131. *Physicochemical Studies of Complex Acids. Part X. The Precipitation of Metallic Vanadates, with a Note on Moser and Brandl's Method of estimating Vanadium.*

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Previous investigations (Parts II and VII; Britton and Robinson, J., 1930, 1261; 1932, 1955) have shown that the nature of solutions of the ortho-, pyro-, and meta-vanadate of sodium, prepared by the action of strong mineral acids on alkaline vanadate solutions, depends on whether the solutions are freshly made, or have been kept or boiled. Moreover, if the solutions had been prepared by boiling, on reaction with silver nitrate they yielded the respective silver vanadates (J., 1930, 2328). Omission of boiling or ageing afforded more complicated vanadate solutions which, as now shown, have a profound effect on the composition of the silver vanadate precipitates.

It was considered of importance to ascertain whether similar reactions occurred with solutions of other metallic vanadates, and to investigate further the nature of the combination occurring between vanadic acid and sodium hydroxide.

Experimental.

1. *Reactions of " Unboiled " Alkali Vanadate Solutions with Silver Nitrate Solutions.*—Solutions corresponding in compn. to $Na_4V_2O_7$ and $NaVO_3$ were prepared by the addition of the calc. amount of H_2SO_4 to solutions of Na_3VO_4 and $Na_4V_2O_7$ respectively *in the cold.* These solutions were yellow. They were treated with various proportions of $AgNO_3$ aq. and the ppts. obtained were analysed after drying at 120°.

Addition of 50 c.c. of $0{\cdot}025M$-Na_2HVO_4 (*i.e.*, sodium pyrovanadate) to 50 c.c. of $0{\cdot}1M$-$AgNO_3$ produced a dark red gelatinous ppt. quite different in appearance from the yellow ppt. obtained by the interaction of $AgNO_3$ with a *boiled* solution of the pyrovanadate similarly prepared. Analysis, however, showed that the ppt. was $2Ag_2O,0{\cdot}99V_2O_5$. By mixing these solutions in equiv. amount, a similar ppt. of $2Ag_2O,0{\cdot}94V_2O_5$ was obtained, which turned yellow while being washed on the filter. When, however, twice as much vanadate solution was added as was sufficient to ppt. all the Ag, an orange-red ppt., $3Ag_2O,1{\cdot}10V_2O_5$, was obtained. A solution of the 1 : 1 vanadate, prep. by addition of H_2SO_4 to Na_3VO_4 in the cold, gave a scarlet ppt., $Ag_2O,0{\cdot}98V_2O_5$, when added to $AgNO_3$ aq. in equiv. amount; but when added in large excess, it gave a yellow ppt., $2Ag_2O,1{\cdot}20V_2O_5$.

A similar metavanadate solution, prep. from the pyrovanadate and added to excess of $AgNO_3$ aq., gave a red ppt. of $1Ag_2O,1{\cdot}64V_2O_5$; if the vanadate was in excess, however, a dark yellow ppt. of $Ag_2O,1{\cdot}09V_2O_5$ was obtained.

Hence the nature of the ppt. depends on the proportion in which the reagents are mixed. The interpretation of the above data is based on two principles : (1) There are three definite vanadates of Ag, the 3 : 1, 2 : 1, 1 : 1 salts, arranged in order of increasing solubility; (2) the addition of acid to boiling Na_3VO_4 aq. produces in succession the pyrovanadate, the metavanadate, and a complex salt approximating to $Na_2O,2{\cdot}5V_2O_5$. In the cold, the p_H titration curves (see Part VII; J., 1932, 1955) show that along with the conversion of the 3 : 1 into the 2 : 1 salt, a certain amount of the complex salt is formed and some 3 : 1 salt is left unattacked. Similarly, the addition of acid to the cold 2 : 1 salt produces both the 1 : 1 salt and the complex salt, and some of the pyro-salt is left unattacked.

