

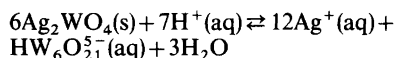
Solubility of Silver Tungstate in Aqueous Solutions at Different Ionic Strengths and Temperatures. Thermodynamic Quantities of Ag_2WO_4

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Freshly precipitated silver tungstate prepared by adding excess of sodium tungstate to silver nitrate is unstable and undergoes slow reactions accompanied by colour changes towards its thermodynamically stable state. The great discrepancies among the reported values of solubility product of silver tungstate may possibly be explained by these slow reactions.

Ionic strength dependence as well as pH dependence of the solubility of stable silver tungstate can be explained by the assumption of the existence of the equilibrium:



for which the equilibrium constant has been determined in 1.0 mol dm⁻³ sodium nitrate solution. In slightly alkaline solutions silver tungstate is dissolved in totally dissociated Ag^+ - and WO_4^{2-} -ions.

Values of solubility of stable silver tungstate are given at six different temperatures ranging from 5.0 to 44.8 °C.

Molar entropy, enthalpy and free energy of solution of silver tungstate as well as standard entropy, enthalpy and free energy are evaluated at 25 °C from the temperature coefficients of solubility.

Standard potential of the $\text{Ag}(\text{s})|\text{Ag}_2\text{WO}_4(\text{s})|\text{WO}_4^{2-}(\text{aq}, \text{hyp})$ electrode is calculated.

Thermodynamic data (ΔH_f , ΔG_f and ΔS_f) for the formation of silver tungstate from its elements at 25 °C are estimated.

Examining literature data concerning solubility product of the sparingly soluble silver tungstate great discrepancies are found. This is illustrated by the reported values determined by means of potentiometric measurements: German and Britton:¹ 5.2×10^{-10} (18 °C), Pan:³ 5.5×10^{-12} (25 °C), Weiner and Boriss:⁵ 6.25×10^{-11} (20 °C), and Saxena and Gupta:⁴ 6.12×10^{-12} (27 °C). Taking into consideration that differences in silver-ion concentrations can be determined potentiometrically by means of a silver electrode with an accuracy of $\pm 1\%$ if the potentials are measured with an accuracy of about ± 0.3 mV, the disagreements are surprisingly great and much greater than would be expected just from statistical considerations. The small temperature differences cannot account for the great disagreements among the cited values, as will be shown later. Obviously some factors related to the precipitation evidently not considered – at least not reported – by the above cited authors must be taken into consideration.

The present paper makes an attempt to clarify some of the discrepancies among the reported values of the solubility product of silver tungstate. We shall restrict ourselves to focus mainly on two factors: (1) the thermodynamic stability of freshly precipitated silver tungstate prepared by adding sodium tungstate to silver nitrate and (2) the pH-dependence of the solubility of stable silver tungstate. In addition some thermodynamic properties, *i.e.* the values of ΔH , ΔG and ΔS of silver tungstate will be given and compared with those of Pan.³ In a following paper the kinetics of the precipitation of silver tungstate will be discussed in more detail.

EXPERIMENTAL

Chemicals. Merck *p.a.* silver nitrate and sodium nitrate (to stabilize the ionic strength) were used without further purification. The nitric acid and the sodium hydroxide solutions (to obtain pH-variations in the solubility measurements) were made by dilution from titrisol ampullae (Merck) containing 1 mol. Sodium tungstate *p.a.* was delivered partly by Riedel de Haën, partly from Ferak (Berlin). Both products contain a small amount of sodium hydroxide (about 0.1 weight %). In order to remove this, the sodium tungstate was recrystallized three times by dissolving in distilled, deionized water. From this solution sodium tungstate was slowly precipitated by adding three times the volume of ethanol. TGA measurements showed that the recrystallized sodium tungstate had the formula $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. Before use it was dried for one week at 50 °C.

Potentiometric measurements were performed on equipment obtained from Radiometer A/S, Copenhagen, Denmark. The indicator electrode was a silver pellet electrode (P4011) on which Ag_2S was deposited by electrolysis. This electrode appears to be very useful in measuring silver ions⁷ and superior to the pure silver electrode. The reference electrode was an $\text{Hg(l)}|\text{Hg}_2\text{SO}_4(\text{s})|\text{Na}_2\text{SO}_4(\text{aq,sat})$ (K501). The electrodes were immersed in a water jacketed cell containing an aqueous solution of silver nitrate in concentrations ranging from 2×10^{-3} to 1.6×10^{-2} mol dm⁻³ and sodium nitrate in the following concentrations: 0, 0.01, 0.05, 0.1, 0.5 and 1.0 mol dm⁻³. In the cell the temperature was kept constant at 25.0 °C (± 0.1). An expanded scale precision pH-meter (PHM26) in connection with a Servograph Recorder (RECS1) was used for continuously measuring and recording the potentials of the indicator electrode *vs.* the reference electrode.

The main purpose in carrying out the potentiometric measurements was to try to imitate the procedure used by the authors cited above^{1,3,5,6} with the hope of perhaps in this way getting some information about some "hidden" sources of error in this procedure.

