142. *Physicochemical Studies of Complex Acids. Part XIV. Vanadic Acid.*

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A series of glass-electrode and conductometric titrations at temperatures ranging from 5° to 90° have been carried on an aqueous solution of vanadium pentoxide with sodium hydroxide. Back-titrations of more concentrated solutions of alkaline vanadate solutions are described. In solution, vanadium pentoxide behaves as a strong polyvanadic acid, $H_2[(V_2O_5)_{2\cdot5}O]$. The bivalent anion is relatively stable towards sodium hydroxide in the cold but not at elevated temperatures, at which it is successively converted into the anions of the so-called meta-, pyro-, and ortho-vanadates. The reverse process with hydrochloric acid is not spontaneous except in hot solutions.

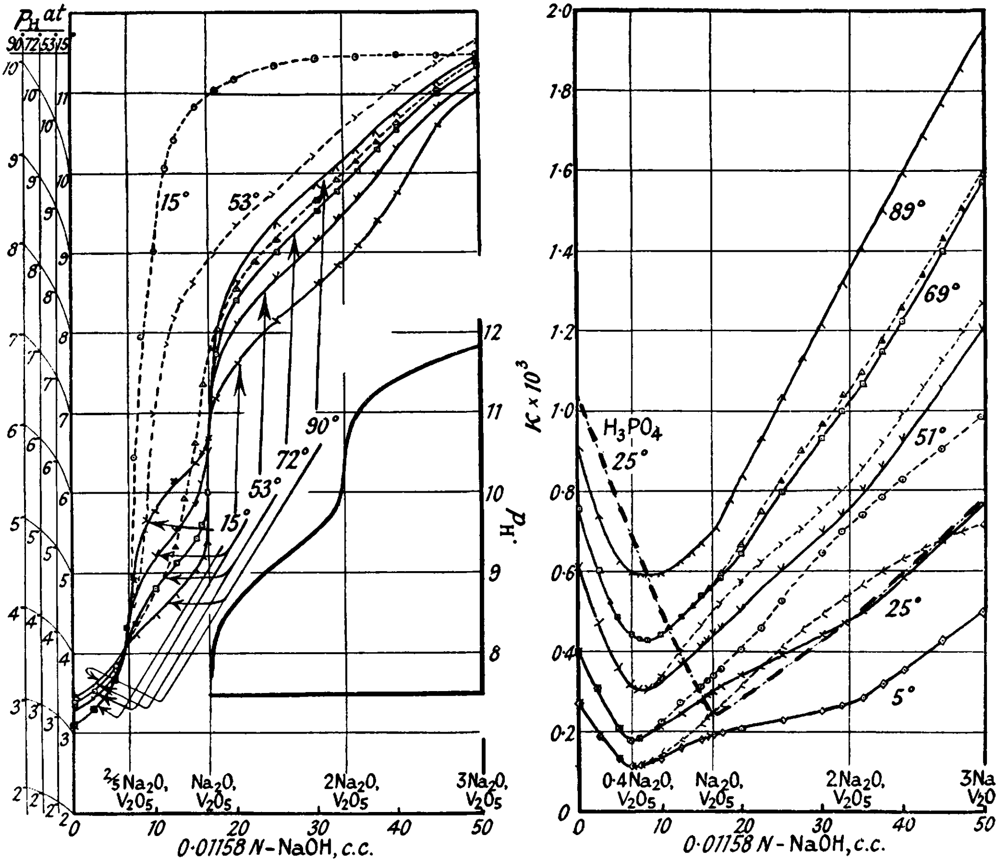
VANADIC acid was investigated by conductometric titrations and later by glass-electrode titrations of alkaline vanadate solutions with hydrochloric acid by Britton and Robinson (J., 1930, 1261; 1932, 1955). Solutions of sodium hydroxide and vanadium pentoxide in appropriate ratios, boiled before measurements, revealed a distinct similarity between the three sodium vanadates and the corresponding trisodium phosphate and the two sodium hydrogen phosphates. There is, however, produced a sodium polyvanadate, $Na_2O,(V_2O_5)_{2\cdot5}$, which, being not readily decomposed by hydrochloric acid, behaves as a salt of a strong acid, the simplest formula of which is $H_2[(V_2O_5)_{2\cdot5}O]$. Vanadium pentoxide is sparingly soluble in water and imparts to it a strongly acid reaction, which, as the subsequent work shows, can be ascribed to the existence of such an acid. Some preliminary glass-electrode titrations of exceedingly dilute solutions of vanadium pentoxide at elevated temperatures (J., 1934, 1842) seemed to indicate that, with increasing temperature, vanadic acid becomes a perfectly normal tribasic acid, that its first stage of ionisation can be represented as $H_3VO_4 \rightleftharpoons H^{\cdot} + H_2VO_4{}'$, and that the abnormal polyvanadic acid consequently disappears. The present work, which consists of electrometric titrations of solutions of (*a*) vanadium pentoxide and (*b*) alkaline vanadate at a series of temperatures ranging from 5° to 90°, shows that, contrary to expectation, the strong polyvanadic acid is not decomposed at elevated temperatures and the apparent analogy between vanadic and phosphoric acids is therefore not complete.

