CCCI.—*Physicochemical Studies of Complex Acids. Part IV. The Vanadates of Silver.*

By HUBERT THOMAS STANLEY BRITTON and
ROBERT ANTHONY ROBINSON.

THE vanadates of silver have received little attention, investigations on the nature of these compounds having been restricted almost entirely to their isolation and analysis.

The 3 : 1 vanadate, $3Ag_2O,V_2O_5$, was prepared by Roscoe (J., 1871, **24**, 23) from the corresponding sodium salt by metathesis; in a similar way he prepared the 2 : 1 salt, $2Ag_2O,V_2O_5$, which was later isolated by Ditte (*Compt. rend.*, 1887, **104**, 1705). The conditions under which 1 : 1 silver vanadate is precipitated from solutions of silver nitrate by ammonium metavanadate were studied by Browning and Palmer (*Amer. J. Sci.*, 1910, **30**, 220), who found that quantitative precipitation of the vanadium occurred from boiling solutions, even when the solutions were first made slightly alkaline with ammonia. Acidification with acetic acid, however, gave rise to a precipitate whose composition varied slightly from that of the 1 : 1 vanadate. Carnelly (J., 1873, **26**, 323) obtained a silver salt of the composition $Ag_6V_4O_{13}$, *i.e.*, the 3 : 2 vanadate, by the action of silver nitrate on solutions of 3 : 2 sodium vanadate. Moser and Brandl (*Monatsh.*, 1929, **51**, 169) showed that in the presence of a certain concentration of sodium acetate, a precipitate corresponding approximately to the yellow 2 : 1 silver vanadate can be obtained from the interaction of solutions of ammonium metavanadate and silver nitrate, whilst if a given amount of ammonium hydroxide is present along with the sodium acetate, a precipitate corresponding exactly to 3 : 1 silver vanadate is formed.

This communication describes some physicochemical measurements made in order to determine which of the many possible compounds of silver and quinquevalent vanadium are true chemical compounds and to investigate the conditions under which they are formed. Further, the results are utilised in a discussion of the more general problem of the constitution of vanadate solutions.

EXPERIMENTAL.

A. *Titrations with the Silver Electrode.*

(1) 3 : 1 *Silver Vanadate*, Ag_3VO_4.—By mixing solutions of silver nitrate and 3 : 1 sodium vanadate, prepared by dissolving vanadium pentoxide in boiling sodium hydroxide solution, a deep orange-red precipitate is obtained having the empirical formula Ag_3VO_4. The course of this precipitation has been followed by titrating 100 c.c. of $0{\cdot}01N$-silver nitrate with $0{\cdot}0333M$-sodium vanadate, the silver electrode being employed to determine the silver-ion concentration at different titres by means of the following cell at 20° :

$$Ag|0{\cdot}1N\text{-}AgNO_3|\text{sat. }KNO_3|0{\cdot}01N\text{-}AgNO_3 + Na_3VO_4|Ag.$$

To ascertain whether the cell and the electrodes were functioning properly, we titrated 100 c.c. of $0{\cdot}01N$-silver nitrate solution with $0{\cdot}1N$-sodium chloride against these electrodes and obtained a value of $1{\cdot}61 \times 10^{-10}$ for the solubility product $[Ag^{\cdot}][Cl']$ at 20°, a value which is in good accord with those previously published. The theoretical end-point of the reaction $Na_3VO_4 + 3AgNO_3 \longrightarrow Ag_3VO_4 + 3NaNO_3$ occurs at 10 c.c. of the vanadate solution. The *E.M.F.*'s registered by the above cell on further addition of this solution are given in Table I, together with the silver-ion concentration calculated from the formula $E_{obs.} = -0{\cdot}063 - 0{\cdot}058 \log [Ag^{\cdot}]$.

TABLE I.

Titration of 100 c.c. of $0{\cdot}01N$-$\mathrm{AgNO_3}$ with $0{\cdot}0333M$-$\mathrm{Na_3VO_4}$.
End point = 10 c.c.

C.c.	11	12	13	14	15	20	25
E.M.F.	0·264	0·274	0·280	0·287	0·290	0·300	0·308
$[\mathrm{Ag}^{\cdot}] \times 10^7$	23·0	15·5	12·2	9·24	8·20	5·51	4·01
$[\mathrm{VO_4}'''] \times 10^3$	0·300	0·595	0·885	1·17	1·45	2·78	4·00
$[\mathrm{HVO_4}''](= [\mathrm{OH}']) \times 10^3$	0·300	0·595	0·885	1·17	1·45	2·78	4·00
$[\mathrm{Ag}^{\cdot}]^3[\mathrm{VO_4}'''] \times 10^{23}$	365	222	161	92	80	47	26
$[\mathrm{Ag}^{\cdot}]^3(\mathrm{HVO_4}''][\mathrm{OH}'] \times 10^{25}$	11·0	13·2	14·2	10·8	11·6	12·9	10·3

C.c.	30	40	50	60	70	80
E.M.F.	0·313	0·319	0·324	0·326	0·328	0·329
$[\mathrm{Ag}^{\cdot}] \times 10^7$	3·29	2·59	2·13	1·96	1·81	1·74
$[\mathrm{VO_4}'''] \times 10^3$	5·13	7·14	8.89	10·4	11·8	13·0
$[\mathrm{HVO_4}''](= [\mathrm{OH}']) \times 10^3$	5·13	7·14	8·89	10·4	11·8	13·0
$[\mathrm{Ag}^{\cdot}]^3[\mathrm{VO_4}'''] \times 10^{23}$	18·3	12·4	8·6	7·8	7·0	6·8
$[\mathrm{Ag}^{\cdot}]^3[\mathrm{HVO_4}''][\mathrm{OH}'] \times 10^{25}$	9·4	8·9	7·6	8·1	8·3	8·9

Mean value of $[\mathrm{Ag}^{\cdot}]^3[\mathrm{OH}'][\mathrm{HVO_4}''] = 1 \times 10^{-24}$.

