# Precipitation Reactions between Silver Nitrate and Sodium Tungstate in 1.0 mol dm⁻³ Aqueous Sodium Nitrate Solution at 25 °C

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Precipitation reactions of silver tungstate have been followed by simultaneous potentiometric registration of pAg and pH. The reactions were initiated by addition of 1.0 cm³ of 1.0 mol dm⁻³ sodium tungstate to 1.0 cm³ of 1.0 mol dm⁻³ silver nitrate in 125 cm³ 1.0 mol dm⁻³ sodium nitrate at 25 °C. The experimental results indicate formation of at least four sparingly soluble silver tungstate compounds. X-Ray powder diffraction, quantitative silver and tungstate analyses and electron microscopy were used to characterize the precipitates. By combining the experimental results with protolytic equilibria given in the literature, a model is outlined which can describe a possible reaction pattern.

A survey of the existing literature [1-6] shows that the precipitation of silver tungstate from sodium tungstate–silver nitrate mixtures must be regarded as somewhat more complicated than expressed by the following reaction:

$$2Ag^+(aq)+WO_4^{2-}(aq)\rightarrow Ag_2WO_4(s) \qquad (1)$$
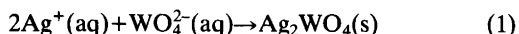
Saxena and Gupta [5] describe in a paper, where potentiometric titration between silver nitrate and sodium tungstate has been treated, that the "direct titration", i.e. addition of sodium tungstate from a burette to silver nitrate, can be performed at different concentrations with no problems, whereas the "reverse titration" only succeeds in concentrated solution. The lower limit for the titrant concentration was given to 0.01 mol dm⁻³. During the titration, two other observations concerning the precipitate were

made: (1) a change in the nature of the precipitate; before the end-point, the silver tungstate was formed as colloid particles which in the vicinity of the end-point began to coagulate and (2) a change in the colour from white to yellow.

Buchholz [3] has carried out conductometric titration of sodium tungstate with silver nitrate and during these experiments he observed that silver tungstate has a great tendency to form supersaturated solutions, especially when it is precipitated from dilute solution (i.e. below 0.01 mol dm⁻³). A similar observation was made by Varughese and Rao [6] who found it necessary to heat the solution in a steam bath for 7–8 h in order to complete the precipitation.

Several titrations – both direct and reverse – have been carried out at this institute. Our experiences from these titrations can be concluded in the following way. Titration of 0.01 mol dm⁻³ sodium tungstate in 1.0 mol dm⁻³ sodium nitrate with 1.0 mol dm⁻³ silver nitrate in 1.0 mol dm⁻³ sodium nitrate solution could be performed problem-free although it was obvious that the precipitation of silver tungstate was not complete at the end of the titration curve. However, contrary to Saxena and Gupta, we did not succeed in getting reproducible results from titration of 0.01 mol dm⁻³ silver nitrate in 1.0 mol dm⁻³ sodium nitrate with 1.0 mol dm⁻³ sodium tungstate in 1.0 mol dm⁻³ sodium nitrate. Twelve experiments gave twelve different titration curves, i.e. different with respect to the position of end-points and different with respect to the appearance. Some of the curves showed two
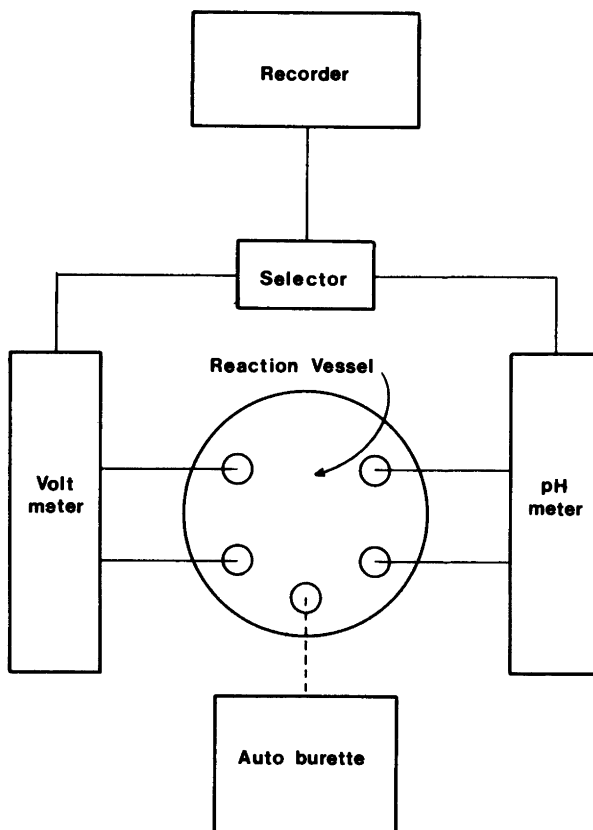
Fig. 1. Diagram of the experimental equipment.

end-points. During the "direct titration", we observed colour-change of the precipitate from yellow to white. Based on the fact that our observations to some extent were contrary to those made by Saxena and Gupta,[5] we decided to study the precipitation mechanism of silver tungstate somewhat more in detail. Some preliminary results from this study have already been published in this journal.[7] The main purpose of the present paper is to include the latest experimental results in order to suggest a precipitation mechanism of silver tungstate.

EXPERIMENTAL

Sodium tungstate *p.a.* was obtained from Riedel de Haén, Ferak and Merck. The three samples were used at random in the experiments. No differences could be observed in the pre-

cipitation experiments. In order to remove traces of sodium hydroxide (about 0.1 weight %), the sodium tungstate was recrystallized three times by dissolving in distilled and deionized water. From this solution, sodium tungstate was slowly precipitated by adding three times the volume of ethanol. Sodium determination on a flame photometer showed that the sodium tungstate used in the experiments had the formula $Na_2WO_4 \cdot 2H_2O$. The nitric acid and the sodium hydroxide solutions were made by dilution from titrisol ampulae (Merck), containing 1 mol. Silver nitrate and sodium nitrate were from Merck (*p.a.*) and used without purification. Silver tungstate was delivered from Alfa Products.

