

XXXVI.—*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 mimetosite, minerals consisting of calcium phosphato-fluoride, lead phosphato-chloride, and lead arsenato-chloride, having the formulæ $3(\text{Ca}_3\text{P}_2\text{O}_8) \cdot \text{CaFl}_2$; $3(\text{Pb}_3\text{P}_2\text{O}_8) \cdot \text{PbCl}_2$, and $3(\text{Pb}_3\text{As}_2\text{O}_8) \cdot \text{PbCl}_2$. The crystalline form of all these minerals is a hexagonal prism terminated by six-sided pyramids. The angle P : P (terminal) found by

* Pogg. Ann. Bd., xeviii, p. 249 (1856).

† Ibid. Bd., c, p. 297

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; | (3) 1 : 0·736; |
| (2) 1 : 0·732; | (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 crystallise 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.

We are indebted to the researches of Berzelius for almost all we know concerning the chemical relations of vanadium and the composition of 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 VO_3 . Hence it is evident that we have here to do with either a case of dissimilarly constituted substances acting as isomorphous bodies and crystallising together, or else the conclusions of Berzelius are erroneous, and the true formula of vanadic acid is V_2O_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 VO_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

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

† Pogg. Ann. Bd. xxii, p. 1 (1831).

‡ Ann. Ch. Pharm. cix, p. 84 (1859).

§ Pogg. Ann. Bd. cxx, p. 33 (1863).

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 VO_3 , that of the oxide prepared by reduction VO , and that of the chloride VCl_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_2O_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.

(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

* I had originally intended to call the first and third oxides of 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

(3.) The so-called terchloride of vanadium VOCl_3 , ($V = 67.3$) contains oxygen; it is an oxychloride having the formula VOCl_3 ($5 = 51.3$); it may be called vanadyl trichloride, or vanadium oxytrichloride, and corresponds to POCl_3 , phosphorus oxychloride.

(4.) Three other solid oxychlorides exist, having the compositions:

(1.) VOCl_2 , vanadyl dichloride, or vanadium oxydichloride.

(2.) VOCl , vanadyl monochloride, or vanadium oxymonochloride.

(3.) $\text{V}_2\text{O}_2\text{Cl}$, divanadyl monochloride.

(5.) All the native vanadates are tribasic:—

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

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

(c.) Arceoxene, analyzed by V. Kobell (J. pr. Chem. l., 496), was found to have a similar composition to eusynchnite.

(d.) An American vanadinite, analyzed by Smith (J. pr. Chem. lxvi., 433), is a tribasic compound.

(e.) Dechenite from the Pfalz is, according to Brush (Sill. Am. Journ. [2], xxxiv., 116), identical with arceoxene, and therefore a tribasic compound.

(f.) Volborthite, according to Credner's analysis (Pogg. Ann. lxxiv., 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 sodium vanadate, or sodium orthovanadate, 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 , Ba_2VO_3 . The so-called bivanadates

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.]

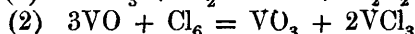
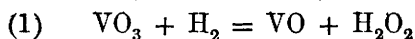
are anhydro-salts, similar in constitution to the anhydro-salts of chromic and boric acids.

(8.) Vanadium nitride has been prepared, which, on analysis, was shown to contain 51·3 parts by weight of vanadium to fourteen 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 $V = 67\cdot3$ can equally well be explained when V_2O_5 ($V = 51\cdot3$) is taken to represent the composition of this substance. That this is the case is seen from the following:—

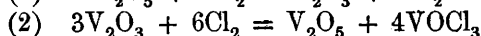
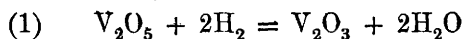
Berzelius's formulæ.

($V = 68\cdot5$. $O = 8$.)



New formulæ.

($V = 51\cdot3$. $O = 16$.)



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 Sand-

stone 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 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, then 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

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

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 recognised 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 then 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 neutralised 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 was 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 recrystallised. 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 vana-

date was separated by filtration from a residue containing silica, phosphates, &c., and was crystallised 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, which, 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 associated 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 crystallisation 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 crystallisation 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 trustworthy, 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 enclosed 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

* 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 milligramme error is ± 0.086 .

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, the presence of the smallest quantity of phosphorus pentoxide rendering, as has been shown, the complete reduction of the vanadic acid impossible.

1. The vanadic acid used in 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.

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.