Curve A of Fig. 1 shows the variation of *E.M.F.* during the titration, and exhibits all the characteristics of a precipitation reaction, the *E.M.F.* first increasing slowly through the diminution in silver-ion concentration consequent on the precipitation of a silver salt, the completion of the reaction being marked by a sharp inflexion at the calculated end-point, after which the curve flattens out, the silver-ion concentration being determined by the equilibrium between the solution and the precipitated silver vanadate.

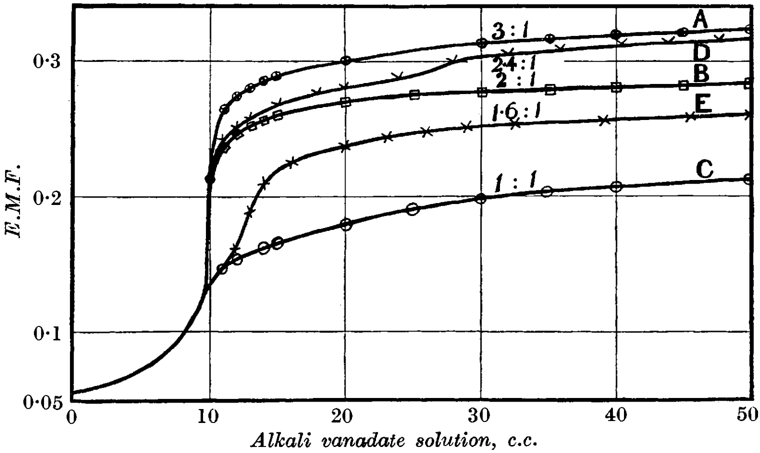
The composition of the precipitate is independent of the ratio of the silver nitrate and sodium vanadate reacting. This was shown by mixing them in the respective ratios of 1, 2, and 4 mols. of silver nitrate to 2 mols. of 3 : 1 sodium vanadate. The character of the precipitate varies, however, since a flocculent, easily filterable precipitate can only be obtained by maintaining an excess of silver nitrate. These analyses refer to precipitations carried out in the cold, but even the precipitate obtained from a boiling solution will not settle readily unless the silver nitrate is in excess. Excess of the other constituent produces a precipitate which can be separated by filtration only with great difficulty. The precipitate was analysed in the following way. A weighed amount, dried at 120°, was dissolved in sulphuric acid, the silver precipitated with the slightest excess of hydrochloric acid, and the vanadium estimated in the filtrate by reduction with sulphur dioxide and titration with potassium permanganate. Estimations carried out on solutions of known silver and vanadium content showed the method to be satisfactory. The mean of four analyses of 3 : 1 silver vanadate gave $\mathrm{Ag_2O}$, 79·36; $\mathrm{V_2O_5}$, 20·81 (Calc. : $\mathrm{Ag_2O}$, 79·26; $\mathrm{V_2O_5}$, 20·74%). The solution in sulphuric acid had a greenish tinge, showing the presence of a small quantity of vanadium in the quadrivalent state; this may have originated in reduction by a small amount of organic impurity during the drying of the precipitate or, more probably, since the two constituents add up to 100·17%, during the dissolution of the vanadate in sulphuric acid. Of the two analyses, that of the silver is probably the more accurate.

Since the solid phase has the composition Ag_3VO_4, it would be expected that the equation $K = [Ag^{\cdot}]^3[VO_4''']$, where K is the solubility product of 3 : 1 silver vanadate, would determine the equilibrium between the solid and its saturated solution. Now, on the assumption that the excess of the 3 : 1 sodium vanadate was completely dissociated into $Na^{\cdot}$ and VO_4''' ions, we have calculated (line 6 of Table I) values of this product at different titres, and it will be seen that it varies continuously over a 50-fold range between 11 and 80 c.c. of the titrant. Hence it would appear that the method adopted to estimate the VO_4''' ion concentration was unsatisfactory. It was shown previously (this vol., p. 1269) that as the p_H of a $0·005M$-sodium vanadate solution is 11·65, hydrolysis of the first stage must be almost complete; and consequently the anions existing in the solution are HVO_4'' and OH' rather than VO_4''', and therefore we are not justified in setting $[VO_4'''] = [Na_3VO_4]$. But the small residual VO_4''' ion concentration must be in equilibrium with its products of hydrolysis, $VO_4''' + H_2O \rightleftarrows HVO_4'' + OH'$, so that $K_h = [VO_4''']/[HVO_4''][OH']$, where K_h is the hydrolysis constant, and hence the true solubility product,

$$K = K_h[Ag^{\cdot}]^3[HVO_4''][OH'].$$

Although the product $[Ag^{\cdot}]^3[HVO_4''][OH']$ is not the true solubility

FIG. 1.



product, since the foregoing expression involves an unknown hydrolysis constant, yet constancy of this product will confirm the postulate that 3 : 1 sodium vanadate undergoes hydrolysis in solution and that there is a small concentration of VO_4''' ions in solution in equilibrium with the precipitate, Ag_3VO_4. In the last line of Table I is given the value of this product, the HVO_4'' and OH′ ion concentrations each being taken equal to the concentration of sodium vanadate, *i.e.*, hydrolysis being assumed to be complete. As predicted by our theory, we find a satisfactorily constant value for $[Ag^{\cdot}]^3[HVO_4''][OH']$ of the order of 10^{-24}.

