140. *Electrometric Studies of the Precipitation of Hydroxides. Part XV. The Amphoteric Nature of Vanadium Tetroxide.*

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Electrometric evidence has been obtained which shows that quadrivalent vanadium exists in hydrochloric and sulphuric acid solutions as vanadyl salts, $VOCl_2$ and $VOSO_4$. The vanadyl ion, $VO^{\bullet\bullet}$, does not react in solution with strong acids to form salts of the type VCl_4. Vanadyl hydroxide is precipitated between p_H 4 and 5. With excess of alkali, vanadites, *e.g.*, $Na_2O,2V_2O_4$ are formed.

BRITTON (J., 1934, 1842) described a glass-electrode titration curve of a sulphuric acid solution of vanadyl sulphate with sodium hydroxide, which supplied evidence of the existence of the vanadyl ion, VO··. The curve also indicated that free alkali did not pass into the solution until slightly more than sufficient to convert the vanadyl sulphate into vanadyl hydroxide had been added. Vanadyl hydroxide, on first precipitation, is greyish-white but it becomes dark brown as precipitation proceeds, and this, coupled with the extreme ease with which it suffers aerial oxidation to the quinquevalent stage, was considered to account for the delayed end-point, although the titration was carried out in an atmosphere of hydrogen. It was therefore considered that vanadyl hydroxide possesses no acidic properties, especially as it did not dissolve when an excess of alkali was added.

The present work, however, shows that both the colour change and the delayed end-point result from the formation of a sparingly soluble sodium vanadite. The acidic nature of vanadyl hydroxide can best be demonstrated by rapidly adding sodium hydroxide to a vanadyl salt, whereupon the vanadyl hydroxide dissolves as soon as a small excess of alkali is added, forming a clear red solution, from which on standing a black crystalline sodium vanadite, $Na_2O,2V_2O_4,xH_2O$, is deposited (Crow, J., 1876, **30**, 453; Koppel and Behrendt, *Z. anorg. Chem.*, 1903, **35**, 154).

With the aid of hydrogen electrode and conductometric titrations of alkali vanadite solutions and of quadrivalent vanadium solutions in sulphuric and hydrochloric acids, definite information regarding the amphoteric nature of vanadyl hydroxide has been obtained.

<div align="center">EXPERIMENTAL.</div>

Solutions of quadrivalent vanadium were obtained by reducing hydrochloric and sulphuric acid solutions of vanadium pentoxide by shaking with mercury (McCay and Anderson, *J. Amer. Chem. Soc.*, 1922, **44**, 1018); after an hour reduction was complete, and, on filtering off the mercurous chloride or sulphate, clear blue vanadyl salt solutions remained. Owing to the fact that mercurous sulphate is somewhat soluble, it was necessary to add the exact amount of hydrochloric acid to convert it into calomel in order to remove the mercury from the solution. The method is quantitative, but in general, the reduction of sulphuric acid solutions of vanadium pentoxide by sulphur dioxide was preferred in the preparation of vanadyl sulphate solutions, the excess of sulphur dioxide being driven off by boiling.

Fig. 1 gives the electrometric curves at 25° of vanadium tetroxide in the presence of sufficient acid to convert it into VR_4, R being Cl' or $\frac{1}{2}SO_4''$. In dilute quadrivalent vanadium solutions the hydrogen electrode gave quite satisfactory and reproducible p_H values, there being no indication of any reduction to tervalent vanadium. The hydrogen not only served the electrode, but its passage through the solution kept this thoroughly agitated and also supplied the necessary inert atmosphere. Curves A (100 c.c. of 0·0025M-V_2O_4 + 0·02N-HCl titrated with 0·4N-NaOH) and B (100 c.c. of 0·0025M-V_2O_4 + 0·02N-H_2SO_4 titrated with 0·4N-NH_4OH) have two distinct sections in the acid range. The first section is that of the neutralisation of the 2 equivs. of acid (per atom of vanadium) which appears not to unite with the vanadyl tetroxide, whereas the second refers to the precipitation of hydrated vanadium tetroxide from the vanadyl salt, *viz.*, $V(OH)_2R_2$ or VOR_2. Precipitation began when the solutions had reached approximately p_H 4, *i.e.*, soon after 2 equivs. of alkali had been added. When 4 equivs. had been added the precipitate had changed from greyish-white to a dark brown, and also the mother-liquor, instead of becoming colourless, which would have occurred if all the quadrivalent vanadium had been precipitated as the hydroxide, had assumed a red coloration. Tests were carried out to ascertain whether any oxidation had occurred, but they proved negative. As the curves show, the solutions did not become alkaline, even when ammonium hydroxide was used, until slightly more than 4 equivs. of alkali were added, despite the fact that no oxidation had taken place. Except for the red colour imparted to the mother-liquor, the precipitates did not dissolve appreciably when the excess of alkali was increased. The curves A and B refer to the p_H values immediately set up; if longer times were allowed to elapse before measurements were taken, the final inflexion slowly receded to the line representing the amount of alkali necessary to convert the vanadium tetroxide into an alkali vanadite, $Na_2O,2V_2O_4$.

