V.—*On some New Vanadium Compounds.*

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THESE compounds are formed by the following remarkable reaction. If a blue solution of hypovanadic sulphate be mixed with a colourless solution of an alkaline metavanadate, a dark-green liquid will be produced, and if to this a slight excess of caustic soda is added, the colour of the solution quickly changes to a deep black. From this dark-

coloured solution, well-defined crystalline salts having a purple or dark-green colour and metallic lustre, can be obtained, in which the condition of oxidation of the metal is intermediate between the tetroxide, V_2O_4 , and the pentoxide V_2O_5 . I have succeeded in preparing five distinct numbers of this group of salts, viz. :—

1. A soluble sodium salt having the composition—

2. A soluble potassium salt—

3. An insoluble potassium salt—

4. A soluble ammonium salt—

5. An insoluble ammonium salt—

Intermediate Oxides.

Professor Roscoe observed long ago that when black vanadium trioxide, V_2O_3 , is exposed to the air for many months, it absorbs oxygen and moisture from the air, its colour changing to a pale grass-green. On analysing a sample of such an oxide which had been freely exposed to the air for a considerable length of time, I found that its composition, as regards its degree of oxidation, corresponds with that of the insoluble potassium and ammonium salts, viz., $V_2O_4, 2V_2O_5 + 8H_2O$.

	Found.	Calculated.
Vanadium	45·08	45·49
Oxygen	33·45	33·19
Water	21·47	21·32
	<hr/> 100·00	<hr/> 100·00

This oxide, dissolved in dilute sulphuric acid and neutralised with caustic potash, yields, when heated, the purple insoluble potassium salt.

Another intermediate dark-green oxide, containing an equal number of molecules of tetroxide and pentoxide, may be obtained by the gentle ignition of the ammonium salt, No. 5. This oxide readily absorbs moisture from the air, its composition then being—

	Found.	Calculated.
Vanadium	51.83	51.62
Oxygen	35.94	36.29
Water	12.23	12.09
	<hr/> 100.00	<hr/> 100.00

This intermediate oxide, V_4O_9 , can also be obtained in solution by adding strong sulphuric acid to a hot saturated solution of ammonium metavanadate, and then passing sulphur dioxide through the solution until the liquid attains a green colour. After driving off the excess of sulphur dioxide by boiling, the solution was titrated with permanganate and found to contain vanadium tetroxide and pentoxide in equal molecular proportions. The green-coloured solutions thus obtained may also be prepared by suspending freshly precipitated hydrated vanadium tetroxide in water, adding an insufficient quantity of dilute sulphuric acid to dissolve it, and allowing the turbid liquid to stand several hours. These solutions are very unstable, gradually changing colour from absorption of atmospheric oxygen, passing through all shades of colour, from dark-green to light-brownish yellow.

Intermediate Salts.

1. *Soluble Sodium Salt*, $2V_2O_4 \cdot V_2O_5 \cdot 2Na_2O + 13H_2O$.—In order to prepare this salt, 12 grams of finely powdered vanadium pentoxide is placed in a flask, an excess of a strong solution of sulphur dioxide poured on to it, and the solution heated to the boiling point, small quantities of sulphuric acid being added from time to time. The deep blue solution thus obtained is then well boiled to expel every trace of sulphur dioxide. Six grams of vanadium pentoxide are separately boiled with an excess of caustic soda until completely dissolved. The two solutions are now mixed hot, and caustic soda added to the dark blackish-green liquid until it is slightly alkaline; after standing for a short time, acetic acid should be added to the liquid in very slight excess only, as an excess of caustic soda decomposes the green salt. On filtration after boiling, the filtrate contains the new salt together with sodium sulphate. As these two salts possess nearly the same degree of solubility they cannot be separated by crystallisation; on adding to the cold solution a cold saturated solution of sodium acetate, however, the new vanadium salt is precipitated in black shining crystals. These are deposited in large quantity and of considerable size if the liquid is heated after addition of the acetate, and then allowed to cool. The crystals should be washed with a saturated solution of sodium acetate until the washings are free from sulphuric acid, and the adhering acetate removed by washing with dilute alcohol