The titration has also been conducted in the reverse manner, 100 c.c. of 0·0083*M*-sodium vanadate being titrated with 0·1*N*-silver nitrate. A curve similar to the upper curve (A) of Fig. 2 was obtained, and the *E.M.F.*'s recorded gave a mean value of $[Ag^{\cdot}][OH'][HVO_4''] = 0{\cdot}9 \times 10^{-24}$, over a range of 25 c.c., in good agreement with the value obtained as above.

(2) 2 : 1 *Silver Vanadate*, $2Ag_2O,V_2O_5$.—In a similar manner, a silver nitrate solution was titrated with a solution of the 2 : 1 sodium vanadate. This solution, which was colourless, was prepared by dissolving vanadium pentoxide in boiling sodium hydroxide solution. The results are given in Table II and Curve B of Fig. 1. The precipitate appeared on the addition of the first few drops of sodium vanadate. It was light yellow and flocculent; after drying at 120°, it contained Ag_2O, 71·60; V_2O_5, 28·36 (Calc.: Ag_2O, 71·82; V_2O_5, 28·18%). Subsequent work suggests that this substance is a definite compound, which on the basis of its composition, might be regarded as either silver pyrovanadate, $Ag_4V_2O_7$, or the secondary silver orthovanadate, Ag_2HVO_4, and consequently the 2 : 1 sodium vanadate used is either $Na_4V_2O_7$, the pyrovanadate, or Na_2HVO_4 respectively. The ionic equilibrium set up between this salt and water would be either $Ag_4V_2O_7 \rightleftarrows 4Ag^{\cdot} + V_2O_7''''$ or $Ag_2HVO_4 \rightleftarrows 2Ag^{\cdot} + HVO_4''$, and the respective solubility products would be $[Ag^{\cdot}]^4[V_2O_7'''']$ and $[Ag^{\cdot}]^2[HVO_4'']$.

Table II gives the values of the two solubility products, and it will be seen that only $[Ag^{\cdot}]^2[HVO_4'']$ gives a constant value; thus this evidence would favour the existence of the HVO_4'' ion rather than that of the V_2O_7'''' ion.

In Part II (this vol., p. 1263) we showed that the colourless 2 : 1 sodium vanadate solution could also be prepared by boiling 1 equiv. of a strong acid with 1 mol. of Na_3VO_4, in contrast to the yellow solution of slightly higher conductivity formed by adding the acid to the cold solution. The colourless solution so prepared gives the same precipitate with silver nitrate, and a titration curve, with the silver electrode, of 100 c.c. of a 0·01*M*-silver nitrate solution with

TABLE II.

Titration of 100 c.c. of 0·01N-$AgNO_3$ with 0·05M-Na_2HVO_4. End-point = 10 c.c.

C.c.	11	12	13	14	15	20	25	30
E.M.F.	0·237	0·248	0·253	0·257	0·261	0·270	0·275	0·278
$[Ag^{\cdot}\} \times 10^6$	6·72	4·34	3·56	3·04	2·59	1·81	1·49	1·32
$[HVO_4] \times 10^8$	0·450	0·893	1·33	1·75	2·17	4·17	6·00	7·69
$[Ag^{\cdot}]^2[HVO_4''] \times 10^{14}$	2·0	1·7	1·7	1·6	1·5	1·4	1·3	1·3
$[Ag^{\cdot}]^4[V_2O_7''''] \times 10^{26}$	46	16	11	7·5	4·9	2·3	1·5	1·2

C.c.	35	40	45	50	60	70	80
E.M.F.	0·281	0·282	0·283	0·284	0·285	0·286	0·287
$[Ag^{\cdot}] \times 10^6$	1·17	1·13	1·08	1·04	1·00	0·96	0·92
$[HVO_4] \times 10^3$	9·26	10·7	12·1	13·3	15·6	17·6	19·4
$[Ag^{\cdot}]^2[HVO_4''] \times 10^{14}$	1·3	1·4	1·4	1·4	1·6	1·6	1·6
$[Ag^{\cdot}]^4[V_2O_7''''] \times 10^{26}$	0·87	0·87	0·82	0·78	0·78	0·75	0·69

Mean value of $[Ag^{\cdot}]^2[HVO_4''] = 1·5 \times 10^{-14}$.

0·025M-Na_2HVO_4 gave $1·6 \times 10^{-14}$ as the mean value for $[Ag^{\cdot}]^2[HVO_4'']$, over a range of 60 c.c. beyond the end-point. The product, $[Ag^{\cdot}]^4[V_2O_7'''']$, however, varied from 1270×10^{-27} to 7×10^{-27}. It will be seen that the solubility products, $[Ag^{\cdot}]^2[HVO_4'']$, obtained in the above two experiments are identical, in spite of the concentration of the precipitant in the second case being one-half of that used in the first titration.

(3) 1 : 1 *Silver Vanadate*, Ag_2O,V_2O_5.—1 : 1 Sodium vanadate, prepared by dissolving ammonium metavanadate in boiling sodium hydroxide solution and passing a stream of carbon dioxide-free air through the boiling solution, gives a deep orange precipitate with silver nitrate solution, which on analysis gives Ag_2O, 56·40; V_2O_5, 43·31 (Calc. for Ag_2O,V_2O_5: Ag_2O, 56·03; V_2O_5, 43·97%). This precipitate is not changed in composition if a large excess of the precipitant is used, unlike the precipitate from a solution of 1·6 : 1 sodium vanadate which, as is shown later, acts as a mixture of 1 : 1 and 2 : 1 silver vanadates, and in the presence of an excess of the vanadate solution, changes into the less soluble 2 : 1 silver vanadate. Table III gives the results of titrating a solution of silver nitrate with 1 : 1 sodium vanadate solution against silver electrodes, and Curve C in Fig. 1 is their graphical representation.

The solubility product $[Ag^{\cdot}][VO_3']$ has been calculated on the assumption that the 1 : 1 sodium vanadate is completely dissociated into VO_3' (or H_2VO_4') ions. A satisfactory constant is obtained.

