LXXVIII.—*The Electrolytic Preparation of Vanadious Sulphate.*

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PROFESSOR ROSCOE observed that when a solution of vanadium trioxide was prepared by reducing the higher oxides dissolved in dilute sulphuric acid, the resulting liquid had sometimes a brown and sometimes a green colour. The brown-coloured liquid is usually obtained when a solution of vanadium dioxide from which the excess of acid has been removed by zinc, is allowed to absorb oxygen from the air, being thereby converted into V_2O_3 . That these two compounds are of the same degree of oxidation has also been shown by Roscoe.

These experiments were repeated very carefully, and it was found that the green trioxide solution could be at once converted into the brown by the addition of zinc oxide; this of course removing the excess of free acid. The resulting brown liquid had still an acid reaction, but when a large excess of zinc oxide was added it became colourless, and ultimately the whole of the vanadium was completely precipitated from solution.

This behaviour of a solution of the trioxide with zinc oxide indicates that the green solution is an acid salt, whilst the brown is probably basic, a conclusion supported, moreover, by the fact that a few drops of acid turned the brown liquid green again.

I endeavoured to isolate a pure solution of the trioxide by reducing a pure solution of V_2O_5 in dilute sulphuric acid with metallic zinc, until the deep green colour of the trioxide was produced. This green solution, filtered and mixed with alcohol, deposited an intensely green oily liquid which could be separated from the lighter watery portion by means of a funnel. I found, however, that it was impossible to separate the vanadium salt from the zinc sulphate by long continued washing with alcohol, or by any other means tried. I then endeavoured to obtain by electrolysis a solution of V_2O_3 in sulphuric acid uncontaminated with any foreign substance. This method was

found to answer satisfactorily, the apparatus being arranged so that all the hydrogen was utilised and the oxygen carried away without interfering with the reduction. Fig. 1 shows the arrangement adopted. The reduction is best commenced on a strong pure solution of V_2O_4 in dilute H_2SO_4 , which is readily obtained by the reducing action of SO_2 . The deep blue tetroxide solution is placed in the platinum dish (*b*) forming the negative electrode of the battery (*d*), whilst the porous cell (*a*) containing the positive electrode of pla-

FIG. 1.

tinum (*c*) and dilute sulphuric acid just touches the surface of the liquid. The reduction proceeds regularly and may be accelerated by heating. In this manner, the reduction and evaporation can go on simultaneously. The end of the reaction is determined by the intense green colour of the solution, a drop of which on being taken out and shaken up with a small quantity of water gives a green liquid with no tinge of blue.

The concentrated green trioxide solution is then mixed with about twice its bulk of strong sulphuric acid, and allowed to remain for 24 hours; at the end of that time the whole of the trioxide separates in combination with sulphuric acid as a pale green sandy crystalline precipitate, which must be placed upon a porous tile, washed with strong alcohol until the free sulphuric acid is entirely removed, and then dried over sulphuric acid in a desiccator filled with coal-gas. The following analyses made with two preparations show that this sulphate of vanadium trioxide has the formula $V_2O_3(SO_3)_4 + 9H_2O$:—

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	Calculated.	Found.	Found.
V_2O_3	23·78	23·93	23·81
SO_3	50·60	50·89	50·82
H_2O	25·62	25·18	25·37
	100·00	100·00	100·00

The vanadium was estimated as V_2O_3 by heating the salt in a crucible to bright redness, a fine crystalline residue of V_2O_3 remaining. The degree of oxidation was confirmed by means of a standard solution of permanganate, 1 c.c. of which was equal to 0·000677 gram of oxygen; 0·1120 gram of salt required 7·9 c.c. = 0·0053483 oxygen. The oxygen required by theory being 0·00566. The variation which is equal to 1 per cent. is only very small when the readiness with which the salt absorbs oxygen is considered.

Sulphate of vanadium trioxide dissolves in water, yielding a bright green solution, from which alkalis precipitate the hydrated trioxide as a dirty green somewhat gelatinous mass, which is rapidly oxidised in the air.

The fact that the brown trioxide solution is more basic than the above was ascertained by the fact that this green hydrated trioxide readily dissolves in a solution of the foregoing green sulphate, forming a deep chocolate-coloured liquid, and on evaporation this liquid yields a shining green amorphous mass, which again dissolves in water, forming a brown solution.

This method of reduction may also be employed for the preparation of the other lower oxides of vanadium. Thus a lavender-coloured solution of vanadium dioxide is obtained on continued reduction, and from this the hydrated dioxide may be precipitated by ammonia as a deep purple gelatinous mass.

It is, however, impossible to isolate these compounds in the solid state on account of their extreme instability.