141. *Electrometric Studies of the Precipitation of Hydroxides. Part XVI. Vanadous Hydroxide. The Nature of Vanadous Chloride and Sulphate Solutions.*

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Vanadous chloride exists in solution as VCl_3, whereas in the presence of an excess of sulphuric acid, vanadous sulphate appears to form an acid salt, $H_2SO_4,V_2(SO_4)_3$, or possibly a complex acid, $HV(SO_4)_2$. Vanadous hydroxide is precipitated from both chloride and sulphate solutions between p_H 4 and 5. It is not amphoteric.

Tervalent vanadium salt solutions are exceedingly readily oxidised by air; nevertheless, several vanadous salts have been isolated. Whereas the halide salts appear to be normal, sulphuric acid gives rise to what is usually regarded as an acid salt,

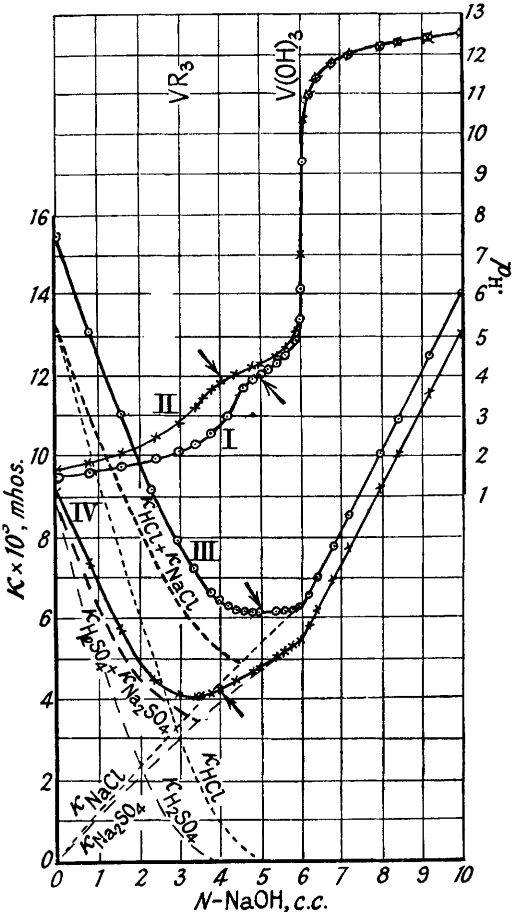
$$H_2SO_4,V_2(SO_4)_3,xH_2O.$$

Solutions of these compounds may be conveniently prepared by electrolytic reduction of acid solutions of quadrivalent vanadium salts. With smooth platinum, lead, or mercury as kathode, reduction may proceed as far as the bivalent stage, but it was found that with platinised platinum reduction ceased at the tervalent stage, with formation of vanadous salts (cf. Rutter, *Z. Elektrochem.*, 1906, **12**, 230). Vanadous salt solutions are brown, but on acidification they undergo a characteristic change to green.

The object of the present work was to follow the changes in p_H and electrical conductivity which result from the progressive addition of sodium hydroxide to acidified vanadous salt solutions in order to ascertain the conditions under which vanadous hydroxide is precipitated.

EXPERIMENTAL.

Electrolytic Preparation of Vanadous Salt Solutions.—Acidified vanadyl solutions were reduced at a cylindrical platinised platinum kathode placed inside the walls of a glass vessel, the capacity of which was about 1200 c.c. A small bright platinum anode was enclosed in an inverted bell-shaped glass tube, and this was separated from the katholyte by means of a diaphragm of porous pot which was fitted securely into the mouth of the bell. The anolyte was a very dilute solution of either hydrochloric or sulphuric acid depending on whether the chloride or sulphate was being prepared. The complete cell was covered with a tightly fitting ebonite cap, and nitrogen was bubbled through the katholyte throughout the electrolysis and an atmosphere of this gas was maintained inside the vessel. The progress of reduction was followed by the titration, at intervals, of portions of the katholyte with potassium permanganate, and no solution was used until two titrations carried out ½ hour apart showed that reduction was complete. Then the solution was siphoned by means of nitrogen pressure into a vessel previously filled with hydrogen and attached to a burette into which the liquid could be run as required.



Electrometric Titrations.—For the titrations, performed at 25°, 100 c.c. of solutions, which were 0·005M with respect to V_2O_3 and 0·06N with respect to hydrochloric or sulphuric acid, were used. These were titrated with N-sodium hydroxide both by using the hydrogen electrode and also conductometrically. In the former titrations, every care was taken to prevent atmospheric oxidation by keeping the liquid in contact with an atmosphere of hydrogen, whereas nitrogen was employed in the conductometric work. The curves obtained are shown in the figure. Curves I and II are the hydrogen electro-titration curves of the hydrochloric and sulphuric acid solutions respectively, whereas III and IV are the corresponding conductometric titration curves. The solutions titrated were so chosen that they contained an excess of acid equivalent to that required to form the vanadous salt. Owing to the presence of the excess of acid these vanadous salt solutions were initially green, but when enough alkali was added (*viz.*, 3 c.c.) to neutralise the excess of acid the solutions became brown. Precipitation of vanadous hydroxide did not begin until the vanadous chloride and sulphate had undergone appreciable decomposition, to the extents corresponding with $V(OH)_2Cl$ and $V(OH)SO_4$ and indicated by arrows in the curves. During the formation of these basic salts in solution the solutions became more intensely brown. Vanadous hydroxide separated as a green gelatinous precipitate, its formation being complete when the stoicheiometric amounts of alkali had been added. The p_H curve of the sulphate solution becomes inflected soon after the excess of sulphuric acid has been neutralised, whereas the chloride curve shows that acid was present at a later stage as indicated by both the delayed inflection and precipitation, which, however, began from both solutions at a p_H slightly below 4.