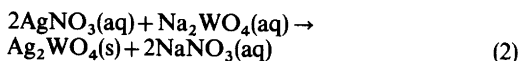
By adding aqueous sodium tungstate to the aqueous silver nitrate – sodium nitrate solution and neglecting the contributions from activity coefficients and liquid junction potentials – as done in this procedure – the free silver-ion concentration can be determined from the observed potential difference by means of eqn. (1) where ΔE is the

$$C_{\text{Ag}^+} = C_{0,\text{Ag}^+} \exp(-\Delta EF/RT) \quad (1)$$

difference between the initial potential established in the pure silver nitrate – sodium nitrate solution and the potential developed when sodium tungstate

is added to this solution, C_{0,Ag^+} is the initial concentration of silver-ions, and the symbols F , R and T have their usual meanings.

In order to obtain a reasonably large ΔE and to ensure precipitation of silver tungstate under alkaline conditions⁴ the amount of added sodium tungstate was larger than that corresponding to the equivalent amount calculated from the expected reaction (2).



Assuming validity of (2), the concentration of free tungstate ions, $C_{\text{wo}_4^{2-}}$, is given by eqn. (3)

$$C_{\text{wo}_4^{2-}} = C_{0,\text{wo}_4^{2-}} \left(\frac{v-v_{\text{eq}}}{V_0+v} \right) + \frac{1}{2} C_{\text{Ag}^+} \quad (3)$$

where $C_{0,\text{wo}_4^{2-}}$ and v are the concentration and volume, respectively, of the added sodium tungstate, V_0 is the initial volume of the silver nitrate – sodium nitrate solution, and v_{eq} is the volume of sodium tungstate solution needed to reach the equivalence point according to reaction (2). The solubility product of silver tungstate, K_c , at the present ionic strength can now be expressed

$$K_c = C_{0,\text{wo}_4^{2-}} \left(\frac{v-v_{\text{eq}}}{V_0+v} \right) \left(\frac{C_{0,\text{Ag}^+}}{\exp(\frac{\Delta EF}{RT})} \right)^2 + \frac{1}{2} \left(\frac{C_{0,\text{Ag}^+}}{\exp(\frac{\Delta EF}{RT})} \right)^3 \quad (4)$$

The ionic strength, I is defined as $I = \frac{1}{2} \sum_i c_i z_i^2$ and

can at any added volume $v > v_{\text{eq}}$ in these experiments be calculated from the formula (5) where C_{0,Na^+} is

$$I = \frac{1}{2} \left[\frac{1}{V_0+v} (V_0(2C_{0,\text{Na}^+} + C_{0,\text{Ag}^+}) + 2C_{0,\text{wo}_4^{2-}}(3v-2v_{\text{eq}})) + \frac{3C_{0,\text{Ag}^+}}{\exp(\frac{\Delta EF}{RT})} \right] \quad (5)$$

the concentration of sodium nitrate in the pure silver nitrate – sodium nitrate solution before adding of sodium tungstate. The other symbols in eqn. (5) have the meanings defined above.

Saturated solutions of silver tungstate were prepared by vigorously rotating well-closed 100 ml bottles in a thermostat with a temperature control of ± 0.1 °C. The bottles were filled with either distilled, deionized water or aqueous solutions of sodium nitrate at well-known concentrations and excess of crystalline thermodynamically stable

silver tungstate. (This was prepared by adding excess of aqueous sodium tungstate to a well-stirred aqueous solution of silver nitrate. In order to obtain thermodynamic stability (see later under discussion) the silver tungstate precipitate was allowed to equilibrate with aqueous solutions at least one year before use.) In some of the bottles some small amounts (from 50 to 500 μl) of nitric acid or sodium hydroxide were added in order to create variations of pH in the saturated solutions. To insure complete saturation the bottles were rotated for at least one week. This procedure was carried out at the following temperatures: 5.0, 10.0, 15.0, 25.0, 35.0 and 44.8 $^{\circ}\text{C}$. To obtain satisfactory thermal stability at 5.0, 10.0 and 15.0 $^{\circ}\text{C}$ and to avoid condensation, the experimental equipment was placed in a cold-storage room with a temperature a little below 5.0 $^{\circ}\text{C}$. By means of a water bath the temperature in the thermostat was controlled at the desired temperature, ± 0.1 $^{\circ}\text{C}$. After rotation the bottles were placed for one day in an upright position in the thermostat to allow the excess of crystalline sodium tungstate to settle, whereupon the solutions were filtered and the concentration of silver-ions determined by titration with potassium iodide.

Solubility determinations were performed on an automatic titration equipment (SBR2, PHM26, TTT11, ABU1). The determinations were carried out on 25 ml of the saturated silver tungstate solution placed in a water-jacketed titration cell in which also the electrodes were immersed. The indicator electrode was the same as utilized for the potentiometric measurements. The reference electrode was either $\text{Hg}(\text{l})|\text{Hg}_2\text{SO}_4(\text{cr})|\text{K}_2\text{SO}_4(\text{aq},\text{sat})$ (K601) or $\text{Hg}(\text{l})|\text{Hg}_2\text{Cl}_2(\text{cr})|\text{KCl}(\text{aq},\text{sat})|\text{NaNO}_3-$

($\text{aq},c=1\text{ mol}/\text{dm}^3$)(K701). In order to avoid precipitation of silver tungstate during titration, the temperature in the titration cell was kept constant at 25.0, 35.0, 45.0 $^{\circ}\text{C}$, ± 0.05 , respectively. (In some cases crystalline sodium nitrate was added to the titration cell to decrease the ohmic resistance in the electrode circuit.)