EXPERIMENTAL.

The glass-electrode and conductometric titration curves shown in Fig. 1 refer to the neutralisation of 50 c.c. of 0·00193M-vanadium pentoxide with 0·01158N-sodium hydroxide at the temperatures indicated.

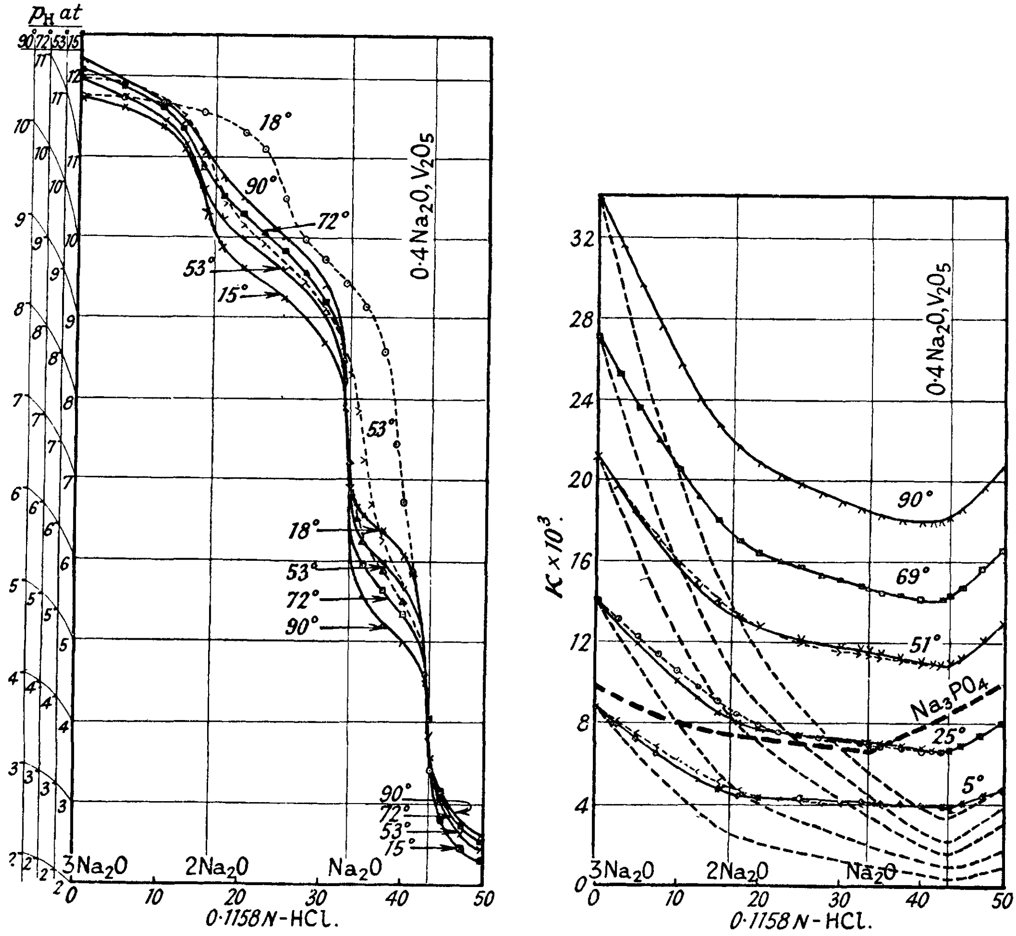
In order to make the $p_{\rm H}$ curves directly comparable with one another at the various temperatures, they are plotted in such a way that the appropriate ordinates are so adjusted that they extend over the same ranges of acidity to alkalinity. This would not have been the case if all the curves had been plotted with respect to the same $p_{\rm H}$ ordinate, because owing to the considerable increase in $K_{\rm w}$ with temperature, the $p_{\rm H}$ range covering the variations from say $[\rm H^{\cdot}] = 1$ to $[\rm OH'] = 1$ is much greater at 0° than at 100° : at 0° such a range would be indicated by 14·9 $p_{\rm H}$ units, with neutrality at $p_{\rm H}$ 7·45, whereas at 100° it is represented by 12·2 units, with neutrality at $p_{\rm H}$ 6·10. In Figs. 1 and 2 the horizontal scale lines refer to 15° only, and the positions of the ordinates at the higher temperatures were ascertained from the appropriate values of $K_{\rm w}$.