Previous experiments (Part II, *loc. cit.*) showed that colourless solutions of 1 : 1 sodium vanadate can be prepared by boiling solutions of either the 3 : 1 or the 2 : 1 vanadate with the requisite quantity of a strong acid. We therefore prepared solutions in this way, 0·0167M and 0·025M, respectively, and used them to titrate

TABLE III.

Titration of 100 c.c. 0·01N-$AgNO_3$ with 0·1M-$NaVO_3$. End-point = 10 c.c.

C.c.	11	12	14	15	20	25	30	35	40	50	60	70	80
E.M.F.	0·148	0·156	0·163	0·166	0·181	0·190	0·198	0·203	0·207	0·212	0·217	0·220	0·221
$[Ag^{\cdot}] \times 10^4$	2·30	1·68	1·27	1·13	0·62	0·43	0·316	0·259	0·221	0·181	0·149	0·132	0·127
$[VO_3'] \times 10^3$	0·901	1·79	3·51	4·35	8·33	12·0	15·4	18·5	21·4	26·7	31·3	35·3	38·9
$[Ag^{\cdot}][VO_3'] \times 10^7$	2·1	3·0	4·5	4·9	5·2	5·2	4·9	4·8	4·7	4·8	4·7	4·7	4·9

Mean value of $[Ag^{\cdot}][VO_3'] = 4·8 \times 10^{-7}$.

100 c.c. of 0·005N-silver nitrate. In spite of the different concentrations of 1 : 1 sodium vanadate employed, constant values of $[Ag^{\cdot}][VO_3']$ were obtained, the mean values, taken over the range 33—90 c.c. in the first case and 22—90 c.c. in the latter, being $4·3 \times 10^{-7}$ and $4·1 \times 10^{-7}$ respectively.

We also used a solution of ammonium metavanadate, NH_4VO_3, to titrate silver nitrate solution, the *E.M.F.*'s observed being given in Table IV. The precipitate, after being dried, had a composition corresponding to $AgVO_3$ (Found : V_2O_5, 43·71; Ag_2O, 56·12%).

TABLE IV.

Titration of 100 c.c. of 0·01N-$AgNO_3$ with 0·04M-NH_4VO_3. End-point = 25 c.c.

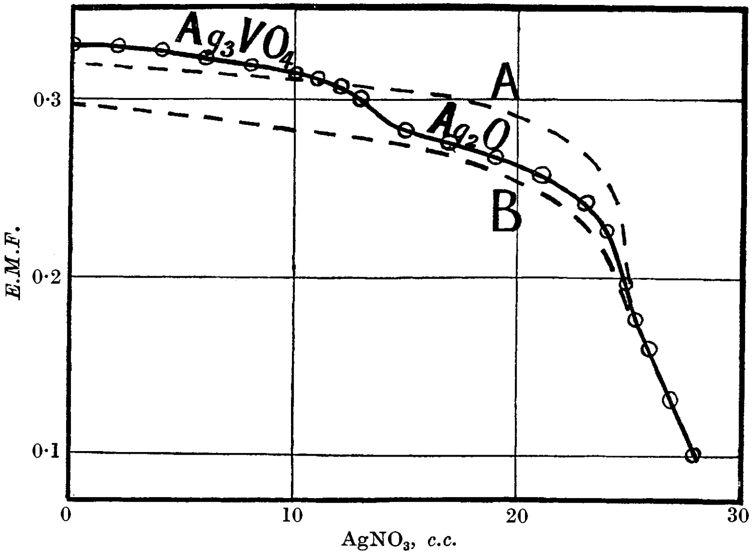
C.c.	26	28	30	35	40	45	50	60	70	80
E.M.F.	0·120	0·130	0·137	0·156	0·163	0·170	0·173	0·178	0·182	0·184
$[Ag^{\cdot}] \times 10^4$	7·00	4·70	3·56	1·68	1·27	0·96	0·85	0·70	0·60	0·55
$[VO_3'] \times 10^3$	0·318	0·938	1·54	2·96	4·29	5·52	6·67	8·75	10·6	12·2
$[Ag^{\cdot}][VO_3'] \times 10^7$	2·2	4·4	5·5	5·0	5·4	5·3	5·7	6·1	6·4	6·7

Mean value of $[Ag^{\cdot}][VO_3'] = 5·3 \times 10^{-7}$.

Hence the same precipitate was obtained from ammonium metavanadate as from 1 : 1 sodium vanadate, and the average of all values of $[Ag^{\cdot}][VO_3']$ may be taken as 5×10^{-7}. Düllberg (*Z. physikal. Chem.*, 1903, **45**, 129) brought evidence, based on depressions of the freezing point, to show that the 1 : 1 sodium vanadate is polymerised probably to $Na_3V_3O_9$, which dissociates : $Na_3V_3O_9 \longrightarrow 3Na^{\cdot} + (V_3O_9)'''$. If this is the case, then the 1 : 1 silver vanadate is in equilibrium, not with VO_3' ions, but with $(V_3O_9)'''$ ions, whence its solubility product would be $[Ag^{\cdot}]^3[V_3O_9''']$. These data, however, would not give even an approximately constant value for this product, and therefore in view of the very satisfactory data we have obtained with different dilutions of 1 : 1 sodium vanadate and also with ammonium metavanadate, we cannot regard polymerisation of the VO_3' ion as a well-established fact and must leave a decision on this question to further experiment.