The conductometric curves show that there was a marked difference between hydrochloric and sulphuric acid solutions initially, and this difference persisted during the neutralisation of the excess of acid. The broken lines, marked κ_{HCl} and $\kappa_{H_2SO_4}$, represent the variation in specific conductivity caused by the respective acids present throughout the early parts of the reactions, the concentrations of which were computed from the p_H values given on the appropriate hydrogen-electrode curve. The broken lines, marked κ_{NaCl} and $\kappa_{Na_2SO_4}$, show the specific conductivities of the sodium salts formed as the alkali was added, whereas the broken lines marked $\kappa_{HCl} + \kappa_{NaCl}$ and $\kappa_{H_2SO_4} + \kappa_{Na_2SO_4}$ represent the contribution to the conductivity by the acid present and the alkali salt formed. It will be observed in both the chloride and the sulphate titrations that these curves run almost parallel to the first parts of the actual conductometric curves; the actual difference in the chloride titration ranging from $2\cdot2 \times 10^{-3}$ mho initially to $1\cdot5 \times 10^{-3}$ mho when the excess of acid had been neutralised, whilst the difference in the sulphate titration was much less and ranged from $0\cdot6 \times 10^{-3}$ to $0\cdot4 \times 10^{-3}$ mho.

DISCUSSION.

Both the hydrogen electro-titration and the conductometric titration show that vanadous sulphate is fundamentally different from vanadous chloride as it exists in solution. An attempt to obtain a clearer insight into this difference was made by calculating the approximate concentrations of free acid present when increasing amounts of alkali had been added, the acid being assumed to be completely ionised so that its concentration was equal to that of the hydrogen-ion concentration. Although such computations may be open to criticism, they do, as results given in the tables show, afford some idea of the nature of the solutions.

Hydrogen-electrode Titration of 100 c.c. *of* 0·005M-V_2O_3 *in* 0·06N-HCl *with* 1·0N-NaOH *at* 25°.

N-NaOH, c.c.	p_H.	Total HCl, equivs.	Equivs. of HCl combined per atom of V.	N-NaOH, c.c.	p_H.	Total HCl, equivs.	Equivs. of HCl combined per atom of V.
0	1·51	6·00	2·91	4·0	2·73	2·00	1·74
0·8	1·62	5·20	2·71	4·2	2·96	1·80	1·62
1·6	1·76	4·40	2·57	4·4	3·20	1·60	1·47
2·4	1·94	3·60	2·37	4·6	3·66	1·40	1·32
3·0	2·14	3·00	2·19	4·8	3·87	1·20	1·13
3·4	2·32	2·60	2·04	5·0	3·97	1·00	0·94
3·8	2·59	2·20	1·86				

The first line of this table shows that in the original solution the excess of hydrochloric acid was almost sufficient to repress the hydrolysis of the vanadous chloride, there being 2·91 equivs. of acid in combination with an atom of tervalent vanadium. As the excess of acid was removed by neutralisation the number of equivalents of combined acid became less: the composition of the basic vanadous chloride changed from $V(OH)_{0\cdot09}Cl_{2\cdot91}$ to $V(OH)_{0\cdot81}Cl_{2\cdot19}$ when the 3 equivs. of excess hydrochloric acid had been removed, and to $V(OH)_{2\cdot06}Cl_{0\cdot94}$ when precipitation just began. The difference between the observed and calculated specific conductivities shown by Curve III must be ascribed to the ionisation of the basic chloride present in the solution.

Somewhat different conclusions are to be drawn from similar p_H calculations relating to sulphuric acid solutions of tervalent vanadium, as shown in the following table. Despite the approximate nature of the calculations, the figures in the last column reveal that in acid solution more than 3 equivs. of sulphuric acid are in a state of combination with the

Hydrogen-electrode Titration of 100 c.c. *of* 0·005M-V_2O_3 *in* 0·06N-H_2SO_4 *with* 1·0N-NaOH *at* 25°.

N-NaOH, c.c.	p_H.	Total H_2SO_4, equivs.	Equivs. of H_2SO_4 combined per atom of V.	N-NaOH, c.c.	p_H.	Total H_2SO_4, equivs.	Equivs. of H_2SO_4 combined per atom of V.
0	1·69	6·00	3·96	3·0	2·84	3·00	2·77
0·8	1·87	5·20	3·68	3·4	3·18	2·60	2·45
1·6	2·10	4·40	3·53	3·8	3·64	2·20	2·20
2·4	2·48	3·60	3·19	4·0	3·80	2·00	1·91

vanadium; in the original solution approximately 4 equivs. of acid appear to have combined to form a compound which, as shown by the difference between the " theoretical " and the actual conductivity (Curve IV), is but slightly ionised. These proportions correspond to the acid sulphate, $H_2SO_4,V_2(SO_4)_3$, which has been isolated. These considerations suggest rather that it was a complex sulphate or perhaps a weak complex acid, $HV(SO_4)_2$. The last column shows that this complex sulphate was gradually decomposed as the alkali was added, approximating to $V_2(SO_4)_3$ when the theoretical excess of acid had been removed. Precipitation began when it had been rendered basic and corresponded with $V(OH)_{1\cdot09}(SO_4)_{0\cdot96}$.

Apparently the brown colour of vanadous chloride and sulphate solutions is associated with the existence therein of soluble basic salts, and the intensification of the brown colour, when alkali is added, is caused by the salts being rendered more basic. The green colour of those solutions containing an excess of acid seems to be accounted for by the conversion of these basic salts into non-basic vanadous compounds, which in the case of the sulphate appears to be of the nature of a weak complex acid.

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