During the precipitation reactions, the continuous measuring and registration of pAg and pH was performed by means of an equipment shown graphically in Fig. 1. pH was measured with a glass electrode with an $Hg(l)$, $Hg_2Cl_2(s)$, $KCl(sat)$, $NaNO_3(1.0 \text{ mol dm}^{-3})$-reference elec-

trode. Both electrodes were obtained from Radiometer A/S, Copenhagen, Denmark (G202C and K701, respectively). (Due to Cl⁻-contamination a "normal" saturated calomel electrode could not be used as reference-electrode.) pAg was measured with an Ag-electrode (P 4011) and an $Hg(l),Hg_2SO_4(s)$, $Na_2SO_4(sat)$-reference electrode (K501) from Radiometer. By means of a selector unit, made at this institute, both pAg and pH were continuously recorded on a Servograph-recorder (REC 51 from Radiometer A/S). The selector unit also allowed us to place the pAg- and pH-signals arbitrary and independent of each other on the recorder paper, whereas the sensitivity of both signals was determined by the recorder. The reaction vessel consists of a water-jacketed 250 cm^3 glass tube with lid, thermostated at 25.0±0.1 °C. Through

the lid the electrodes were immersed into the reaction mixture. An additional hole in the lid was used for addition of reactants. In order to stabilize the ionic strength, all experiments were carried out in 1.0 mol dm^{-3} sodium nitrate. Initial concentration of silver nitrate was selected to $8 \cdot 10^{-3}$ mol dm^{-3} achieved by adding 1.0 cm^3 of 1.0 mol dm^{-3} $AgNO_3$ to 125 cm^3 of 1.0 mol dm^{-3} $NaNO_3$. (According to Saxena and Gupta,[5] it is expected that the greatest difficulties in explaining the precipitation reactions of silver tungstate should arise from solutions with initial concentrations below 0.01 mol dm^{-3}.) To this solution a 1.0 mol dm^{-3} Na_2WO_4 was added, sometimes at once with a 1 cm^3 Carlsberg-pipette, and sometimes from an autoburette (ABU 13 from Radiometer A/S) with a speed of $31.25 \cdot 10^{-3}$ cm^3 min^{-1}. This autoburette was also used in experiments with
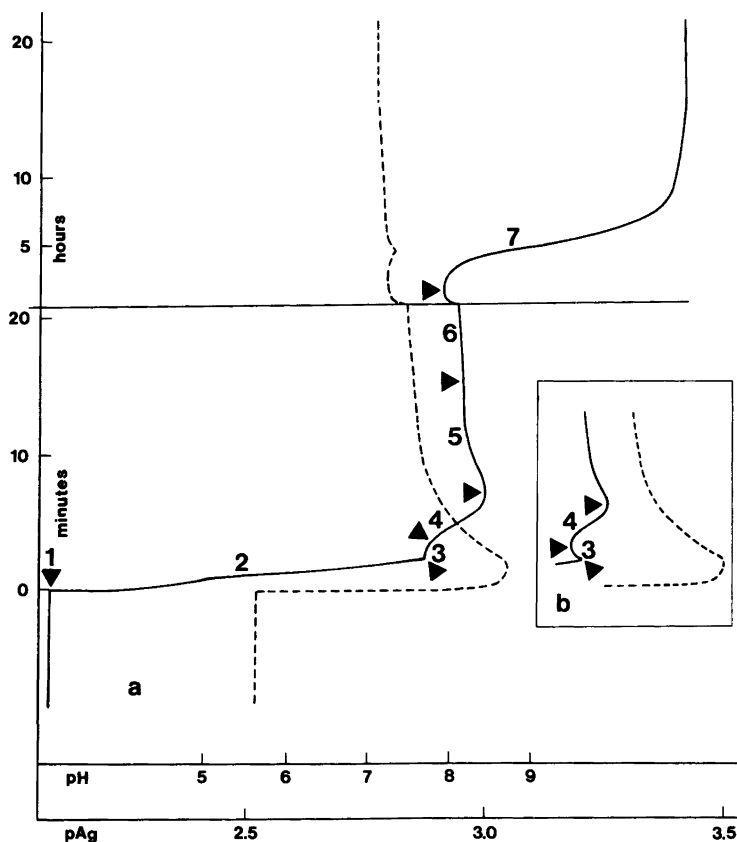

Fig. 2. Time variation of pAg (fully drawn line) and pH (dotted line). Precipitation reactions started at $t=0$, when 1.0 cm^3 of 1.0 mol dm^{-3} sodium tungstate quickly was added to a solution of 1.0 cm^3 of 1.0 mol dm^{-3} silver nitrate in 125 cm^3 of 1.0 mol dm^{-3} sodium nitrate. Two slightly different patterns (indicated by a and b) are shown of the initial course of the reactions. The horizontal line indicates a change in recorder velocity from 1 cm min^{-1} to 0.5 cm h^{-1}.

continuous addition of NaOH.

Titration curves were performed by an automatic titration equipment (Radiometer A/S) which was also used in experiments carried out with constant pH.

Sodium determinations were carried out on a flame photometer (FLM 3, Radiometer A/S).

The X-ray powder diffractometer was a vertical type (Philips PW 1049/01). The copper target was operated at 40 kV and 20 mA.

Photos of precipitates were taken by application of a scanning electron microscope (Philips SEM 505), operated at 19.0 and 24.4 kV.

Silver content of the precipitate was determined in two ways: (a) by dissolving the precipitate in an aqueous NH_3-solution and potentiometric titration of the $Ag(NH_3)_2^+$-complex with aqueous KI-solution, (the strength of the KI-solution was determined by means of $AgNO_3$ dissolved in aqueous NH_3) and (b) by electron micro probe analysis (Applied Research Laboratories, type EMX).

Tungstate content of the precipitate was determined by electron micro probe analysis.