The conductometric curves C, D, and E (C, 100 c.c. of 0·01M-V_2O_4 + 0·08N-H_2SO_4 titrated with 1·6N-NaOH; D, as in C but titrated with 1·6N-NH_4OH; E, 100 c.c. of 0·0025M-V_2O_4 + 0·02N-HCl titrated with 0·4N-NaOH), which represent titrations carried out in an atmosphere of oxygen-free nitrogen, confirm that (i) vanadium tetroxide reacts as a base, as

VO(OH)$_2$, to form vanadyl sulphate and chloride, for the first branch of each of the three curves corresponds very closely to the neutralisation of free acid, and (ii) the attack of the alkali continues after 4 equivs., the amount required to precipitate VO(OH)$_2$, have been added. After the alkali which has combined reaches the quantity required by the formula Na$_2$O,2V$_2$O$_4$, no further reaction occurs and the extra alkali merely passes into the solution. This is shown by the final slopes of C and E being identical with those indicated by the broken lines shown above the titration graphs. They represent the theoretical increases in specific conductivity caused by excess of alkali produced by the respective titrants. The intersections of the " salt lines " labelled (NH$_4$)$_2$SO$_4$, Na$_2$SO$_4$, and NaCl with the conductometric graphs at the points corresponding with the addition of 4 equivs. of alkali show that initially vanadyl hydroxide was precipitated. The broken lines which run almost parallel
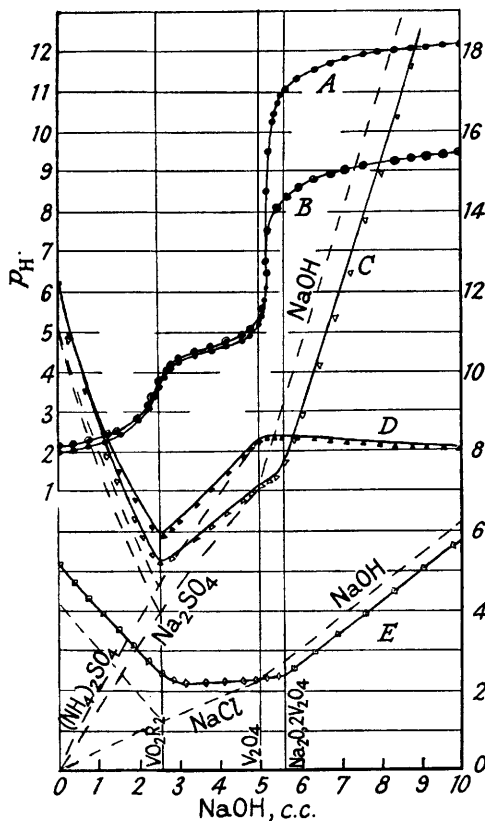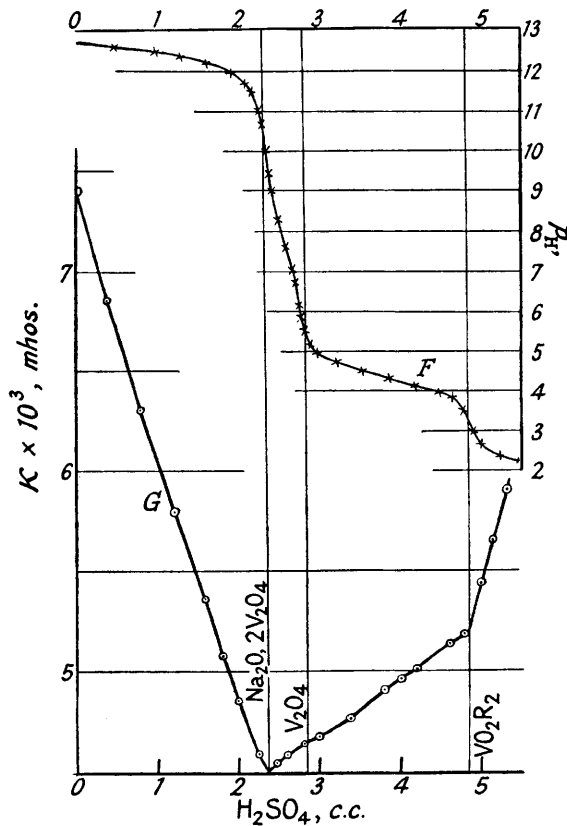