(4) *Vanadates of the Formula* xAg_2O,V_2O_5, *where* $x>3$.—In order to find whether a vanadate could be obtained of the composition xAg_2O,V_2O_5 where $x>3$, we titrated a mixture of 100 c.c. of $0{\cdot}00416M$-Na_3VO_4 and $0{\cdot}0125N$-sodium hydroxide with $0{\cdot}1N$-silver nitrate against the silver electrode. Fig. 2 shows the plot of *E.M.F.* against c.c. of silver solution and clearly indicates a " break " in the curve at half the amount of silver nitrate required to complete the precipitation of both the vanadate and the hydroxide. For comparison, the calculated titration curves are given for a titration with $0{\cdot}1N$-silver nitrate of (*a*) a solution of 3 : 1 sodium vanadate of the same total sodium concentration, *i.e.*, $0{\cdot}00833M$-Na_3VO_4, Curve A, and (*b*) a solution of sodium hydroxide of the same total sodium concentration, *i.e.*, $0{\cdot}025N$, Curve B.

FIG. 2.



The precipitate obtained in the first half of the titration had the appearance of 3 : 1 silver vanadate, and that in the second half seemed to be silver oxide. The data are reproduced in Table V.

To a mixture of 3 : 1 sodium vanadate and sodium hydroxide in equimolecular amounts (corresponding to 6 : 1 sodium vanadate), was added half the amount of silver nitrate required for complete precipitation of silver vanadate and silver oxide, and the precipitate filtered off and analysed (Found : V_2O_5, 20·41 ; Ag_2O, 79·67%, corresponding to 3 : 1 silver vanadate). The residual solution contained no vanadium and gave a titre against acid corresponding to the original alkali concentration. This remaining alkali caused silver oxide to be precipitated during the second half of the precipitation.

TABLE V.

Titration of 100 c.c. of 0·00416*M*-Na_3VO_4 and 0·0125*N*-NaOH with 0·1*N*-$AgNO_3$.

C.c.	1	2	4	6	8	10	11	15	17	19	21	23
E.M.F.	0·329	0·328	0·326	0·322	0·318	0·313	0·311	0·282	0·275	0·268	0·257	0·242
$[\mathrm{Ag}^{\cdot}] \times 10^6$	0·174	0·181	0·196	0·230	0·270	0·329	0·356	1·13	1·49	1·96	3·04	5·51
$[\mathrm{OH}'] \times 10^3$	16·2	15·7	14·7	13·9	13·0	12·2	11·8	8·70	6·84	5·04	3·31	1·63
$[\mathrm{HVO}_4''] \times 10^3$	3·79	3·43	2·72	2·04	1·39	0·76	0·45					
$[\mathrm{Ag}^{\cdot}]^3[\mathrm{OH}'][\mathrm{HVO}_4''] \times 10^{25}$	3·3	3·2	3·0	3·5	3·6	3·3	2·4					
$[\mathrm{Ag}^{\cdot}][\mathrm{OH}'] \times 10^8$	0·3	0·3	0·3	0·3	0·4	0·4	0·4	1·0	1·0	1·0	1·0	0·9

Mean value of $[\mathrm{Ag}^{\cdot}][\mathrm{OH}'] = 1 \times 10^{-8}$.
„ „ $[\mathrm{Ag}^{\cdot}]^3[\mathrm{HVO}_4''][\mathrm{OH}'] = 3\cdot3 \times 10^{-25}$.

Hence the precipitation occurs in two stages, first the precipitation of 3 : 1 silver vanadate, and then that of silver hydroxide. The reason for this order will be apparent from Table V, in which are recorded the values of $[\mathrm{Ag}^{\cdot}][\mathrm{OH}']$ calculated from the *E.M.F.*'s obtained. During the second half of the titration they acquired a value equal to the actual solubility product of silver hydroxide, and one which is in good agreement with that given by Britton (J., 1925, **117**, 2956). In the first half of the titration, it has been assumed that each molecule of 3 : 1 sodium vanadate gives rise to one HVO_4'' ion and one hydroxyl ion; the concentration of the latter added to the hydroxyl-ion concentration derived from the sodium hydroxide yields the total hydroxyl-ion concentration given in the fourth line.

Although the hydroxyl ions from the sodium hydroxide may repress the hydrolysis of 3 : 1 sodium vanadate to a certain extent, yet, as the hydrolytic reaction is almost complete, and therefore Na_3VO_4 has the characteristics of a " strong " base, we have thought it reasonable to take the HVO_4''-ion concentration as equal to that of the 3 : 1 sodium vanadate.

With these data have been calculated the values of

$$[Ag^{\cdot}]^3[HVO_4''][OH'].$$

The mean value, $3{\cdot}3 \times 10^{-25}$, is of the same order as that obtained in the direct precipitation of 3 : 1 silver vanadate, the lack of complete agreement being attributed to the decreased accuracy of the silver electrode when placed in a solution of vanadate poor in silver ions : it is probable that true equilibrium is then established only after a long time, whereas in the previous titrations the silver electrode was immersed in a silver nitrate solution and the solution titrated with the appropriate solution—in these circumstances equilibrium is established almost immediately and the electrode responds readily to changes in the silver-ion concentration.

The last line of Table V shows that the value of the ionic product of silver hydroxide, $[Ag^{\cdot}][OH']$, is always smaller than $1{\cdot}5 \times 10^{-8}$, the solubility product of silver hydroxide, as long as there is 3 : 1 sodium vanadate present in solution, thus accounting for the non-precipitation of silver hydroxide in the first stage of the titration. The values of the HVO_4''- and hydroxyl-ion concentrations, however, are such as to lead to a precipitation of the less soluble 3 : 1 silver vanadate.

This evidence leads to the conclusion that no vanadates can be obtained from dilute solutions richer in silver than the 3 : 1 silver vanadate.