RESULTS AND DISCUSSION

Precipitation reaction between sodium tungstate and silver nitrate in 1.0 mol dm^{-3} sodium nitrate has been followed during a period of about 24 h by continuously registrating changes in pAg- and pH-values. The results are shown in Fig. 2. Immediately after the reactants have been brought together, a yellow precipitate appeared. The yellow colour gradually changed to white and later to light grey. The instantaneous changes in both pAg- and pH-values together with colour changes of the precipitate and the peculiar appearance of both curves during the first 10–15 min of the reaction, strongly indicate that the precipitate initially formed *cannot* be described with the (simple) formula Ag_2WO_4. The S-shape on the pAg-curve (period 7 on Fig. 2a) formed during the following 5–6 h might indicate the dissolution of one sparingly soluble silver tungstate compound followed by formation of another (more sparingly soluble) compound.
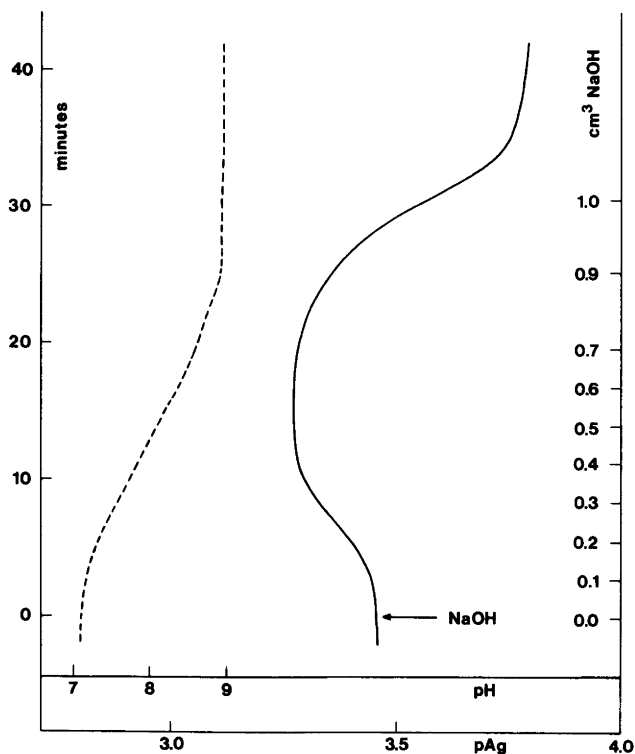

Fig. 3. Continuation of Fig. 2 after a reaction period of 24 h. By slow addition of 1.0 mol dm^{-3} sodium hydroxide (autoburette) pH was raised from about 7.1 to 9.0 after which pH was kept constant at this value.
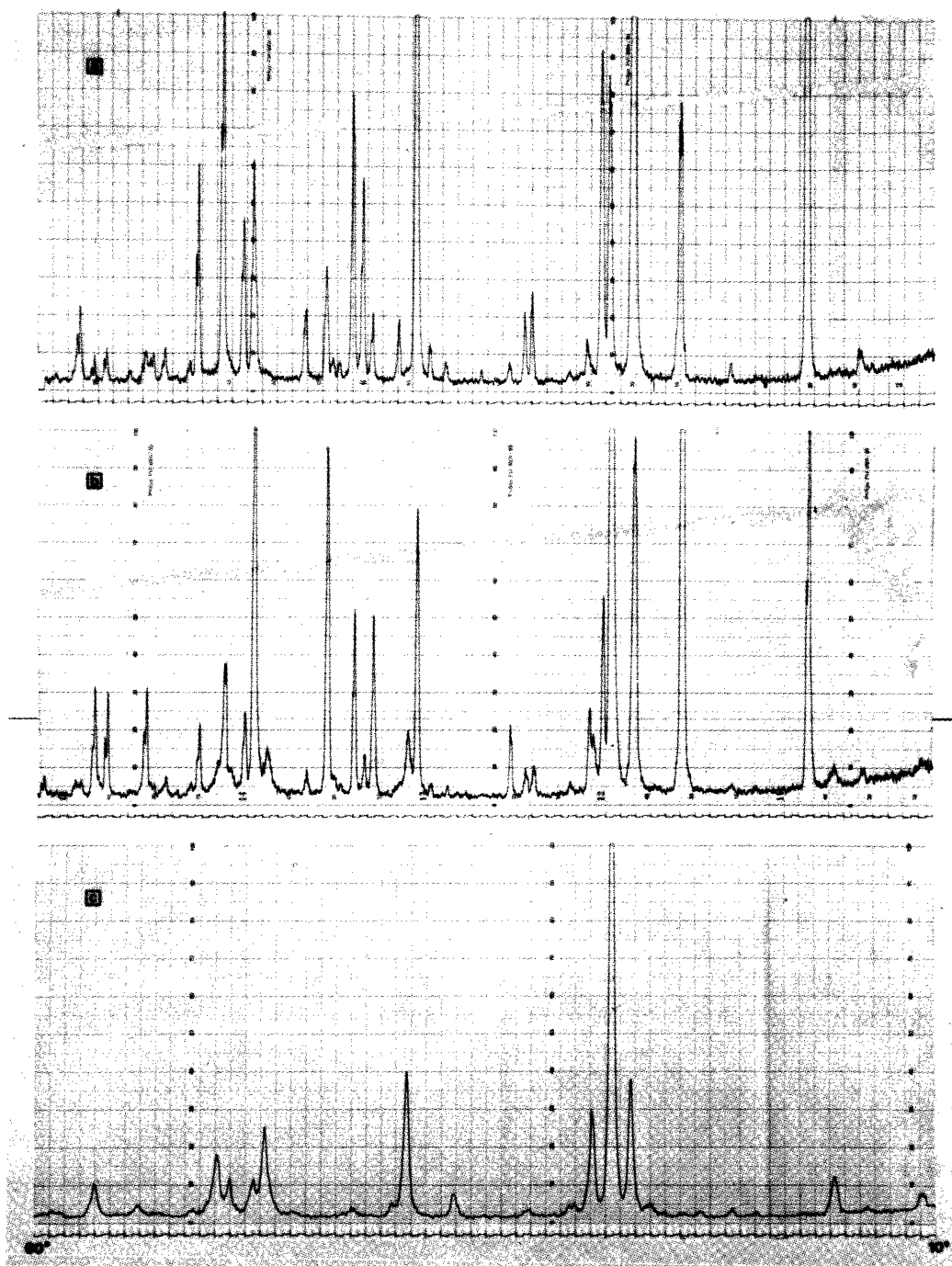
Fig. 4. X-Ray diffraction patterns of precipitates isolated from (a) period 6 (*cf.* Fig. 2), (b) period 7 (*cf.* Fig. 2) and (c) commercial Ag$_2$WO$_4$ from Alfa Products.
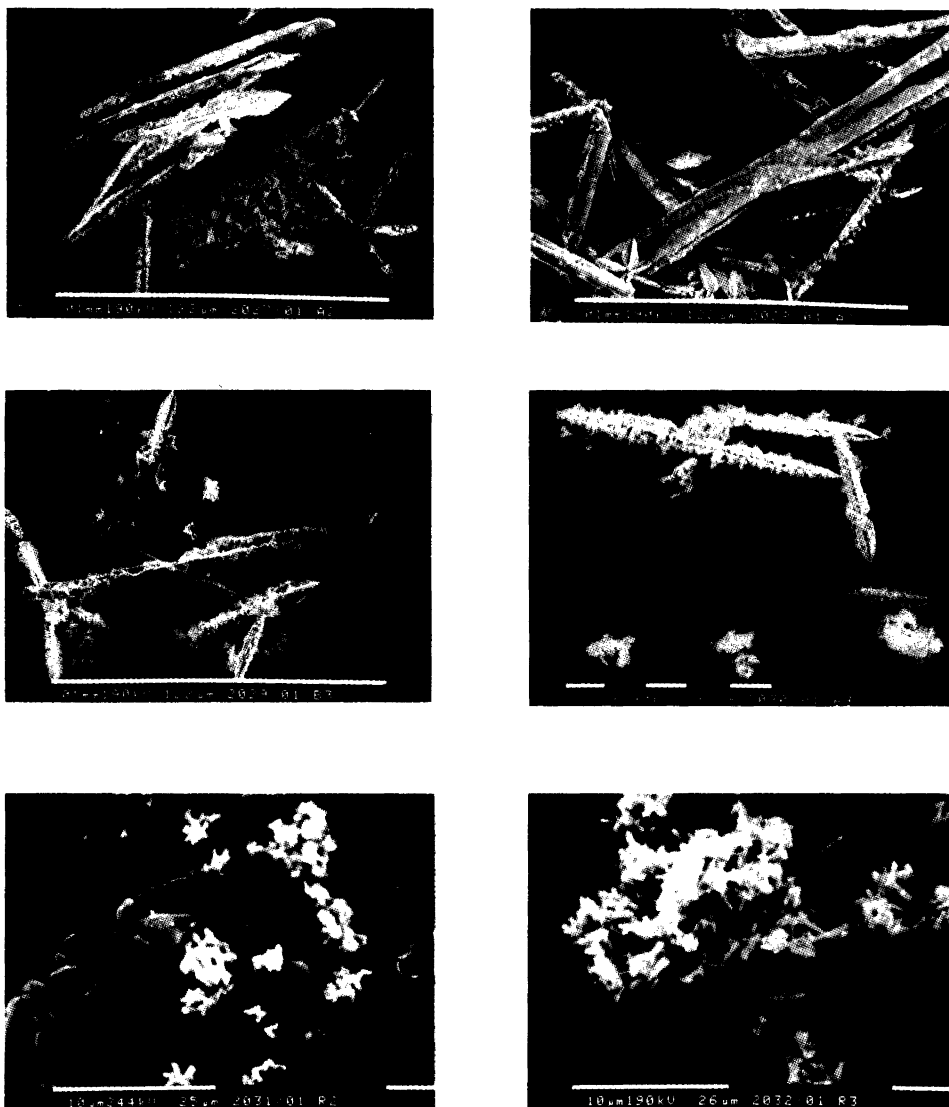
Fig. 5. Electron microscopy of precipitates from period 6 and 7 (*cf.* Fig. 2) and of commercial Ag_2WO_4. The dimensions are indicated by the white bars at the bottom of the pictures.

