

<b>COMPONENTS:</b> 1. Mercury(I) selenite; $\text{Hg}_2\text{SeO}_3$ ; [15855-76-2] 2a. Sulfuric acid; $\text{H}_2\text{SO}_4$ ; [7664-93-9] 2b. Nitric acid; $\text{HNO}_3$ ; [7697-37-2] 3. Water; $\text{H}_2\text{O}$ ; [7732-18-5]	<b>ORIGINAL MEASUREMENTS:</b>  Chukhlantsev, V.G.; Tomashevsky, G.P. <i>Zh. Anal. Khim.</i> <u>1957</u> , 12, 296-301; * <i>J. Anal. Chem. USSR</i> <u>1957</u> , 12, 303-9.																																													
<b>VARIABLES:</b>  Sulfuric and nitric acid concentrations One temperature: 293 K	<b>PREPARED BY:</b>  Mary R. Masson																																													
<b>EXPERIMENTAL VALUES:</b> <p style="text-align: center;">All concentrations are expressed in units of <math>\text{mol dm}^{-3}</math>.</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">Soln.</th> <th style="text-align: center;">Initial pH</th> <th style="text-align: center;">Final pH</th> <th style="text-align: center;"><math>[\text{Hg}^+]</math></th> <th style="text-align: center;">pHg</th> <th style="text-align: center;"><math>\log \alpha_{\text{L}(\text{H})}</math></th> <th style="text-align: center;"><math>p[\text{SeO}_3^{2-}]</math></th> <th style="text-align: center;"><math>pK_{\text{SO}}</math></th> </tr> </thead> <tbody> <tr> <td rowspan="2" style="text-align: center;"><math>\text{H}_2\text{SO}_4</math></td> <td style="text-align: center;">2.69</td> <td style="text-align: center;">2.72</td> <td style="text-align: center;"><math>5.8 \times 10^{-5}</math></td> <td style="text-align: center;">4.24</td> <td style="text-align: center;">5.49</td> <td style="text-align: center;">10.05</td> <td style="text-align: center;">18.53</td> </tr> <tr> <td style="text-align: center;">2.06</td> <td style="text-align: center;">2.20</td> <td style="text-align: center;"><math>1.3 \times 10^{-4}</math></td> <td style="text-align: center;">3.89</td> <td style="text-align: center;">6.20</td> <td style="text-align: center;">10.39</td> <td style="text-align: center;">18.17</td> </tr> <tr> <td rowspan="3" style="text-align: center;"><math>\text{HNO}_3</math></td> <td style="text-align: center;">2.95</td> <td style="text-align: center;">3.05</td> <td style="text-align: center;"><math>2.6 \times 10^{-5}</math></td> <td style="text-align: center;">4.58</td> <td style="text-align: center;">5.03</td> <td style="text-align: center;">9.92</td> <td style="text-align: center;">19.08</td> </tr> <tr> <td style="text-align: center;">2.40</td> <td style="text-align: center;">2.59</td> <td style="text-align: center;"><math>7.2 \times 10^{-5}</math></td> <td style="text-align: center;">4.14</td> <td style="text-align: center;">5.66</td> <td style="text-align: center;">10.10</td> <td style="text-align: center;">18.38</td> </tr> <tr> <td style="text-align: center;">2.08</td> <td style="text-align: center;">2.22</td> <td style="text-align: center;"><math>1.1 \times 10^{-4}</math></td> <td style="text-align: center;">3.96</td> <td style="text-align: center;">6.18</td> <td style="text-align: center;">10.44</td> <td style="text-align: center;">18.36</td> </tr> </tbody> </table> <p>The average value is <math>K_{\text{SO}} = 3.8 \times 10^{-19} \text{ mol}^3 \text{ dm}^{-9}</math>.            (<math>pK_{\text{SO}} = 18.42</math>)</p> <p><b>Notes.</b>  <math>[\text{Se}_{\text{tot}}] = [\text{Hg}^+]</math> and <math>[\text{SeO}_3^{2-}] = [\text{Se}_{\text{tot}}]/\alpha_{\text{L}(\text{H})}</math>            where <math>\alpha_{\text{L}(\text{H})} = (1 + [\text{H}^+]/K_2 + [\text{H}^+]^2/K_1K_2)</math>            and the acid dissociation constants have the values <math>K_1 = 4 \times 10^{-3}</math> and  <math>K_2 = 1.0 \times 10^{-8}</math> (ref. 1).</p> <p style="text-align: right;">(continued on next page)</p>		Soln.	Initial pH	Final pH	$[\text{Hg}^+]$	pHg	$\log \alpha_{\text{L}(\text{H})}$	$p[\text{SeO}_3^{2-}]$	$pK_{\text{SO}}$	$\text{H}_2\text{SO}_4$	2.69	2.72	$5.8 \times 10^{-5}$	4.24	5.49	10.05	18.53	2.06	2.20	$1.3 \times 10^{-4}$	3.89	6.20	10.39	18.17	$\text{HNO}_3$	2.95	3.05	$2.6 \times 10^{-5}$	4.58	5.03	9.92	19.08	2.40	2.59	$7.2 \times 10^{-5}$	4.14	5.66	10.10	18.38	2.08	2.22	$1.1 \times 10^{-4}$	3.96	6.18	10.44	18.36
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<b>AUXILIARY INFORMATION</b>																																														
<b>METHOD APPARATUS/PROCEDURE:</b> Solutions of nitric and sulfuric acids were saturated with mercury(I) selenite by shaking in a thermostat at $20 \pm 0.05^\circ\text{C}$ 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 mercury(I) concentration was determined by titration with 0.01N ammonium thiocyanate.	<b>SOURCE AND PURITY OF MATERIALS:</b> C.P.-grade reagents were used. Mercury(I) selenite was prepared by mixing 0.1N solutions of mercury(I) nitrate and sodium selenite in the cold. The precipitate was washed with water and dried at $20^\circ\text{C}$ . Mercury was determined by titration with ammonium thiocyanate, and selenium was determined gravimetrically as the element after precipitation with hydrazine.																																													
<b>ESTIMATED ERROR:</b> $\pm 2.2 \times 10^{-19}$ . (The spread in the results is 0.91 of a log unit.) Temperature: $\pm 0.05 \text{ K}$																																														
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1. Mercury(I) selenite; $\text{Hg}_2\text{SeO}_3$ ; [15855-76-2]		Chukhlantsev, V.G.; Tomashevsky, G.P.					
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3. Water; $\text{H}_2\text{O}$ ; [7732-18-5]							
COMMENTS AND/OR ADDITIONAL DATA:							
The authors were in error in treating the mercury(I) ion as $\text{Hg}^+$ , instead of as $\text{Hg}_2^{2+}$ , and in expressing $K_{\text{SO}}$ as $[\text{Hg}^+]^2 \cdot [\text{SeO}_3^{2-}]$ instead of as $[\text{Hg}_2^{2+}] \cdot [\text{SeO}_3^{2-}]$ . The compiler has recalculated the results in the correct form.							
Soln.	Initial pH	Final pH	$[\text{Hg}_2^{2+}]$	$\text{pHg}_2^{2+}$	$\log \alpha_{\text{L(H)}}$	$\text{p}[\text{SeO}_3^{2-}]$	$\text{p}K_{\text{SO}}$
$\text{H}_2\text{SO}_4$	2.69	2.72	$2.9 \times 10^{-5}$	4.54	5.49	10.05	14.59
	2.06	2.20	$6.5 \times 10^{-5}$	4.19	6.20	10.39	14.58
$\text{HNO}_3$	2.95	3.05	$1.3 \times 10^{-5}$	4.89	5.03	9.92	14.81
	2.40	2.59	$3.6 \times 10^{-5}$	4.44	5.66	10.10	14.54
	2.08	2.22	$5.5 \times 10^{-5}$	4.26	6.18	10.44	14.70
The average value is $K_{\text{SO}} = 2.3 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$ .							
$\text{p}K_{\text{SO}} = 14.64$ .							

