assume $V=51\cdot3$ and $O=16$, these salts will be expressed by the formulæ $(NH_4)_2V_4O_{11}$ and $Na_2V_4O_{11}$; or they may be represented as *anhydro-salts*, either $2(NH_4VO_3)+V_2O_5$ and $2(NaVO_3)+V_2O_5$, or else as $Na_4V_2O_7+3(V_2O_5)$ as an anhydro-salt of sodium pyro-vanadate.

*Constitution of the Normal Vanadates.*—That vanadic acid in its normal state is tribasic is shown by the fact first pointed out by CZUDNOWICZ†, that when vanadium pentoxide is fused with an excess of sodium carbonate three molecules of carbon dioxide ($3CO_2$) are displaced for every molecule of vanadium pentoxide ($V_2O_5$) entering into combination. In an experiment carefully conducted, in which sodium carbonate was heated to redness with 0·4323 grm. of vanadium pentoxide until no further loss of weight occurred, the pentoxide was found to expel 0·3078 grm. carbon dioxide ($CO_2$); this corresponds to a ratio of 2·957 molecules of carbon dioxide to 1 of $V_2O_5$, or nearly in the proportion of 3 to 1. Normal- or ortho-sodium vanadate is $Na_3VO_4$, or $\left.\begin{matrix}Na_3\\VO\end{matrix}\right\}O_3$. Hence there is no doubt that vanadic acid in its normal state acts as a tribasic acid.

It is my intention fully to investigate the constitution and properties of the vanadates at a future time.

## V. VANADIUM OXYCHLORIDES.

1. *Vanadium Oxytrichloride*, or *Vanadyl Trichloride*, $VOCl_3$, molec. weight 173·67 (terchloride of vanadium of BERZELIUS).—The fact that the lemon-yellow-coloured liquid chloride of vanadium prepared by the action of chlorine upon the trioxide does contain oxygen, contrary to the distinct statements of previous experimenters, was ascertained in various ways:—

(1) A few grammes of the lemon-coloured liquid chloride was placed in a bulb attached to a long combustion-tube half filled with pure sugar-charcoal and half with metallic copper. A current of dry hydrogen, purified from oxygen according to the method previously described, was then passed over the bulb and cold tube until every trace of air was expelled; the carbon and copper were then heated to redness, and as soon as the escaping gases had ceased for fifteen minutes to render baryta-water turbid, Liebig's bulbs containing clear baryta-water were attached. The bulb containing the oxychloride, which up to this point had been kept cool, was now warmed, and the chloride distilled into the heated carbon in the tube; as soon as the vapour of the chloride was carried forward by the hydrogen, a dense precipitate of barium carbonate, which effervesced on the addition of hydrochloric acid, was thrown down in the Liebig's bulbs, proving that the liquid contains oxygen and undergoes partial decomposition when mixed with hydrogen and brought in contact with red-hot charcoal.

This experiment was repeated twice with identical results. It is not possible in this

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* Journ. Prak. Chem. Bd. lxix. p. 388 (1856).

† POGG. Ann. Bd. cxx. p. 33.

manner to estimate the quantity of oxygen which the oxychloride contains, as only a small portion of the oxygen combines with the carbon, by far the greater portion remaining in combination with the metal to form dioxide or the lower solid oxychlorides yet to be described.

(2) The vapour of the lemon-yellow chloride was passed over metallic magnesium heated in a current of pure hydrogen; the action was violent, and the metal took fire. On cooling the tube the excess of magnesium was carefully removed, and the boat was found to contain a dark-coloured powder which, on extraction with water, contained both magnesium and chlorine; after repeated boiling with water, hydrochloric acid extracted from this powder large quantities of magnesia, the oxygen of which could only be derived from the vanadyl trichloride.

(3) The foregoing experiment, made with sodium instead of magnesium, showed that a thick crust of caustic soda was formed on the tube close to the boat in which the metal was placed.