Two upper pictures. Precipitate from period 6, white bar=100 μm.

Two middle pictures. Precipitate from the end of period 7, white bar=100 μm (left-hand) and=10 μm (right hand).

Two lower pictures. Precipitate isolated after one year of reaction (left-hand) and crystals from commercial Ag_2WO_4 (right-hand), white bars=10 μm.

Note: The crystals in the two lower figures must be regarded as identical confirming the statement that the final product consists of pure Ag_2WO_4.

During this period the white to light grey colour change of the precipitate was observed.* The observation that both pAg and pH, after a reaction period of 24 h, obviously approach stable values, might suggest that an equilibrium is to be established, which means that the final step (formation of Ag_2WO_4 only[7]) of the reaction is approached. However, the following facts reject this suggestion:

(1) Using the pAg-value at the end of period 7 (Fig. 2), the solubility product of Ag_2WO_4 is calculated to be about $4 \cdot 10^{-9}$ mol^3 cm^{-9}. This value is quite different and much higher than the value previously reported $(1.63 \cdot 10^{-11}$ mol^3 $cm^{-9})$.[7]

(2) If Ag_2WO_4 – and only Ag_2WO_4 – was formed at the end of period 7, then an increase in pH (addition of NaOH to the reaction vessel) must be followed by either no change or by an increase of pAg. (Increase is due to further precipitation of Ag_2WO_4 or a possible precipitation of Ag_2O.) The actual situation is illustrated in Fig. 3. About 24 h after mixing the reactants, almost stable values are read for pAg and pH (pH=7.1 and pAg=3.5). When pH was raised to 9 by addition of NaOH, it was seen that pAg initially decreased, then later increased, obviously going towards a new steady state, (maybe an equilibrium). This means that the precipitate at the end of period 7 must consist of a mixture of at least two sparingly soluble silver tungstate compounds which again means that the final step of the precipitation reaction has not yet been reached after a reaction of 24 h.

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* A possible explanation of the pAg and pH variations in Fig. 2 and the colour changes could be that an ion exchange takes place between protons from the precipitates and sodium ions from the solution. However, precipitates isolated from periods 6 and 7 contained not even traces of sodium (determined by flame photometry), which means that mechanisms involving ion exchanges can totally be excluded.
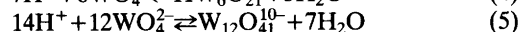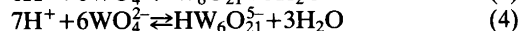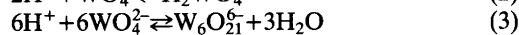
(3) X-Ray measurements on precipitate isolated from this period showed a completely different pattern compared with the curve on pure Ag_2WO_4 (from Alfa Products) (Fig. 4).

(4) Electron microscopy on precipitate relating to this period shows a mixture of crystals – different in both shape and size – compared with Ag_2WO_4 crystals (Fig. 5).