Four experiments gave the following results:—

I.	$a = 7.7397$;	$b = 6.3827$;	therefore $V = 51.257$
II.	$a = 6.5819$;	$b = 5.4296$;	„ $V = 51.391$
III.	$a = 5.1895$;	$b = 4.2819$;	„ $V = 51.485$
IV.	$a = 5.0450$;	$b = 4.1614$;	„ $V = 51.353$

Mean 51.371

Hence we may assume the atomic weight of vanadium, as obtained from the reduction of pentoxide to trioxide, to be 51.4 and probably true to within ± 0.07 .

Berzelius's mean number, calculated for V_2O_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.

The fact that these older determinations all give a higher number than the above experiments, shows either that the acid was not fully oxidised, 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 $\text{VO} = 76.5$.

2. Vanadic oxide, to which Berzelius gave the formula $\text{VO}_2 = 84.5$, 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, $\text{VO}_3 = 92.5$, was shown to contain three times as much oxygen as the suboxide.

Berzelius describes several other intermediate oxides, but he did not isolate or analyse 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 ($\text{O} = 16$), 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 ($\text{V} = 51.3$):—

1. Vanadium dioxide, or vanadyl, V_2O_2 .
2. Vanadium trioxide (Berzelius's suboxide), V_2O_3 , or $\text{V}_2\text{O}_2 + \text{O}$.
3. Vanadium tetroxide (Berzelius's vanadic oxide), V_2O_4 , or $\text{V}_2\text{O}_2 + \text{O}_2$.
4. Vanadium pentoxide (vanadic acid), V_2O_5 , or $\text{V}_2\text{O}_2 + \text{O}_3$.

* Since the above was written I have been fortunate enough, through the kindness of Dr. Frankland, to be able to examine a specimen of ammonium vanadate, sent by Berzelius to Faraday in 1831, and I find that this contains very considerable quantities of phosphorus.—H. E. R., July 1868.

1. *Vanadium Dioxide (or Vanadyl)*, $V_2O_2 = 134.6$.—In its power of uniting with oxygen, vanadium surpasses even uranium, as observed by Peligot.* Like uranium, the metal vanadium is so extremely difficult to separate from its last atom of oxygen, 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 ($VOCl_3$), mixed with excess of hydrogen, through a combustion-tube containing red-hot carbon. Lower solid oxychlorides (see page 347) 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.

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 ($V_2O_2 = 134.6$) 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 having proved that this point is that of maximum

* Ann. Ch. Phys., 3 sér., tomes v and xii.

oxidation (V_2O_5), and that it can be accurately reached provided an excess of sulphuric acid be present.*

The calculated loss of oxygen on 100 vanadium pentoxide, when reduced to the dioxide V_2O_3 , is 26.3; the mean experimental number obtained was 26.53.

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.

The mean of these six determinations thus made gave 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 338). 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

* 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.

green, and the vanadium is contained in solution as trioxide (see trioxide, page 336). 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), $V_2O_3 = 150\cdot6$.—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 glowing rapidly 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 338).

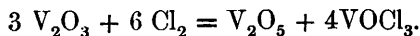
Vanadium Trioxide in solution.—The trioxide is insoluble in acids, but it may be obtained in solution as follows:—If solutions of vanadium pentoxide in sulphuric acid are diluted and treated with excess of metallic magnesium, the changes of colour which are observed when zinc, cadmium, or sodium amalgam are used do not continue beyond the green, and the liquid contains vanadium trioxide in solution. Thus the observed loss of oxygen on 100 V_2O_5 was 17·6, whilst the calculated loss is 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 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.

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

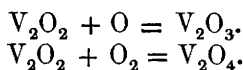
If a few drops of acid are added to the brown solution, which does not undergo change even when air is passed through for several days, it immediately turns green, but does not undergo any alteration as regards its oxygen. Thus a brown solution was divided into two equal parts; the one which was oxidized 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 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:—



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* by precipitating the hydrated oxide from a sulphate with sodium carbonate, washing, and igniting in a vacuum 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 30.36 per cent. of V_2O_3 :—



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, having been 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

* Pogg. Ann. Bd. xxii, p. 19.

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.

The experiments gave 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. 100 parts of vanadium dioxide were found to have absorbed (1) 20.9, and (2) 23.4 parts of oxygen; 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 analysed by Berzelius, 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 con-

* Pogg. Ann. Bd. cxii, p. 160.

† Ibid. Bd. xxii, p. 49.

sidered as metavanadates when the atomic weight of the metal is taken to be 51·3.

Berzelius's formulæ. $V = 68\cdot5$, $O = 8$.