The titration of silver ions at the present concentrations with potassium iodide was carried out without any problem in getting a titration curve which covered several hundreds of millivolts and with a very easily detectable end point. Duplicate experiments showed that the concentration of silver ions in this way could be determined with a relative accuracy below 1 %.

RESULTS AND DISCUSSION

By means of potentiometric measurements the solubility products, K_c , of freshly prepared silver tungstate were calculated (eqn. 4) at different ionic strengths (eqn. 5). In Fig. 1 $-\log K_c$ ($\text{p}K_c$) is plotted against $\sqrt{I}/(1+\sqrt{I})$. Assuming validity of the Debye-Hückel theory one would expect to find — at least in the dilute area — a straight line correlation by means of which K_a could be determined by extrapolating to ionic strength zero. The fully drawn line in Fig. 1 represents the best straight line determined by means of the least squares method. The dotted lines indicate the uncertainties of intersect and slope determined by this line. From the intersect, K_a is determined to $(2.7 \pm 1.5) \times 10^{-10} \text{ mol}^3 \text{ dm}^{-9}$. The slope is determined to (3.2 ± 0.6) compared

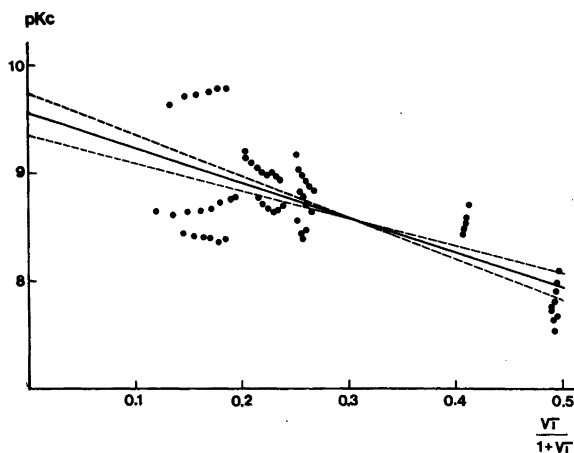


Fig. 1. Estimated values of solubility products of freshly prepared silver tungstate as a function of ionic strength. For further discussions see text.

with the theoretical Debye-Hückel slope 3.055.⁸ As can be seen from the figure the straight line fit is really poor (correlation coefficient of the line is 0.57) and, quite in contrast to what would be expected from the Debye-Hückel theory, the scattering of points are greatest in the dilute area.

The discrepancy is much greater than can be explained by a possible lack of validity in the Debye-Hückel theory and probably is responsible for the great differences among the reported values of solubility products of silver tungstate. A possible contribution to the explanation of this discrepancy may be taken from the results shown in Fig. 2, representing the following experimental conditions

$$C_{o,Ag^+} = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$$

$$C_{o,WO_4^{2-}} = C_{o,Na^+} = 1.0 \text{ mol dm}^{-3}$$

$$V_o = 125 \text{ ml}, v = 1000 \mu, \text{ and } v_{eq} = 875 \mu.$$

Immediately after the addition of sodium tungstate to the silver nitrate–sodium nitrate mixture a yellow precipitate appeared. During about half an hour the colour of the precipitate changed from yellow to white. This colour was stable for some hours but then slowly changed from white to light grey and during the same period of about eight hours the potential change progressed along an S-curve. The potential was recorded for three weeks during which period a slow and continuous decrease in potential was observed; some times the decrease was following S-curves.

From Fig. 2 it can be seen that in the white coloured period the potential is almost stable and can be measured with a precision of ± 0.1 mV, but if this value is taken as the true value in calculating ΔE , then, of course, the estimated value of K_c will be too high and will not correspond to the solubility product of the stable silver tungstate in the present experimental conditions. Thus it would be expected that solubility products of stable silver tungstate found by the potentiometric method would always be too high. This seems also to be true.

The duration of the potential-stable, white-coloured period is affected by many factors such as pH, the ionic strength, the preparation of sodium tungstate, *etc.* The discrepancies shown in Fig. 1 as well as the discrepancies in the reported values of K_c may be explained by the influence from these factors. A detailed discussion will be given in a subsequent paper. In the remaining part of this paper, the discussion shall be limited to conditions relating to the solubility of stable silver tungstate. The term "stable silver tungstate" is used as an indication of silver tungstate precipitate, which has been allowed to equilibrate at least one year in aqueous solutions.

