CLXII.—*Physicochemical Studies of Complex Acids. Part II. Vanadic Acid.*

By HUBERT THOMAS STANLEY BRITTON and ROBERT ANTHONY ROBINSON.

A NUMBER of alkali-metal vanadates have been described and have generally been prepared either by fusion of carbonates with vanadium pentoxide or by crystallisation of solutions containing various amounts of acid or alkali. Vanadates are said to exist having the general formula $n\mathrm{Na_2O,V_2O_5,}x\mathrm{H_2O}$, where $n = 3, 2, 1, \frac{5}{8}, \frac{4}{7}, \frac{1}{2}, \frac{3}{7}, \frac{2}{5}, \frac{1}{3}$, etc. Nevertheless, little work has been done on the constitution of alkali vanadates in solution, the most comprehensive investigation being that of Düllberg (*Z. physikal. Chem.*, 1903, **45**, 129), who studied the conductometric titration of sodium orthovanadate solutions with hydrochloric acid under various conditions, determined the freezing-point depressions of different vanadate solutions, and postulated the existence in solution of a hexavanadic acid, $H_4V_6O_{17}$.

Since the addition of the slightest quantity of acid to a sodium orthovanadate solution produces a yellow coloration, it is interesting to note that while the ortho-, pyro-, and meta-salts are white or a faint yellow, the higher vanadates are orange or red. Thus, $\mathrm{Na_2O,2V_2O_5,9H_2O}$ has been obtained in orange-red crystals (von Hauer, *Sitzungsber. Akad. Wien*, 1856, **21**, 337; 1860, **39**, 455), and on being heated on the water-bath gives the metavanadate and $\mathrm{Na_2O,3V_2O_5}$ (Norblad, *Acta Lund Univ.*, 1874, **2**, 1). Norblad also isolated orange-red crystals of $\mathrm{2Na_2O,3V_2O_5,10H_2O}$, which Rammelsberg (*Wied. Ann.*, 1883, **20**, 938) obtained with $\mathrm{16H_2O}$.

Conductometric and potentiometric titrations of sodium vanadates and vanadic acid are now described, and the results are explained on the hypothesis that vanadium tends to form a heavy molecule, on the border-line between a true solute and a colloidal micelle, and corresponding to $\mathrm{Na_2O,2V_2O_5}$ or $\mathrm{Na_2O,3V_2O_5}$.

EXPERIMENTAL.

Nomenclature.—There is considerable confusion as to a suitable nomenclature for the large number of compounds of the alkali oxides with vanadium pentoxide. The use of the prefixes " ortho," " pyro," and " meta " for three of the vanadates stresses a false analogy between them and the phosphates and, moreover, tends to single out three of the vanadates from others of equal or greater importance. We therefore propose in this and succeeding communications to designate an alkali vanadate by a prefix denoting the ratio of M_2O to V_2O_5 (M = alkali metal); thus sodium orthovanadate becomes the 3 : 1-vanadate, the pyro-salt becomes the 2 : 1-vanadate, and the compound $\mathrm{Na_2O,2V_2O_5}$ will be called the 1 : 2-vanadate.

A. *Conductometric Titrations.*

1. *Direct Titration of Sodium* 3 : 1-*Vanadate.*—Vanadium pentoxide dissolves slowly in cold sodium hydroxide solution giving a clear yellow solution, whose colour disappears on standing for some time. If, however, the pentoxide be dissolved in boiling sodium

hydroxide solution, a clear colourless solution is immediately obtained. Such a solution may also be prepared by treating ammonium metavanadate with hot sodium hydroxide solution. In view of the different appearance of the solutions obtained by various methods of preparation, it was of interest to see if the behaviour of the vanadate solutions towards hydrochloric acid could be in any way correlated with their method of preparation.