(5) Quantitative silver and tungstate analyses on precipitates isolated from periods 6 and 7 show nearly identical composition. The calculated average formula is $Ag_{1.93}WO_4$ (Table 1).

(6) An experiment similar to that shown in Fig. 2 was carried out and pAg and pH were recorded for three weeks. During this period pH was almost constant (a slight increase of about 0.2 pH was observed), whereas a slow and continuous increase in pAg was observed. Sometimes the pAg increase followed an S-curve. At the end of the three-week period pAg was about 3.9 but still not enough to explain the saturation equilibrium of Ag_2WO_4 (≈ 4.2).

In order to try to give some reasonable semi-quantitative explanation of the precipitation reactions between sodium tungstate and silver nitrate under the present experimental conditions, the protolytic equilibria of sodium tungstate in aqueous solutions must be taken into account.[3,8-16] Arnek and Sasaki[16] found the following protolytic equilibria in 3 M $Na(ClO_4)$ at 25 °C:

$$2H^+ + WO_4^{2-} \rightleftharpoons H_2WO_4 \tag{2}$$
$$6H^+ + 6WO_4^{2-} \rightleftharpoons W_6O_{21}^{6-} + 3H_2O \tag{3}$$
$$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O \tag{4}$$
$$14H^+ + 12WO_4^{2-} \rightleftharpoons W_{12}O_{41}^{10-} + 7H_2O \tag{5}$$

and determined the equilibrium constants, K_2, K_3, K_4, K_5. Further, Arnek and Sasaki found the non proton-involving equilibrium to be "practically instantaneously" established:

Table 1. Quantitative analyses of precipitates from period 6 and 7 together with analyses of Ag_2WO_4 (own preparation). The theoretical figures for pure Ag_2WO_4 are: Ag 46.54 and W 39.66.

	Potentiometric, % Ag	Electron micro probe	
		% Ag	% W
Precipitate from period 6 (A2)	45.6±0.1	45.4±0.5	40.7±0.3
Precipitate from period 7 (B3)	45.5±0.1	45.1±1.0	40.3±0.6
Ag_2WO_4 (own preparation, R2)	46.6±0.2	46.6±0.5	39.7±0.2

$$2HW_6O_{21}^{5-} \rightleftharpoons W_{12}O_{41}^{10-} + H_2O \tag{6}$$
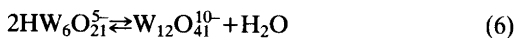
The protolytic equilibria (2)–(5) are also assumed to be practically instantaneously established, $e.g.$ faster than the considered precipitation reactions. Assuming also that the values for K_2, K_3, K_4 and K_5 are valid in 1.0 mol dm^{-3} NaNO$_3$ solution at 25 °C – maybe a somewhat bold assumption – then concentrations of the various tungstate compounds can be calculated at different pH-values.

The following mass-balance holds:

$$C_0 = C_{WO_4^{2-}} + C_{H_2WO_4} + 6C_{HW_6O_{21}^{5-}} +$$

$$6C_{W_6O_{21}^{6-}} + 12C_{W_{12}O_{41}^{10-}} \tag{7}$$

Introducing (2)–(5) in eqn. (7):

$$C_0 = C_{WO_4^{2-}} + K_2(C_{H^+})^2 C_{WO_4^{2-}} +$$

$$6K_3(C_{H^+})^6(C_{WO_4^{2-}})^6 + 6K_4(C_{H^+})^7(C_{WO_4^{2-}})^6 +$$

$$12K_5(C_{H^+})^{14}(C_{WO_4^{2-}})^{12} \tag{8}$$
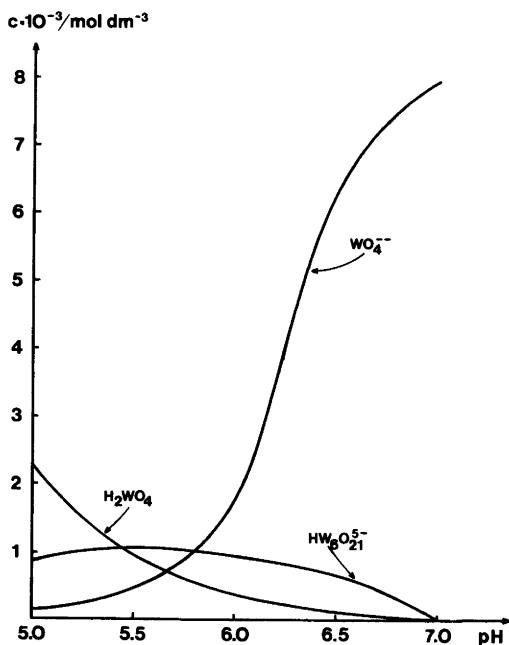
$c \cdot 10^{-3}/$mol dm^{-3}

Fig. 6. Calculated distribution of H$_2$WO$_4$, HW$_6$O$_{21}^{5-}$ and WO$_4^{2-}$ as a function of pH utilizing equilibrium constants determined by Arnek and Sasaki.[16] Total concentration of tungstate=8 · 10^{-3} mol dm^{-3} (calculated as WO$_4^{2-}$).

where C_0 denotes the initial concentration of tungstate calculated as WO$_4^{2-}$. In our experiments $C_0 = 8 \cdot 10^{-3}$ mol dm^{-3}. Utilizing eqn. (8), the complete distribution among the five different tungstate ions can be calculated at different pH-values. The result is shown in Fig. 6. Above pH 7 the WO$_4^{2-}$ ion is totally dominating and is practically equal to C_0. Therefore the distribution is only shown for the pH-interval 5<pH<7. The two ionic species W$_6$O$_{21}^{6-}$ and W$_{12}$O$_{41}^{10-}$ turn out to be present in so small concentrations that they cannot be shown on the figure. A consequence of this could be that only two ions, $i.e.$ HW$_6$O$_4^{5-}$ and WO$_4^{2-}$ were able to take part in the precipitation processes.