The pH-dependence of the solubility of stable silver tungstate has been investigated by titrimetric determinations of silver ions in saturated aqueous solutions at 25.0 °C. The ionic strength was kept constant = 1.0 by means of sodium nitrate. The variation of pH was performed by adding small amounts of HNO₃ or NaOH. In such solutions the solubility of silver tungstate can be expressed

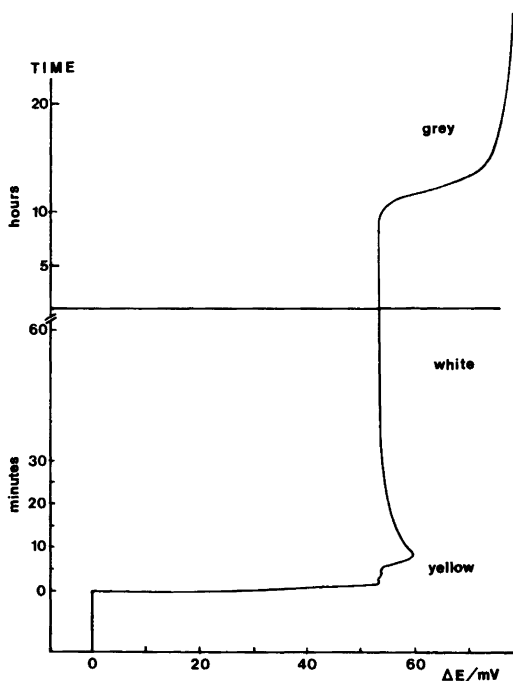


Fig. 2. Potential variation of a Ag/Ag₂S-electrode during precipitation of silver tungstate when sodium tungstate quickly is added to a silver nitrate–sodium nitrate mixture. Experimental conditions $C_{o,Ag^+} = 1.4 \times 10^{-2} \text{ mol dm}^{-3}$, $C_{o,WO_4^{2-}} = C_{o,Na^+} = 1.0 \text{ mol dm}^{-3}$, $V_o = 125 \text{ ml}$, $v = 1000 \mu$, and $v_{eq} = 875 \mu$. For explanation of symbols see text relating eqns. (3) and (4). At the horizontal line the recorder velocity was changed from 5 min cm⁻¹ to 2 h cm⁻¹. Colourchanges during precipitation are indicated on the right side of the figure.

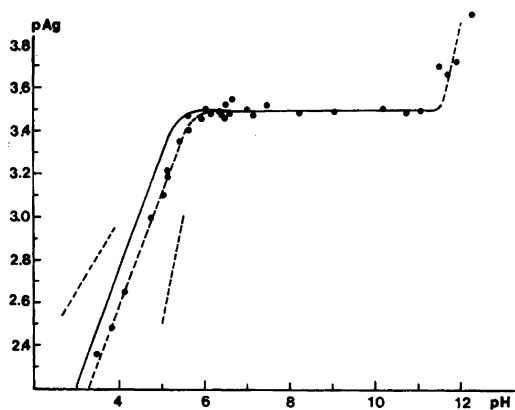
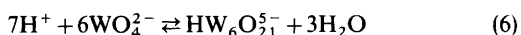


Fig. 3. Solubility of stable silver tungstate as a function of pH. The two dotted line sections have the slopes 1/3 (eqn. 10a) and 1 (eqn. 12a), respectively.

solely by the concentration of free silver ions. When the experimentally determined concentrations of silver ions (expressed as pAg) are plotted against pH, the result appears as shown in Fig. 3. Clearly some protolytic reactions occur in weak acidic and strong alkaline medium, whereas pAg is constant in the pH-interval $6 < \text{pH} < 11$. As suggested by Sasaki,⁹ Arnek,¹⁰ and Arnek and Sasaki¹¹ the first step in the acidification of WO_4^{2-} ions can be expressed by the equilibrium (6) with



the equilibrium constant in 3 M NaClO_4 $\log \beta_6 = 60.76$. Combining eqn. (6) and the two equations (7) and (8), the concentration of the silver ions can

$$C_{\text{Ag}^+} = 2(C_{\text{WO}_4^{2-}} + 6C_{\text{HW}_6\text{O}_{21}^{5-}}) \quad (7)$$

$$(C_{\text{Ag}^+})^2 \times C_{\text{WO}_4^{2-}} = K_c \quad (8)$$

be expressed by eqn. (9), where $\beta'_6 = \frac{\beta_6}{(C_{\text{H}_2\text{O}})^3}$.

$$(C_{\text{Ag}^+})^{13} - 2K_c(C_{\text{Ag}^+})^{10} - 12\beta'_6 K_c^6 (C_{\text{H}^+})^7 = 0 \quad (9)$$

Combining eqn. (6) with the equilibrium (10), for



which Arnek and Sasaki¹¹ have determined the value of the equilibrium constant, $\log \beta_{10} = 11.30$, the complete distribution of the components H_2WO_4 , $\text{HW}_6\text{O}_{21}^{5-}$ and WO_4^{2-} as a function of pH can be calculated (two other components also mentioned by Arnek and Sasaki turn out to be completely without significance under the experimental conditions described in this paper and will be disregarded). Such distribution is shown in Fig. 4. The total concentration of tungstate is $5 \times 10^{-4} \text{ mol dm}^{-3}$ – an approximate average of the values in Fig. 3. As can be seen from this figure, $C_{\text{HW}_6\text{O}_{21}^{5-}}$ can be regarded as equal to zero when $\text{pH} > 6.5$, which means that eqn. (6) is completely shifted to the left side, which again means

