XXV. *Researches on Vanadium.*—Part II. *By* HENRY E. ROSCOE, *B.A.*, *Ph.D.*, *F.R.S.*

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On the Chlorides of Vanadium and Metallic Vanadium.

IN the first part of these researches* I stated that the nitride of vanadium forms the point from which the study of the vanadium compounds, properly so called, must be commenced. I now proceed to describe the composition and mode of preparation of the compounds of the metal with chlorine, and also the properties of the metal itself.

The process for preparing vanadium mononitride which I described in the last communication, was that proposed by BERZELIUS for obtaining the substance which he conceived to be metal. It consists in the action of dry ammoniacal gas upon vanadyl trichloride ($VO\,Cl_3$).

Owing, however, to the difficulty of properly regulating the very violent action which occurs when the two bodies come into contact, and the consequent loss of trichloride, this method was unsuited for the preparation of the nitride in quantity. Seeking for an easier and more economical method, I found that if the black residue left on calcining ammonium metavanadate in the air (probably an oxynitride) be heated to whiteness for a sufficiently long time in a current of dry ammoniacal gas, pure vanadium mononitride is left behind. A portion of ammonium-salt was placed in a platinum boat inside a porcelain tube, through which a stream of dry ammonia was passed. The tube was then heated to whiteness for three days.

Analysis 1.—Determination of Vanadium.

Weight of Nitride employed . . . 0·1705.

Constant weight of vanadium pentoxide obtained by roasting . . . . 0·2415.

Hence the nitride contained 79·6 per cent. of vanadium. The formula requires 78·6 per cent.

Determination of Nitrogen according to SIMPSON'S method.

Weight of nitride taken . . . 0·2070.

Observed vol. of nitrogen (measured moist).	Pressure. millims.	Temp.	Vol. at 0° and 760 millims.
111·2 vol.	746·2	17·0°	100·5

(1 vol. =0·331 cub. centim.)

This corresponds to 20·2 per cent. of nitrogen.

Vanadium mononitride contains 21·4 per cent.

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* Bakerian Lecture, Philosophical Transactions, 1868, p. 1.

The substance used in the following analysis was prepared by heating about 3 to 4 grms. of the ammonia-salt in a platinum tube to whiteness in a current of dry ammonia. The tube was imbedded in a chalk crucible, and the central portions were heated to whiteness by the blast of a powerful blowpipe until no alteration of weight was observed. In this way, after a long and tedious series of operations, no less than 40 grms. of pure nitride (see analysis No. 2) was prepared.

Analysis No. 2.—Determination of Nitrogen.

Weight of nitride taken . . . 0·2250.

Observed vol. of nitrogen (measured moist).	Pressure. millims.	Temp. °	Vol. at 0° C. and 760 millims.
123·3	740·5	21·5	108·5

(1 vol. $=0·331$ cub. centim.)

This corresponds to 20·1 per cent. of nitrogen. A third and still more simple mode of obtaining the nitride is that of exposing the trioxide to the action of ammonia gas at a white heat. It is a remarkable fact, and one of which we know of but two other examples, that in presence of nitrogen and hydrogen the whole oxygen of an oxide is displaced by nitrogen.

THE CHLORIDES OF VANADIUM.

I have succeeded in preparing three chlorides of vanadium, viz. (1) vanadium tetrachloride, VCl_4, (2) vanadium trichloride, VCl_3, (3) vanadium dichloride, VCl_2.

(1) *Vanadium Tetrachloride*, VCl_4, molecular weight $=193·3$, vapour-density $=96·6$ ($H=1$).—This chloride is formed as a dark reddish-brown volatile liquid when metallic vanadium or the mononitride is burnt in excess of chlorine.

Method 1.—The first method adopted for the preparation of the tetrachloride was by passing dry chlorine gas over the mononitride heated to redness; the whole of the nitride volatilizes, and a reddish-brown liquid is obtained. In one operation 16·96 grms. of the mononitride yielded, on treatment with excess of chlorine, 44·3 grms. of the crude tetrachloride, the theoretical yield being 50·1 grms. Owing to the inevitable presence of traces of oxide in the nitride, the first few drops of the distillate consisted of the more volatile light-yellow oxytrichloride, and this portion was collected separately before much of the dark tetrachloride had come over.

The crude product thus obtained was first saturated with chlorine, and then distilled upwards for some hours in a current of dry carbonic acid. On fractionating, the liquid was found to begin to boil at 148°, slowly rising to 154°, between which points the whole of the liquid came over.