FIG. 1.



The curves represented by continuous lines refer to the $p_{\rm H}$ values and conductivities which were reached at the temperatures only after prolonged standing or almost instantaneously after boiling and then cooling. The broken lines indicate the values obtained immediately after each addition of alkali and stirring. Both the initial $p_{\rm H}$ values and specific conductivities of the vanadium pentoxide solutions indicate the formation in solution of a strong acid. The curves show that this strong acid is neutralised when 0·4 mol. of $\rm Na_2O$ per mol. of $\rm V_2O_5$ has been added, for well-defined inflexions occur in the $p_{\rm H}$ curves and " breaks " in the conductometric curves marking the end of rapid diminutions in conductivity. It is also significant that during this stage of the neutralisation neither the p_H nor the conductivity undergoes any change as the result of either boiling or standing.

FIG. 2.



An approximate estimate of the strength of polyvanadic acid, $H_2[(V_2O_5)_{2\cdot5}O]$, existing in aqueous vanadium pentoxide solutions may be obtained from Table I. The vanadium pentoxide

TABLE I.

Temp.	$\kappa \times 10^4$.	Λ.	p_H.	α.	Λ_∞.	$l_{H^\bullet}$.	$l_{X''}$.
5°	2·72	176	3·05	0·58	305	252	53
25	4·00	259	3·04	0·59	438	350	88
51	6·05	392	3·03	0·60	649	464	185
69	7·53	488	2·99	0·66	736	—	—
89	9·11	590	2·96	0·71	831	—	—

is regarded as 0·000772M-$H_2[(V_2O_5)_{2\cdot5}O]$. The equivalent conductivities (col. 3) were calculated by assuming the acid to ionise into $2H^\bullet + [(V_2O_5)_{2\cdot5}O]''$. The degree of ionisation, α, was estimated from the p_H value and by combining α with the data given for Λ, Λ_∞ was calculated. Using the values of $l_{H^\bullet}$, an estimate was thereby made of the ionic mobility, $l_{X''}$, of the assumed bivalent anion. Although these calculations are necessarily approximate, the magnitude of the ionic mobility at the temperatures recorded suffices to show that the anion is a true rather than a colloidal ion. This view is confirmed by a consideration of the equivalent conductivity of the sodium salt, $Na_2O,(V_2O_5)_{2\cdot5}$, formed in the course of the neutralisation at 25° and denoted by the first " break ". The equivalent conductivity is 131 mhos. Assuming the salt to be completely ionised and taking $l_{Na^\bullet} = 50$, we have $l_{X''} = 81$.