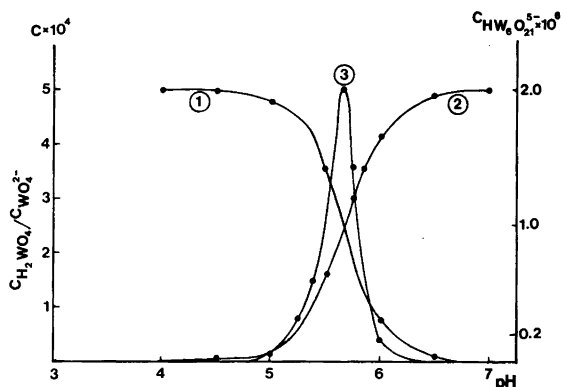
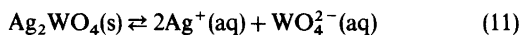


Fig. 4. Calculated distributions of the components H_2WO_4 (curve 1), WO_4^{2-} (curve 2), and $\text{HW}_6\text{O}_{21}^{5-}$ (curve 3) as a function of pH utilizing equilibrium constants determined by Arnek and Sasaki.¹¹ Total concentration of tungstate = $5 \times 10^{-4} \text{ mol dm}^{-3}$. Concentration axis on the left side is valid for curves 1 and 2. Curve 3 is related to concentration axis on the right side.

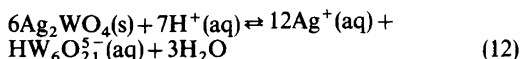
that for $\text{pH} > 6.5$ the term $\beta'_6 K_c^6 (\text{C}_{\text{H}^+})^7$ vanishes in eqn. (9) and K_c can be determined from the value of C_{Ag^+} at the horizontal line in Fig. 3. Here pAg has the value 3.496 ± 0.007 and the solubility product of Ag_2WO_4 in 1.0 M NaNO_3 , K_c , can now be calculated, $K_c = (1.63 \pm 0.08) \times 10^{-11} \text{ mol}^3 \text{ dm}^{-2}$. Using this value in eqn. (9) together with the value $\text{C}_{\text{H}_2\text{O}} = 55.5 \text{ mol dm}^{-3}$ to calculate β'_6 the function $\text{pAg} = f(\text{pH})$ can be derived for any given value of pH . This function is shown as a fully drawn curve in Fig. 3. Clearly the curve does not fit experimental values in the acidic part of the figure, *i.e.* in the pH interval from 3.5 to 5.5. A very likely reason for the poor fit is that the value of β'_6 determined by Arnek and Sasaki is valid in 3 M NaClO_4 . In order to find a value of β'_6 valid in 1.0 M NaNO_3 -solution – the medium used in this experiment – the best straight line determined by least squares method was placed through the experimental points in the pH interval $3.5 < \text{pH} < 5.5$ (shown in Fig. 3 as the dotted line). The equation for this line was found to be $\text{pAg} = 0.526 \text{ pH} + 0.485$ with a correlation coefficient $r^2 = 0.9962$. The uncertainties in the slope and intercept were, respectively, $\pm 1.45 \times 10^{-2}$ and $\pm 7.07 \times 10^{-2}$. According to the theory outlined in eqns. (6) to (10), the slope of the straight line should be $\frac{7}{13} = 0.5385$. This value is covered by the uncertainty of the slope which means that the experimental points support the validity of the theory. From the intercept the value of β'_6 in 1.0 M NaNO_3 was found to be $\log \beta'_6 = 62.58 \pm 0.25$. (If the first step in the acidification of WO_4^{2-} -ions instead of eqn. (6) is described by the "normal" equilibrium (10a), the $\text{pAg} = f(\text{pH})$



function would in acidic medium be a straight line with the slope $= \frac{1}{3}$. Such a straight line is drawn on the left side of the experimental results in Fig. 3. Obviously eqn. (10a) must be disregarded, whereas eqn. (6) seems to describe the experimental points nicely.) By combining eqn. (6) with the saturation equilibrium (11), for which K_c is known, the equi-

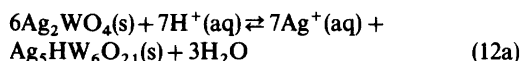


librium (12) can be evaluated.



Using K_c and the value of the intercept of the straight line, the equilibrium constant, β_{12} , was found to be $\log \beta_{12} = -(2.1 \pm 0.1)$.

Actually, eqn. (12) describes the equilibrium situation for saturated solutions of silver tungstate in acidic medium. Now the question arises: how to be sure that the solutions besides being saturated with Ag_2WO_4 also are saturated with $\text{Ag}_5\text{HW}_6\text{O}_{21}$, *i.e.* that the precipitate consists of a two-compound crystalline system. If this is the case, then eqn. (12) can be written in the form (12a) and the relation



between pAg and pH can be expressed as a line with a slope $= 1$, and the solubility product of $\text{Ag}_5\text{HW}_6\text{O}_{21}$ could have been determined from the value of the intercept with this line and the pAg -axis. (It has not been possible to find any data of solubility product of this compound.)