(4) The vapour of the liquid oxychloride mixed with pure hydrogen was passed through a red-hot tube; the chloride was decomposed, black shining crystals of vanadium trioxide were deposited in the first portions of the tube, a mixture of lower solid oxychlorides filled up the further portions, and small quantities of a dark-red liquid were formed. The black crystals on analysis were found to be free from chlorine; 0·0860 grm. of these crystals gave on oxidation 0·1051 grm. vanadium pentoxide, or the substance contained 99·2 per cent. of vanadium trioxide.

(5) When vanadyl trichloride is rapidly distilled over heated carbon, or when it is prepared by treating a mixture of trioxide and carbon with chlorine, a dark reddish-brown liquid is formed consisting of a mixture of the oxychloride and another chloride. The analysis of this dark liquid yielded results which, when calculated for chlorine and vanadyl ($VO = 67·3$), always added up to from 103 to 105 per cent. on the quantity taken, showing the presence in this liquid of a vanadium chloride containing no oxygen.

(i.) *Preparation of Vanadyl Trichloride.*—Finely divided vanadium pentoxide is intimately mixed with pure sugar-charcoal, and the mixture heated to redness in a current of hydrogen. After cooling in hydrogen the mixture of trioxide and carbon is removed to a hard glass retort, heated by a large Bunsen's lamp, and a current of dry chlorine gas passed in. The crude oxychloride comes off as a reddish-yellow* liquid, of which 180 grms. were collected in one operation. In order to purify this liquid it is distilled upwards in a current of carbonic acid for several hours, and afterwards rectified several times over clean sodium in a current of carbonic acid, when the sodium becomes coated with a dark substance due to the decomposition of some other chlorides. The liquid gradually assumes a light amber-colour, and on continued distillation it attains a permanent lemon-yellow tint; it began to boil at 126° C., and all came over before 130°.

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* The dark colour of the chloride thus prepared is not due to the presence of vanadic acid as SCHAFARIK supposes, as the acid is insoluble in the chloride, but rather to some dark-coloured vanadium chlorides containing no oxygen.

When perfectly pure the boiling-point was accurately determined with 100 grms. of substance; the temperature corrected for freezing-point of the thermometer and mean temperature of the column was found to be 126°·7 under 767·0 millims. of mercury.

(ii.) Vanadyl trichloride is obtained at once of a bright lemon-yellow colour, and free from the compounds which accompany its formation in the preceding reaction, by passing dry chlorine over the trioxide gently heated. The reaction is as follows, viz.—

$$3(V_2O_3) + 6Cl_2 = V_2O_5 + 4(VOCl_3).$$

The liquid thus obtained requires only to be distilled upwards for a short time in a current of carbonic acid, to remove excess of chlorine and hydrochloric acid, and then rectified once over sodium to obtain the substance chemically pure.

The general properties of vanadyl trichloride have been already described by BERZELIUS.

The specific gravity of this liquid was carefully determined at three temperatures, and found to be—

| | |
|---|---|
| at 14°·5 . . . . | 1·841. |
| 17°·5 . . . . | 1·836. |
| 24°·0 . . . . | 1·828. |

The trichloride remains liquid at temperatures above −15° C. As the coefficient of expansion of this liquid has not been yet determined above 24°, it is not possible to calculate the atomic volume of this liquid, or to compare it with that of phosphorus oxychloride ($PO Cl_3$).

The vapour-density of vanadyl trichloride was determined according to DUMAS's method with the following results:—

| | |
|---|---|
| Weight of bulb and air at 11° C. and under 776·5 millims. . . | 6·5172 grms. |
| Weight of bulb and vapour at 18°·6 C. and 780 millims. . . | 7·0003 grms. |

Residual air =0·0 cub. centim. Capacity of bulb 135·13 cub. centims.

Hence the vapour-density is found to be 88·20 (H=1) or 6·108 (air =1); the calculated density is 86·8 (H=1) or 6·000 (air =1).