Vanadate of ammonia, $NH_3VO_3 + HO$.

Vanadate of baryta, $BaOVO_3$.

New formulæ. $V = 51\cdot3$, $O = 16$.

NH_4VO_3 , ammonium metavanadate, or $\left. \begin{smallmatrix} NH_4 \\ VO \end{smallmatrix} \right\} O_2$.

BaV_2O_6 , barium metavanadate, or $\left. \begin{smallmatrix} Ba \\ 2VO \end{smallmatrix} \right\} O_4$.

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 been analyzed by Von Hauer.* The ammonium and sodium bivanadates were found to correspond with the formulæ $NH_4O\cdot2VO_3$ and $NaO\cdot2VO_3$, 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 $2NH_4VO_3 + V_2O_5$ and $2NaVO_3 + V_2O_5$, or else as $Na_4V_2O_7 + 3V_2O_5$ 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 sodium vanadate or sodium orthovanadate, is Na_3VO_4 , or $\left. \begin{smallmatrix} Na_3 \\ VO \end{smallmatrix} \right\} O_3$. Hence there is no doubt that vanadic acid in its normal state acts as a tribasic acid.

* Journ. prak. Chem. Bd. lxi, p. 388 (1856).

† Pogg. Ann. Bd. cxi, p. 33.

It is my intention to investigate fully 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 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 were 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 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 were found on analysis 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.

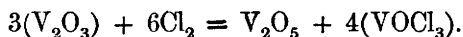
(5.) When vanadyl trichloride is rapidly distilled over heated carbon, or when it is prepared by treating a mixture of trioxide and carbon with chlorine, a dark reddish-brown liquid is formed consisting of a mixture of the oxychloride and another chloride. The analysis of this dark liquid yielded results 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

* 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.

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° . 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 $126\cdot7^{\circ}$ 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:—



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 $14^{\circ}\cdot 5$	1·841.
$17^{\circ}\cdot 5$	1·836.
$24^{\circ}\cdot 0$	1·828.

The trichloride remains liquid at temperatures above -15°C. As the co-efficient 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 (POCl_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 $18^{\circ}\cdot 6\text{C.}$, 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 weight 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 verification 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 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-fourths 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

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

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

‡ Idem, p. 62.

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 analysis 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.

No. of experiment.	Weight of tri-chloride 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	7.3799	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

* Stas's numbers are here used, viz., O = 16, Ag = 107.93, Cl = 35.457.

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 tri-chloride 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—

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

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.

Nos.	Weight of tri-chloride 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.....			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	—
<hr/> 173.67	<hr/> 100.00	

2. *Vanadium Oxydichloride*, or *Vanadyl Dichloride*, $\text{VOCl}_2 = 138.21$.—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_2O_3 , as on treatment with dilute acid it bleaches strongly.

Vanadium oxydichloride is a grass-green body crystallising 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.

	Calculated.	Found.
V = 51.3	37.12	37.58
Cl ₂ = 70.91	51.39	50.73
O = 16.0	11.59	—
<hr/> 138.21	<hr/> 100.00	

3. *Vanadium Oxymonochloride*, or *Vanadyl Monochloride*, $\text{VOCl} = 102\cdot76$.—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.

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

4. *Divanadyl Monochloride*, $\text{V}_2\text{O}_2\text{Cl} = 170\cdot06$.—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 analysed, as above described.

Hence we have—

	Calculated.	Found.
$\text{V}_2 = 102\cdot60$	60·33	61·69
Cl = 35·46	20·84	18·93
$\text{O}_2 = 32\cdot00$	18·83	—
<hr/>	<hr/>	
170·06	100·00	

VI. VANADIUM NITRIDES.

1. *Vanadium Monotride*, $VN = 65.3$.—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 monotride 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 volatilised. 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 oxidises, 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 mononitride readily evolves ammonia.

Its composition is as follows:—

	Calculated.		Found.		
Vanadium.....	51.3	78.6	77.8	—	—
Nitrogen	14.0	21.4	—	20.3	20.0
	<hr/> 65.3				

2. *Vanadium Dinitride*, $VN_2 = 79.3$.—This substance is obtained as a black powder by passing dry ammonia over vanadyl trichloride heated in a glass tube to expel sal-ammoniac, 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

* Pogg. Ann. Bd. ciii, p. 134.

three determinations, the substance contains 64.1 per cent. of vanadium, the formula VN_2 requiring 64.6 per cent.

The existence of vanadium mononitride, VN , 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.
