

COMPONENTS: 1. Silver selenite; Ag_2SeO_3 ; [7784-05-6] 2a. Nitric acid; HNO_3 ; [7697-37-2] 2b. Sulfuric acid; H_2SO_4 ; [7664-93-9] 3. Water; H_2O ; [7732-18-5]	ORIGINAL MEASUREMENTS: Chukhlantsev, V.G. <i>Zh. Neorg. Khim.</i> <u>1956</u> , 1, 2300; *Russ. <i>J. Inorg. Chem.</i> <u>1956</u> , 1, 132.																																						
VARIABLES: HNO_3 and H_2SO_4 concentrations One temperature: 293 K	PREPARED BY: Mary R. Masson																																						
EXPERIMENTAL VALUES: Concentrations are expressed in units of mol dm^{-3} . <table border="1" data-bbox="197 504 1158 715"> <thead> <tr> <th>Soln.</th> <th>Initial pH</th> <th>Final pH</th> <th>$[\text{Ag}^+]$</th> <th>pAg</th> <th>$\log \alpha_{\text{L(H)}}$</th> <th>$\text{p}[\text{SeO}_3^{2-}]$</th> <th>$\text{p}K_{\text{SO}}$</th> </tr> </thead> <tbody> <tr> <td rowspan="2">HNO_3</td> <td>2.24</td> <td>2.43</td> <td>8.52×10^{-4}</td> <td>3.07</td> <td>5.83</td> <td>9.20</td> <td>15.34</td> </tr> <tr> <td>2.00</td> <td>2.27</td> <td>1.59×10^{-3}</td> <td>2.80</td> <td>6.10</td> <td>9.20</td> <td>14.80</td> </tr> <tr> <td rowspan="2">H_2SO_4</td> <td>2.35</td> <td>2.61</td> <td>6.12×10^{-4}</td> <td>3.21</td> <td>5.60</td> <td>9.11</td> <td>15.53</td> </tr> <tr> <td>2.06</td> <td>2.31</td> <td>1.51×10^{-3}</td> <td>2.82</td> <td>6.05</td> <td>9.17</td> <td>14.81</td> </tr> </tbody> </table> <p>The average value is $K_{\text{SO}} = 9.7 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$. ($\text{p}K_{\text{SO}} = 15.01$)</p> <p>Notes. $[\text{Se}_{\text{tot}}] = [\text{Ag}^{2+}]$ and $[\text{SeO}_3^{2-}] = [\text{Se}_{\text{tot}}]/\alpha_{\text{L(H)}}$ where $\alpha_{\text{L(H)}} = (1 + [\text{H}^+]/K_2 + [\text{H}^+]^2/K_1K_2)$ (refs. 1 and 2) and the acid dissociation constants have the values $K_1 = 4 \times 10^{-3} \text{ mol dm}^{-3}$ and $K_2 = 1.0 \times 10^{-8} \text{ mol dm}^{-3}$ (ref. 1).</p>		Soln.	Initial pH	Final pH	$[\text{Ag}^+]$	pAg	$\log \alpha_{\text{L(H)}}$	$\text{p}[\text{SeO}_3^{2-}]$	$\text{p}K_{\text{SO}}$	HNO_3	2.24	2.43	8.52×10^{-4}	3.07	5.83	9.20	15.34	2.00	2.27	1.59×10^{-3}	2.80	6.10	9.20	14.80	H_2SO_4	2.35	2.61	6.12×10^{-4}	3.21	5.60	9.11	15.53	2.06	2.31	1.51×10^{-3}	2.82	6.05	9.17	14.81
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METHOD APPARATUS/PROCEDURE: Solutions of nitric and sulfuric acids were saturated with silver selenite by stirring in a thermostat at 20°C for 8 hr. The remaining solid phase was removed by centrifugation, then the pH was measured ("Moskip" pH meter, to 0.01 pH unit) and the silver concentration was determined (method not stated).	SOURCE AND PURITY OF MATERIALS: C.P.-grade reagents were used. Silver selenite was prepared by mixing stoichiometric amounts of 0.1N solutions of selenious acid and silver nitrate in the dark, then the precipitate was washed with water and dried at 40°C. Silver was determined by the Volhard method and selenium gravimetrically after precipitation with hydrazine. ESTIMATED ERROR: The spread in the results is 0.73 of a log unit. REFERENCES: 1. Rumpf, P. <i>Compt. Rendu</i> <u>1933</u> , 197, 686.																																						