For this purpose solutions of the sodium 3 : 1-vanadate were prepared in the following ways and titrated conductometrically with hydrochloric acid at 25° : (1) Ammonium metavanadate, NH_4VO_3, was boiled with the stoicheiometrical quantity of sodium hydroxide solution, a current of carbon dioxide-free air being drawn through the solution. (2) Vanadium pentoxide was boiled with the calculated amount of sodium hydroxide solution. Both these solutions were colourless. (3) Vanadium pentoxide was dissolved in the same amount of cold sodium hydroxide solution; this solution was yellow. (4) Solution (3) was kept for 48 hours, and had then become colourless. In all cases, the solutions were $0{\cdot}005M$ with respect to Na_3VO_4. Solutions (1) and (2) were titrated directly with $0{\cdot}1N$-, and (3) and (4) with $0{\cdot}0933N$-hydrochloric acid, the liberation of the vanadic acid according to the equation $2Na_3VO_4 + 6HCl \longrightarrow V_2O_5,3H_2O + 6NaCl$ corresponding to 15·0 c.c. in the first two cases and to 16·1 c.c. in the last two. The specific conductivities, κ, at different titres are given in Table I.

TABLE I.

Specific conductivities ($\kappa \times 10^3$) *of* 100 c.c. *of* $0{\cdot}005M\text{-}Na_3VO_4$ *prepared in different ways and titrated directly with* HCl.

$Na_2O : V_2O_5$ =	3 : 1	2·5 : 1	2 : 1	1·5 : 1	1 : 1	0·5 : 1	0·25 : 1	0 : 1
Soln. 1	2·14	1·92	1·72	1·58	1·54	1·58	1·73	1·98
,, 2	2·13	1·92	1·73	1·57	1·53	1·58	1·73	2·01
,, 3	2·14	1·93	1·74	1·56	1·52	1·61	1·78	2·06
,, 4	2·09	1·88	1·68	1·53	1·49	1·54	1·75	2·00

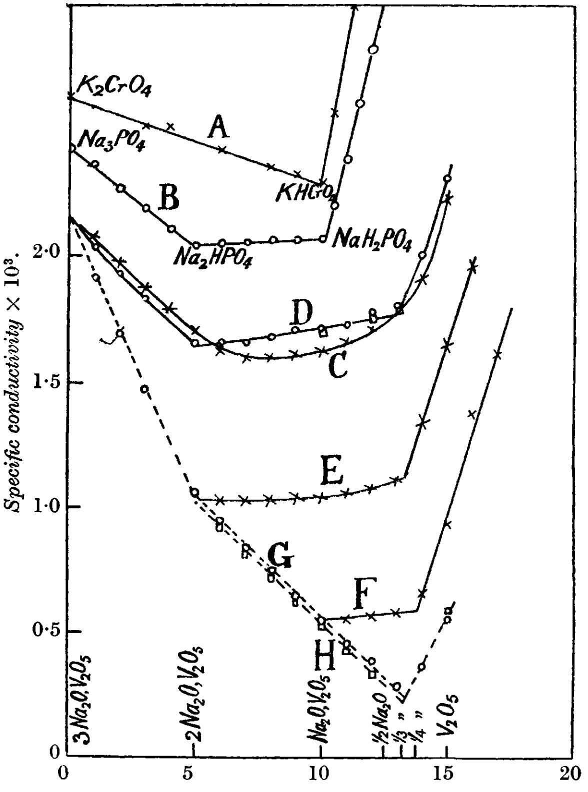
Continuation of titration of Solution 2 *beyond liberation of vanadic acid at* 15 c.c. *of* HCl :

HCl, c.c. ...	15	16	17	18	19	20	21	22	23	24	25
$\kappa \times 10^3$	2·01	2·20	2·46	2·74	2·97	3·19	3·45	3·68	3·91	4·14	4·34

Table I indicates that all the vanadate solutions reacted with hydrochloric acid in the same way, irrespective of the manner in which they were prepared. The small differences between the conductivities of Solutions 3 and 4 may perhaps be ascribed to the disappearance of the yellow colour on ageing. When the results are plotted, curves are obtained very similar to Curve C (Fig. 1), which will be discussed later.

2. *Effects of Ageing and Boiling.*—In view of the remarkable observation of Düllberg (*loc. cit.*), that the conductivity of solutions of sodium 3 : 1-vanadate, to which varying quantities of hydrochloric acid had been added, underwent a change on standing, we have repeated and confirmed his experiments. In addition, we have investigated the effect of boiling such solutions. Three series of experiments were performed; a series of solutions, 100 c.c. in volume and 0·005M with respect to Na_3VO_4, were prepared containing 0·1N-hydrochloric acid in various quantities from 0 to 15 c.c., and their conductivities were measured (a) immediately, and (b) after they had stood for six days; a similar series of solutions was boiled and the conductivity then measured (c) at 25°.