A considerable quantity of a solid mass of peachblossom-coloured crystals, consisting of vanadium trichloride, remains behind in the bulb after each distillation. A second preparation of 50 grms. of the pure tetrachloride gave a constant boiling-point at 152°–154°.

Method 2.—When vanadium oxytrichloride is prepared according to BERZELIUS's reaction by passing dry chlorine over a mixture of the trioxide and charcoal heated to redness, the distillate possesses a port-wine colour, and it is only by frequent rectifications over sodium that the canary-yellow colour of the pure oxychloride is obtained. This coloration, though ascribed by SCHAFARIK to the presence of traces of vanadic acid, is really due, as I have formerly pointed out, to the presence of a dark-coloured vanadium chloride produced in the reaction and decomposed on rectification over sodium. This observation, coupled with the fact already made use of to demonstrate the existence of oxygen in the oxytrichloride, viz. that this substance yields up oxygen to red-hot charcoal, points the way to the second method for the preparation of the tetrachloride.

This consists in passing the vapour of the oxytrichloride, together with an excess of dry chlorine, slowly over a long column of pure sugar-charcoal heated to dull redness. This operation has to be repeated four or five times before the last traces of oxygen are withdrawn. Even after one distillation the product attains a dark reddish-brown tint, and boils at 152°; but it still contains 1 per cent. of oxygen, and needs three or four very slow repetitions of the process in order to obtain it perfectly pure. The solid trichloride is always found in the bulb from which the tetrachloride is distilled; but this, if carefully heated, slowly burns away in the excess of chlorine.

The portions of substance used for analyses 1, 2, and 3 were prepared from nitride, those in Nos. 4, 5, and 6 were obtained directly from the oxytrichloride. The chloride in analysis 4 was distilled three times over charcoal, and still contained a little oxygen; after another distillation (analysis 5) the oxygen was reduced to 0·2 per cent., and after a fifth distillation (analysis 6) the whole of the oxygen had been removed. The determinations were made by breaking a bulb containing a weighed quantity of substance in a closely stoppered bottle containing water; the chlorine was then estimated as silver-salt, nitric acid being added after the nitrate of silver, whilst the vanadium, either in the filtrate or in another portion of chloride, was weighed as pentoxide.

No.	Weight of tetra-chloride found.	Silver chloride found.	Vanadium pentoxide found.	Percentages	
				of chlorine.	of vanadium.
1.	0·4272	1·2555	——	72·68	——
	0·6645	——	0·3195	——	27·02
2.	0·9644	2·8560	——	73·24	——
	1·0362	——	0·4890	——	26·52
3.	1·0438	3·0441	——	72·14	——
	0·9875	——	0·4632	——	26·36
4.	0·8935	2·6266	——	72·73	——
	1·1465	——	0·5440	——	26·65
5.	0·2940	0·8667	——	72·95	——
	0·4950	1·5760	0·2370	72·83	26·89
6.	0·4080	1·2086	0·1960	73·28	27·05

Hence we have for the composition of this chloride:

	Calculated.		Found.						Mean of 1,2,5&6.
			(1)	(2)	(3)	(4)	(5)	(6)	
V =	51·3	26·54	27·02	26·52	26·36	26·65	26·89	27·05	26·87
Cl_4=	142·0	73·46	72·68	73·24	72·14	72·73	72·89	73·28	73·02
	193·3	100·00	99·70	99·76	98·50	99·38	99·78	100·33	99·89

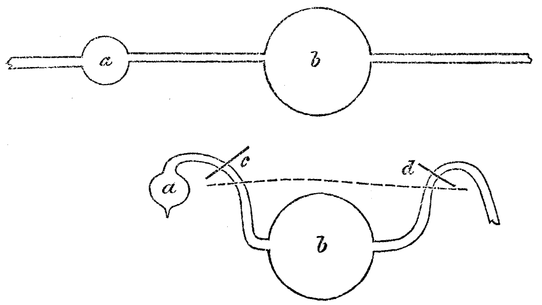
Vapour-density of Vanadium Tetrachloride.—Owing to the ease with which the tetrachloride decomposes into the trichloride and free chlorine, a solid residue is always left in the bulb when the determination is made by DUMAS's method in the ordinary way, and the experimental number is rather too high, as the following numbers show.

No. 1.—Weight of bulb and air at 10° C. and under 763·7 millims. . 11·1507 grms.
Weight of bulb and vapour at 219° and under 763·7 millims. 11·5900 grms.
Capacity of bulb 118 cub. centims., vol. of residual air 0·0 cub. centim.

Hence the vapour-density is found to be 99·06 (H=1) or 6·86 (air=1), the calculated density being 96·6 (H=1) or 6·69 (air=1).