COMPONENTS: 1. Silver selenite; Ag_2SeO_3 ; [7784-05-6] 2. Water; H_2O ; [7732-18-5]	ORIGINAL MEASUREMENTS: Selivanova, N.M.; Leshchinskaya, Z.L.; Klushina, T.V. <i>Zhur. Fiz. Khim.</i> <u>1962</u> , <i>36</i> , 1349; * <i>Russ. J. Phys. Chem.</i> <u>1962</u> , <i>36</i> , 719.																																																								
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EXPERIMENTAL VALUES: All concentrations are expressed in units of mol dm^{-3} . <table border="1" data-bbox="87 487 1223 701"> <thead> <tr> <th>Time of mixing (days) at 25°C</th> <th>Concentration of Ag^+</th> <th>Solubility Product</th> <th></th> </tr> </thead> <tbody> <tr> <td>6</td> <td>8.26×10^{-6}</td> <td></td> <td></td> </tr> <tr> <td>7</td> <td>8.28×10^{-6}</td> <td></td> <td>Hydrolysis of selenite neglected.</td> </tr> <tr> <td>7</td> <td>8.30×10^{-6}</td> <td></td> <td></td> </tr> <tr> <td>8</td> <td>8.30×10^{-6}</td> <td></td> <td></td> </tr> <tr> <td>10</td> <td>8.34×10^{-6}</td> <td></td> <td>Has equilibrium been reached?</td> </tr> <tr> <td>Mean</td> <td>8.31×10^{-6}</td> <td>$2.85 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$</td> <td></td> </tr> </tbody> </table> <p>The compiler has recalculated the results to take account of the hydrolysis of the selenite ions; the computer program HALTAFALL (2) was used, and the values for the dissociation constants were those of Hagişawa (3) - $\text{p}K_1 = 2.62$, $\text{p}K_2 = 8.32$.</p> <table border="1" data-bbox="87 802 1223 1012"> <thead> <tr> <th>Concentration of Ag^+</th> <th>Total conc. of selenite</th> <th>Conc. of SeO_3^{2-}</th> <th>Solubility Product</th> </tr> </thead> <tbody> <tr> <td>8.26×10^{-6}</td> <td>4.13×10^{-6}</td> <td>2.058×10^{-6}</td> <td></td> </tr> <tr> <td>8.28×10^{-6}</td> <td>4.14×10^{-6}</td> <td>2.065×10^{-6}</td> <td></td> </tr> <tr> <td>8.30×10^{-6}</td> <td>4.15×10^{-6}</td> <td>2.072×10^{-6}</td> <td></td> </tr> <tr> <td>8.30×10^{-6}</td> <td>4.15×10^{-6}</td> <td>2.072×10^{-6}</td> <td></td> </tr> <tr> <td>8.34×10^{-6}</td> <td>4.17×10^{-6}</td> <td>2.085×10^{-6}</td> <td></td> </tr> <tr> <td>8.31×10^{-6}</td> <td>4.155×10^{-6}</td> <td>2.075×10^{-6}</td> <td>$1.433 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$ ($\text{p}K_{\text{SO}} = 15.84$)</td> </tr> </tbody> </table> <p>It should be noted that the calculation of $[\text{SeO}_3^{2-}]$ assumes that the water used for dissolution of the silver selenite was extremely pure and had a pH not significantly differing from 7. If the pH was significantly different from 7 (e.g. because of the presence of dissolved carbon dioxide) hydrolysis of the selenite ion would have occurred to a greater or lesser extent.</p>		Time of mixing (days) at 25°C	Concentration of Ag^+	Solubility Product		6	8.26×10^{-6}			7	8.28×10^{-6}		Hydrolysis of selenite neglected.	7	8.30×10^{-6}			8	8.30×10^{-6}			10	8.34×10^{-6}		Has equilibrium been reached?	Mean	8.31×10^{-6}	$2.85 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$		Concentration of Ag^+	Total conc. of selenite	Conc. of SeO_3^{2-}	Solubility Product	8.26×10^{-6}	4.13×10^{-6}	2.058×10^{-6}		8.28×10^{-6}	4.14×10^{-6}	2.065×10^{-6}		8.30×10^{-6}	4.15×10^{-6}	2.072×10^{-6}		8.30×10^{-6}	4.15×10^{-6}	2.072×10^{-6}		8.34×10^{-6}	4.17×10^{-6}	2.085×10^{-6}		8.31×10^{-6}	4.155×10^{-6}	2.075×10^{-6}	$1.433 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$ ($\text{p}K_{\text{SO}} = 15.84$)