Fig. 1.



In all cases, the addition of even the slightest amount of acid to a colourless vanadate solution produced a yellow coloration, which increased in intensity with addition of hydrochloric acid until about half the amount required to liberate H_3VO_4 had been added, *i.e.*, 7 or 8 c.c. Boiling the coloured solutions decolorised those containing 10 c.c. of hydrochloric acid or less, and ageing decolorised those containing 8 c.c. or less. The results of these experiments are given in Table II and shown graphically in Fig. 1.

TABLE II.

Specific conductivities of 100 c.c. *of* 0·005M-Na_3VO_4 *containing* x c.c. *of* 0·1N-HCl, (a) *immediately,* (b) *after standing for* 6 *days,* (c) *boiling, after addition of acid.*

x	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Na_2O/V_2O_5	3	2·8	2·6	2·4	2·2	2	1·8	1·6	1·4	1·2	1	0·8	0·6	0·4	0·2	0
$\kappa \times 10^3$ (*a*)	2·15	2·08	1·97	1·87	1·79	1·70	1·62	1·58	1·60	1·61	1·62	1·67	1·71	—	1·91	2·23
(*b*)	2·15	2·03	1·93	1·83	—	1·65	1·65	1·65	1·68	1·70	1·71	1·73	1·78	1·80	2·01	2·31
(*c*)	2·09	2·00	—	1·76	—	—	—	1·64	—	1·70	1·70	—	1·75	1·78	—	2·30

The results of the first experiment (Curve C) are almost identical with the direct titrations described above, the small difference being due to the dilution of the solution in the course of the former titration. No break appears in the curve corresponding to a 2 : 1- or a 1 : 1-vanadate. The effect of ageing is shown in Curve D. The effect of boiling is almost identical, as will be seen from the data in Table II. A break occurs at a point corresponding with the 2 : 1-vanadate, and another which approximates to the 1 : 3-vanadate. These breaks are shown more clearly by Curve G, constructed by subtracting from the total conductivity of the solution that due to the sodium chloride formed. Thus, Curve G represents the conductivity of the solution due to the vanadate at different points. For comparison, the titration curves of a potassium chromate (A) and a sodium phosphate (B) solution are shown on the same graph, but the scale of the conductivity axis has been moved. Breaks are found in these curves corresponding with $KHCrO_4$, Na_2HPO_4, and NaH_2PO_4, and it is evident that the vanadate curves are anomalous.

3. *Titration of the Sodium* 1 : 1-*Vanadate.*—Curves C and D of Fig. 1 show that the variation of conductivity during titration with hydrochloric acid of a solution corresponding in composition with the 3 : 1-vanadate depends on whether the measurement is made immediately, or after boiling or ageing, after each addition of acid.

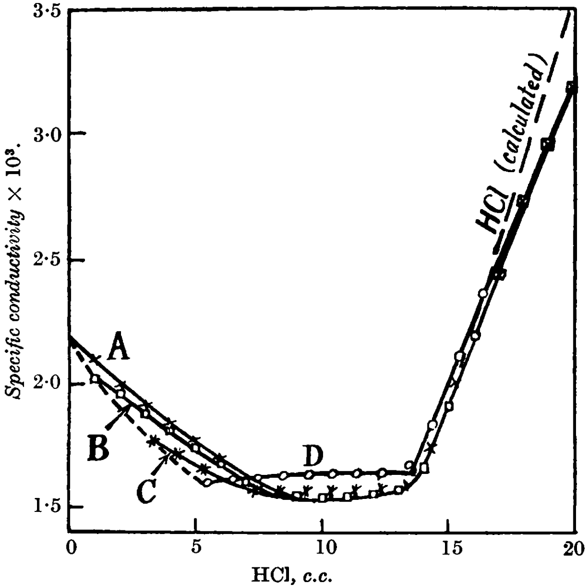
In order to study this matter further, a solution was prepared of the 1 : 1-vanadate by boiling the pentoxide with the calculated amount of sodium hydroxide solution. The vanadium content was the same as in the previous experiments. 100 C.c. of the solution were then titrated directly with 0·1N-hydrochloric acid; the conductivities found were as follows, the corresponding curve being F (Fig. 1), which starts at 10 c.c. :