(5) *Vanadates of the Formula* xAg$_2$O,V$_2$O, *where* $3>x>2$.—A solution corresponding to the 2·5 : 1 sodium vanadate was added to silver nitrate solution, first in such quantity that the silver concentration was equal to that of the sodium, and secondly that there was a large excess of the sodium vanadate. In the first case the precipitate contained Ag_2O, 76·16; V_2O_5, 24·54 (Calc. for $2{\cdot}5Ag_2O,V_2O_5$: Ag_2O, 76·11; V_2O_5, 23·89%). If this is a true compound, however, we should expect the composition of the precipitate to be unchanged in the presence of an excess of the sodium salt; the precipitate then, however, contained Ag_2O, 78·44; V_2O_5, 21·15%, which is close to that required for Ag_3VO_4, namely, Ag_2O, 79·26; V_2O_5, 20·74%. It would appear, therefore, that as long as the silver nitrate is in excess, the reaction consists of the co-precipitation of two vanadates, the 3 : 1 and the 2 : 1, according to the following equations

$$3Na_2O,V_2O_5 + 6AgNO_3 \longrightarrow 2Ag_3VO_4 + 6NaNO_3$$
$$2Na_2O,V_2O_5 + 4AgNO_3 + H_2O \longrightarrow 2Ag_2HVO_4 + 4NaNO_3$$

the resulting precipitate, of course, corresponding in composition to

$2·5Ag_2O,V_2O_5$. Addition of excess of the sodium vanadate results in the 2 : 1 silver vanadate in the mixed precipitate being converted into the less soluble 3 : 1 vanadate through some vanadium pentoxide contained in the 2 : 1 salt dissolving in the added sodium vanadate.

A solution was made by mixing 0·0333*M*-Na_3VO_4 and 0·050*M*-Na_2HVO_4 in equal volumes, the resulting solution corresponding to the 2·4 : 1 sodium vanadate, and used to titrate 100 c.c. of 0·01*N*-silver nitrate. The co-precipitation of the 3 : 1 and the 2 : 1 silver vanadate was complete after 10 c.c., and the complete conversion of the precipitate into the 3 : 1 vanadate was complete at 20 c.c. The *E.M.F.* plotted against the titrant (Curve D, Fig. 1) shows a change of direction between 10 and 20 c.c., corresponding to the conversion of the mixed precipitate into the 3 : 1 vanadate.

In Table VI, the hydroxyl-ion concentration of the solution has been calculated from the amount of 3 : 1 sodium vanadate added, and that of the HVO_4'' ion as the sum of the HVO_4'' ion derived from the 2 : 1 and the 3 : 1 vanadate, it being assumed that there is but little buffering action of the HVO_4'' on the hydrolytic reaction. On this basis a value of $[Ag^{\bullet}]^3[OH'][HVO_4'']$ has been calculated for that part of the titration where the 3 : 1 silver vanadate is the solid phase.

TABLE VI.

C.c.	24	28	32	36	40	44	47
E.M.F.	0·288	0·299	0·304	0·308	0·310	0·312	0·314
$[Ag^{\bullet}] \times 10^7$	8·88	5·74	4·70	4·01	3·71	3·42	3·16
$[OH'] \times 10^3$	0·54	1·04	1·52	1·96	2·38	2·78	3·06
$[HVO_4''] \times 10^3$	5·38	6·51	7·58	8·58	9·52	10·4	11·1
$[Ag^{\bullet}]^3[OH'][HVO_4''] \times 10^{24}$	2·0	1·3	1·2	1·1	1·2	1·2	1·1

Mean value of $[Ag^{\bullet}]^3[OH'][HVO_4''] = 1·2 \times 10^{-24}$.

This value is in good agreement with that obtained by the direct titration of silver nitrate solution with 3 : 1 sodium vanadate.

(6) *Vanadates of the Formula* xAg_2O,V_2O_5, *where* $2 > x > 1$.—The selective precipitation encountered in the case of 2·5 : 1 sodium vanadate is also found in the case of vanadates between the 2 : 1 and the 1 : 1. A solution made up of composition 1·6 : 1 sodium vanadate and added to a solution of silver nitrate in the ratio Ag : Na = 1 : 1, gave a precipitate corresponding to $1·6Ag_2O,V_2O_5$ (Found : Ag_2O, 67·31 ; V_2O_5, 32·86. Calc. for $1·6Ag_2O,V_2O_5$: Ag_2O, 67·09 ; V_2O_5, 32·91%). In all probability this precipitate was a mixture of $2Ag_2O,V_2O_5$ and Ag_2O,V_2O_5, so that on addition of excess of the sodium vanadate the 1 : 1 silver vanadate would be converted into the less soluble 2 : 1 vanadate. The precipitate thereby obtained contained Ag_2O, 70·60 ; V_2O_5, 28·57 (Calc. for

$2Ag_2O,V_2O_5$: Ag_2O, 71·82; V_2O_5, 28·18%), again proving that the excess of sodium vanadate solution extracted some vanadium pentoxide from the initially precipitated silver vanadate.

100 C.c. of 0·005*N*-silver nitrate were titrated with a solution of 1·6 : 1 sodium vanadate, *i.e.*, with a solution corresponding to 0·0122*M*-Na_2HVO_4 + 0·0083*M*-$NaVO_3$. The precipitation of the 1·6 : 1 silver vanadate was complete at 15·3 c.c., and at 20·5 c.c. the solid phase was assumed to be completely converted into 2 : 1 silver vanadate. In Table VII are given the concentrations of HVO_4'' ions calculated on this assumption, and from this, values of $[Ag^{\bullet}]^2[HVO_4'']$ have been computed. The course of the titration is shown by Curve E of Fig. 1.

TABLE VII.

