265. *Physicochemical Studies of Complex Acids. Part VII. Glass-electrode Titrations of Vanadic Acid.*

By HUBERT THOMAS STANLEY BRITTON and ROBERT ANTHONY ROBINSON.

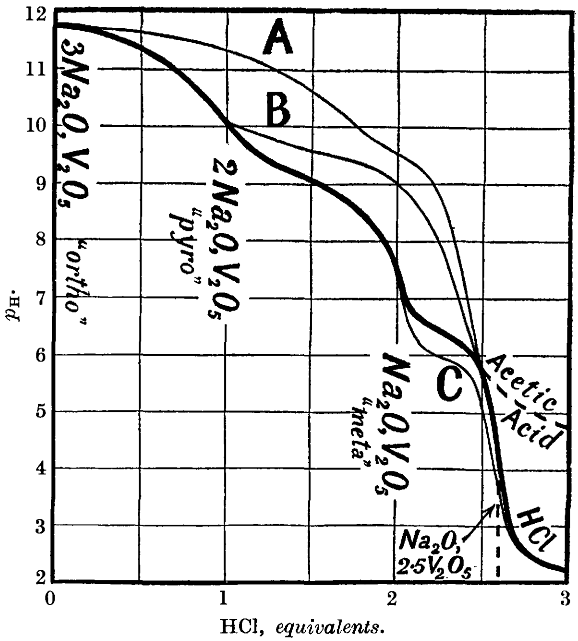
CONDUCTIVITY measurements (Part II, J., 1930, 1261) have shown that the various sodium vanadates on treatment in solution with hydrochloric acid are readily converted into a stable complex vanadate of the approximate composition, $Na_2O,2V_2O_5$. If, however, the acid be insufficient to form such a complex, there occurs a gradual change with time in the constitution of the alkali vandate. As a rule, this change requires several days, but boiling was found to bring it to completion almost instantaneously. The electrodes normally employed to measure p_H fail in the presence of vanadic acid, and the complete investigation of its acidic nature was not then possible, but the glass electrode has now been found not to suffer from this disadvantage, and experiments performed with its aid are described.

EXPERIMENTAL.

Solutions of the three sodium vanadates, $3Na_2O,V_2O_5$, $2Na_2O,V_2O_5$, and Na_2O,V_2O_5, were prepared and back-titrated with hydrochloric acid at 18°. The p_H values were measured throughout these titrations by means of the glass electrode, a condenser, and a sensitive ballistic galvanometer (see Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531). In another set of experiments, three series of alkali vanadate solutions were treated with various amounts of hydrochloric acid corresponding to different stages of the previous titrations, each mixture was heated to boiling, cooled to 18°, and the p_H value then determined. Solutions of the first two vanadates, *viz.*, the so-called ortho- and pyro-vanadates, were prepared by boiling vanadium pentoxide with sodium hydroxide solution in the requisite proportions, whilst the solutions of the so-called metavanadate were made by boiling ammonium metavanadate with the stoicheiometric amount of a sodium hydroxide solution in a current of carbon dioxide-free air. All these solutions developed a yellow colour on the addition of the even the smallest amount of acid, the colour becoming more intense in the case of the solutions of low p_H. Boiling, however, caused those solutions containing vanadates of composition between 3 and 1 mols. of Na_2O to 1 mol. of V_2O_5 to become colourless again. Those solutions which had been treated with more acid than that required to form the 1 : 1-vanadate could not be decolorised, even on boiling. Red precipitates could be obtained from solutions to which more acid had been added than was required to liberate " vanadic acid," although the precise point at which the separation began depended, not only on the concentration of the free hydrochloric acid, but also on the vanadium concentration and on the duration of boiling.

The p_H data obtained during the three immediate titrations at 18° are plotted in Fig. 1 as curves A, B, C, beginning respectively with abscissæ at 0, 1, and 2 equivs. of hydrochloric acid. The undulating curve shown by the heavy line represents the variation in hydrogen-ion concentration brought about by boiling each solution. With the exception of that part of the curve lying below p_H 3, the three curves are coincident over the corresponding stages of the reaction. The observations from which the major part of the heavy curve was constructed are given in Table I : in each case, after the addition of the acid, the solution was boiled and then cooled to 18°. The ratios HCl/Na_3VO_4, etc., are expressed in mols.