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<p>VARIABLES:</p> <p>One temperature, probably 293 or 298 K</p>	<p>PREPARED BY:</p> <p>Mary R. Masson</p>																								
<p>EXPERIMENTAL VALUES:</p> <p>A solution in contact with a precipitate of <math>\text{Hg}_2\text{SeO}_3</math> was found to contain <math>4.97 \times 10^{-5} \text{ mol dm}^{-3}</math> mercury(I) and <math>7 \times 10^{-3} \text{ mol dm}^{-3}</math> total selenite at pH 3.4, and <math>4.57 \times 10^{-4} \text{ mol dm}^{-3}</math> mercury(I) and <math>1.3 \times 10^{-5} \text{ mol dm}^{-3}</math> total selenite at pH 2.2. Values for the solubility product can be calculated as follows (compiler).</p> <table border="1" data-bbox="162 664 1229 807"> <thead> <tr> <th>pH</th> <th><math>\log \alpha_{\text{L(H)}}</math></th> <th><math>[\text{Se}_{\text{tot}}]</math></th> <th><math>[\text{SeO}_3^{2-}]</math></th> <th><math>[\text{Hg(I)}]</math></th> <th><math>[\text{Hg}^{2+}]</math></th> <th><math>K_{\text{sO}}</math> <math>\text{mol}^2 \text{ dm}^{-6}</math></th> <th><math>\text{p}K_{\text{sO}}</math></th> </tr> </thead> <tbody> <tr> <td>3.4</td> <td>4.64</td> <td><math>7 \times 10^{-3}</math></td> <td><math>1.6 \times 10^{-7}</math></td> <td><math>4.97 \times 10^{-5}</math></td> <td><math>2.48 \times 10^{-5}</math></td> <td><math>4.0 \times 10^{-12}</math></td> <td>11.40</td> </tr> <tr> <td>2.2</td> <td>6.21</td> <td><math>&lt;1.3 \times 10^{-3}</math></td> <td><math>2.98 \times 10^{-10}</math></td> <td><math>4.57 \times 10^{-4}</math></td> <td><math>2.27 \times 10^{-4}</math></td> <td><math>&lt;1.8 \times 10^{-15}</math></td> <td><math>&gt;14.74</math></td> </tr> </tbody> </table> <p>If it is assumed that the wrong pH values have been assigned to the two solutions, the values 12.97 and <math>&gt;13.17</math> can be calculated for <math>\text{p}K_{\text{sO}}</math> and <math>1.07 \times 10^{-13}</math> and <math>&lt;6.76 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}</math> for <math>K_{\text{sO}}</math>.</p> <p>The temperature of the determination is not stated.</p> <p>*Calculated with <math>K_1 = 4 \times 10^{-4}</math> and <math>K_2 = 1 \times 10^{-8}</math> (ref. 1).</p>		pH	$\log \alpha_{\text{L(H)}}$	$[\text{Se}_{\text{tot}}]$	$[\text{SeO}_3^{2-}]$	$[\text{Hg(I)}]$	$[\text{Hg}^{2+}]$	$K_{\text{sO}}$ $\text{mol}^2 \text{ dm}^{-6}$	$\text{p}K_{\text{sO}}$	3.4	4.64	$7 \times 10^{-3}$	$1.6 \times 10^{-7}$	$4.97 \times 10^{-5}$	$2.48 \times 10^{-5}$	$4.0 \times 10^{-12}$	11.40	2.2	6.21	$<1.3 \times 10^{-3}$	$2.98 \times 10^{-10}$	$4.57 \times 10^{-4}$	$2.27 \times 10^{-4}$	$<1.8 \times 10^{-15}$	$>14.74$
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<p>METHOD APPARATUS/PROCEDURE:</p> <p>The results were obtained from the analysis of the filtrates obtained in two experiments. In one, the precipitation was done with excess of selenite, and in the other equivalent amounts were used. Mercury(I) was determined with dithizone after oxidation to mercury(II) with conc. nitric acid; and selenite was determined with 3,3'-diaminobenzidine.</p>	<p>SOURCE AND PURITY OF MATERIALS:</p> <p>Not stated.</p> <hr/> <p>ESTIMATED ERROR:</p> <hr/> <p>REFERENCES:</p> <p>1. Rumpf, P. <i>Compt. Rendu</i> <u>1933</u>, 197, 686.</p>																								