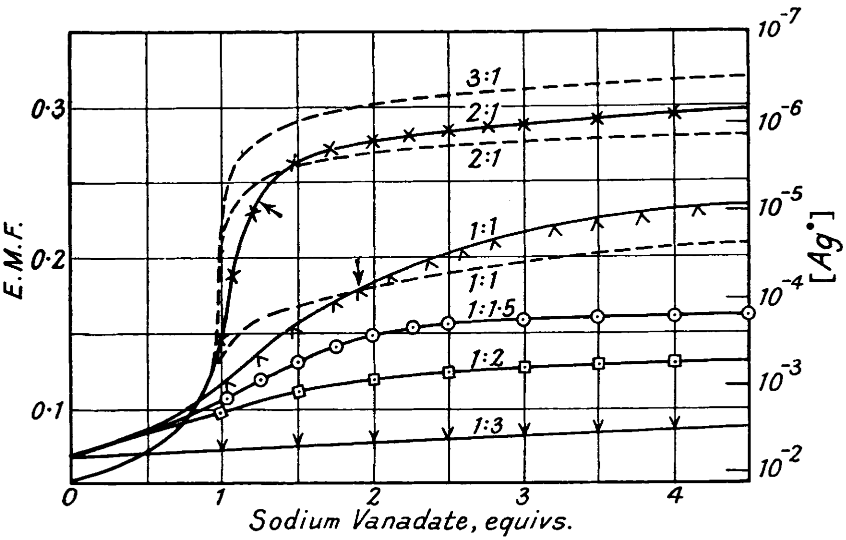
On these two principles the reactions of the yellow vanadate solutions with $AgNO_3$ can be explained satisfactorily, and conversely they offer supporting evidence for these views of the constitution of alkali vanadate solutions. The first addition of the yellow pyrovanadate solution to one containing excess of $AgNO_3$ produces a mixed ppt. of the 3 : 1, 2 : 1, and 1 : 2·5 salts,

$$Na_3VO_4 + 3AgNO_3 \longrightarrow Ag_3VO_4 + 3NaNO_3; \quad Na_2HVO_4 + 2AgNO_3 \longrightarrow Ag_2HVO_4 + 2NaNO_3;$$
$$Na_2O,2{\cdot}5V_2O_5 + 2AgNO_3 \longrightarrow Ag_2O,2{\cdot}5V_2O_5 + 2NaNO_3.$$

The ppt. is red, and pptn. proceeds in this manner until all the Ag is removed. Further addition causes decomp. of the ppt., with formation of the least sol. Ag vanadate, in this case the 3 : 1 salt:

$$3Ag_2HVO_4 + 2Na_3VO_4 \longrightarrow 2Ag_3VO_4 + 3Na_2HVO_4;$$
$$3Ag_2O,2{\cdot}5V_2O_5 + 2Na_3VO_4 \longrightarrow 2Ag_3VO_4 + 3(Na_2O,2{\cdot}5V_2O_5).$$

FIG. 1.