During the addition of alkali corresponding with 0·4—1·0 mol. of Na_2O per mol. of V_2O_5, another distinct stage in the neutralisation of vanadic acid occurs, as may be seen by the inflexions and breaks in the continuous curves. The attack of the alkali on the complex polyvanadate anion is so slow that if the solutions are not allowed to stand or are not boiled, they readily acquire high p_H values and conductivities, as shown by the broken lines. These approach the continuous lines as the temperature is raised, and, in fact, coincide at 90°.

The solutions represented by the broken lines are yellow, whereas those indicated by the continuous lines gradually become less yellow as the amount of alkali is increased from 0·4 to 1·0 mol., whereupon they become quite colourless. It would appear that the polyvanadate ion is yellow, whilst the anion, probably H_2VO_4', arising from the salt formed by the complete interaction of 1 mol. of each oxide (*viz.*, either NaH_2VO_4 or $NaVO_3$) is colourless. Represented in the simplest way, the equilibrium involved in the second stage of the neutralisation is

$$\frac{13}{2}H_2O + O(V_2O_5)_{2\cdot5}'' \rightleftharpoons 5H_2VO_4' + 3H^{\bullet}$$

or perhaps

$$13H_2O + O_2(V_2O_5)_5'''' \rightleftharpoons 10H_2VO_4' + 6H^{\bullet}$$

On the assumption that the law of mass action governs the conversion of the polyvanadate ion into the simpler ion, the former equilibrium requires

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

The values of K, expressed as $-\log K$ or p_K, in Table II, have been calculated for three stages in the neutralisation from the p_H values, *viz.*, at each successive quarter of the total amount of sodium hydroxide required to complete the conversion.

TABLE II.

Titrations.	Temp. NaOH.	15°. p_H.	15°. p_K.	53°. p_H.	53°. p_K.	72°. p_H.	72°. p_K.	90°. p_H.	90°. p_K.
I.									
50 C.c. of 0·00193M-V_2O_5 with 0·01158N-NaOH	0·25	5·54	29·5	4·66	26·9	4·10	25·2	3·78	24·2
	0·50	5·88	28·8	4·97	26·1	4·40	24·4	4·00	23·2
	0·75	6·22	28·6	5·32	25·9	4·67	23·9	4·25	22·7
II.									
50 C.c. of 0·0386M-Na_3VO_4 with 0·1158N-HCl	0·25	5·93	26·7	5·66	24·4	4·10	25·2	4·27	21·7
	0·50	6·28	26·0	5·50	23·7	4·40	24·4	4·54	20·8
	0·75	6·50	25·4	5·30	23·3	4·67	23·9	4·75	20·2

The values of p_K in both titrations I and II at the different temperatures show that the conversion of $(V_2O_5)_{2\cdot5}O''$ into H_2VO_4' does not strictly follow the mass law, except perhaps in a qualitative sense. As will be seen from a comparison of the data referring to titrations I and II, the value of K increases with the concentration of the reactants. The increase in the value of K with temperature is, however, apparent. This is also reflected in the relative positions of the second stage of the p_H curves, so much so that it is easy to see why the preliminary glass-electrode titration of vanadium pentoxide solution (*loc. cit.*) seems to point to the disappearance of polyvanadic acid at elevated temperatures. Although small, the p_H curve at 90° is definitely inflected, but it is more clearly seen that a strong polyvanadic acid exists in the 89° conductometric titration.

The addition of the second equivalent of alkali, being the amount required to convert NaH_2VO_4 into Na_2HVO_4, is marked in the conductometric curves, except the one at 89°, by small " breaks ", but owing to the low concentrations employed, the p_H curves do not give the corresponding inflexions. If the two vanadates exist in solution in the form of the simple acid vanadates (cf. NaH_2PO_4 and Na_2HPO_4), then the equilibrium involved during the addition of the second equivalent of sodium hydroxide may be represented as $H_2VO_4' \rightleftharpoons H^{\bullet} + HVO_4''$, and Table III gives the values of $K = [H^{\bullet}][HVO_4'']/[H_2VO_4']$ as calculated from the p_H values.