C.c.	22	25	30	35	40	45	50	60	70	80	90
E.M.F.	0·210	0·227	0·239	0·245	0·249	0·252	0·254	0·257	0·259	0·260	0·262
$[Ag^{\bullet}] \times 10^6$	19·6	10·0	6·21	4·89	4·18	3·71	3·42	3·04	2·81	2·70	2·49
$[HVO_4''] \times 10^3$	0·15	0·44	0·89	1·31	1·70	2·06	2·40	3·01	3·55	4·03	4·46
$[Ag^{\bullet}]^2[HVO_4''] \times 10^{14}$	5·8	4·4	3·4	3·1	3·0	2·8	2·8	2·8	2·8	2·9	2·8

Mean value of $[Ag^{\bullet}]^2[HVO_4''] = 2{\cdot}9 \times 10^{-14}$.

The value obtained for $[Ag^{\bullet}]^2[HVO_4'']$ compares well with that obtained from direct titration with 2 : 1 sodium vanadate. This experiment explains why Carnelly (J., 1873, **26**, 323) obtained a vanadate of composition $3Ag_2O,2V_2O_5$ from a solution of $1{\cdot}5Na_2O,V_2O_5$ by adding excess of silver nitrate solution. Indeed, a precipitate of any composition between Ag_2O,V_2O_5 and pure silver oxide can be obtained by the action of silver nitrate *in excess* on a solution of the corresponding sodium salt, *i.e.*, between Na_2O,V_2O_5 and NaOH. It is only when the sodium salt is in excess that evidence can be obtained regarding the different vanadates of silver, although precipitates obtained in this manner, even from boiling solutions, are unsuitable for exact analytical work, on account of the difficulty of their filtration. The above experiments afford evidence of only three vanadates of silver, *viz.*, the 3 : 1, 2 : 1, and 1 : 1.

B. *Conductometric Titrations.*

100 C.c. of solutions of 0·0083*M*-Na_3VO_4, 0·0125*M*-Na_2HVO_4 and 0·025*M*-NaH_2VO_4 were titrated with 0·1*N*-silver nitrate, and the specific conductivities at 25° measured at different titres.

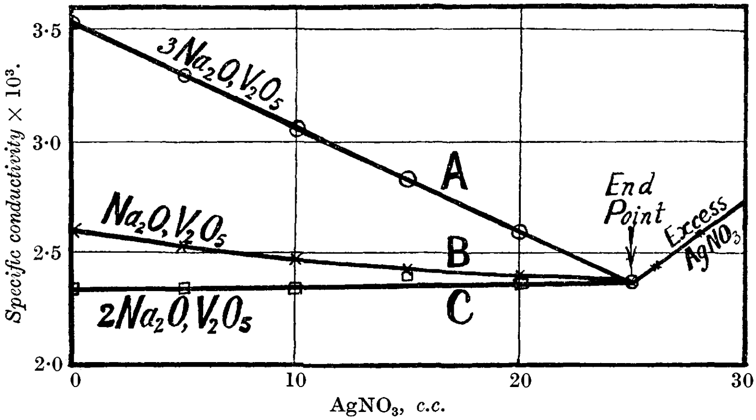
Table VIII gives the specific conductivities, $\kappa_{obs.}$, which are represented graphically in Fig. 3.

TABLE VIII.

AgNO$_3$, c.c.	0	5	10	15	20	25	30
$\kappa_{Na_3VO_4} \times 10^3$	3·54	3·30	3·05	2·83	2·59	2·35	2·73
$\kappa_{Na_2HVO_4} \times 10^3$	2·33	2·32	2·33	2·29	2·31	2·33	2·74
$\kappa_{NaH_2VO_4} \times 10^3$	2·58	2·52	2·49	2·41	2·37	2·33	2·71

In all cases we get a uniform change in conductivity, with a sharp inflexion at the calculated end-point, 25 c.c., where the observed specific conductivity, 0·00234 mho, allowing for the conductivity of the small amount of silver vanadate still in solution, agrees with that calculated for the amount of sodium nitrate theoretically present, *i.e.*, 0·00221 mho. Afterwards, the curve rises with the slope expected from the addition of silver nitrate. It is remarkable that, while the precipitation of the 2 : 1 and 1 : 1 silver vanadates is accompanied by only small changes in specific conductivity, there is a very marked diminution in the case of the 3 : 1 vanadate. The former precipitations consist essentially in the replacement in solution of HVO_4'' and VO_3' (or H_2VO_4') ions respectively by nitrate ions, *i.e.*, $2Na^{\cdot} + HVO_4'' \longrightarrow 2Na^{\cdot} + 2NO_3'$ and $Na^{\cdot} + VO_3' \longrightarrow Na^{\cdot} + NO_3'$; therefore, unless sodium nitrate and 2 : 1 sodium vanadate undergo dissociation to markedly different extents, the mobility of the HVO_4'' ion must be of the same order as that of the nitrate ion. In the case of the precipitation of 3 : 1 silver vanadate, the specific conductivities found are entirely in agreement with the hypothesis that hydrolysis of the VO_4''' ion is almost complete, *i.e.*, $VO_4''' + H_2O \longrightarrow HVO_4'' + OH'$, and the precipit-

FIG. 3.