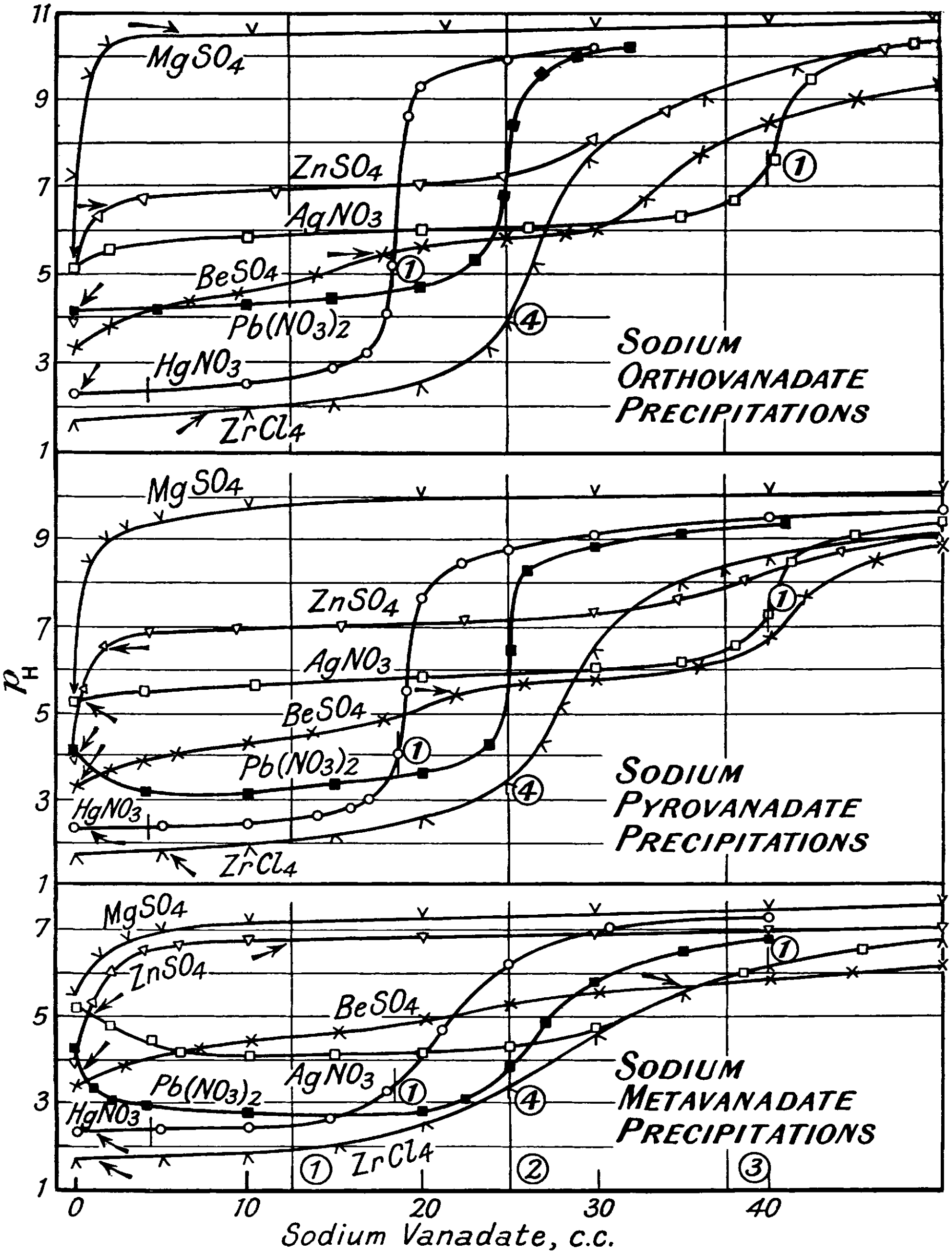
Similarly, the yellow metavanadate solution probably consists of a mixture of the 2 : 1, 1 : 1, and 1 : 2·5 salts. The first reaction of this solution with $AgNO_3$ will be a co-precipitation of the corresponding three Ag salts, which, on addition of an excess of the vanadate solution, decompose to yield the least sol. Ag salt that can be formed in these circumstances, in this case $Ag_4V_2O_7$. The final ppt. is, therefore, yellow and corresponds closely to the 2 : 1 salt.

The conclusions are borne out by some Ag-electrode titrations on 0·01*M*- and 0·005*M*-$AgNO_3$ with alkali vanadates prepared by the action of acids, both *with boiling* and *in the cold,* on more alkaline vanadates. The cell combination used in the titrations was

$$Ag|0{\cdot}1N\text{-}AgNO_3|KNO_3,\ \text{satd.}|AgNO_3 + x\text{-Sodium vanadate}|Ag.$$

Fig. 1 gives the obs. *E.M.F.*'s and the corresponding $Ag^{\cdot}$ concns. set up during the titrations. The broken lines, marked 3 : 1, 2 : 1, and 1 : 1, are reproduced from Part VII (*loc. cit.*) for comparison, and correspond to the reactions of 100 c.c. of 0·01*N*-$AgNO_3$ with 0·1*N*-solutions of the ortho-, pyro-, and meta-vanadates respectively, that were prepared by boiling. The complete curves represent titrations of $AgNO_3$ with yellow sodium vanadate solutions that were prepared by suitable acidification in the cold and had not been boiled. The curve 2 : 1 is that of the titration of 100 c.c. of 0·01*N*-$AgNO_3$ with 0·05*N*-Na_2HVO_4, prepared from Na_3VO_4. A similar titration performed with a vanadate solution prepared from one of $Na_4V_2O_7$ gave an identical curve. The curve 1 : 1·5 is that of 100 c.c. of 0·005N-$AgNO_3$ with 0·025N-Na_2O,1·5V_2O_5, prep. from $Na_4V_2O_7$; that marked 1 : 2 refers to a titration of 100 c.c. of 0·005N-$AgNO_3$ with 0·0125N-Na_2O,2V_2O_5, prep. from $Na_4V_2O_7$, and the bottom curve, 1 : 3, is that of 100 c.c. 0·005N-$AgNO_3$ with 0·017N-Na_2O,3V_2O_5, prep. from $NaVO_3$.

FIG. 2.