In order to avoid the error arising from the deposition of a solid residue, an arrangement shown in fig. 1 was used. The tetrachloride was first placed in the small bulb (*a*); the large bulb (*b*) was then submerged, and the oil heated above the boiling-point of the chloride. The chloride was then boiled and the vapour passed through the bulb (*b*), and the tube sealed at *c*. The bulb was then turned round in the oil so as to bring the point (*c*) below the surface, and the temperature of the bath allowed to rise above 200° C.; and when the temperature had become constant, the tube was again sealed at *d*.

Fig. 1.



No. 2.—Weight of bulb and air at 15° C. and under 751 millims. . . 19·8945 grms.
Weight of bulb and vapour at 205° and under 758·1 millims. 20·3015 grms.
Capacity of bulb 112 cub. centims., residual air 2 cub. centims. No solid residue was left in the bulb.

Hence the vapour-density is found to be 96·6 (H=1), or 6·69 (air =1).

No. 3.—Another determination made at a higher temperature gave a somewhat lower number, indicating that a portion of the tetrachloride had been decomposed.

Weight of bulb and air 9° C. and under 762 millims. . . . 24·4722 grms.
Weight of bulb and vapour at 215° C. and under 762 millims. 25·0102 grms.
Capacity of bulb 169·5 cub. centims. No solid residue left in the bulb. Volume of mercury entering the bulb 157 cub. centims.

Hence the vapour-density is found to be 93·3 (H=1) or 6·48 (air =1).

Vanadium tetrachloride is a dark brownish-red, thickish liquid, which evolves white fumes when exposed to moist air. Its specific gravity was carefully determined at three temperatures, and found to be:

at 0° C.	1·8584
at 8° C.	1·8363
at 32° C.	1·8159.

It does not solidify at temperatures above −18° C.; nor does it at this, or any higher temperature, undergo any change of properties on treatment with chlorine. The boiling-point of vanadium tetrachloride is 154° C. (corrected) under a pressure of 760 millims.

Vanadium tetrachloride not only decomposes (as has been stated) on boiling into the trichloride and free chlorine, but the same decomposition takes place slowly at the ordinary temperature of the air. The liquid tetrachloride, sealed up in glass tubes and exposed to the light, was found on standing for some months to be changed to a dark blackish powder, whilst free chlorine was liberated in such quantity as not only to exhibit its characteristic greenish-yellow colour, but in several cases by its pressure to have burst the tubes. This powder on analysis was found to consist of the trichloride (see analysis, p. 685) moistened with tetrachloride; on removing this latter liquid in a current of dry carbonic acid at 170°, the pure violet solid trichloride was left behind. Thrown into water the tetrachloride is at once decomposed, yielding a blue solution identical in colour with the liquids obtained by the action of oxalic, sulphurous, or sulphydric acids on vanadic acid in solution, and containing a vanadous salt (derived from the tetroxide, V_2O_4).

In order to prove that a vanadous salt is formed when the tetrachloride is decomposed by water, the quantity of oxygen which this salt absorbs in conversion into vanadic acid was determined with a standard permanganate solution according to the method described in Part I. of these researches (Phil. Trans. 1868, p. 17).

Action of Potassium Permanganate on the aqueous solution of Vanadium Tetrachloride.

	(1)	(2)	(3)	(4)
Weight of VCl_4 taken	0·2375	0·5353	0·4628	0·5687
Cub. centim. of permanganate solution required (1 cub. centim. = 0·00066 grm. oxygen)	15·0	33·2	28·8	35·4
Percentage gain of oxygen found . .	4·17	4·09	4·10	4·09

The calculated percentage gain of oxygen according to the equation

$$2VCl_4 + O + 4H_2O = V_2O_5 + 8HCl \quad \text{is } 4{\cdot}14.$$

The solution of the tetrachloride in water does not bleach litmus-paper; but if the vapours of the boiling tetrachloride are condensed in water, a liquid is obtained which contains free chlorine, as it bleaches litmus-paper and liberates iodine from potassium iodide. At higher temperatures, as, for instance, when the vapours are led through a red-hot tube, much larger quantities of chlorine are evolved. Vanadium tetrachloride acts violently upon both dry alcohol and ether, giving in the first case a deep green, and in the second a deep red-coloured liquid. I am at present engaged with the examination of the products of this action.

Action of Bromine on Vanadium Tetrachloride.—Vanadium tetrachloride, heated with excess of bromine in a sealed tube to 180°, yielded a solid mass, which on drying in a stream of carbonic acid at 160°, presented the appearance of the peach-coloured trichloride, and subsequent analysis proved that this body was formed. It is thus seen that, heated in excess of both chlorine and bromine, the tetrachloride splits up into trichloride and free chlorine, so that vanadium does not readily form a pentad compound with the chlorous elements*.