*Analysis of Vanadyl Trichloride. Determination of the atomic weight of Vanadium. Method* 2.—The difficulty attending determinations of the atomic weights of the metals from analysis of their volatile chlorides has already been pointed out by PIERRE* in the case of titanium. The errors here referred to, arising from absorption of moisture by these hygroscopic chlorides, may, however, be avoided by sealing up several portions of the chloride for analysis at once from a large mass of liquid.

The following seventeen determinations were most carefully made, and the numbers obtained, closely coinciding as they do with the results of the reduction experiments already given, serve as a most important control of the reliability of the original method.

*Volumetric Determination of the Chlorine.*—Before employing GAY-LUSSAC's method to this determination, it was ascertained that when the chloride is decomposed by water in

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* Ann. de Ch. et de Phys. 3 sér. t. xx. p. 257.

presence of nitric acid and silver solution added, no trace of vanadium goes down with the silver.

Pure silver was prepared with all the precautions detailed by STAS* in his first memoir, and the analyses were conducted in the manner described by him†. The nitric acid was prepared by distilling a large quantity of pure acid until three-fifths had come over; the remainder was then distilled and collected, and on careful testing with silver showed not the slightest indication of chlorine. The distilled water used had been carefully redistilled, and likewise gave no indication of chlorine. The weight of silver to be taken was calculated from a careful gravimetric analysis, and several volumetric determinations were made at one time. The weighed quantity of silver was placed with ten times its weight of pure nitric acid, sp. gr. 1·2, in well-stoppered 300 cubic centimetre bottles, and heated to about 40° C. until all the silver had dissolved. After cooling, the bulb containing the weighed quantity of vanadyl trichloride was brought into the bottle, the bottle closed, and the bulb broken by shaking; distilled water was then added, so that the weight of the whole liquid amounted to from forty to fifty times that of the silver employed. The lower oxides of nitrogen present in solution in the acid reduced the vanadium to a bright blue solution, in which the slightest turbidity of silver chloride could be well seen.

In the volumetric determination of chlorine it has already been noticed, both by GAY-LUSSAC and STAS, that when one or two milligrammes of silver per litre still remain in solution, a turbidity is produced by the addition of both silver and chloride solution. This fact was also observed in the volumetric analyses of vanadyl trichloride; and in order to render the results comparable, the course proposed by STAS was invariably adopted, viz. that of adding the decimal chloride solution until all turbidity ceased. The error thus introduced is, however, extremely small (less than 0·0005), and is counterbalanced by the error arising from a trace of impurity contained in the silver.

In several cases the vanadium in the filtrate was estimated by precipitating the excess of silver, expelling the acid by evaporation, again filtering from the trace of silver chloride which separates out, and evaporating the filtrate to dryness in porcelain, transferring to platinum, oxidizing by nitric acid, and weighing the fused acid.

The following Table contains the results of nine chlorine determinations made according to the above method with trichlorides of various preparations. Nos. 1, 2, 3, and 4 were made with substances of one preparation, Nos. 5 and 6 of a second preparation, Nos. 7 and 8 of a third preparation.

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* Recherches sur les Rapports réciproques des Poids atomiques. Bruxelles, 1860, p. 25.

† Idem, p. 62.

| No. of experiment. | Weight of trichloride taken. | Weight of silver required for complete precipitation. | Percentage of chlorine*. | |
|---|---|---|---|---|
| 1. | 2·4322 | 4·5525 | 61·49 | Analyst A. |
| 2. | 4·6840 | 8·7505 | 61·37 | „ |
| 3. | 4·2188 | 7·8807 | 61·37 | „ |
| 4. | 3·9490 | 7·3792 | 61·39 | „ |
| 5. | 0·9243 | 1·7267 | 61·37 | „ |
| 6. | 1·4330 | 2·6769 | 61·37 | „ |
| 7. | 2·8530 | 5·2853 | 60·86 | Analyst B. |
| 8. | 2·1252 | 3·9535 | 61·11 | „ |
| 9. | 1·4248 | 2·6642 | 61·43 | „ |
| | | Mean result . . . | 61·306 | |

*Gravimetric Determination of the Chlorine.*—As a check on the volumetric analysis, weight estimations were made in the usual way, it having been proved that no trace of vanadium is carried down with the silver in nitric acid-solution.