From boiled solutions, ppts. were obtained immediately on addition of the first drop of vanadate solution to the $AgNO_3$ aq. With yellow, unboiled solutions, however, pptn. was often delayed beyond the stage at which it should be stoicheiometrically complete. With solutions containing more V_2O_5 than the meta-salt, no pptn. occurred, but only a turbidity or a red suspension. The points of pptn. are marked in Fig. 1 by arrows. The curve for the pyrovanadate titration is above that corresponding to a boiled pyrovanadate solution; this shows that the Ag· concn. is less, but since the HVO_4'' concn. cannot possibly be proportionately greater, it follows that the *E.M.F.* cannot be governed by the solubility product of the 2 : 1 salt.

2a. *Precipitation of Basic Vanadates with " Boiled " Alkali Vanadate Solutions.*—The following table and Fig. 2 refer to a series of glass-electrode titrations of typical metallic salt solutions with 0·1*N*-solutions of the three sodium vanadates (*i.e.*, 0·1*N* with respect to Na). Pptn. began at p_H values that were approx. those at which the corresponding metallic hydroxides would normally separate. The ratios V_2O_5/(Metal oxide) at this stage are lower than those (in parentheses) which would have been found if the respective vanadates had been pptd. The V_2O_5 contents of the ppts. obtained in the pyro- and meta-vanadate titrations of the acid $HgNO_3$ aq. were, however, slightly higher, probably owing to the action of the excess HNO_3 on the precipitant. The ratios in the Mg and Be titrations correspond to ppts. formed by twice the stoicheiometrical amount of titrant, and those for the remaining titrations were obtained from analyses of the ppts. when exactly theo. amounts had been added.

The " hydroxide p_H " was not reached in the pyro- and meta-vanadate titrations of $MgSO_4$; hence no ppts. were produced. In all other reactions, the respective " hydroxide p_H " was exceeded and pptn. took place, the points at which it began being marked by arrows in Fig. 2. As a rule, it began very soon after the first few drops of alkali vanadate had been added, but in the Be titrations it was considerably delayed owing to the peculiar property of this metal of forming " soluble basic salts." It was also delayed in those titrations in which the particular alkali vanadate was only just able to establish the p_H conditions for basic pptn. : *e.g.*, in the reaction of Na_3VO_4 with $MgSO_4$ the requisite p_H was not reached until 0·56 equiv. had been added, whilst in the titration of $ZnSO_4$ with $NaVO_3$ 0·96 equiv. was necessary. In both these reactions, excess of the precipitants did not greatly raise the p_H of the mother-liquors, and in consequence, pptn. was partial, the extents depending on the actual amounts employed. Comparison of the sections of the curves corresponding to excess of the three sodium vanadates with the vanadic acid curve in Fig. 1 in Part VII (*loc. cit.*), shows that the p_H values set up tend to approach the values given by solutions of the respective vanadates. The p_H values due to excess of the precipitants, together with any V_2O_5 remaining in solution, appear, however, to be higher than would have been the case if the solutions had been kept or boiled.

Titration of 100 *c.c. of metallic salt solutions by* 0·1N-*sodium vanadates* : p_H *and oxide ratio at precipitation.*

Salt.		$3Na_2O,V_2O_5$.	$2Na_2O,V_2O_5$.	Na_2O,V_2O_5.	Hydroxide pptn. p_H.
0·0125*M*-$MgSO_4$	p_H	10·50	no ppt.	no ppt.	10·49
	V_2O_5/MgO	0·105 (0·333)	—	—	
0·0125*M*-$ZnSO_4$	p_H	6·63	6·72	6·74	6·80
	V_2O_5/ZnO	0·235 (0·333)	0·226 (0·5)	0·272 (1·0)	
0·0125*M*-$BeSO_4$	p_H	5·50	5·54	5·75	5·69
	V_2O_5/BeO	0·052 (0·333)	0·100 (0·5)	0·175 (1·0)	
0·00625*M*-$ZrCl_4$	p_H	1·85	1·79	1·70	1·86
	V_2O_5/ZrO_2	0·471 (0·667)	0·649 (1·0)	0·610 (2·0)	
0·0143*M*-$HgNO_3$ + 0·0042*M*-HNO_3	p_H	2·5	2·5	2·5	2·5—3·0
	V_2O_5/Hg_2O	0·273 (0·333)	0·588 (0·5)	1·111 (1·0)	