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METHOD APPARATUS/PROCEDURE: Solid silver selenite was equilibrated with water for 7 - 10 days, in a thermostat at $25^\circ\text{C} \pm 0.1^\circ\text{C}$. The concentration of silver in the solution was determined turbidimetrically as follows. To 2 - 10 ml of the solution were added 10 drops of a 1% gelatin solution and 2 ml of HCl (1:1), and the solution was diluted to 100 ml. After 15 min, the absorbance was measured (blue filter) (ref. 1).	SOURCE AND PURITY OF MATERIALS: Silver selenite was prepared by mixing 0.1N solutions of silver nitrate and sodium selenite in stoichiometric proportions, washing several times with warm water, and drying at 40°C .																																																								
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METHOD APPARATUS/PROCEDURE: Precipitations were done in 100-ml standard flasks kept in a water bath at 25°C . The ligand was always added last. The initial concentration of silver ions was $4.79 \times 10^{-3}M$ and of selenous acid $4.79 \times 10^{-2}M$. The pH was adjusted to the required value by addition of sodium hydroxide or perchloric acid. Sealed flasks were equilibrated for six days. pH and pAg were measured potentiometrically in the aqueous phase after removal of the solid phase by filtration through a frit, under nitrogen. The potentiometric determination of silver was done with a silver metal electrode and a calomel electrode filled with 1M sodium perchlorate solution. E° for this cell was determined by measuring its potential with solutions of known $[\text{Ag}^+]$ in 1M sodium perchlorate.	SOURCE AND PURITY OF MATERIALS: The water used was demineralized and deoxygenated, and stored under nitrogen. The selenous acid used was of reagent grade. ESTIMATED ERROR: $s = 0.2$ log units for all the data. (compiler) REFERENCES:																																																																																																																								

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<p>COMMENTS AND/OR ADDITIONAL DATA</p> <p>The compiler used the values for K_1 and K_2 determined by the authors to allow a value for K_{SO} based on the complete set of data to be evaluated. That is, a value for $[\text{SeO}_3^{2-}]$ was calculated for each point as follows.</p> <p>Amount of Ag precipitated = initial Ag - free Ag</p> <p>Total Se in solution = initial Se - precip. Se = initial Se - (ppt Ag/2)</p> $[\text{SeO}_3^{2-}] = (\text{Total Se in solution}) / (1 + [\text{H}^+]/K_2 + [\text{H}^+]^2/K_1K_2).$ <p>The $K_{\text{SO}} = [\text{Ag}^+]^2[\text{SeO}_3^{2-}]$.</p> <p>A value of $2.36 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$ was found for K_{SO} ($\text{p}K_{\text{SO}} = 15.63$). The standard deviation estimate, s expressed in logarithmic terms is 0.2.</p>	