HCl, c.c.	0	1	2	3	4	5	6	7
$\kappa \times 10^3$	0·544	0·550	0·562	0·573	0·657	0·935	1·38	1·61

Since the initial conductivity of this solution is due entirely to the 1 : 1-vanadate, we should expect it to agree with the conductivity of the corresponding solution in Curve D, after correction has been made for the sodium chloride in the latter. Satisfactory agreement is obtained. Moreover, if from Curve F we subtract the conductivity of the sodium chloride formed during the reaction, a curve is obtained identical with the latter part of Curve G.

4. *Titration of the Sodium* 2 : 1-*Vanadate*.—In a similar manner, 100 c.c. of a 0·005M-solution corresponding in composition with the 2 : 1-vanadate (Na_2HVO_4) were prepared and titrated with 0·1N-hydrochloric acid (see Curve E, Fig. 1, starting at 5 c.c.):

FIG. 2.



HCl, c.c.	0	1	2	3	4	5	6	7	8	9	10	11
$\kappa \times 10^3$	1·01	1·03	1·03	1·03	1·04	1·05	1·06	1·07	1·12	1·34	1·65	1·95

Again, satisfactory agreement was obtained between the initial conductivity of this solution and that of the solution in Curve D corresponding with 5 c.c. of hydrochloric acid when corrected for the conductivity of its sodium chloride. Also, if correction is made in Curve E for the sodium chloride formed, giving Curve H, the resulting conductivities are only slightly lower than those in Curve G.

Since Curves E and F relate to a direct titration of the 2 : 1- and 1 : 1-vanadate solutions respectively, it would appear that no influence of boiling or ageing on the solutions of Curves D and C should appear beyond the point relating to 5 c.c. of hydrochloric acid. To check this deduction, a solution of 100 c.c. of 0·005M-Na_3VO_4 was treated with sufficient hydrochloric acid to form the 2 : 1-vanadate, and boiled. It was then titrated directly with 0·0933N-acid without further boiling on addition of acid. A curve was obtained almost identical with that portion of Curve D beyond 5 c.c. of added acid.

We also showed that a solution of the 2 : 1-vanadate, prepared by dissolving the pentoxide in *cold* sodium hydroxide solution, and titrated directly with hydrochloric acid, gave a curve only slightly lower than Curve E in Fig. 1 and identical with it in form, although, unlike the above, this solution was yellow in colour.

It is therefore concluded that boiling or ageing effects are only to be obtained with solutions less acid than the 2 : 1-vanadate, although the effect of omitting the boiling or ageing operation with such solutions may be apparent in the subsequent titration after the 2 : 1-vanadate stage is passed.

5. *Effects of Boiling on Solutions between the* 3 : 1- *and the* 2 : 1-*Vanadate.*—Since boiling or ageing has little or no influence on solutions of the 2 : 1-vanadate, but considerable effect on the 3 : 1-vanadate, an experiment was carried out with solutions intermediate between these two vanadates. To four portions of a solution of the 3 : 1-vanadate, x c.c. of 0·0933N-hydrochloric acid were added, where $x = 0, 1, 3{\cdot}25$, and 5·40 c.c. respectively. Each solution was boiled, diluted to 100 c.c. and 0·005M with respect to the vanadium content, and titrated directly, without any subsequent boiling, with acid of the same concentration.

The conductivities found are shown in Table III and plotted in Fig. 2. The initial broken-line curve corresponds to the boiling effect shown in Curve D in Fig. 1. This experiment shows that initial boiling of solutions between the 3 : 1- and the 2 : 1-vanadate lowers their conductivity, but on direct titration they tend to revert to a curve of the type C of Fig. 1. Initial boiling of a solution corresponding with the 2 : 1-vanadate leads, however, on titration with