Except in the Mg titrations and those of $ZnSO_4$ with ortho- and pyro-vanadate, the mother-liquors were yellow and were more intense in those reactions where pptn. occurred at a low p_H. Hence some of the added vanadate must have remained in solution in the form of yellow alkali polyvanadates, and, as judged from the colour produced in the more acid solutions, their compn. must have approached that of the stable complex, *viz.*, $Na_2O,2{\cdot}5V_2O_5$. The colourless mother-liquors during the titrations in which pptn. occurred in the alk. zone are due to the inability of the low concn. of H· ions to decompose the alkali vanadates; H_3BO_3, for instance, does not cause colourless alkali vanadates to become yellow, but KH_2PO_4 readily does so. A pale yellow coloration accompanied the ppt. from $ZnSO_4$ aq. with $NaVO_3$; this was due to the fact that a " basic metavanadate " was separating and some sodium polyvanadate consequently being formed in the solution.

If the view be accepted that 1 equiv. of the H_2SO_4 in combination with $Be(OH)_2$ is loosely bound, and that this acid reacts with the alkali vanadates so as to convert them into the stable salt $Na_2O,2{\cdot}5V_2O_5$, calculation shows that this amount of acid (12·5 c.c. of *N*/10) would require

14·4 c.c. of Na_3VO_4, 15·6 c.c. of $Na_4V_2O_7$, and 20·8 c.c. of $NaVO_3$; *i.e.*, these amounts of titrant would set up a p_H of 4 (cf. Fig. 1, Part VII) and therefore more alkali vanadate would be necessary before p_H 5·7 [the pptn. p_H of $Be(OH)_2$] could be reached. Pptn. actually occurred when 18, 22, and 35 c.c. of the respective alkali vanadate had been added.

2b. *Other Precipitates obtained with "Boiled" Alkali Vanadate Solutions.*—Fig. 2 also contains the p_H curves of some titrations in which normal ortho-, pyro-, and meta-vanadates were pptd. The p_H values obtaining during the process were considerably below the hydroxide p_H's, and with $Pb_2V_2O_7$, $Pb(VO_3)_2$, and $AgVO_3$ there occurred increases in [H$^\bullet$] as the first portions of the precipitant were added; these were evidently caused by hydrolysis of the ppts., for, as will be shown in a subsequent paper, V_2O_5 is slightly sol. in H_2O to give a strong acid, having the approx. formula, $H_2V_4O_{11}$. Fairly well-defined inflexions were given when the theo. amounts of the alkali vanadates were added.

For the Ag titrations, 100 c.c. of 0·01*M*-$AgNO_3$ were titrated with 0·025*N*-solutions of the three alkali vanadates. Ag_3VO_4 was pptd. between p_H 5·8 and 6·5, $Ag_4V_2O_7$ at p_H 5·5—6·0, and $AgVO_3$ at p_H 4·25—4·75. For analysis, the ppts. were washed, and dried at 120° [Found: (1) Ag_2O, 78·96; V_2O_5, 21·14. Calc. for Ag_3VO_4: Ag_2O, 79·36; V_2O_5, 20·74. (2) Ag_2O, 71·59; V_2O_5, 28·49. Calc. for $Ag_4V_2O_7$: Ag_2O, 71·82; V_2O_5, 28·18. (3) Ag_2O, 56·01; V_2O_5, 43·78. Calc. for $AgVO_3$: Ag_2O, 56·03; V_2O_5, 43·97%].

The curves in Fig. 2 illustrate the p_H changes during the reactions of 0·1*N*-alkali vanadate with 100 c.c. of 0·0125*M*-$Pb(NO_3)_2$. The ppt. obtained with Na_3VO_4 was pure white and consisted largely of $Pb_3(VO_4)_2$ [Found, in dried ppt.: PbO, 76·78, 77·01; V_2O_5, 22·37, 22·74. Calc. for $Pb_3(VO_4)_2$: PbO, 78·61; V_2O_5, 21·39%]; in spite of numerous attempts to obtain it pure, the orthovanadate always contained excess of V_2O_5. It is considered that as the ppts. were obtained from solns. containing a small excess of precipitant, a little PbO may have dissolved in the NaOH formed by hydrolysis of Na_3VO_4. $Na_4V_2O_7$ afforded a pale yellow ppt. of $Pb_2V_2O_7$ (Found, in ppt. dried at 120°: PbO, 69·87; V_2O_5, 29·20%; PbO : V_2O_5 = 2·00 : 1·02). Double decomp. also occurred between $NaVO_3$ and $Pb(NO_3)_2$, giving a red ppt. (Found: PbO, 55·80; V_2O_5, 44·34%; PbO : V_2O_5 = 1·00 : 0·97).