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EXPERIMENTAL VALUES: Concentrations are expressed in terms of $-\log$ of mol dm^{-3} . <table border="1" data-bbox="154 541 1263 1032"> <thead> <tr> <th>pH</th> <th>$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.00646 \text{ mol dm}^{-3}$</th> <th>$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.1 \text{ mol dm}^{-3}$</th> <th>$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.1995 \text{ mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>1.0</td><td>2.26</td><td>-</td><td>-</td></tr> <tr><td>1.5</td><td>2.76</td><td>3.16</td><td>-</td></tr> <tr><td>2.0</td><td>3.18</td><td>3.66</td><td>-</td></tr> <tr><td>2.5</td><td>3.57</td><td>4.10</td><td>4.42</td></tr> <tr><td>3.0</td><td>3.93</td><td>4.42</td><td>4.61</td></tr> <tr><td>3.5</td><td>4.18</td><td>4.68</td><td>4.80</td></tr> <tr><td>4.0</td><td>4.42</td><td>4.90</td><td>(5.00)</td></tr> <tr><td>4.5</td><td>(4.64)</td><td>(5.07)</td><td>(5.19)</td></tr> <tr><td>5.0</td><td>(4.87)</td><td>(5.24)</td><td>(5.38)</td></tr> <tr><td>5.5</td><td>(5.10)</td><td>(5.41)</td><td>(5.57)</td></tr> <tr><td>6.0</td><td>5.32</td><td>5.58</td><td>5.75</td></tr> <tr><td>6.5</td><td>5.49</td><td>5.65</td><td>5.76</td></tr> <tr><td>7.0</td><td>5.60</td><td>5.65</td><td>5.77</td></tr> <tr><td>7.5</td><td>5.65</td><td>5.59</td><td>5.48</td></tr> <tr><td>8.0</td><td>5.65</td><td>5.43</td><td>5.22</td></tr> <tr><td>8.5</td><td>5.65</td><td>5.28</td><td>5.05</td></tr> <tr><td>9.0 - 12.0</td><td>5.65</td><td>5.20</td><td>5.00</td></tr> </tbody> </table> <p>The compiler summarized the results by plotting all the authors' experimental points, drawing smooth curves through them, then abstracting values at regular intervals of pH. Values in brackets are in regions of pH where there were no experimental points, but where interpolation seems to be justified.</p> <p>The initial concentration of silver ions was $3.63 \times 10^{-3} \text{ mol dm}^{-3}$ for the first two sets of results, and $3.98 \times 10^{-4} \text{ mol}^{-3}$ for the third. (continued on next page)</p>		pH	$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.00646 \text{ mol dm}^{-3}$	$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.1 \text{ mol dm}^{-3}$	$[\text{H}_2\text{SeO}_3]_{\text{tot}} = 0.1995 \text{ mol dm}^{-3}$	1.0	2.26	-	-	1.5	2.76	3.16	-	2.0	3.18	3.66	-	2.5	3.57	4.10	4.42	3.0	3.93	4.42	4.61	3.5	4.18	4.68	4.80	4.0	4.42	4.90	(5.00)	4.5	(4.64)	(5.07)	(5.19)	5.0	(4.87)	(5.24)	(5.38)	5.5	(5.10)	(5.41)	(5.57)	6.0	5.32	5.58	5.75	6.5	5.49	5.65	5.76	7.0	5.60	5.65	5.77	7.5	5.65	5.59	5.48	8.0	5.65	5.43	5.22	8.5	5.65	5.28	5.05	9.0 - 12.0	5.65	5.20	5.00
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<p>The compiler has used the values calculated by the authors for $\text{p}K_{\text{SO}}$, β_1 and β_2 to do a back-calculation of the solubility expressed as $[\text{Ag}]_{\text{tot}}$. The calculated values for pAg corresponding to listed experimental ones are tabulated below.</p>																																																																																	
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<p>COMMENTS AND/OR ADDITIONAL INFORMATION</p> <p>The authors deduced that the two complexes formed are AgSeO_3^- and $\text{Ag}(\text{SeO}_3)_2^{3-}$ from the behaviour of the solubility, expressed in terms of $[\text{Ag}]_{\text{tot}}$ as a function of the concentration of selenite. A plot of $\log [\text{Ag}]_{\text{tot}}$ vs. $[\text{SeO}_3^{2-}]$ has two distinct linear regions with slopes of -0.5 and -1.5. A value for β_2 was calculated from the data corresponding to a slope of -1.5, by assuming that essentially all the silver in solution would be present as $\text{Ag}(\text{SeO}_3)_2^{3-}$; <i>i.e.