The trichloride used in these experiments was taken from four different preparations; analyses Nos. 4, 5, and 7 were made from the same sample by two different experimenters.

| No. of experiment. | Weight of trichloride taken. | Weight of silver chloride obtained. | Percentage of chlorine. | |
|---|---|---|---|---|
| 1. | 1·8521 | 4·5932 | 61·33 | Analyst B. |
| 2. | 0·7013 | 1·7303 | 61·01 | „ |
| 3. | 0·7486 | 1·8467 | 61·00 | „ |
| 4. | 1·4408 | 3·5719 | 61·30 | „ |
| 5. | 0·9453 | 2·3399 | 61·21 | „ |
| 6. | 1·6183 | 4·0282 | 61·55 | „ |
| 7. | 2·1936 | 5·4309 | 61·22 | Analyst A. |
| 8. | 2·5054 | 6·2118 | 61·31 | „ |
| | | Mean result . . . | 61·241 | |

The atomic weight of vanadium calculated from the mean (61·276) of the above seventeen determinations is

$$\frac{(106{\cdot}371 \times 100) - (122{\cdot}371 \times 61{\cdot}276)}{61{\cdot}276} = 51{\cdot}29.$$

Taking the mean of the numbers found (1) by the reduction of vanadium pentoxide in hydrogen, viz. 51·37, and (2) by the determination of chlorine in vanadyl trichloride, viz. 51·29, *we have the number* 51·33 *as the mean atomic weight of vanadium.*

*Determinations of Vanadium.*—The vanadium in vanadyl trichloride was directly estimated in some instances (Nos. 1 and 4) in separate portions of the trichloride, whilst in other cases (Nos. 2 and 3) it was estimated in the filtrate from the chlorine determinations.

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* STAS's numbers are here used, viz. O = 16, Ag = 107·93, Cl = 35·457.

| Nos. | Weight of trichloride taken. | Weight of vanadium pentoxide found. | Percentage of vanadium. |
|---|---|---|---|
| 1. | 1·4188 | 0·7368 | 29·20 |
| 2. | 0·7013 | 0·3679 | 29·47 |
| 3. | 0·7486 | 0·3959 | 29·71 |
| 4. | 1·1731 | 0·6252 | 29·94 |
| | | Mean result . . . . | 29·58 |

These results give as the composition of vanadyl trichloride,—

| | | Calculated. | Found. |
|---|---|---|---|
| V | = 51·3 | 29·54 | 29·58 |
| $Cl_3$ | =106·37 | 61·25 | 61·27 |
| O | = 16·00 | 9·21 | —— |
| | 173·67 | 100·00 | |

2. *Vanadium Oxydichloride*, or *Vanadyl Dichloride*, $VO\,Cl_2=138{\cdot}21$.—This substance is formed, together with other lower solid oxychlorides, when the vapour of vanadyl trichloride mixed with hydrogen is passed through a red-hot tube. It is easily obtained, however, in the pure state by the action of metallic zinc on the oxytrichloride in sealed tubes at 400°. For this purpose strips of zinc and slight excess of the liquid chloride are heated in a strong tube placed in an inclined position in an air-bath for three or four days in a temperature considerably above the boiling-point of mercury; the oxytrichloride is decomposed, a black oxide of vanadium is formed together with zinc chloride, and a sublimate of splendid grass-green tabular crystals of the oxydichloride collects in the upper part of the tube. On opening the tube, the portion containing the crystals was quickly pushed inside a wider tube heated to 130° in a paraffin bath through which a current of dry carbonic acid was passed; the excess of liquid oxychloride was thus easily expelled and the green crystals obtained of a constant weight. The black oxide formed together with the green crystals consists of the lowest oxide, $V_2\,O_2$, as on treatment with dilute acid it bleaches strongly.