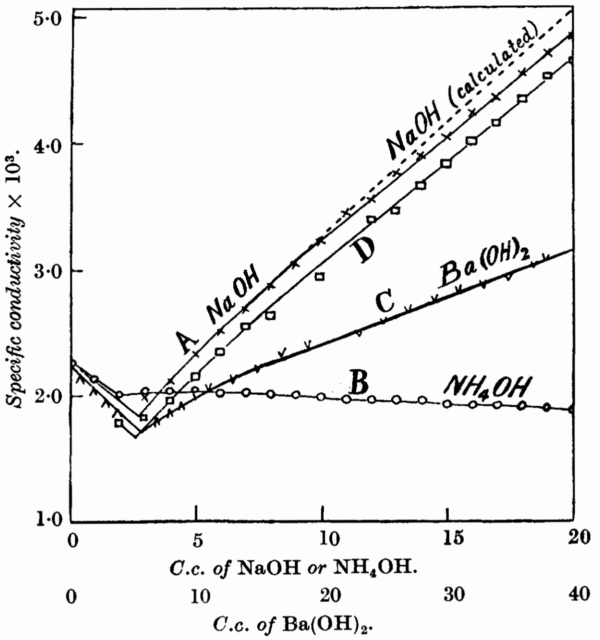
TABLE III.

Specific conductivities of 100 c.c. *of* (a) 3 : 1-, (b) 2·8 : 1-, (c) 2·35 : 1-, (d) 2 : 1-*vanadate, boiled initially and titrated directly with* 0·0933N-HCl.

$Na_2O : V_2O_5$...	3 : 1	2·8 : 1	2·35 : 1	2 : 1	1·5 : 1	1 : 1	0·5 : 1	0 : 1
$\kappa \times 10^3$ (*a*)	2·17	2·10	1·89	1·73	1·55	1·54	1·60	2·21
(*b*)	—	2·02	1·86	1·71	1·56	1·54	1·60	2·21
(*c*)	—	—	1·78	1·64	1·57	1·56	1·62	2·21
(*d*)	—	—	—	1·61	1·62	1·64	1·66	2·30

acid, to a different type of curve, identical in form with Curve D of Fig. 1, which was obtained by boiling the solution after each addition of acid.

FIG. 3.



Alkali, c.c.	0.	2.	4.	6.	10.	15.	19.
$\kappa \times 10^3$ (*a*)	2·30	1·96	2·10	2·50	3·20	4·03	4·70
(*b*)	2·26	2·04	2·04	2·02	1·98	1·93	1·91
(*c*)	2·28	2·05	1·88	1·81	2·01	2·23	2·38
(*d*)	1·78	1·95	2·34	2·61	3·39	4·16	4·84

6. *Titration of Vanadic Acid with Alkalis.*—The effect of hydrochloric acid on vanadate solutions having been determined, the reverse titration of vanadic acid with alkalis was investigated. 0·005*M*-Vanadic acid (H_3VO_4) was formed by the addition of hydro-

chloric acid to the 3 : 1-vanadate and 100 c.c. were titrated with (*a*) 0·1*N*-sodium hydroxide, (*b*) 0·1023*N*-ammonia, and (*c*) 0·0487 *N*-baryta. Also (*d*) 100 c.c. of a solution corresponding with the minimum conductivity in Curve G of Fig. 1 (*i.e.*, prepared by diluting a mixture of 13 c.c. of 0·1*N*-hydrochloric acid and 25 c.c. of 0·02*M*-Na_3VO_4) were titrated with 0·1*N*-sodium hydroxide. The conductivities are given above and are plotted in Fig. 3, the Curve D starting from 2 c.c., because 13 c.c. of 0·1*N*-acid were used in making up this solution, whereas 15 c.c. would have been required to give H_3VO_4 (see Fig. 1).

The first part of the curve, in all three cases, consists of a sharp drop, corresponding with the neutralisation of some excess acid; in the sodium hydroxide titration, the curve then rises regularly, showing no break which could be attributed to the 1 : 1-, 2 : 1-, or 3 : 1-vanadates.

The slow fall in the ammonium hydroxide curve is to be explained by the gradual dilution of the solution, which is more than sufficient to counterbalance the conductivity due to the ammonium hydroxide added; moreover, the ammonium chloride exerts a buffering effect. The baryta curve resembles that for sodium hydroxide, and a similar explanation applies, although here there is the added complication of a precipitation of a barium vanadate, which appears slowly during the course of the titration.