Just to the right of the experimental points in Fig. 3 a straight line with the slope $= 1$ is drawn. Obviously eqn. (12a) must be disregarded under the present experimental conditions.

From Fig. 4 it can be seen that $\text{C}_{\text{HW}_6\text{O}_{21}}$ has its greatest value at $\text{pH} = 5.65$, where $\text{C}_{\text{HW}_6\text{O}_{21}} \approx 2 \times 10^{-6}$. At this pH -value C_{Ag^+} was found to be 3.7×10^{-4} . This means that the solubility product of $\text{Ag}_5\text{HW}_6\text{O}_{21}$ defined as $(\text{C}_{\text{Ag}^+})^5 \text{C}_{\text{HW}_6\text{O}_{21}^{5-}}$ in 1.0 M NaNO_3 -solution is greater than 1.4×10^{-23} .

The decrease in solubility observed at $\text{pH} = 11.5$ is most probably due to precipitation of Ag_2O corresponding to a solubility product of AgOH in 1.0 M NaNO_3 -solution of approx. 1.1×10^{-7} , a most reasonable value compared with data from literature.

The temperature dependence of the solubility of stable silver tungstate has been investigated utilizing the same analytical method as performed in the pH dependence measurements. At each temperature pH was adjusted to 7 or a little above by means of NaOH in order to be sure that reaction (6) was shifted completely to the left side, and the solubility was determined at at least seven different ionic strengths. In no case was the ionic strength greater than $3.5 \times 10^{-2} \text{ mol dm}^{-3}$. Assuming that (1) the precipitate consists solely of Ag_2WO_4 (the pH dependence measurements support this assumption), (2) the soluble Ag_2WO_4 is completely dissociated, and (3) that the Debye-Hückel theory expressed in

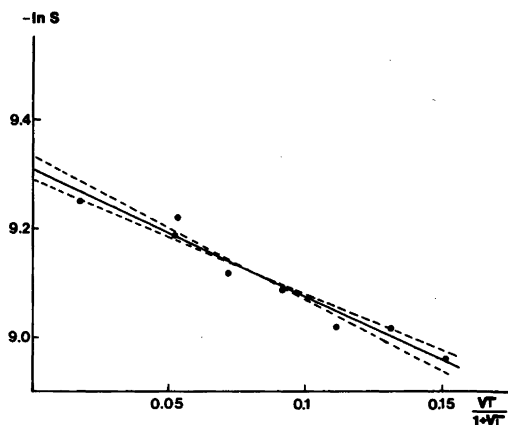


Fig. 5. Güntelberg-plot (eqn. 13) for estimated values of solubility of stable silver tungstate. The fully drawn line indicates the best straight line through the values. The dotted lines indicate the 67% uncertainty limit for the straight line ($t = 44.8^\circ\text{C}$).

the Güntelberg equation is valid in the present measurements the relation (13) holds, where s is

$$\ln s = \ln s_0 + k \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (13)$$

the solubility at the ionic strength I and s_0 is the solubility at infinite dilution. The constant, k , is related to the Debye-Hückel constant, A , by $k = 2.30 \times 2A$. The value of A is tabulated for example by Robinson and Stokes.⁸

In Fig. 5 is shown a plot of $\ln s$ vs. $\sqrt{I}/(1 + \sqrt{I})$. The correlation coefficient of the best straight line is 0.95. The slope of the line is -2.32 ± 0.22 compared with the theoretical value -2.44 .

The good fit of the straight line together with the nice agreement between the experimental and theoretical values of the slope of the line support

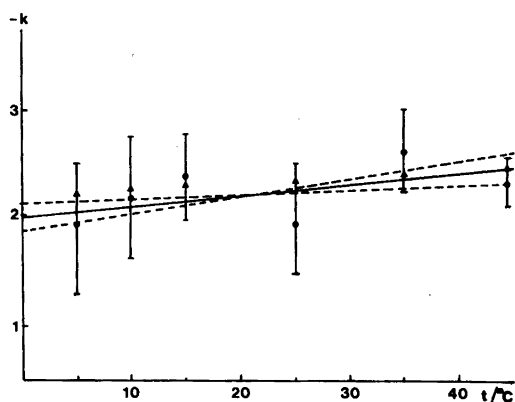


Fig. 6. Slope of Güntelberg-plots as a function of temperature. ● = estimated values; ▲ = values from Robinson and Stokes.⁸ The vertical lines through the points indicate 67% uncertainty limit. From estimated values the temperature dependence of the slope is calculated to $(9 \pm 7) \times 10^{-3}$ compared with the theoretical value 4.3×10^{-3} .

the assumptions (1)–(3). Plots similar to the one shown in Fig. 5 were made at the following temperatures: 5.0, 10.0, 15.0, 25.0 and 35.0 °C. At these temperatures the straight line correlation as well as the agreement between calculated and theoretical values of the slope are well established. In Fig. 6 are shown the estimated values of the slopes with uncertainties together with the theoretical values. From the extrapolated s_0 -values the solubility product at infinite dilution, K_a , can be calculated from $K_a = 4s_0^3$. Values of K_a and s_0 are collected in Table 1.