until the latter no longer yields an acid distillate. Finally the crystals are dried over calcium chloride. The sodium salt thus obtained consists of black shining plates which, under the microscope, are seen to consist of groups of short hexagonal prisms, and have a sp. gr. of 1.327 at 15° compared with water at 15°. A solution of the pure salt, on slow crystallisation, yields hexagonal plates of considerable size, having the form shown in the figure, and an angle between the faces of the pyramid and prism of 133° 45'. The salt is readily soluble in water, yielding a dark blackish-green solution which, on acidification with a few drops of sulphuric acid, instantly changes to a light grass-green, whilst alkalis restore the black colour, unless an excess be added, when the compound is decomposed with formation of a red-brown solution. The sodium salt is insoluble in strong saline solutions—especially in those of the acetates in the cold; if boiled with potassium or ammonium acetate, purple insoluble salts of these metals are formed.

The quantity of the two oxides of vanadium present was ascertained by titration with a standard permanganate solution, care being taken, in the determination of the tetroxide, to use cold solutions, to displace all air by carbon dioxide, and to use well boiled water for dissolving the salt. The total vanadium was estimated by the same method after complete reduction with sulphur dioxide. In order to estimate the alkaline metal, the vanadium was precipitated as lead salt by basic lead acetate, the excess of lead removed by sulphuretted hydrogen, and the sodium weighed as sulphate.

For the purpose of determining the water of crystallisation, the salt was heated to redness in a combustion-tube in a current of dry air, and the water collected in a weighed calcium chloride tube.

The following are the results obtained :—

	Found.		Calculated.
	1st preparation.	2nd preparation.	$2V_2O_4, V_2O_5, 2Na_2O + 13H_2O.$
V_2O_4	37·67	36·80	38·12
V_2O_5	21·19	21·00	20·88
H_2O	26·05	25·34	26·80
Na_2O	14·15	13·88	14·20
	<hr/> 99·06	<hr/> 97·02	<hr/> 100·00

2. *Soluble Potassium Salt*, $2V_2O_4, V_2O_5, 2K_2O + 6H_2O$.—In order to prepare this salt, 20 grams of vanadium pentoxide were reduced by sulphur dioxide, and 10 grams also were converted into potassium metavanadate, the filtered solutions being mixed and caustic potash added to slight alkalinity. The resulting greenish-black liquid was then heated to the boiling point, filtered, mixed with a cold saturated solution of potassium acetate, and the mixed liquids evaporated on the water-bath to a small bulk. On cooling and standing, a mass of small dark crystals separated which, under the microscope, were seen to consist of imperfectly formed octohedrons having a purple colour, mixed with other dark-green four-sided crystals. The mixed crystalline mass was then well washed on a filter with hot water, which dissolved the greenish-black crystals, leaving the purple insoluble salt behind. The dark-green filtrate was, as before, mixed with a concentrated solution of potassium acetate, heated until the separated crystals redissolved, and the solution left to cool. On standing, fine greenish-black crystals were deposited from which all trace of potassium sulphate was removed by continued washing with weak alcohol. This compound has a sp. gr. of 1·389 at 15°, compared with water at 15°.

Analysis of this salt gave the following:—

	Found.			Calculated.
	1st preparation.	2nd preparation.		$2V_2O_4, V_2O_5, 2K_2O + 6H_2O.$
V_2O_4	42·02	40·83	40·16	41·04
V_2O_5	23·54	23·90	22·58	22·48
H_2O	11·11	12·82	13·84	13·31
K_2O	21·04	21·21	21·58	23·17
	<hr/> 97·71	<hr/> 98·76	<hr/> 98·16	<hr/> 100·00

Preparation No. 1 contains 5 mols. H_2O .