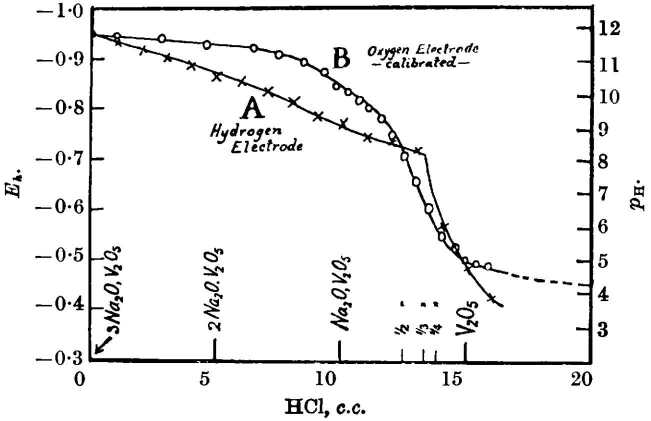
B. *Potentiometric Titrations.*

An attempt has been made to follow the course of the titration of sodium 3 : 1-vanadate with hydrochloric acid potentiometrically. In a 0·005*M*-Na_3VO_4 solution, the hydrogen electrode was found to give steady, reproducible potentials, the *E.M.F.* in eight determinations varying only between —0·948 and —0·950, measured against the normal calomel electrode. This corresponds to p_H 11·65 and $[OH'] = 0{\cdot}0045N$, indicating 30% hydrolysis. The cell used was $H_2(Pt)|0{\cdot}005M\text{-}Na_3VO_4|\text{sat.}KCl|1{\cdot}0N\text{-}KCl,Hg_2Cl_2|Hg$. On titration of the solution with 0·1*N*-hydrochloric acid, the electrode ceased to give satisfactory results: it showed a slight but steady fall in potential up to 13 c.c., but then became very erratic, the *E.M.F.* falling rapidly. A typical titration is illustrated in Fig. 4. That reduction was proceeding, at any rate in the more acid solutions, was evident from their blue colour after hydrogen had been passing for a short time.

Titration with the oxygen electrode also yielded unsatisfactory results. As is well known, this electrode does not give reproducible readings even under favourable conditions; it was therefore calibrated against the value of —0·950 volt, obtained for the hydrogen electrode in 0·005M-Na_3VO_4 solution, and then afforded qualitative results, as may be seen from a typical curve in Fig. 4; in agreement with the hydrogen electrode, there is no sharp fall, but a considerable lowering of the p_H of the solution in the region of the 1 : 2-, 1 : 3-, and 1 : 4-vanadates.

Attempts were made to use the quinhydrone electrode in the titration of vanadic acid solutions with alkali. Its behaviour was very erratic, however, a fact which is not surprising in view of the closeness of the normal reduction potential of quinone–quinol to that of quinquevalent–quadrivalent vanadium.

FIG. 4.



Discussion.

The foregoing experiments may be summarised as follows : The sodium 3 : 1-vanadate, when titrated directly with hydrochloric acid, shows but little analogy with the formally similar phosphate (compare Curves B and C, Fig. 1) : while the phosphate shows breaks corresponding with the primary and secondary salts, the vanadate has a continuously varying conductivity, although, when allowance is made for the conductivity due to the sodium chloride in the solution, a break appears at a point corresponding with 13/15ths decomposition. If these solutions are boiled or aged after each addition of acid in the course of the titration, the nature of the curve changes, a break being obtained at the 2 : 1-vanadate and, according to Düllberg (*loc. cit.*), in the more concentrated solutions, at the 1 : 1-vanadate. The main divergence from the phosphate analogy, however, lies in the break at 13/15ths decomposition, which appears in all the titrations. These boiling (or ageing) effects are not operative in all vanadate solutions. Solutions of the 3 : 1-vanadate, when titrated directly with acid, follow what we may term the " abnormal " smooth curve, typified by C in Fig. 1. If these solutions are boiled after every addition of acid until the 2 : 1-vanadate is reached, another type of curve, exemplified by D in Fig. 1, which we will call the " normal " type, is obtained. Boiling a solution corresponding to the 2 : 1-vanadate, or a more acid vanadate, produces no change in its titration with hydrochloric acid. Omission of the boiling operation at any stage previous to the 2 : 1-vanadate, however, results in the solution reverting to the " abnormal " curve on further titration.