FIG. 1.



The inflexions marking the termination of the first two sections of the heavy curve in Fig. 1 occur when 1 and 2 mols. respectively of hydrochloric acid are added to 1 mol. of Na_3VO_4. The shapes of these sections are similar to those produced during the addition of 2 equivs. of a strong acid to the sodium salt of a tribasic acid

TABLE I.

(*a*) p_H Values of 100 c.c. of 0·00833M-Na_3VO_4 + x c.c. of 0·2N-HCl.

Third Stage :

x	0	1·04	1·56	2·08	2·60	3·13	3·65	4·17
HCl/Na_3VO_4	0	0·25	0·375	0·50	0·625	0·75	0·875	1·0
p_H	11·74	11·60	11·49	11·35	11·12	10·83	10·45	10·12
Hydrolysis, %	49	48	45	41	32	25	21	
p_{K_3}	11·72	11·79	11·77	11·72	11·58	11·47	11·41	

Second Stage :

x	5·0	6·0	6·25	7·0	7·5	8·3
HCl/Na_3VO_4	1·20	1·44	1·50	1·68	1·80	2·0
p_H	9·46	9·14	9·07	8·63	8·47	7·50
p_{K_2}	8·86	9·04	9·07	8·96	9·07	—

First Stage :

x	9·0	10·0	12·5	15·0	30·0
HCl/Na_3VO_4	2·16	2·40	3·0	3·6	7·2
p_H	6·50	6·21	2·60	2·09	1·54
p_H (calc.)	—	—	2·53	2·14	1·53

$Na_2O,2·5V_2O_5$ assumed at 10·83 c.c.

(*b*) p_H Values of 100 c.c. of 0·0125M-Na_2HVO_4 + x c.c. of 0·2N-HCl.

Second Stage :

x	0·78	1·56	2·34	3·13	3·91	4·69	5·47
HCl/Na_2HVO_4	0·125	0·25	0·375	0·5	0·625	0·75	0·875
p_H	9·67	9·36	9·17	9·04	8·85	8·61	8·20
p_{K_2}	8·82	8·88	8·95	9·04	9·07	9·09	9·05

First Stage :

x	6·25	9	11	12	12·5	16	29
HCl/Na_2HVO_4	1·0	1·44	1·76	1·92	2·0	2·56	4·64
p_H	7·60	6·15	2·98	2·70	2·30	2·10	1·60
p_H (calc.)	—	—	2·74	2·45	2·35	1·99	1·53

$Na_2O,2·5V_2O_5$ assumed at 10·0 c.c.

(*c*) p_H Values of 100 c.c. of 0·025M-NaH_2VO_4 + x c.c. of 0·2N-HCl.

First Stage, Part 2.

x	0·78	1·56	2·34	3·13	3·91	4·69	5·47	7·0
HCl/NaH_2VO_4	0·06	0·125	0·18	0·25	0·32	0·375	0·44	0·56
p_H	6·85	6·65	6·53	6·44	6·35	6·24	6·06	4·90

First Stage, Part 1.

x	8·0	8·6	9·0	10·0	12·5	16·0	26·0
HCl/NaH_2VO_4	0·64	0·69	0·72	0·80	1·0	1·28	2·08
p_H	3·37	2·76	2·61	2·40	2·20	1·86	1·56
p_H (calc.)	3·03	2·69	2·56	2·34	2·05	1·83	1·53

$Na_2O,2·5V_2O_5$ assumed at 7·5 c.c.

of which K_2 is about 10^{-9} and K_3 about $10^{-11·5}$. Accordingly, values of p_{K_3} and p_{K_2} have been calculated (see Britton, "Hydrogen Ions," 2nd Edn., 1932, p. 145) and are given in Table I (*a*) and (*b*) corresponding to numerous p_H values recorded for increasing amounts of hydrochloric acid. The values of p_{K_3} show greater variations (11·41—11·79) than can be attributed to experimental error, whilst the mean values of p_{K_2} in the two sections are 8·99 and 9·00 respectively, the deviations being attributable to experimental error. In view of the difference in concentration of the vanadate solutions, this constancy and agreement of p_{K_2} appear to provide definite evidence for the existence of the ionic equilibrium $H_2VO_4' \rightleftharpoons H^{\bullet} + HVO_4''$. In spite of their variation, the values of p_{K_3} might be considered to afford some indication of the further ionisation $HVO_4'' \rightleftharpoons H^{\bullet} + VO_4'''$. Hence the first two sections of the heavy curve would correspond to the reactions $Na_3VO_4 + HCl \longrightarrow NaCl + Na_2HVO_4$ and $Na_2HVO_4 + HCl \longrightarrow NaCl + NaH_2VO_4$.