However, according to the experimental results above and the three to four plateaus in the pAg-curve mentioned in Fig. 7, two different sparingly soluble silver tungstate compounds are probably not enough to explain the results shown in Fig. 2. (Two sparingly soluble silver tungstate compounds are in this paper defined to be different when they create two different saturated concentrations of silver ions at the same pH.) The initial conditions in Fig. 7 were exactly the same as those in Fig. 2, $i.e.$ 1.0 cm^3 of 1.0 mol dm^{-3} sodium tungstate was quickly added to a solution consisting of 1.0 cm^3 of 1.0 mol dm^{-3} silver nitrate in 125 cm^3 sodium nitrate, but now a pH-state equipment was attached to the reaction vessel. By means of NaOH pH was not allowed to go below 8.0, so when this value was reached (about 5 min after the reaction was started) and during the following 48 h, pAg was registrated at constant pH (8.0). During this registration, three distinct plateaus were observed on the pAg-curve and, at the end of the registration period, plateau number four was obviously approached (Fig. 7). This can be explained by formation of at least four different sparingly soluble silver tungstate compounds being created during the precipitation reactions either before or during the pH-state conditions. Further information of the different silver tungstate compounds can be obtained from Figs. 8 and 9. In Fig. 8 the reactants, $i.e.$ silver nitrate and sodium tungstate, were mixed together at pH 5.25. No visible precipitate was formed at the mixing, but gradually a slightly visible precipitate was created. To this mixture a solution of 1.0 mol dm^{-3} NaOH was gradually added from an autoburette. Initially a moderate increase in pAg was registrated,
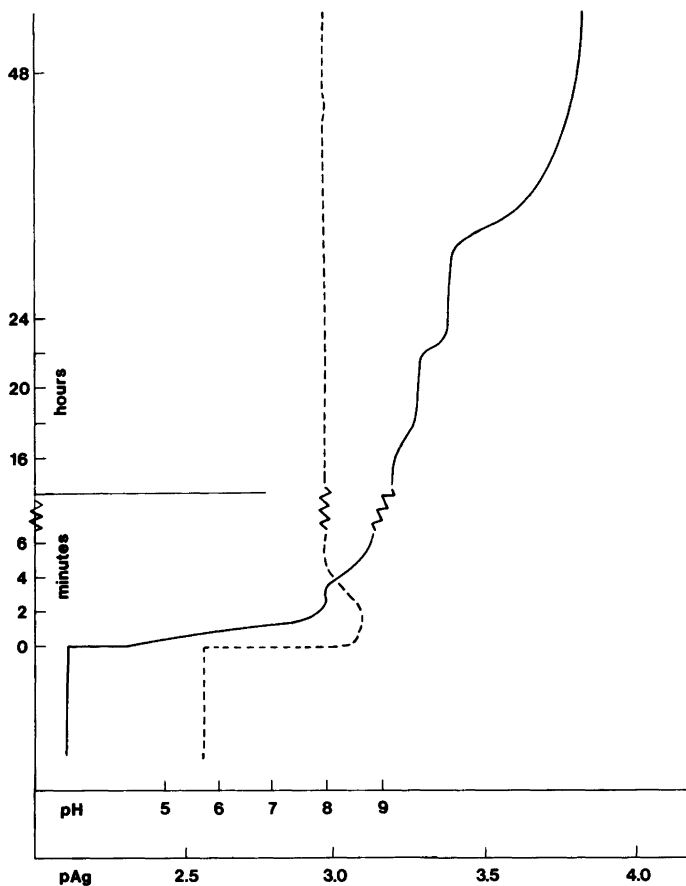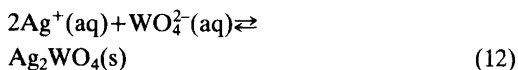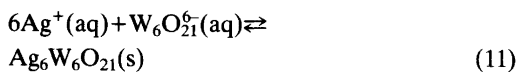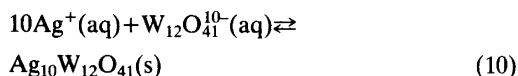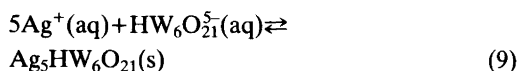
Fig. 7. Initial conditions as in Fig. 2. From t≈5 min pH was kept constant (8.0) in the reaction vessel by means of a pH-state. During the progress of the reactions three plateaus were formed by the pAg curve and obviously the fourth plateau was approached.

but at pH≈6.6 a considerable increase in pAg suddenly occurred, followed by a small decrease. After this an increase in pAg again is observed. We interpret this behaviour in the following way: initially an acidic silver tungstate compound is quickly precipitated (*cf.* Fig. 2). When the precipitation of this compound is almost completed, the precipitation of a second silver tungstate compound is initiated at higher pAg and pH values. However, at these new values the acidic compound is unstable and dissolves initially faster than the second compound precipitates, with the result that both pAg and pH decrease. Later on, the acidic compound is completely dissolved and an increase in both pAg and pH is again observed. The interpretation above is

supported by the results shown in Fig. 9, where a solution of sodium tungstate gradually was added to a silver nitrate–sodium nitrate solution. The transistory decrease in pH observed at pH≈6.7 can be explained by dissolution of the acidic silver tungstate compound, due to the fact that this component becomes unstable at higher pH.

Based on the experimental facts, we found it permissible to assume that at least four different silver tungstate compounds must be considered in order to explain the precipitation reaction shown in Fig. 2. Assuming further the protolytic equilibria (2)–(5) to be valid, we suggest that the following precipitations take place:

$$5Ag^+(aq)+HW_6O_{21}^{5-}(aq)\rightleftarrows$$
$$Ag_5HW_6O_{21}(s) \qquad\qquad (9)$$

$$10Ag^+(aq)+W_{12}O_{41}^{10-}(aq)\rightleftarrows$$
$$Ag_{10}W_{12}O_{41}(s) \qquad\qquad (10)$$

$$6Ag^+(aq)+W_6O_{21}^{6-}(aq)\rightleftarrows$$
$$Ag_6W_6O_{21}(s) \qquad\qquad (11)$$

$$2Ag^+(aq)+WO_4^{2-}(aq)\rightleftarrows$$
$$Ag_2WO_4(s) \qquad\qquad (12)$$

The solubility products are denoted by the letter L and defined in the following way:

$$L_9=(C_{Ag^+})^5 C_{HW_6O_{21}^{5-}} \qquad\qquad (13)$$

$$L_{10}=(C_{Ag^+})^{10} C_{W_{12}O_{41}^{10-}} \qquad\qquad (14)$$

$$L_{11}=(C_{Ag^+})^6 C_{W_6O_{21}^{6-}} \qquad\qquad (15)$$

$$L_{12}=(C_{Ag^+})^2 C_{WO_4^{2-}} \qquad\qquad (16)$$

When L is known and utilizing eqns. (7) and (8), the saturation concentration of the silver ions, $C_{Ag^+,sat}$, belonging to each of the four slightly soluble silver tungstate compounds can be calculated at different pH-values. The shape of the curves is determined from the pH-distribution of the different tungstate ions. This distribution is known (eqn. (8)). The exact position of the curves is determined from the L-values. However, only L_{12} is known precisely[7] ($1.63 \cdot 10^{-11}$ mol^3 dm^{-9} in 1.0 mol dm^{-3} NaNO$_3$). $C_{Ag^+,sat(12)}$ is calculated and shown as 1 in Fig. 10. Concerning L_9, L_{10} and L_{11}, no exact values can be given. Reasonable estimates might possibly be made from the experimental results shown in Figs. 2, 8 and 9. Utilizing the pH$-$pAg relation L_9 and L_{10} can roughly be estimated to 10^{-15} and 10^{-48}, and two saturation curves 2 and 3 can be drawn in
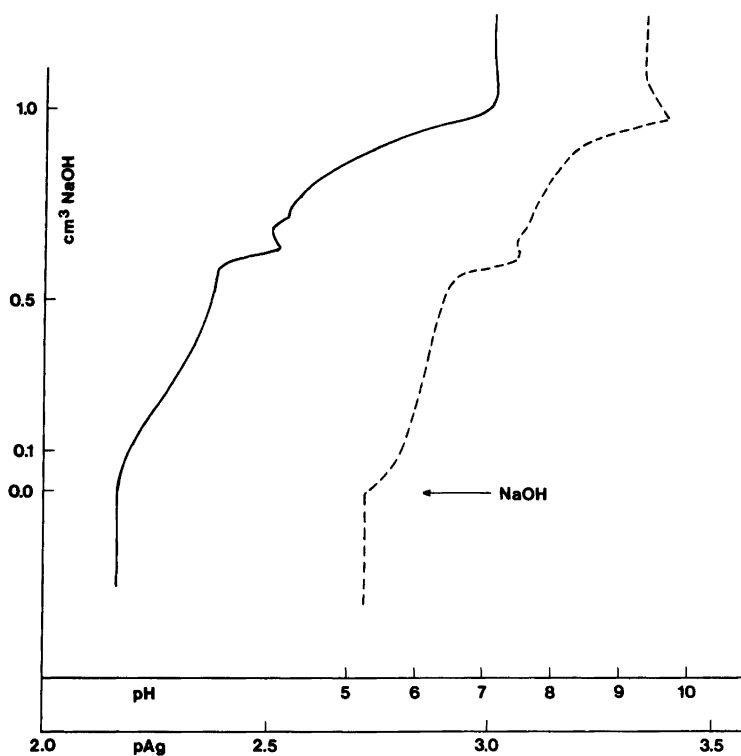

Fig. 8. Time variations of pAg (fully drawn line) and pH (dotted line) when 1.0 mol dm^{-3} sodium hydroxide from an autoburette is slowly added to a mixture of (1.0 cm^3 of 1.0 mol dm^{-3} sodium tungstate +1.0 cm^3 of 1.0 mol dm^{-3} silver nitrate) in 125 cm^3 of 1.0 mol dm^{-3} sodium nitrate. Initial pH value 5.25. Note the small decrease in both pAg and pH at pH$\approx$7.5.
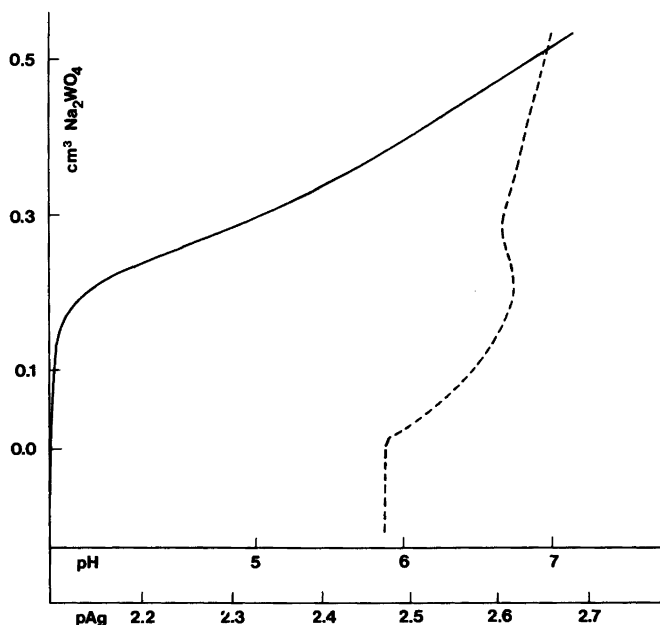
Fig. 9. Time variations of pAg (fully drawn line) and pH (dotted line) when 1.0 mol dm^{-3} sodium tungstate from an autoburette is slowly added to a mixture of 1.0 cm^3 of 1.0 mol dm^{-3} silver nitrate in 125 cm^3 1.0 mol dm^{-3} sodium nitrate. Initial pH value 5.9. Note the decrease in pH at pH=6.7.
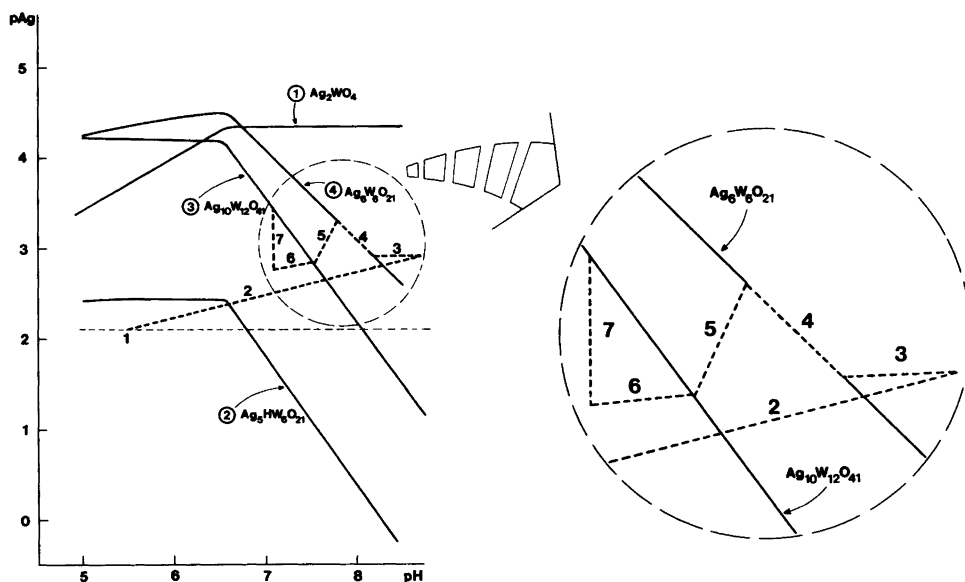