(2) *Vanadium Trichloride*, $VCl_3 = 157{\cdot}8$.—The trichloride is a solid body, crystallizing in splendid peachblossom-coloured shining tables, closely resembling in appearance the crystals of chromium sesquichloride. It is non-volatile when heated in hydrogen, and decomposes when heated in the air, red fumes of oxytrichloride being given off in small quantity, whilst the solid mass glows with absorption of oxygen, forming the pentoxide. Heated in hydrogen it loses, first, one atom of chlorine, forming the dichloride (VCl_2), and afterwards, on exposure to a higher temperature, loses the whole of its chlorine, metallic vanadium being left as a grey lustrous powder.

Vanadium trichloride is an extremely hygroscopic substance; it instantly changes colour on exposure to moist air, deliquescing to a dark-brown liquid, which on the addition of a drop of hydrochloric acid becomes green, containing a solution of vanadium trioxide (V_2O_3), or rather of the corresponding hypovanadic salts.

The trichloride is obtained (1) by the slow decomposition of the tetrachloride at the ordinary atmospheric temperatures, (2) by the decompositions of the tetrachloride at its boiling-point, (3) together with dichloride, when the vapour of the tetrachloride is passed mixed with hydrogen through a red-hot tube. Method No. 2 is that which yields the trichloride in largest quantity and in the purest state, large quantities of the peach-coloured crystals remaining behind in the bulb-retort; and these only require heating in a current of carbon dioxide at 160° in order to yield the pure trichloride. The substance

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* The only other case of an element of a decidedly triad character yielding compounds of a tetrad nature, appears to be the nitrosyl-dichloride, $NOCl_2$, of GAY-LUSSAC, and the corresponding bromine compound, $NOBr_2$, discovered by LANDOLT.

used in analysis (1) was obtained by the first method, that used for analyses 2, 3, and 4 was prepared by the second process.

No.	Weight of trichloride taken.	Silver chloride found.	Vanadium pentoxide found.	Percentages of	
				chlorine.	vanadium.
1.	1·6615	4·5704	0·9240	68·05	31·25
2.	0·2295	——	0·1320	——	32·31
	0·2550	0·6931	——	67·25	——
3.	0·1965	0·5298	0·1140	66·71	32·59
4.	0·1094	0·2993	——	67·67	——
	0·2188	——	0·1290	——	33·12

Hence we have for the composition of this chloride:

	Calculated.	Found.				Mean.
		(1)	(2)	(3)	(4)	
V = 51·3	32·5	31·25	32·31	32·59	33·12	32·57
Cl_3=106·5	67·5	68·05	67·25	66·71	67·67	67·42
157·8	100·0	99·30	99·56	99·30	100·79	99·99

When the trichloride is thrown into water it does not at once dissolve, the peachblossom-coloured crystals floating in the liquid; these, however, gradually dissolve, forming a brown-coloured solution, which on addition of a drop of acid turns to a bright green colour, identical in tint with the liquid obtained by reducing vanadic acid in solution with nascent hydrogen evolved by magnesium, and containing a hypovanadic salt. Like the solution obtained by reduction, the green-coloured solution of the trichloride absorbs oxygen on standing, passing into the blue solution of the vanadous salts. A solution of hypovanadic salt obtained by dissolving 0·293 grm. of trichloride in water required 45 cub. centims. of permanganate solution in order to oxidize it completely (1 cub. centim. permanganate=0·00066 grm. oxygen). Hence the quantity of oxygen needed to oxidize the solution was 10·10 per cent. (on the trichloride), whilst that required by the formula $2V\,Cl_3 + O_2 + 3H_2O = V_2O_5 + 6H\,Cl$ is 10·14 per cent.

The specific gravity of vanadium trichloride at 18° is 3·00. Vanadium trichloride dissolves readily in absolute alcohol, forming a greenish-blue solution; in ether it also dissolves, giving a green-coloured solution.