Vanadium oxydichloride is a grass-green body crystallizing in thin plates and possessing an unctuous feel. It is slowly decomposed by water, and on exposure to moist air it deliquesces; it easily dissolves in dilute nitric acid. Its specific gravity at 13° C. is 2·88.

The composition of the oxydichloride is readily determined by precipitating the chlorine in nitric-acid solution, and estimating the vanadium in the filtrate.

| Nos. | Weight of oxydichloride taken. | Ag Cl. Found. | $V_2\,O_5$. Found. | Percentages | |
|---|---|---|---|---|---|
| | | | | of chlorine. | of vanadium. |
| 1. | 0·3765 | 0·7683 | 0·2498 | 50·40 | 37·30 |
| 2. | 0·3207 | 0·6631 | 0·2160 | 51·07 | 37·87 |

Hence we have as the composition of this substance:—

| | | Calculated. | Found. |
|---|---|---|---|
| V | = 51·3 | 37·12 | 37·58 |
| $Cl_2$ | = 70·91 | 51·39 | 50·73 |
| O | = 16·0 | 11·59 | —— |
| | 138·21 | 100·00 | |

3. *Vanadium Oxymonochloride,* or *Vanadyl Monochloride,* $VOCl$=102·76.—Vanadyl monochloride is a brown, light, powdery solid, formed by the action of hydrogen upon vanadyl trichloride. It is obtained by passing the vapour of the trichloride together with hydrogen through a red-hot tube, and is deposited at the end nearest to the point where the trichloride enters the tube. It is insoluble in water, but easily soluble in nitric acid. It may readily be distinguished and separated from the preceding and following oxychlorides by its appearance and light flocculent nature. The analysis was made in the manner already described, the substance being dried at 130° in a stream of carbon dioxide till its weight was constant.

| Nos. | Weight of substance taken. | Weight of silver chloride found. | Weight of vanadium pentoxide found. | Percentages | |
|---|---|---|---|---|---|
| | | | | of chlorine. | of vanadium. |
| 1. | 0·1393 | 0·1823 | 0·1240 | 32·35 | 50·03 |
| 2. | 0·2631 | 0·3912 | 0·2285 | 36·71 | 48·82 |

Hence we have—

| | | Calculated. | Found. |
|---|---|---|---|
| V | = 51·3 | 49·92 | 50·21 |
| Cl | = 35·46 | 34·51 | 34·53 |
| O | = 16·0 | 15·57 | —— |
| | 102·76 | 100·00 | |

4. *Divanadyl Monochloride,* $V_2O_2Cl$=170·06.—This substance is likewise formed in a similar manner to the foregoing oxychlorides. It has a bright, shining, metallic lustre and a brownish-yellow colour, closely resembling the tin disulphide known as "mosaic gold." This substance is always deposited in the portion of the heated tube furthest from the trichloride, and it adheres firmly to the glass. From its heavy coherent nature it can easily be separated from the preceding compound. Under the microscope it is seen to consist of brilliant-yellow metallic crystals, and it has been mistaken for metallic vanadium by SCHAFARIK.

It is insoluble in water, but dissolves like the other solid oxychlorides easily in nitric acid. The brown shining crystals were heated in carbon dioxide at 140° until their weight was constant, and then they were analyzed as above described.

| Nos. | Weight of substance taken. | Weight of silver chloride found. | Weight of vanadium pentoxide found. | Percentages | |
|---|---|---|---|---|---|
| | | | | of chlorine. | of vanadium. |
| 1. | 0·2130 | 0·1777 | 0·2443 | 19·72 | 64·48 |
| 2. | 0·6098 | 0·4767 | 0·6390 | 18·15 | 58·91 |

Hence we have—

| | Calculated. | Found. |
|---|---|---|
| $V_2$=102·60 | 60·33 | 61·69 |
| Cl= 35·46 | 20·84 | 18·93 |
| $O_2$= 32·00 | 18·83 | —— |
| 170·06 | 100·00 | |

## VI. VANADIUM NITRIDES.

1. *Vanadium Mononitride*, V N=65·3.—The process described by **Berzelius** for preparing metallic vanadium by heating the ammonio-oxychloride in an atmosphere of ammonia does not yield the metal but a nitride.