Fig. 10. Calculated saturation concentrations of silver ions corresponding to four different sparingly soluble silver tungstate compounds [eqns. (9)−(12)] as a function of pH. The solubility products of the silver tungstate compounds are estimated from experimental data.

Fig. 10. The position of 4 is restrained to lie between curve 1 and curve 3 for pH>7. In Fig. 10, L_{11} is selected to be 10^{-32}. Fig. 5 shows that the precipitate from period 6 (two upper pictures) consists of rod-shaped crystals. No traces of Ag_2WO_4-crystals (shown on the two lower pictures) can be seen. The two middle pictures show that the rod-shaped crystals are not stable (under the present pH-values) but dissolve into smaller crystals. The final result of this process is pure Ag_2WO_4-crystals (two lower pictures).

In order to interpret these results in accordance with the proposed equilibria (9)–(12) we shall assume that the sparingly soluble silver tungstate compounds formed according to these equilibria do not exist as monomers in acidic medium but are built together in a polymer structure (forming rod-shaped crystals). In alkaline medium the polymer structure breaks down (slowly) under formation of the monomer compounds. Utilizing the results from Table 1, it must be concluded that the polymer is built up mainly of Ag_2WO_4-units. This again means that only small amounts of $Ag_5HW_6O_{21}$, $Ag_{10}W_{12}O_{41}$ and $Ag_6W_6O_{21}$ are formed during the dissolution of the polymer. However, it must be emphasized that the pure existence of these compounds is enough to create a silver ion concentration different from that defined by pure Ag_2WO_4.

The precipitation is initiated in acidic medium (Fig. 2), so it must be expected that the rod-shaped crystals are created at the initial stage of the reaction. According to this a semi-quantitative consistent explanation of the reactions * shown in Fig. 2 can be given with simultaneous reference to Fig. 10. The progress of the reaction is divided into seven periods indicated by the numbers 1 to 7 on both figures. These periods shall be discussed separately.

Period 1. Registration of pAg and pH in an aqueous nitrate–sodium nitrate solution.

Period 2. The protolytic equilibria (2)–(5) are established and the precipitation reactions (9)–(12) occur from left to right, immediately followed by a polymerization of the precipitate.

Period 3. Due to the high pH-value, the polymer will start to dissolve and reactions (9)–(11) occur from right to left. At the end of

* By the term "consistent explanation" we mean an explanation consistent with our experimental results and the protolytic equilibria from literature. Other "consistent explanations" might probably exist.

this period the system can be described with a point on the saturation curve 4 for $Ag_6W_6O_{21}$.

Period 4. The polymer still dissolves. Reactions (9) and (10) occur from right to left and reaction (11) occurs from left to right. The system moves along the saturation curve for $Ag_6W_6O_{21}$. (According to Buchholz[3] practically no further precipitation of Ag_2WO_4 occurs.)

Period 5. Reactions as in period 4, but reactions (9) and (10) are now "faster" than reaction (11), so an increase in the concentration of silver ions is observed and the system moves from curve 4 to curve 3 (precipitation curve for $Ag_{10}W_{12}O_{41}$). The system "delays" a short time on curve 3. This is visualized by the very small shoulder seen in Fig. 2a between periods 5 and 6.

Period 6. The polymer still dissolves and is still the main component as can be seen from Fig. 5. The results from Table 1 seem to indicate that the polymer here mainly consists of Ag_2WO_4-units. The following reactions are proposed:

Reaction (9) occurs from right to left and reactions (10)–(12) occur from left to right. The dissolution of $Ag_5HW_6O_{21}$ goes "faster" than the precipitation of $Ag_{10}W_{12}O_{41}$, $Ag_6W_6O_{21}$ and $AgWO_4$ so a decrease in both pAg and pH is observed. At the end of this period $Ag_5HW_6O_{21}$ is completely dissolved so that in:

Period 7. Reactions (10) and (11) occur from left to right and the system will move towards the saturation curve for $Ag_{10}W_{12}O_{41}$. The results from Table 1 say that the average composition of the precipitate from the start of this period is almost identical with the average composition of the precipitate from period 6. At the end of this period the precipitate probably consists of a mixture of $Ag_{10}W_{12}O_{41}$, $Ag_6W_6O_{21}$ and pure Ag_2WO_4. We know that the reactions continue until the precipitate consists of pure Ag_2WO_4.

CONCLUSIONS

Since the appearance of the paper of Zettnow[17] concerning the precipitation of silver tungstate from sodium tungstate–silver nitrate solutions, only little attention has been paid to explain the reaction mechanism of this reaction.[1-6] The complexity of the reaction is illustrated by Fig. 2 in this paper. We found the behaviour of the silver ion concentration in the solution during

the precipitation very strange. In order to explain the experimental results shown in Fig. 2 and the following figures, we were forced to operate with the theory that the precipitate consists of a mixture of silver tungstate components of which one should have a polymer structure. Based on reported protolytic equilibria the following sparingly soluble silver tungstates are assumed to be formed: $Ag_5HW_6O_{21}$, $Ag_6W_6O_{21}$, $Ag_{10}W_{12}O_{21}$, Ag_2WO_4 and a polymer which, according to Table 1, can be given the formula $(Ag_{1.93}WO_4)_n$. The relations between these compounds are given by (9)−(12). Previously it has been reported[7] that at the final step of the precipitation reactions the precipitate consists of pure Ag_2WO_4.

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