(3) *Vanadium Dichloride*, $V\,Cl_2$=122·3.—Vanadium dichloride is a solid body crystallizing in fine bright apple-green plates, having a micaceous lustre and an hexagonal form. It is prepared by passing the vapour of vanadium tetrachloride mixed with dry and pure hydrogen through a glass tube heated to dull redness. If the distillation of the tetrachloride be conducted slowly, and the mixture of vapour and hydrogen brought at once into the heated portion of the tube, the pure dichloride is deposited in light pearly scales, which can easily be shaken out of the tube. If the operation be conducted too quickly, or if the hydrogen be not present in large excess, a considerable quantity of

the peach-coloured trichloride is formed in the anterior portion of the tube, and the green crystals of dichloride collect in one spot and are fixed firmly to the glass. If the temperature be raised to a bright red heat during the preparation, the dichloride is further reduced, a black crystalline powder containing a mixture of lower chlorides and metal being produced, whilst the glass tube becomes opaque with formation of the silicon-vanadium compound. When heated for a long time in a platinum boat in a current of pure and dry hydrogen the dichloride loses all its chlorine, metallic vanadium being left in the form of bright greyish-white lustrous metallic grains. The dichloride prepared as above, gave the following analytical results:—

No.	Weight of dichloride taken.	Silver chloride found.	Vanadium pentoxide found.	Percentages of	
				chlorine.	vanadium.
1.	0·3317	0·7693	0·2510	57·40	42·53
2.	0·2490	0·5876	——	58·37	——
	0·2462	——	0·1832	——	41·80

Hence we have for the composition of the chloride:

	Calculated.	Found.		Mean.
		(1)	(2)	
$V = 51{\cdot}3$	41·95	42·53	41·80	42·16
$Cl_2 = 71{\cdot}0$	58·05	57·40	58·37	57·88
122·3	100·00	99·93	100·17	100·04

Vanadium dichloride, when heated in hydrogen or in carbon dioxide, does not volatilize without decomposition. It is extremely hygroscopic, instantly absorbing moisture from the air, deliquescing to a brown liquid: a portion of this chloride exposed to the air for five minutes gained 4 per cent. in weight, and in standing for sixteen hours the increase amounted to 50 per cent. When thrown into water the dichloride does not at once dissolve, the scales floating on the water without becoming wet; soon, however, they dissolve, forming a violet-coloured liquid identical in tint with the solution of hypovanadous sulphate obtained by reducing a solution of vanadic acid in sulphuric acid by hydrogen evolved from zinc or sodium. Like this latter liquid, the solution of the dichloride in water acts as a very powerful reducing agent, bleaching litmus and indigo solutions.

A solution of hypovanadous salt obtained by dissolving 0·2875 grm. of vanadium dichloride in water required 81·8 cub. centims. of permanganate solution completely to oxidize it (1 cub. centim.=0·00066 grm. oxygen). Hence the percentage (on the dichloride) of oxygen needed to oxidize the solution was 18·78, whereas the formula $2V\,Cl_2 + O_3 + 2H_2O = V_2O_5 + 4H\,Cl$ requires 19·6 per cent.; the difference between the found and calculated numbers is due to the great difficulty of preventing the solution absorbing some little oxygen during the analysis, which must of course be conducted in an atmosphere of carbon dioxide. When the dichloride placed in a platinum boat is heated to whiteness in a current of dry ammonia, dense fumes of ammonium chloride are given off, and on cooling after an hour's heating, the boat contains vanadium mononitride in bronze-coloured pseudomorph crystals, which exhibit by reflected light a bright metallic lustre.

The specific gravity of vanadium dichloride at 18° C. is 3·23 as a mean of two well-agreeing determinations. Vanadium dichloride dissolves slowly in alcohol and in ether, giving in the one case a blue and in the other a greenish-yellow solution.

Metallic Vanadium, V=51·3.—From what we now know of the character of vanadium, we learn without surprise that the metal cannot be prepared in the free state by any of the methods given in the books.

BERZELIUS (POGG. Ann. vol. xx. p. 1) obtained a brilliant metallic scale by heating the oxytrichlorides, placed in a bulb-tube, in an atmosphere of ammonia; but this substance, as SCHAFARIK observes, is mononitride, and not metal. The great Swedish chemist also states that the metal can be prepared in a pulverulent form by exploding fused vanadic acid with potassium. The black powder which is obtained by lixiviating the fused mass is, however, not metal but an indefinite mixture of oxides. SCHAFARIK (Ann. der Ch. und Pharm. vol. cix. p. 97) describes as metal the brownish-yellow lustrous crystals obtained by passing the vapour of the oxytrichloride mixed with hydrogen through a red-hot tube. The body thus prepared, as I have already shown, is not the metal, but a mixture of the lower oxychlorides of vanadium.

JOHNSTON (N. Edin. Journ. of Sc. vol. v. pp. 166, 318) obtained a hard brittle metallic globule by reducing vanadic acid with carbon at a white heat; this was certainly not metallic vanadium, probably the alloy with silicon.