The high p_H values prevailing during the addition of the first equivalent of hydrochloric acid to the sodium orthovanadate solution reveal that the salt must be considerably hydrolysed, apparently in consequence of the ionic reaction $VO_4''' + H_2O \rightleftharpoons HVO_4'' + OH'$. Calculations have been made of the extent of the hydrolysis of the sodium orthovanadate remaining in solution after the various amounts of hydrochloric acid had been added. The figures given in Table I (*a*) show that the 0·00833*M*-sodium orthovanadate solution was hydrolysed to the extent of 49%. During the decomposition reaction with hydrochloric acid, owing to the increasing concentration of HVO_4'' ions, this amount became gradually reduced to 21% when 0·875 equiv. of acid had reacted. In comparison, solutions of so-called sodium pyrovanadate, $Na_4V_2O_7$ or more probably Na_2HVO_4, are but little hydrolysed. This is in agreement with the conductometric curve of sodium orthovanadate given in Fig. 1 of Part II (*loc. cit.*), which shows that a rapid diminution in specific conductivity occurred during the reaction with the first equivalent of hydrochloric acid at which a definite " break " appeared. This change was brought about by the removal of the hydroxyl ions by the direct conversion of the hydrolysed alkali into sodium chloride.

After the reaction with 1 equiv. of hydrochloric acid, there was a gradual variation in conductivity until 2·57 equivs. had reacted. From the heavy curve in Fig. 1 it is seen that this amount of acid corresponds almost to the middle point of the final inflexion. The actual points of flex in each of the curves given by the data in Tables I (*a*) and (*c*) correspond more closely to 2·6 equivs., the complex vanadate in solution then being $Na_2O,2{\cdot}5V_2O_5$. There is but little, if any, definite indication in the conductivity curve of the variation in the type of sodium vanadate existing during the reaction from 2·0 to 2·6 equivs. of acid, but the p_H curve provides adequate evidence.

As previously stated, there appears to be satisfactory evidence that under equilibrium conditions solutions of sodium 1 : 1-vanadate (considered to be the salt of metavanadic acid, $NaVO_3$) contain the salt in the form NaH_2VO_4. If this be the case, then the reaction with the 0·6 equiv. of hydrochloric acid required to bring about a considerable increase in hydrogen-ion concentration might be expressed by the equation

$$2{\cdot}5NaH_2VO_4 + 3HCl = Na_2O{,}2{\cdot}5V_2O_5 + 3NaCl + 5H_2O$$

$$\textit{i.e.,}\quad 5H_2VO_4{}' + 3H^{\bullet} \longrightarrow (V_2O_5)_{2\cdot5}O'' \quad\text{or}\quad 10H_2VO_4{}' + 6H^{\bullet} \longrightarrow (V_2O_5)_5O_2{}''''.$$

If this is so then that part of the titration curve corresponding to the addition of 0·6 equiv. of acid to the 1 : 1-salt should be governed by equations of the type

$$K_1 = [H_2VO_4{}']^5[H^{\bullet}]^3/[(V_2O_5)_{2\cdot5}O'']$$

or

$$K_2 = [H_2VO_4{}']^{10}[H^{\bullet}]^6/[(V_2O_5)_5O_2{}''''].$$

Calculations made on this basis yield the following table :

HCl, c.c.	0·78	1·56	2·34	3·13	3·91	4·69	5·47
p_{K_1}	25·5	25·5	25·6	25·8	26·15	26·4	26·7
p_{K_2}	53·6	53·4	53·5	53·7	54·3	54·8	55·2

In calculations involving complex equilibria of this type it is easy to let an arithmetical calculation outrun the experimental accuracy; consequently it is not claimed that the moderate agreement between the above p_K values establishes the existence of definite chemical anions of the type $(V_2O_5)_{10}O_2$. It does, however, furnish evidence that polymerisation occurs in these solutions, the heavy ions formed probably not being definite in structure and possibly not homogeneous in composition.