3. *Insoluble Potassium Salt*, $2V_2O_4, 4V_2O_5, 5K_2O + H_2O$.—The purple insoluble salt above mentioned can be easily obtained pure from the mother-liquors of the sodium salt. This dark-green solu-

tion containing sodium acetate and sulphate is heated and filtered hot, to the hot liquid some solid potassium acetate is added, and the whole is well boiled. Small crystals having a metallic lustre soon form on the surface of the liquid, and, if the boiling be continued, the whole of the soluble sodium salt may thus be converted into the insoluble potassium compound. The sp. gr. of this salt is 1.213 at 15° compared with water at 15°. In order to determine the potassium in this insoluble salt, it was oxidised with strong nitric acid, and the pentoxide converted into the ammonium salt; this was then precipitated with lead acetate as before, and the alkali weighed as sulphate.

	Found.		Calculated.
	1st preparation.	2nd preparation.	$2V_2O_4, 4V_2O_5, 5K_2O + H_2O.$
V_2O_4	20.75	22.81	21.48
V_2O_5	47.47	45.98	47.05
K_2O	28.24	29.82	30.32
H_2O	2.26	1.17	1.15
	<hr/> 98.72	<hr/> 99.78	<hr/> 100.00

The amount of water in Preparation No. 1 corresponds with 2 mols H_2O , whilst that in No. 2 agrees with 1 mol. H_2O .

4. *Soluble Ammonium Salt*, $2V_2O_4, 2V_2O_5, (NH_4)_2O + 14H_2O$.—This salt is formed by boiling vanadium pentoxide with ammonia until solution takes place, reducing two-thirds of the resulting solution to V_2O_4 , mixing this with the unreduced third, and adding ammonia to slightly alkaline reaction. A dark-green solution of the above ammonium salt is thus formed; this cannot be boiled, as the salt is thereby converted into the insoluble compound. By adding acetic acid to the solution until faintly acid, and then alcohol, and allowing the mixture to stand after well shaking, a black crystalline precipitate separates. The supernatant liquid is decanted, and the precipitate thrown on a filter, and washed with a mixture of equal volumes of alcohol and water until free from sulphuric acid. The salt thus obtained is then dried over calcium chloride. It consists of greenish-black crystals which are very unstable, readily absorbing oxygen from the air. In order to determine the ammonia, the salt placed in a platinum boat was heated in a combustion-tube, and the ammonia collected and weighed as platinochloride. Analysis gave :—

	Found. 1st preparation.	Calculated.
V_2O_4	33·20	33·23
V_2O_5	35·62	36·43
$(NH_4)_2O$.	5·67	5·19
H_2O^*	25·51	25·15
	<hr/> 100·00	<hr/> 100·00

* Water by difference.

5. *Insoluble Ammonium Salt*, $2V_2O_4, 4V_2O_5, 3(NH_4)_2O + 6H_2O$.—The foregoing soluble salt is readily converted into this insoluble compound by adding ammonium chloride to its solution rendered alkaline by ammonia, and gently heating the liquid for some time. Small purple crystals having a metallic lustre separate out—first on the sides of the vessel, and afterwards on the surface of the hot liquid. It is not necessary for this purpose to prepare the pure soluble ammonium salt, as the dark-green liquid obtained by mixing equal parts of solutions of V_2O_4 and of ammonium metavanadate readily yields this salt when rendered alkaline with ammonia and heated. The crystalline precipitate is well washed with hot water until it is seen under the microscope to be perfectly homogeneous.

It crystallises in small purple octagonal plates, of a metallic lustre, and yields a brown powder. Its sp. gr. at 15° is 1·335 compared with water at 15° . Analysis gave:—

	Found.			Calculated.
	1st preparation.	2nd preparation.		$2V_2O_4, 4V_2O_5, 3(NH_4)_2O$ $+ 6H_2O$.
V_2O_4	25·64	24·77	25·15	25·09
V_2O_5	55·48	55·29	55·42	55·01
$(NH_4)_2O$..	11·68	12·40	11·51	11·76
H_2O^*	7·20	7·54	7·92	8·14
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

* Water by difference.

In concluding my paper, I must thank Mr. Harden, of Owens College, for kindly confirming several of my results.