TABLE III.

Temp. NaOH, equivs.	15°. p_H.	15°. p_K.	53°. p_H.	53°. p_K.	72°. p_H.	72°. p_K.	90°. p_H.	90°. p_K.
1·25	7·68	8·16	7·68	8·16	7·70	8·18	7·72	8·20
1·50	8·14	8·14	8·15	8·15	8·16	8·16	8·22	8·22
1·75	8·52	8·04	8·52	8·04	8·53	8·05	8·60	8·12

At each of the temperatures, the p_K values are approximately constant, although they tend to become smaller as more Na$_2$HVO$_4$ is formed. They also remain sensibly constant with increase in temperature.

A somewhat surprising property of solutions containing 1 mol. each of the two oxides (corresponding with NaH$_2$VO$_4$) is that, after they have been rendered colourless either by ageing or by boiling, they react immediately with alkali to give p_H values and conductivities that remain unchanged after subjection to either boiling or ageing. For instance, the p_H curve inset in Fig. 1 represents a glass-electrode titration of 100 c.c. of 0·01M-NaH$_2$VO$_4$ with 0·25N-NaOH, obtained by measuring the p_H values immediately after each addition of alkali at 18° and also by boiling and cooling to 18° before making the determinations. The effect of the increased concentration of the vanadate solution is seen in the well-defined inflexion denoting the formation of Na$_2$HVO$_4$. Another effect is on the p_H values themselves and the resulting values of p_K. This may be deduced from the following table :

NaOH, equivs.	0·25	0·50	0·75
p_H	8·70	9·05	9·40
p_K	9·18	9·05	8·92

The values of p_K are similar in magnitude to those obtained by Britton and Robinson (J., 1932, 1957). A comparison of this table with Table III shows that the concentration has a marked effect in diminishing the dissociation constant of the assumed ion, H$_2$VO$_4'$. This might possibly be due to the ions involved being in a polymerised form. On the other hand, the spontaneity with which the 1 : 1 sodium vanadate, once it is formed in solution, reacts with alkali would rather point to the simple character of the H$_2$VO$_4'$ ion. Furthermore, an investigation of the specific conductivities recorded in the course of the titrations and plotted in Fig. 1, when the salts NaH$_2$VO$_4$ and Na$_2$HVO$_4$ respectively were formed, leads to equivalent conductivities which are somewhat smaller than those of sodium chloride at the corresponding dilutions and temperatures. These comparisons, which are given in Table IV, show that if the degree of ionisation of the two sodium vanadates is similar to that of sodium chloride at the various temperatures, the ionic mobilities of the assumed ions, H$_2$VO$_4'$ and HVO$_4''$, must be lower than that of the Cl$'$ ion. This might possibly be attributed to the two vanadate ions being polymerised in solution (cf. Robinson and Sinclair, J., **1934**, 642), although it should be remarked that at 25° the equivalent conductivities of NaH$_2$PO$_4$ and Na$_2$HPO$_4$ at the precise dilutions reached in the titration, *i.e.*, when NaH$_2$VO$_4$ and Na$_2$HVO$_4$ respectively were formed, are lower than those of the corresponding vanadates, *viz.*, 85 and 104 mhos compared with 104 in the two cases.

TABLE IV.