Although it appeared unlikely that any compound of vanadium containing oxygen would yield the metal by direct reduction, I have nevertheless repeated the above experiments, but without success. In order to test the second method proposed by BERZELIUS, the fused pentoxide was mixed with excess of sodium, and the mixture heated in a closed wrought-iron crucible; after the explosion the black mass was washed until free from alkali. A black powder is thus obtained which glitters when suspended in water, and this powder on oxidation only gained 16 per cent., showing that it contained even more oxygen than the trioxide.

JOHNSTON'S experiment was also repeated by exposing a mixture of trioxide, charcoal, and oil contained in a graphite crucible for several hours to the heat of a wind-furnace in which manganese can be fused. Not a trace of either a bead or metallic powder was obtained, and the black powder gained on oxidation only 16 per cent.

In order to ascertain whether under other circumstances the trioxide can be reduced, a portion of this oxide was heated to whiteness in a current of hydrogen, both when alone and mixed with excess of sodium; in neither case was the metal formed, a black residue of oxide remaining behind in the boats. The trioxide heated in a graphite crucible to bright redness with magnesium also yielded a black powder consisting of mixed oxides.

Another reaction consisted in passing the vapour of oxytrichloride mixed with hydrogen over metallic sodium heated in a porcelain boat; a black shining powder was thus obtained, which after lixiviation and drying was burnt to vanadium pentoxide, and gained only 11 per cent. in weight.

The only methods which promised possible results were:

1. The reduction of a vanadium chloride (free from oxygen) in hydrogen gas.
2. The reduction of the mononitride in a current of hydrogen.

The first of these methods has been found to be successful, the second does not appear to yield the metal; for in two experiments in which the mononitride was ignited in a platinum-tube to whiteness in a current of hydrogen, in one case for 3½ and in another for 2 hours, the loss of weight was only 8·8 and 8·4 per cent. respectively, whereas the nitride must lose 21·4 per cent. when converted into the metal.

Reduction of the Metal from Vanadium Dichloride in Hydrogen.—The only method by which it has been found possible to obtain metallic vanadium is by the reduction of a chloride free from oxygen, in an atmosphere of perfectly pure hydrogen. Although this process appears simple enough, yet there is, I believe, no metal more difficult to obtain than vanadium.

This arises from the circumstance that while vanadium appears to be stable at ordinary atmospheric temperatures, it absorbs oxygen at a red heat with the greatest avidity, and that therefore every trace of air or of moisture must be excluded. Another difficulty consists in the preparation of sufficiently large quantities of the solid chlorides free from oxygen or moisture, as also in the length of time necessary in order to reduce these chlorides in hydrogen at a red heat, during which time diffusion (which can never be wholly prevented) brings traces of oxygen in contact with the heated metal.