ation is therefore essentially $3Na^{\cdot} + OH' + HVO_4'' + 3AgNO_3 \longrightarrow 3Na^{\cdot} + 3NO_3' + Ag_3VO_4 + H_2O$. This may be considered as two simultaneous reactions :

$$3AgNO_3 + \left\{\begin{array}{l} Na^{\cdot} + OH' \longrightarrow Na^{\cdot} + NO_3' \\ 2Na^{\cdot} + HVO_4'' \longrightarrow 2Na^{\cdot} + 2NO_3' \end{array}\right\} + Ag_3VO_4 + H_2O \quad \begin{array}{l} (1) \\ (2) \end{array}$$

i.e., as a replacement in the solution during precipitation of (1) each hydroxyl ion by a nitrate ion and (2) each HVO_4'' ion by two nitrate ions. The change in the specific conductivity resulting from the replacement of hydroxyl by nitrate ions can be calculated. The second line of the following table gives the observed conductivities of the 3 : 1 vanadate solution at different titres; the third line, the calculated conductivity caused by the sodium hydroxide assumed to be present, *i.e.*, if complete hydrolysis of all the 3 : 1 vanadate left in solution at any stage of the titration occurs as above stated; the fourth line, the calculated conductivity at each titre due to the sodium nitrate *which has replaced the sodium hydroxide.* The sum of these two specific conductivities will give the change in the conductivity of the solution as a result of reaction (1), whilst if this sum is subtracted from the corresponding observed conductivity of the solution, the residual conductivity, given in the last line of the table, will correspond to different stages of reaction (2). The differences given in the last line suggest that very little change in conductivity might be expected during the addition of silver nitrate to a solution of 2 : 1 sodium vanadate. Curve C in Fig. 3 shows that this is actually the case.

$AgNO_3$, c.c.	0	5	10	15	20
$\kappa_{Na_3VO_4} \times 10^3$	3·54	3·30	3·05	2·83	2·59
$\kappa_{NaOH} \times 10^3$	1·89	1·45	1·04	0·66	0·32
$\kappa_{NaNO_3} \times 10^3$	0·00	0·19	0·34	0·48	0·62
$[\kappa_{Na_3VO_4} - \kappa_{NaOH} - \kappa_{NaNO_3}] \times 10^3$	1·65	1·66	1·67	1·69	1·65

That this is the correct interpretation of the steep slope of the Na_3VO_4 curve, A, of Fig. 3 is confirmed by a comparison of the equivalent conductivities of 2 : 1 sodium vanadate calculated from the conductivity of the 3 : 1 vanadate solution and that of the 2 : 1 vanadate. The specific conductivity of $0{\cdot}0083M$-Na_3VO_4 is found to be 0·00354 mho, and after subtracting κ_{NaOH} we get 0·00165 mho for the specific conductivity of $0{\cdot}0083M$-Na_2HVO_4, which gives an equivalent conductivity of 100. Direct observation on a solution of $0{\cdot}0125M$-Na_2HVO_4 gives an equivalent conductivity of 93 at this concentration.

In the following table are collected the equivalent conductivities of solutions of the three vanadates, obtained from data in this paper and in Part II (*loc. cit.*).

	Na_3VO_4.		Na_2HVO_4.			NaH_2VO_4.	
Conc., *M*......	0·0083	0·005	0·0125	0·0083	0·005	0·025	0·005
Mhos	142	143	93	100	101	103	109

The above conductometric titrations, therefore, confirm the hydrolysis of the VO_4''' ion in solution. We have the following evidence to support this view: (1) the p_H value of a solution of 3 : 1 sodium vanadate is 11·65; (2) the precipitation of 3 : 1 silver vanadate proceeds in accordance with predictions based on the theory of almost complete hydrolysis; (3) the precipitation of 3 : 1 silver vanadate from a mixture of $Na_3VO_4 + 3NaOH$ also agrees with this hypothesis, which in this case leads to the conclusion that 3 : 1 silver vanadate will be precipitated rather than silver oxide in the presence of a deficit of silver nitrate, and this has been confirmed experimentally; (4) the precipitation of 3 : 1 silver vanadate from a solution intermediate between 3 : 1 and 2 : 1 sodium vanadate can also be brought into harmony with the hypothesis; (5) finally, the above conductometric titrations form additional independent evidence.

Summary.

1. Titrations have been carried out, using the silver electrode, of silver nitrate solutions with sodium vanadate whose $Na_2O : V_2O_5$ ratios were 3 : 1, 2·4 : 1, 2 : 1, 1·6 : 1, and 1 : 1 respectively. Also the reverse titration of vanadate solutions with silver nitrate solution has been investigated.

2. 3 : 1, 2 : 1, and 1 : 1 Sodium vanadates have been titrated conductometrically with silver nitrate.

3. Evidence has been found for the existence of only three vanadates of silver, *viz.*, the 3 : 1, 2 : 1, and 1 : 1.

4. A solution containing more sodium hydroxide than is required by $3Na_2O,V_2O_5$ can be selectively precipitated with silver nitrate; if the alkali is in excess, 3 : 1 silver vanadate will first be precipitated, it being less soluble than silver oxide.

5. Hydrolysis of 3 : 1 sodium vanadate renders the law of the solubility product in its ordinary form inapplicable to this salt. It has been shown that both theory and experiment lead to a constant value for the product $[Ag^{\cdot}]^3[HVO_4''][OH']$ of the order of 10^{-24}.

6. The titration of silver nitrate solution with 2 : 1 sodium vanadate gives a value for $[Ag^{\cdot}]^2[HVO_4'']$ of the order of 2×10^{-14}, and shows that 2 : 1 sodium vanadate solutions contain the HVO_4'' ion, rather than the V_2O_7'''' ion.

7. The solubility product $[Ag^{\cdot}][VO_3']$ is 5×10^{-7}.

8. Addition of silver nitrate in excess to a solution of sodium vanadate of the composition xNa_2O,V_2O_5 results in the precipitaion

of mixed vanadates of silver whose analyses are in agreement with the formula $x\text{Ag}_2\text{O},\text{V}_2\text{O}_5$; addition of excess of the sodium vanadate solution, however, precipitates the less soluble silver vanadate, the 3 : 1 vanadate if the composition of the solute lies between 2 : 1 and 3 : 1 sodium vanadate, and the 2 : 1 vanadate in the case of solutes between 1 : 1 and 2 : 1 sodium vanadate.

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UNIVERSITY COLLEGE OF THE SOUTH WEST OF ENGLAND,
EXETER.

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