Direct titration by alkali of a solution corresponding with vanadic acid shows no evidence of salt formation corresponding to the 1 : 1-, 2 : 1-, or 3 : 1-vanadates.

Potentiometric titration of the 3 : 1-vanadate with hydrochloric acid, using the hydrogen electrode, indicates that there is a steady fall in p_H from 11·65 in the 3 : 1-vanadate solution to about 8·4 when 13/15ths of the decomposition is complete, after which the solution rapidly becomes acid.

Düllberg explained his titration curves by postulating a hexavanadic acid, $H_4V_6O_{17}$ (*i.e.*, $3V_2O_5,2H_2O$). At the point corresponding to 12·5/15ths of the decomposition, he supposed that the monohydrogen salt of this acid was formed, *viz.*, $HNa_3V_6O_{17}$ or $Na_2O,2V_2O_5,\frac{1}{3}H_2O$, and that the ion HV_6O_{17}''' did not readily dissociate. In this way he accounted for the decomposition apparently ceasing at 5/6ths of the expected titration.

Against this hypothesis it must be urged that only a small number of vanadates can be derived by simple substitution of hexavanadic acid. Moreover, our figures tend to show that the break occurs somewhat beyond 5/6ths of the decomposition.

By subtracting the conductivity of the sodium chloride from that of the sodium vanadate–sodium chloride mixtures, as in Curves G and H of Fig. 1, an estimate can be made of the minimum conductivity; averaging these values from eight experiments, we estimate this conductivity to be 0·00029 mho, the minimum value occurring at 12·83/15ths of the acid required to liberate vanadic acid; in all cases the solution was 0·005*M* with respect to vanadium. This is a surprisingly low conductivity, indicating a very heavy molecule, *i.e.*, polymerisation.

A more feasible, and at the same time a more fruitful, hypothesis is to postulate the existence of a complex with a high $V_2O_5 : Na_2O$ ratio, corresponding with 12·85 c.c. of hydrochloric acid. Such a complex would have the approximate composition $Na_2O,2V_2O_5$ or

$Na_2O,3V_2O_5$, but as we shall show that this can only exist in a polymerised form, it would appear to be on the border line between a true solute and a colloidal micelle, and consequently a simple ratio between Na_2O and V_2O_5 is not to be expected.

Such a complex could easily give rise to a series of salts by addition of small amounts of acids and evaporation, especially as it is by no means certain that many of these more complex vanadates are of definite chemical composition.

Now, Düllberg has shown that a solution, 0·1*M* with respect to vanadium, and corresponding with 12·5 c.c. of hydrochloric acid in our graph (Fig. 2), has a freezing point of —0·0751°. For a solution of 0·1*M*-$\frac{1}{4}$($Na_2O,2V_2O_5$) we should expect a depression of —0·186° if the solution were un-ionised; for a doubly polymerised molecule we should expect —0·093°, and for a trebly polymerised molecule —0·0465°. The last figure would be somewhat higher if the molecule were ionised, and if it be assumed that our complex contains three atoms of vanadium, the freezing point would indicate about 21% dissociation. Moreover, Düllberg has demonstrated that the 1 : 1-vanadate is probably trebly polymerised, showing that condensation of molecules is occurring even at this stage of the titration.

In one case (Soln. 2 in Section 1), the conductometric titration of a 0·005*M*-3 : 1-vanadate solution with hydrochloric acid was carried beyond the liberation of vanadic acid at 15 c.c. of 0·1*N*-acid. The latter portion of this titration, from 15 to 25 c.c. of acid, is shown in Fig. 2, where it is contrasted with the calculated conductivity of the added hydrochloric acid, assumed present as free acid. The observed conductivities at titres of 15 and 25 c.c. were 0·00201 and 0·00434 mho, respectively, a difference of 0·00233 mho. The conductivity due to the addition of 10 c.c. of 0·1*N*-acid is calculated as 0·00320 mho, or, after allowing for the decrease in the conductivity of the sodium chloride on dilution from 115 to 125 c.c., which is approximately 0·00016 mho, the calculated difference becomes 0·00304. The observed increase in conductivity is therefore about 23% less than the calculated, showing that the complex is not entirely resistant to the action of acids, but that some replacement of sodium by hydrogen occurs.