The standard potential, $E_{\text{Ag}/\text{Ag}_2\text{WO}_4}^\ominus$, relating the electrode equilibrium (14) at a given temperature,

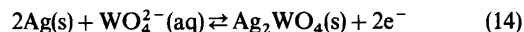


Table 1. Solubilities (mol dm^{-3}) and solubility products ($\text{mol}^3 \text{dm}^{-9}$) of silver tungstate temperatures calculated from potentiometric measurements. Values extrapolated to ionic strength = 0.

$t/^\circ\text{C}$	5	10	15	20	25	30	35	40	44.8
Pan ³									
$K_a \times 10^{-12}$	—	—	—	3.8	5.5	7.8	—	14.8	—
This paper									
$K_a \times 10^{-13}$	0.7 ± 0.2	1.8 ± 0.5	2.9 ± 0.5	—	7.5 ± 0.7	—	15 ± 2	—	30 ± 2
$s_0 \times 10^{-5}$	2.6 ± 0.2	3.5 ± 0.3	4.2 ± 0.2	—	5.7 ± 0.2	—	7.2 ± 0.3	—	9.1 ± 0.2

can be calculated when the standard potential relating the silver-silver ion equilibrium and the solubility product of silver tungstate are known at this temperature, *i.e.*

$$E_{\text{Ag}/\text{Ag}^+}^{\ominus} + \frac{RT}{2F} \ln K_a = E_{\text{Ag}/\text{Ag}_2\text{WO}_4}^{\ominus} \quad (15)$$

Latimer¹² gives $E_{\text{Ag}/\text{Ag}^+}^{\ominus} = 799.1$ mV at 25.0 °C. At this temperature we found $K_a = 7.5 \times 10^{-13}$, which gives

$$E_{\text{Ag}/\text{Ag}_2\text{WO}_4}^{\ominus} = 440.7 \text{ mV (25.0 °C vs. SHE)} \quad (16)$$

compared with the value 466 from Pan.³ (SHE = standard hydrogen electrode.)

Determination of thermodynamic quantities. The solubility product, K_a , and the solubility, s_o , connecting the equilibrium of dissolution (11) are related to thermodynamic quantities by eqns. (17)–(19), where $\Delta_s^1 G^\ominus$, $\Delta_s^1 H^\ominus$ and $\Delta_s^1 S^\ominus$ indicate

$$-\Delta_s^1 G^\ominus = RT \ln K_a = RT \ln (4 s_o^3) \quad (17)$$

$$\left(\frac{\partial \ln s_o}{\partial (1/T)} \right)_p = - \frac{1}{3} \frac{\Delta_s^1 H^\ominus}{R} \quad (18)$$

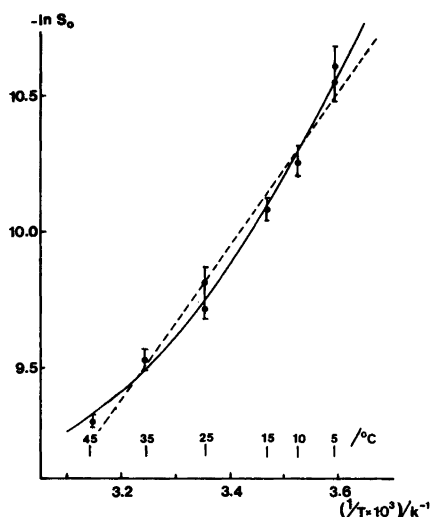


Fig. 7. Estimated solubilities at ionic strength=0 as a function of reciprocal temperature. The vertical lines through the points indicate 67 % uncertainty limit. Both the best straight line as well as the best parabolic curve fitting the points are drawn.

$$\Delta_s^1 H^\ominus = \Delta_s^1 G^\ominus + T \Delta_s^1 S^\ominus \quad (19)$$

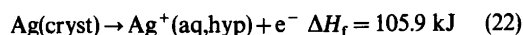
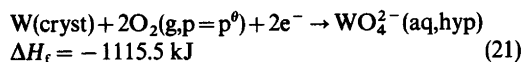
changes in standard free energy, enthalpy and entropy, respectively, accompanying (11). Knowing s_o as a function of temperature, $\Delta_s^1 H^\ominus$ and so also $\Delta_s^1 S^\ominus$ can be calculated from an $\ln s_o$ vs. $1/T$ plot. Such a plot is shown in Fig. 7. The best curve describing the experimental results is expected to be either a straight line ($\Delta C_p^\ominus = 0$) or a parabolic curve ($\Delta C_p^\ominus \neq 0$). Both, the best straight line as well as the best parabolic curve, are shown in Fig. 7, and it is seen that both curves fit the experimental points very well. (The correlation coefficient of the straight line has the value = 0.947.) However, a chi-square evaluation gave the following results: straight line: $\chi^2 = 3.7 \times 10^{-3}$, parabolic curve: $\chi^2 = 1.3 \times 10^{-3}$, *i.e.* a slightly better performance of the parabolic curve compared with the straight line. The thermodynamic quantities can now be calculated. At 25.0 °C the following molar values were obtained: $\Delta_s^1 H^\ominus = (65 \pm 2)$ kJ; $\Delta_s^1 G^\ominus = (69.2 \pm 0.2)$ kJ; $\Delta_s^1 S^\ominus = (-14 \pm 7)$ J K⁻¹. (From the straight line: $\Delta_s^1 H^\ominus = 69 \pm 5$ kJ.) From Pan³ the following values are obtained: $\Delta_s^1 H^\ominus = 50.6$ kJ; $\Delta_s^1 G^\ominus = 64.4$ kJ; $\Delta_s^1 S^\ominus = -62.7$ J K⁻¹. Assuming ideality in the aqueous solutions saturated with silver tungstate then $\Delta_s^1 H^\ominus = \Delta_s^1 H$ (because $(\partial \Delta H / \partial c)_{T,p} = 0$ in ideal solutions). Hence, in the case of ideality, the value of $\Delta_s^1 H^\ominus$ given above expresses the enthalpy change connecting the transference of 1 mol Ag_2WO_4 (1) from the solid state to the hypothetical ideal aqueous solution, and (2) from the solid state to the saturated aqueous solution. At equilibrium $\Delta G = 0$ so the entropy change relating the transference of 1 mol Ag_2WO_4 from solid state to the saturated aqueous solution, $\Delta_s^1 S$ can be calculated from (20). At 25.0 °C $\Delta_s^1 S = (218 \pm 7)$ J K⁻¹.