Conductivity measurements showed that only 2·6 equivs. of hydrochloric acid react with each mol. of sodium orthovanadate, for it was found that beyond that amount the acid remained as such. Similar observations are now obtained from the p_H data in Table I. The last line of each table gives p_H values calculated on the assumption that after sufficient acid had been added to form the complex, $Na_2O{,}2{\cdot}5V_2O_5$, no further decomposition of the polyvanadate occurred. These values are seen to be in fair agreement with those actually observed (preceding lines), especially in the more acid solutions. It appears, therefore, that vanadium pentoxide does not exist alone in strongly acid solutions, but in the state of an alkali polyvanadate, of approximate composition $Na_2O{,}2{\cdot}5V_2O_5$.

Curves A and B in Fig. 1, which refer to the action of hydrochloric acid at 18° on sodium ortho- and pyro-vanadate solutions respectively, show that higher p_H values prevailed than in the case of the corresponding solutions that had been boiled. Except for a slight inflexion in curve A, no well-defined inflexions were produced until the acid was added in the amounts necessary to form the complex salt, $Na_2O,2{\cdot}5V_2O_5$. Further, the two solutions became coloured immediately on the addition of the first drops of hydrochloric acid, and remained yellow throughout the whole titrations. It has already been stated that only those solutions which contain vanadates, xNa_2O,V_2O_5, in which $x<1$, can be decolorised by boiling. In view of the foregoing observations on the direct formation in solution of the complex polyvanadate from sodium metavanadate, it seems certain that the yellow coloration must be attributed to the production of the sodium polyvanadate.

On comparing the analogous conductometric curves (Fig. 1, C, and D, Part II) corresponding to the addition of hydrochloric acid to sodium orthovanadate solutions, it is seen that the slope of the direct titration curve is similar to that obtained with boiled solutions until 1 equiv. of acid had been added. The conductivities observed in the direct titration were, however, slightly higher. Since the 3 : 1-salt is hydrolysed to a considerable extent into free alkali and the 2 : 1-salt, it would appear that much of the diminution in the specific conductivity is due to the neutralisation of this free alkali; nevertheless, curve A of Fig. 1 shows that even when sufficient acid has been added to form the 2 : 1-salt more alkali is present than would have been the case if conversion had been complete, and similarly for curve B. It must, therefore, be concluded that, accompanying the conversion of the 3 : 1-salt successively into the 2 : 1- and the 1 : 1-salt, there is a direct formation of the complex vanadate $Na_2O,2{\cdot}5V_2O_5$. It is not clear why curve C is slightly lower than the curve obtained as the result of boiling.

It is now possible to understand the conductometric curves (Fig. 2, Part II) representing the acid titration of salts intermediate in composition between the 3 : 1- and the 2 : 1-vanadate. Each solution underwent an initial diminution in conductivity on the addition of acid, the extent of this diminution becoming less as the composition of the 2 : 1-salt was approached. This decrease in conductivity is to be attributed to the neutralisation of the free alkali which is present in any solution containing a vanadate of composition between these limits. On the other hand, the conversion of the 2 : 1- into either the 1 : 1-salt or the complex and equivalent amounts of sodium chloride produces very little change in the total conductivity of the solution, and consequently the acid titration of salts richer in vanadium pentoxide than the 2 : 1-salt proceeds with little change in conductivity and is practically independent of any intermediate boiling during the titration, although such boiling produces a considerable change in the nature of the p_H curves.

Titration of Sodium Vanadates with Acetic Acid.—Solutions of the 3 : 1-, 2 : 1-, and 1 : 1-vanadates were boiled with acetic acid in ratios similar to those recorded in Table I, and their p_H values were determined at 18°. From these data the titration curves of the three vanadates were constructed; they were identical with the corresponding curves for hydrochloric acid over the major portion of the titration, *i.e.*, from the orthovanadate to the formation of the complex at 2·5 equivs. of acid. Beyond this point p_H values were registered corresponding to buffered solutions of sodium acetate–acetic acid. Solutions of the three vanadates were also titrated directly with acetic acid, and the titration curves resembled the corresponding curves with hydrochloric acid (Fig. 1; curves A, B, and C), but were about 0·1p_H unit lower during most of the titration. It is evident that hydrochloric and acetic acid act in a similar way on the vanadates of sodium, leading ultimately to the formation of a complex, in composition between the metavanadate and the hypothetical vanadic acid.