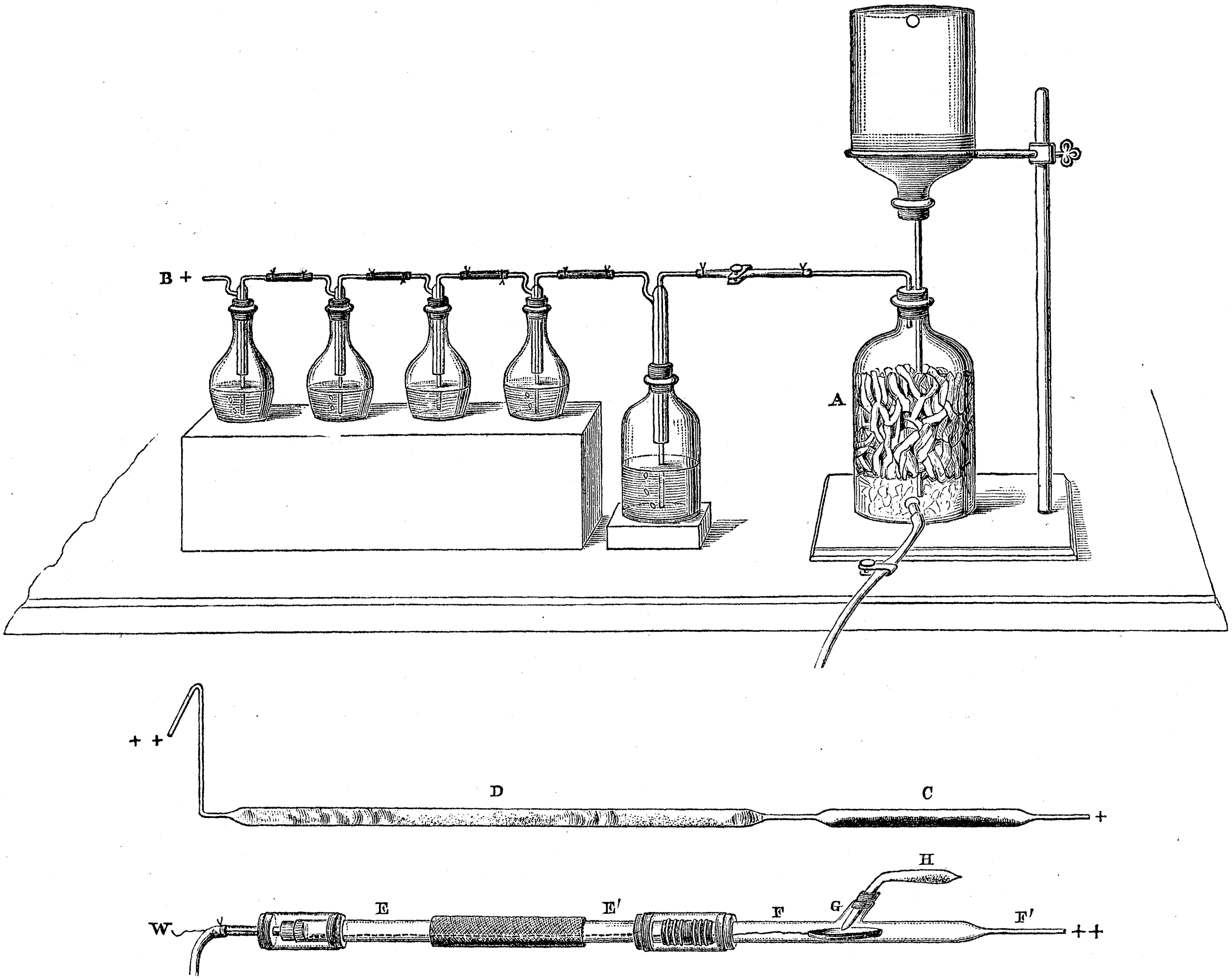
Then, again, the destructive action of the metal on glass and porcelain prevent these substances being used to contain the metal, whilst tubes of platinum and wrought iron become so porous at a red heat as to admit sufficient oxygen to convert the whole vanadium into trioxide. The only means which can be adopted is to heat the chloride in a platinum boat placed in a porcelain tube.

A laborious series of preliminary experiments on the reduction of the metal in this way proved that, in order to obtain a substance even approaching to the metal, many precautions must be taken, whilst they showed that, in spite of every care, it is extremely difficult to obtain the metal itself. Thus no less than ten experiments made by different modifications of this method yielded mixtures of metal with more or less oxide, of which the analyses showed an increase on complete oxidation varying from 60 to 67 per cent., that for pure metal being 78, whilst in every case in which the pure metal was prepared a considerable quantity of black sesquioxide was formed at the end of the boat nearest the inflow of hydrogen, showing that the source of error lay in the presence of diffused oxygen.

The apparatus which, after many alterations, was found best adapted for the preparation of the metal is represented on fig. 2.

It consists of a hydrogen generator (A) yielding a stream of hydrogen which can be kept constantly passing through the wash-bottles day and night for a week at a time,

Fig. 2.



by occasionally adding fresh acid to the upper bottle and drawing off the zinc-sulphate solution from the lower bottle by the caoutchouc tube. The first wash-bottle contains a solution of lead acetate, the second silver nitrate, and the other three boiled sulphuric acid. In order to remove any trace of oxygen which may have accompanied the hydrogen arising either from diffusion or from air absorbed in the dilute acid used, a tube (C D) is attached to the end of the last washing bottle; the first portion of this tube contains a quantity of platinum sponge (C), which is heated to redness during the whole time the hydrogen is passing through the apparatus, whilst the further portion of the tube D is filled with phosphorus pentoxide and plugs of cotton-wool. The greatest care was taken to have all caoutchouc stoppers and joints made as tight as possible with copper wire and paraffin. At right angles to the drying-tube (C D) is placed the reducing arrangement shown in the lowest part of the drawing. This consists of a porcelain tube (E E′) placed in a Hofmann's furnace and protected in the central portions, where it is heated, by an outer casing of sheet iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (F F′) provided with the tubulus (G), and narrowed down to join the drying-tube at F′. The joint between the porcelain and glass tubes is made of seamless caoutchouc well wired, and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The introduction of the anhydrous dichloride without exposure to the air is effected by means of the tubulus (G), the dichloride being contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. After the whole arrangement has been set up, the platinum boat being in position as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours to dry it completely and clear out the air; the caoutchouc stopper of the tubulus is then withdrawn and the end of the tube containing the dichloride cut off, and the tube and stopper quickly replaced, so that the crystals lie in the horizontal portions of the tube. The bent tube is next so turned in the stopper that the crystals of dichloride fall out and are collected in the platinum boat placed below. This boat, charged with dichloride, is then drawn into the centre of the porcelain tube by means of the platinum wire, the end of which (W) passes through a small hole in the caoutchouc tube at the end of the apparatus. As soon as the boat is in position, the wire is cut off short at the end of the glass tube, a proper joint made, and an exit-tube attached dipping under sulphuric acid.