</i> $[\text{Ag}(\text{SeO}_3)_2^{3-}] = [\text{Ag}]_{\text{tot}}$. A value for β_1 was calculated then from the data corresponding to a slope of -0.5, by setting $[\text{Ag}]_{\text{tot}} = [\text{AgSeO}_3^-] + [\text{Ag}(\text{SeO}_3)_2^{3-}]$, and utilizing the value already calculated for β_2 to calculate $[\text{Ag}(\text{SeO}_3)_2^{3-}]$. For both calculations, $[\text{Ag}^+]$ was calculated from $K_{\text{SO}} = [\text{Ag}^+]^2 \times [\text{SeO}_3^{2-}]$.</p> <p><u>Compiler's comments:</u> the compiler felt that the extensive sets of data from experiments B and C should be further utilized to confirm and improve the value derived for K_{SO} from the first series of experiments (A). However, this was not found to be possible; in fact, the sets of data are not consistent, and even the three subsets of data in the second series of experiments are not consistent with one another. The conclusion has to be that one or other, or both, of the experimental procedures must be faulty. In view of the lack of consistency even among the data of the second series of experiments, it seems that the radiochemical technique is the one that is more likely to be faulty. Also, the potentiometric technique used in the first series would have been expected to be more reliable in any case. It is therefore suggested tentatively that the results from series one be regarded as reliable, but that the values for $\log \beta_1$ and $\log \beta_2$ be regarded with suspicion.</p>	

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<p>VARIABLES:</p> <p>One temperature: 293 K</p>	<p>PREPARED BY:</p> <p>Mary R. Masson</p>
<p>EXPERIMENTAL VALUES:</p> <p>The ionic strength was constant at 0.1 mol dm^{-3} (medium not stated)</p> $\text{p}K_{\text{SO}} = 15.45 \pm 0.15 \quad K_{\text{SO}} = 3.55 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$ <p>Concentrations are given in units of mol dm^{-3}.</p> <p><u>Compiler's note</u></p> <p>The values used for the acid dissociation constants of selenious acid are not given, but if the determination was done at pH 11.0, as it was for silver arsenite (1), the values would have an almost negligible influence on the value obtained for the solubility product. Therefore, this value is probably a reasonably good estimate of the concentration solubility product.</p> <p>The value would refer to a freshly precipitated solid, and may therefore be expected to differ from values found by equilibrium of solutions with aged solids.</p>	
<p>AUXILIARY INFORMATION</p>	
<p>METHOD APPARATUS/PROCEDURE:</p> <p>The solubility product was determined from data obtained by potentiometric titration of a selenite solution with a silver nitrate solution. Silver ion activities were measured by means of an Orion silver sulfide electrode (94-16) and an Orion double junction reference electrode (90-02). Emf readings were taken with a Corning model 10 pH meter with expanded scale. Method of calculation is given in ref. (1). This involved determining, from the E value, pAg at the point of incipient precipitation of silver selenite.</p>	<p>SOURCE AND PURITY OF MATERIALS:</p> <p>Reagent-grade chemicals were used.</p> <p>ESTIMATED ERROR:</p> <p>Range in $\text{p}K_{\text{SO}} = \pm 0.15$</p> <p>REFERENCES:</p> <p>1. Chao, E.E. <i>Ph.D. Dissertation</i> University of Missouri, Kansas City, Mo. <u>1975</u>.</p>