Note on the Estimation of Vanadium as Silver Meta-, Pyro-, and Ortho-vanadates.

Browning and Palmer (*Amer. J. Sci.*, 1910, **30**, 220) devised a method of estimating V by pptn. as $AgVO_3$, wherein a HNO_3 solution of V_2O_5 is made alk. by NH_3 and boiled until the remaining vanadate solution becomes faintly yellow. As shown by the authors (*locc. cit.*), the existence of a permanent yellow coloration indicates that the VO_3' ion is present, and moreover the p_H of such a solution is between 6 and 7. Addition of $AgNO_3$ aq. then leads to quant. pptn. of $AgVO_3$ of exactly correct compn., as confirmed by Moser and Brandl (*Monatsh.*, 1929, **51**, 169) and ourselves.

Moser and Brandl have recently described a method by which they claim that V may also be accurately determined as Ag_3VO_4 provided the necessary conditions be established in the solution by adding NaOAc and a little conc. NH_3 (3 g. and 0·5 c.c. respectively for 200 c.c. of neutral solution containing 0·2 g. of V_2O_5) before adding $AgNO_3$, and then boiling for ½ hr. Besides making the solution alk., the relative large conc. of NH_3 would form complex silver-ammine kations and thus tend to keep the Ag$^\bullet$ conc. low, and this in turn would tend to dissolve some Ag from the pptd. vanadate (see Britton, J., 1925, **127**, 2956). Britton and Robinson (J., 1930, 2328) have shown that addition of Na_3VO_4aq. to $AgNO_3$ aq. results in pptn. of Ag_3VO_4. This salt is the most insol. of the various silver vanadates and would appear to be the most suitable for analytical purposes.

We have subjected this method to a systematic examination (1) by using various amounts of NaOAc alone and (2) by varying both the NaOAc and the NH_3 concn. The test solutions were prepared from Kahlbaum's NH_4VO_3 (purity 99·9%), and the results are recorded in the table given on p. 517.

It will be seen from the series (1) that the ppt. obtained by using NaOAc alone consisted of a mixture of $Ag_4V_2O_7$ and $AgVO_3$, and that the presence of much NaOAc yielded a ppt. that was almost entirely $Ag_4V_2O_7$. Series (2) reveals that in every case the use of NH_3 led to ppts. that were much heavier than would have been obtained if $Ag_4V_2O_7$ alone had been pptd. They were, however, not quite heavy enough to correspond to Ag_3VO_4, being as a rule about 2% low. That they were contaminated with some unconverted $Ag_4V_2O_7$ is evident from the slightly low Ag_2O contents of ppts. Nos. 11 and 18, which were respectively 78·05 and 78·75% (for calc. values, see above).

(1) NaOAc without NH_3: V_2O_5 = 0·0869 g. Theo. wts.: $AgVO_3$, 0·1078 g.; $Ag_4V_2O_7$, 0·3087 g.; Ag_3VO_4, 0·4196 g.

No.	1	2	3	4	5	6	7
NaOAc, g.	0·03	0·06	0·25	0·38	1·12	5·38	12·8
Silver vanadate, g.	0·2197	0·2352	0·2745	0·2796	0·3060	0·3106	0·3176

(2) NaOAc with NH_3: V_2O_5 = 0·1046 g. Theo. wts.: $AgVO_3$, 0·2380 g.; $Ag_4V_2O_7$, 0·3714 g.; Ag_3VO_4, 0·5048 g.

No.	8	9	10	11	12	13
NaOAc, g.	1·2	1·14	1·4	3·0	3·0	3·0
NH_3, *N*-	0·0182	0·0109	0·026	0·01	0·0182	0·0187
Silver vanadate, g.	0·4871	0·4963	0·4912	0·4899	0·4894	0·4914

No.	14	15	16	17	18
NaOAc, g.	3·0	3·0	6·0	6·0	9·0
NH_3, *N*-	0·0274	0·0547	0·0182	0·0274	0·0182
Silver vanadate, g.	0·4926	0·4871	0·4888	0·4930	0·4857

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