From the p_H values of solutions to which more acetic acid was added than was required to form the complex, the composition of this complex was determined as follows: from the p_H value the ratio of acetate ion to undissociated acetic acid can be calculated, and since the total amount of acetic acid added is known, the amount which has formed sodium acetate by decomposition of the vanadate can be found; *i.e.*, the extent to which the sodium vanadate is broken down can be calculated. The degree of dissociation of the sodium acetate was taken as 90%. Table II illustrates the results of calculations with the p_H values. corresponding to the addition of excess acetic acid to the 2 : 1-vanadate, both with and without boiling after addition of acid.

TABLE II.

Glass electrode titration at 18° of 100 c.c. of 0·025*M*-NaH_2VO_4 with 0·16*N*-acetic acid: (*a*) immediately, (*b*) after boiling.

HOAc, c.c.	10	12	12·5	15	20	25	40	50
(*a*) p_H	5·15	—	4·83	4·68	4·44	4·26	4·03	3·87
[OAc′]/[HOAc]	2·83	—	1·26	0·89	0·51	0·34	0·20	0·14
V_2O_5/Na_2O	2·0	—	1·9	1·9	1·9	1·8	1·9	1·7
(*b*) p_H	—	4·93	—	—	4·44	4·33	—	3·93
[OAc′]/[HOAc]	—	1·58	—	—	0·51	0·40	—	0·16
V_2O_5/Na_2O	—	2·0	—	—	1·9	2·0	—	1·9

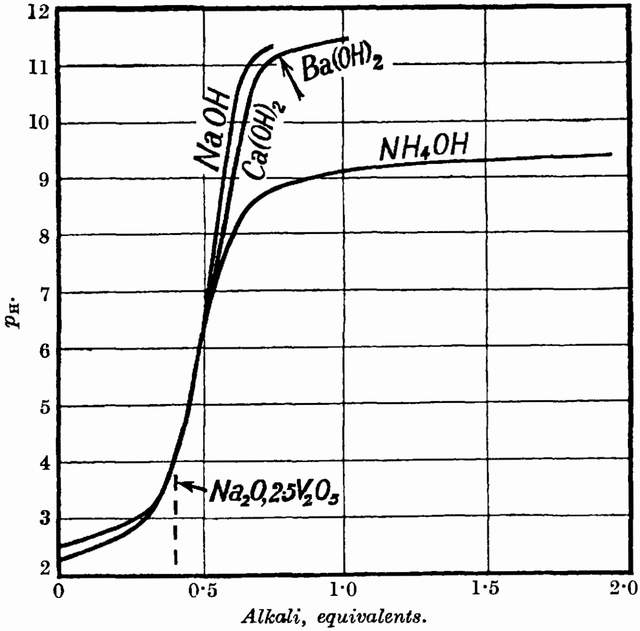
The composition of the complex in this case is $Na_2O,1·9V_2O_5$. Similar experiments with the pyrovanadate led to the same formula. Apparently, therefore, the complex formed with acetic acid is somewhat richer in base than that formed with a strong acid. The curves in Fig. 1 show that the formation of $Na_2O,2V_2O_5$ occurs at p_H 5·7, while a p_H of 4 is required for the formation of $Na_2O,2{\cdot}5V_2O_5$; although the latter p_H is easily attained by the addition of a strong acid, it is difficult to reach it with acetic acid, unless large amounts are used. It is possible that the $Na_2O,2V_2O_5$ complex is also formed during the addition of a strong acid, but, owing to the lower p_H subsequently attained, it is further transformed into $Na_2O,2{\cdot}5V_2O_5$ or possibly into a mixture of $Na_2O,2V_2O_5$ and $Na_2O,3V_2O_5$.