The mononitride is obtained by passing dry ammonia gas over vanadyl trichloride contained in a bulb-tube, and igniting the ammonio-oxychloride formed until the ammonium chloride has volatilized. The black powder thus produced (vanadium dinitride ?) is then placed in a platinum boat, which is exposed for some hours to the white heat of a wind-furnace in a porcelain tube through which dry ammonia (or rather a mixture of its constituent gases) passed. The substance thus obtained is a greyish-brown powder, which does not undergo change on exposure to air at ordinary temperatures, and remains unaltered when it is again strongly heated in ammonia. When roasted in the air it slowly oxidizes, glows, and forms a blue oxide; on further heating it melts, and ultimately forms pure vanadium pentoxide. Heated with soda-lime in a glass tube, the mono-nitride readily evolves ammonia.

The nitride employed in the following analyses had been repeatedly heated to whiteness in a current of ammonia until no further diminution of weight occurred.

Boat and nitride after second ignition in ammonia 6·285 grms.
,, ,, third ,, for three hours 6·284 ,,

(1) *Determination of Vanadium.*—
Weight of nitride employed 0·3126 grm.
Constant weight of vanadium pentoxide, obtained by roasting, 0·4359.
Hence the nitride contained 77·8 per cent. of vanadium.
The formula V N requires 78·6 per cent. of metal.

(2) *Determination of Nitrogen.*—The nitrogen was determined according to **Simpson's** method, by heating the nitride with a mixture of the oxides of mercury and copper, and passing the gases over red-hot metallic copper.

*Analysis* (1). Weight of nitride taken=0·2683 grm.

| Observed vol. of nitrogen (measured dry). | Pressure. | Temp. | Vol. at 0° and 760 millims. |
|---|---|---|---|
| 142·1 vols. | 718 millims. | 9°·2 | 43·2 cub. centims. |

(1 vol.=0·331 cub. centim.).

This corresponds to a percentage of 20·3 nitrogen.

*Analysis* (2). Weight of nitride taken=0·2000 grm.

| Observed vol. of nitrogen (measured moist). | Pressure. | Temp. | Vol. at 0° and 760 millims. |
|---|---|---|---|
| 112 vols. | 682·1 millims. | 13° | 31·8 cub. centims. |

(1 vol.=0·331 cub. centim.).

This corresponds to a percentage of 20·0 nitrogen.

| | Calculated. | | Found. | | |
|---|---|---|---|---|---|
| Vanadium . . | 51·3 | 78·6 | 77·8 | —— | —— |
| Nitrogen . . . | 14·0 | 21·4 | —— | 20·3 | 20·0 |
| | 65·3 | | | | |

2. *Vanadium Dinitride*, $V N_2=79·3$.—This substance is obtained as a black powder by passing dry ammonia over vanadyl trichloride heated in a glass tube to expel salammoniac, washing with ammonia-water, and drying *in vacuo* over sulphuric acid.

This nitride was obtained in 1858 by UHRLAUB*, but this chemist made no direct determination of the nitrogen, by which alone the true nature of these compounds can be discovered; and he, adopting, as a matter of course, the atomic weight 68·5, showed that the body obtained as above described cannot be represented by any simple formula. If, however, UHRLAUB'S experimental results be calculated with the true atomic weight 51·3, it is seen that, according to the mean of three determinations, the substance contains 64·1 per cent. of vanadium, the formula $V N_2$ requiring 64·6 per cent.

The existence of vanadium mononitride, V N, not only demonstrates with absolute certainty the true atomic weight of the metal, but it also serves as the starting-point from which to commence the study of the metal, as well as of an entirely new class of bodies, viz. the compounds of the metal vanadium with chlorine and the other halogens, which I have in vain endeavoured to obtain from vanadyl compounds. In the next communication I hope to describe these interesting substances.

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[*] POGG. Ann. Bd. ciii. p. 134.