FIG. 1.   FIG. 2.

with the first section of the three graphs represent the specific conductivities caused by the mixture of free acid, calculated on the assumption that only 2 equivs. of acid can react with each VO(OH)$_2$, and the sodium salt formed as the result of the neutralisation of some of this acid. The difference in the specific conductivities indicated by the experimental graph and the respective broken lines must therefore refer to the specific conductivities of the vanadyl salts present in the solutions. For instance, in the conductometric titration shown by E the initial specific conductivity was $5 \cdot 09 \times 10^{-3}$ mho; if the 2 equivs. of hydrochloric acid in excess of the amount required to form vanadyl chloride, VOCl$_2$, were present in the solution, it would set up a specific conductivity of $4 \cdot 12 \times 10^{-3}$ mho; whence it follows that the specific conductivity produced by the vanadyl chloride is $0 \cdot 97 \times 10^{-3}$ mho, *i.e.*, corresponding with an equivalent conductivity of 92. On addition of 2 equivs. of sodium hydroxide, thus neutralising the free acid, the conductivity fell to $2 \cdot 26 \times 10^{-3}$ mho, the sodium chloride formed being responsible for $1 \cdot 16 \times 10^{-3}$ mho, showing that the specific conductivity to be attributed to the vanadyl chloride is $1 \cdot 10 \times 10^{-3}$ ($\Lambda = 112$). This increase in conductivity from $0 \cdot 97 \times 10^{-3}$ to $1 \cdot 10 \times 10^{-3}$,

resulting from the neutralisation of the free acid, is most probably to be accounted for by the increased hydrolysis of the vanadyl chloride. The p_H set up by the vanadyl chloride alone was 3·68; it follows therefrom that the hydrolysis of the salt is approximately 2%, and that the specific conductivity caused by the hydrolysed acid is $0·18 \times 10^{-3}$ mho. Hence the specific conductivity of the unhydrolysed vanadyl chloride is $0·92 \times 10^{-3}$ mho, which is slightly less than that at the beginning of the titration. Similar conclusions are to be drawn from the vanadyl sulphate solutions, except that the extrapolated equivalent conductivity of vanadyl sulphate is of the order of 40 mhos. It would appear, therefore, that vanadyl chloride is fairly well ionised, presumably as $VOCl_2 \rightleftharpoons VO^{\cdot\cdot} + 2Cl'$, whereas the ionisation of the sulphate is considerably less. This does not necessarily suggest that ionisation does not take place according to the above equation yielding vanadyl ions, for similar differences are to be seen between the ionisation of bivalent metal salts, *e.g.*, copper chloride and sulphate.

The curves F and G in Fig. 2 represent the back-titrations, followed respectively by the hydrogen electrode and conductometrically, of alkaline solutions of sodium vanadite with a strong acid; F refers to the titration with N-H_2SO_4 of 100 c.c. of 0·025M-VOSO$_4$ + 0·0037N-H$_2$SO$_4$ to which 12·5 c.c. of N-NaOH had been added rapidly, so as to effect the redissolution of the precipitated vanadyl hydroxide; and G refers to a similar titration of 100 c.c. of 0·01M-VOSO$_4$ + 0·00147N-H$_2$SO$_4$ + 5 c.c. of N-NaOH. The solutions were initially clear and red. The first branch of each of the graphs indicates that free alkali was being neutralised. The point at which the minimum conductivity was reached corresponds with an amount of the alkali still left in combination with the vanadium tetroxide required by the sodium vanadite, Na$_2$O,2V$_2$O$_4$. The completion of the neutralisation of the excess of alkali is also shown at the same point in the p_H curve by a downward inflexion. At this stage the solution became deep red, and as the acid decomposed the vanadite, the solution became almost black and precipitation commenced when approximately one half of the vanadite had been decomposed. As the p_H curves show, the acid decomposed the vanadite completely when the stoicheiometric quantity was added. The remaining sections of F and G refer to the gradual redissolution of the vanadyl hydroxide to form soluble vanadyl sulphate and the introduction of free acid into the solution as soon as the necessary 2 equivs. of acid per mol. of VO(OH)$_2$ had been added.