Similar conclusions are to be drawn from the alkali titration of vanadic acid. In Fig. 3 the titration of 0·005*M*-vanadic acid with 0·1*N*-sodium hydroxide is contrasted with the calculated increase in conductivity due to the sodium hydroxide calculated as free alkali. Between the titres of 3 c.c. and 20 c.c. of caustic soda the conductivity increased by 0·00289 mho. The addition of 17 c.c.

of 0·1N-sodium hydroxide would give a calculated increase of 0·00333 mho, or 0·00305 mho after 0·00028 mho is allowed for the decrease in conductivity owing to the dilution of the solution from 103 to 120 c.c. The observed increase is, therefore, 5% less than the calculated increase in conductivity, showing that there is a small interaction between the complex and the sodium hydroxide.

The decomposition of sodium 3 : 1-vanadate, when the solution is boiled or aged after each addition of acid, would appear to proceed as follows: The 3 : 1-vanadate is hydrolysed almost completely into sodium hydroxide and the 2 : 1-vanadate; addition of hydrochloric acid neutralises the hydroxide, and at one-third decomposition the solution consists, therefore, of sodium chloride and the 2 : 1-vanadate. The first reaction may be represented as $NaOH + Na_2HVO_4 \longrightarrow NaCl + Na_2HVO_4$. Now in Expt. B of Section 2 we found that the conductivity at one-third decomposition was 0·00165 mho, of which 0·000585 mho was due to sodium chloride. Thus the conductivity of the 2 : 1-vanadate is 0·001065 mho, and, adding to this the conductivity of an equimolecular amount of sodium hydroxide, *viz.*, 0·001175 mho, we get 0·00224 mho for the calculated value of the conductivity of the 3 : 1-vanadate, compared with 0·00215 mho for the observed. The discrepancy is probably due in the first place to the hydrolysis of the 3 : 1-vanadate being not quite complete, and secondly, to the 2 : 1-vanadate being itself hydrolysed to some extent.

The next stage, between one-third and two-thirds decomposition, consists of the formation of a condensed 1 : 1-vanadate: $3Na_2HVO_4 + 3HCl \longrightarrow Na_3V_3O_9 + 3NaCl + 3H_2O$. Further addition of acid results in an abstraction of soda from this heavy 1 : 1-vanadate molecule until a ratio of Na : V between 1 : 2 and 1 : 3 is reached, whereupon the molecule becomes sufficiently stable, and the residual soda is so closely bound in the complex that further addition of the acid causes no change, or only a very gradual and partial replacement. No break appears at two-thirds neutralisation, where the 1 : 1-vanadate begins to be converted into the complex, but this is marked by the fact that solutions containing the complex cannot be decolorised by boiling.

In the case of direct titration of the 2 : 1- or 1 : 1-vanadates, the same sequence of changes occurs.

The potentiometric curves given in Fig. 4, though by no means satisfactory, explain why Rosenheim and Yang (*Z. anorg. Chem.*, 1923, **129**, 181) found that, on titration of solutions of the 3 : 1-vanadate with sulphuric acid, phenolphthalein became decolorised when approximately 2 equivs. of acid had been added. The curves show that the solutions are buffered at this stage so that the change-point could not possibly be sharp.

The same problem has been approached in another direction by Dumanski (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 703), who prepared vanadium pentoxide sols by the method of Biltz (*Ber.*, 1904, **37**, 1095), *i.e.*, grinding ammonium metavanadate with hydrochloric acid, filtering off the residue, and shaking it with water. On dilution of the red solution, a yellow solution was obtained, having a higher electrical conductivity *and having no particles visible in the ultra-microscope.* On coagulation with barium chloride, a small amount of barium was absorbed, increasing to a constant value after several hours' standing, whereupon the solid approximated to the composition $BaH_2V_6O_{17}$. The conductivity of the solution increased at the same time, consistent with a replacement of barium ions by hydrogen ions. From the amount absorbed in the first stage, the formula $[H_2V_6O_{17}(V_2O_5)_6]'' + 2H^{\bullet}$ was deduced.

The authors wish to thank the Chemical Society for a grant from the Research Fund.

UNIVERSITY COLLEGE, EXETER. [*Received, April* 16*th*, 1930.]