Before the porcelain tube is heated, the caoutchouc stopper of the tubulus is surrounded by a bath of paraffin, and the hydrogen is allowed to bubble through for six hours. The temperature of the porcelain tube is then gradually raised to the highest point (a bright red heat) which the Hofmann's furnace will yield, and kept constant until the reduction is complete. Torrents of hydrochloric acid gas at once come off, and the process must be continued for some hours after the last trace of acid can be detected in the hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grms.

Metallic vanadium prepared by reduction from the dichloride in hydrogen is a light whitish grey-coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline metallic mass possessing a silver-white lustre. It is remarkable that vanadium thus prepared does not oxidize or even tarnish in the air at the ordinary atmospheric temperature, nor does it decompose water at the ordinary temperature, and it may be moistened and dried *in vacuo* frequently without gaining in weight. Vanadium is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with the most brilliant scintillations, and when slowly heated in a current of air it glows brightly with absorption of oxygen, forming in the first place a brown oxide (V_2O or V_2O_2); and on further heating this oxide again glows, and passes through the black trioxide and blue tetroxide to pentoxide. The metal-powder is not magnetic, and it could not be pressed into a coherent form. Its specific gravity at 15° was found to be 5·5 as a mean of three determinations. The metal is not attacked by hydrochloric acid[*], either when hot or cold; neither strong nor dilute sulphuric acid act on the metal in the cold, but when heated with the strong acid the metal slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen, and formation of a green solution, whilst nitric acid of all strengths oxidizes it with violence, evolving nitrous fumes and forming a blue liquid. Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved and a vanadate formed.

The metallic powder obtained by reduction contains a quantity of combined or absorbed hydrogen, the amount of which frequently rose up to 1·3 per cent. The weight of this hydrogen must be determined by burning the metal placed in a platinum boat, in a glass tube through which first a stream of dry air, and afterwards of pure oxygen is passed. A drying-tube placed in front of the combustion-tube gives the weight of water formed.

Analysis No. 1.—0·1365 grm. of substance, containing 0·0005 grm. of hydrogen, yielded on oxidation 0·2420 grm. of vanadium pentoxide in long clear needle-shaped crystals. Hence the percentage gain is 77·94, whereas that calculated from metal is 77·98.

Analysis No. 2.—0·2305 grm. of metal from a different preparation, containing 0·0022 grm. of hydrogen, yielded 0·3915 grm. V_2O_5. Hence the percentage gained was 70·8.

Metallic vanadium burns in excess of dry chlorine, forming the tetrachloride. A portion of dark reddish-brown chloride, formed by combustion of the metal in chlorine, gave the following results: 0·6958 grm. chloride yielded 1·9939 grm. Ag Cl, and 0·3383 grm. V_2O_5. Hence the chloride contained 70·8 per cent. of chlorine and 27·3 per cent. of vanadium; the difference between these and the theoretical numbers (73·46 and 26·54) being explained by the fact that the metal operated upon contained a slight admixture of oxide.

Heated in an atmosphere of pure nitrogen, metallic vanadium at once absorbs this gas and is converted into mononitride.

Vanadium attacks all glass or porcelain in which it is heated, a compound of silicon and the metal being formed. This compound coats all tubes of glass or porcelain in which the chlorides have been heated and reduced, as a grey lustrous metallic mirror, the formation of which renders the tubes very brittle and liable to crack. The silicon compound is not attacked by hydrochloric, and only slightly by nitric acid, but it tarnishes after a time on exposure. The metal also forms an alloy with platinum. All the platinum boats and tubes in which the reduction has been made are found after the operation to be completely saturated with vanadium, and require to be frequently ignited in

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[*] Hydrochloric acid readily dissolves the trioxide.

the air, and as often boiled out with a solvent for vanadic acid, before they can be freed from the absorbed metal. If the platinum be frequently used for the reduction without this purification, it becomes brittle and dark-coloured from absorption of metal in quantity.

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