Temp.	5°.	25°.	51°.	69°.	89°.
$\Lambda_{NaH_2VO_4}$	65	104	152	195	243
Λ_{NaCl}	76	123	201	250	311
$\Lambda_{Na_2HVO_4}$	58	104	164	221	292
Λ_{NaCl}	75	121	199	247	309

The final stage of the ionisation of vanadic acid, *viz.*, HVO$_4'' \longrightarrow$ VO$_4''' +$ H$^{\bullet}$, is not clearly indicated by the p_H and conductometric curves in Fig. 1. This is no doubt largely caused by the very dilute solution of vanadic acid which had, of necessity, to be employed. This stage is, however, shown in the back-titrations of alkali vanadate solutions of higher vanadium concentration. In Fig. 2, which illustrates the changes at various temperatures which occur when 0·1158N-HCl is added to 50 c.c. of a solution of 0·0386M-Na$_3$VO$_4$, the stages corresponding with the formation of Na$_2$HVO$_4$, NaH$_2$VO$_4$, and Na$_2$O,2·5V$_2$O$_5$ are well-defined, and this is particularly the case with the broken lines which lie in the lower portion of the conductivity diagram. They represent the effect obtained by deducting the specific conductivities, due to the increasing amounts of sodium chloride produced as the hydrochloric acid was added, from the observed specific conductivities. Another point which is more clearly shown in Fig. 2 than in Fig. 1, owing to the necessarily dilute solutions to which Fig. 1 refers, is that the strongly acid stage, H$_2$O,2·5V$_2$O$_5$, is not destroyed as the temperature is raised. The last stage of the titrations, *i.e.*, when once Na$_2$O,2·5V$_2$O$_5$ has been formed, corresponds with the introduction into the solution of free hydrochloric acid, for the polyvanadate, being the salt of a relatively strong acid, is only slowly decomposed by the slightly stronger mineral acid.

The broken p_H curves in Fig. 2 give the p_H values recorded after each addition of hydrochloric acid. The solutions immediately assume a yellow colour, which, from the fact that these curves do not overstep the stage caused by the formation of $Na_2O,2{\cdot}5V_2O_5$, would suggest that some of the colourless vanadate existing in alkaline solution is, in the first place, converted into the coloured sodium polyvanadate, which on standing or boiling is eventually converted into simpler and colourless vanadate ions, if not more than 2 mols. of hydrochloric acid have been added to 1 mol. of Na_3VO_4. With increasing temperature these broken curves approach more closely the equilibrium curves, and also less intense yellow colorations are produced.

In both sets of conductivity curves, Figs. 1 and 2, the titration curves at 25° of phosphoric acid and sodium phosphate respectively are given, the same concentrations being used as in the vanadium titrations. Except for the abnormality in forming the polyvanadate, $Na_2O,(V_2O_5)_{2{\cdot}5}$, the phosphoric acid and vanadic acid curves are similar in indicating salts with 1 and 2 mols. of Na_2O per atom of phosphorus and vanadium.

The very dilute solutions of vanadium pentoxide which can be obtained by prolonged shaking are not colloidal, unless the anion involved is such, but ionise as a polyvanadic acid, which in its simplest form may be represented as $H_2O(V_2O_5)_{2{\cdot}5}$. Alkali neutralises it as if it were a strong acid, but, in the cold, alkali does not readily decompose the polyvanadate anion, for the solutions immediately become alkaline. Boiling with alkali, or adding the alkali to hot solutions causes $Na_2O,2{\cdot}5V_2O_5$ to be converted successively into Na_2O,V_2O_5, $2Na_2O,V_2O_5$, and $3Na_2O,V_2O_5$. On the contrary, hydrochloric acid, when added to a cold solution of the so-called orthovanadate, $3Na_2O,V_2O_5$, does not bring about the reverse process immediately. This occurs only at a temperature of 70° and above. Instead, a yellow solution is produced, suggestive of the presence of $Na_2O,2{\cdot}5V_2O_5$, and moreover, the solution becomes acid as soon as the polyvanadate has been completely formed.

Although parts of the electrometric curves corresponding with the neutralisation of hot solutions of vanadic acid are similar to the comparable parts of phosphoric acid curves, it is highly probable that the various vanadate ions are fundamentally different in nature from those of phosphoric acid. There is no spontaneity in the change from one vanadate ion to another, except the change from the anion present in the 1 : 1 salt to that of the 2 : 1 salt and thence to that of 3 : 1 salt by the addition of alkali.

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