The titration curves with acetic acid are of interest in considering the crystallisation of polyvanadates from solutions of the metavanadates acidified with acetic acid under different conditions. A large number of alkali-metal polyvanadates have been described, but the existence of so many separate compounds is very doubtful. It is remarkable, however, that Lachartre (*Bull. Soc. chim.*, 1924, **35**, 321) isolated the ammonium 2 : 3-vanadate by the action of 4% acetic acid on the 1 : 1-vanadate, whereas 10% acetic acid yielded the 1 : 3-salt. Similarly, Ditte (*Compt. rend.*, 1887, **104**, 1061) obtained the sodium 2 : 3-vanadate from the 1 : 1-vanadate acidified with small quantities of acetic acid, and Rammelsberg (*Wied. Ann.*, 1883, **20**, 934) found that a large excess of acetic acid was required to form the 2 : 5-salt. Similar principles explain the observation of Friedheim and Michaelis (*Z. anorg. Chem.*, 1893, **5**, 441), that according to the amount of sodium dihydrogen phosphate added to a solution of sodium 1 : 1-vanadate the 4 : 7- or the 5 : 8-compound can be crystallised.

Titration of " Vanadic Acid " with Alkalis.—To see whether any evidence could be obtained for a normal behaviour of vanadic acid, comparable with that of phosphoric acid, solutions were prepared by adding hydrochloric acid to alkali vanadate solutions in amounts calculated to give " vanadic acid," H_3VO_4 or HVO_3; these were then titrated with alkalis, as follows: (*a*) $0{\cdot}025M$-H_3VO_4 with $0{\cdot}2N$-NaOH, (*b*) $0{\cdot}025M$-H_3VO_4 with $0{\cdot}14N$-NH_4OH, (*c*) $0{\cdot}01M$-H_3VO_4 with $0{\cdot}04N$-$Ca(OH)_2$, (*d*) $0{\cdot}01M$-H_3VO_4 with $0{\cdot}05N$-$Ba(OH)_2$.

The solutions were yellow at the beginning of the titration and remained so throughout. A precipitate appeared in the titration with baryta when 0·75 equiv. had been added. No precipitate appeared during the titration with lime-water, although there was considerable precipitation when the solution to which excess of lime-water had been added was allowed to stand. The p_H values observed during these titrations are shown in Fig. 2. These curves are quite unlike the corresponding curves for the titration of phosphoric acid with alkalis. There is a very rapid decrease in the hydrogen-ion concentration after the addition of approximately 0·4 equiv. of alkali, corresponding to $Na_2O,2{\cdot}5V_2O_5$. The "break," however, is not sharp as in the titration of a simple acid, but extends over the addition of 0·2 equiv. of alkali. Moreover, except in the ammonia titration, the addition of 70% of the amount of alkali required stoicheiometrically for the formation of the metavanadate raises the p_H of the solution to about 11, a value in excess of that required to form the pyro-salt and comparable with that set up by the orthovanadate.

FIG. 2.



These titrations can, however, be accounted for if a stable complex molecule is formed by the addition of acid to the metavanadate during the formation of "vanadic acid," corresponding approximately to the ratio $Na_2O,2{\cdot}5V_2O_5$. The first part of the curves then corresponds to the neutralisation of the free hydrochloric acid present in the solution. During the somewhat protracted increase in the p_H in the vicinity of 0·4 equiv. of alkali, most of the added alkali remains free, but a portion slowly breaks down the polymerised complex into simpler molecules containing a somewhat greater amount of alkali, the reaction being slow owing to the complex nature of the vanadate ion. After this depolymerisation, the complex resists further attack by the alkali, and the titration curve then corresponds to the excess alkali added, no inflexions appearing in the curve at points corresponding to the pyro- or the ortho-vanadate since these salts are only formed on long standing of the alkaline solution of the complex.

These potentiometric titrations are consistent with the parallel conductometric titrations recorded in Fig. 3 of Part II of this series. These curves also illustrate the initial neutralisation of free hydrochloric acid, followed by an increase in conductivity due to the added alkali. The conductometric curves show no evidence of the formation of pyro- or ortho-salts on direct addition of alkali to "vanadic acid."

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UNIVERSITY COLLEGE OF THE SOUTH WEST,
EXETER.

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