$$\Delta_s^1 S = \frac{\Delta_s^1 H^\ominus}{T} \quad (20)$$

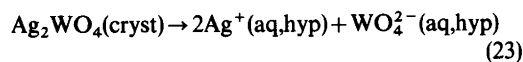
For comparison, the value of $\Delta_s^1 H$ for the sparingly soluble, totally dissociated salts AgCl and $\text{Pb}(\text{IO}_3)_2$ have been calculated. Utilizing values of solubility products at different temperatures from Handbook of Chemistry and Physics¹³ the following values were obtained: $\Delta_s^1 H^\ominus$ (AgCl , 25.0 °C) = 68.6 kJ mol⁻¹ and $\Delta_s^1 H^\ominus$ ($\text{Pb}(\text{IO}_3)_2$, 25.0 °C) = 67.1 kJ mol⁻¹. These values are very close to the value found for silver tungstate. In the case of AgCl and $\text{Pb}(\text{IO}_3)_2$ the ions take place in no other reaction but dissolution. The close agreement between the $\Delta_s^1 H^\ominus$ values

seems to indicate that this is also the case when preparing saturated solutions of stable silver tungstate in slightly alkaline solutions, *i.e.* reaction (6) is completely shifted to the left side.

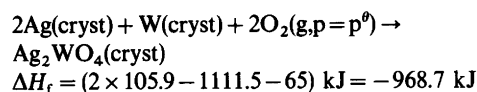
Combining the values of molar heats of formation of WO_4^{2-} and Ag^+ -ions at 25.0 °C from selected values of Chemical Thermodynamic Properties¹⁴



with those evaluated above for the solution of silver tungstate



the molar heat of formation of silver tungstate at 25.0 °C can be evaluated



The term "aq,hyp" used in eqns. (21), (22) and (23) indicates the standard state for a solute in aqueous solution which is defined as the hypothetical ideal state of unit concentration.

Further, the relation (24) holds

$$\Delta G_f(\text{Ag}_2\text{WO}_4) = 2\mu_{\text{Ag}^+}^\theta + \mu_{\text{WO}_4^{2-}}^\theta + RT \ln K_a \quad (24)$$

Utilizing the values from Latimer¹² at 25.0 °C

$$\mu_{\text{Ag}^+}^\theta = 77.1 \text{ kJ} \quad \text{and} \quad \mu_{\text{WO}_4^{2-}}^\theta = 920.5 \text{ kJ}$$

together with the present results $K_a = 7.5 \times 10^{-13}$.

$$\Delta G_f(\text{Ag}_2\text{WO}_4) = -835.5 \text{ kJ.}$$

From these data the entropy change for formation of silver tungstate is estimated as $\Delta S_f = -447 \text{ J K}^{-1}$.

Conclusion. The following main conclusions can be drawn:

(1) The great variety in reported values of solubility product of silver tungstate may be explained by the exceptional way silver tungstate is precipitated (Figs. 1 and 2). The precipitation kinetics will be discussed in a following paper.

(2) The pH influence on the solubility of silver tungstate supports the theory of Arnek and Sasaki about the existence of $\text{HW}_6\text{O}_{21}^{5-}$ -ions in slightly acidic media (Figs. 3 and 4).

(3) The results in Figs. 5 and 6 show that it is most likely that silver tungstate in neutral and slightly alkaline solutions dissolves only into completely dissociated Ag^+ and WO_4^{2-} -ions.

(4) In the temperature range observed, the best description of the temperature dependence on the solubility of silver tungstate is given by a parabolic curve (Fig. 7). From this curve the thermodynamic quantities $\Delta_s^1 H^\theta$, $\Delta_s^1 H$, $\Delta_s^1 G^\theta$, $\Delta_s^1 S^\theta$ and $\Delta_s^1 S$ relating the dissolution process can be determined.

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