COMPONENTS:
1. Calcium selenite; CaSeO₃; [13780-18-2]
2. Water; H₂O; [7732-18-5]

VARIABLES:
One temperature: 291 K

EXPERIMENTAL VALUES:

<table>
<thead>
<tr>
<th>Concentration (mol dm⁻³)</th>
<th>Kₐ₀ (mol dm⁻⁶)</th>
<th>Mean Kₐ₀</th>
<th>pKₐ₀ (mol² dm⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.540 x 10⁻³</td>
<td>2.37 x 10⁻⁶</td>
<td>1.8 ± 1.1 x 10⁻⁶</td>
<td>5.74</td>
</tr>
<tr>
<td>1.557 x 10⁻³</td>
<td>2.42 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.581 x 10⁻³</td>
<td>2.50 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.095 x 10⁻³</td>
<td>1.20 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.127 x 10⁻³</td>
<td>1.26 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.052 x 10⁻³</td>
<td>1.10 x 10⁻⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The concentration c in the saturated solution was calculated from the measured conductivity K from the equation

\[ c = \frac{1000K}{\Lambda^0} \]

Compiler's note
Neither in the determination of the ionic conductivity of the selenite ion nor in the evaluation of the solubility product was hydrolysis of the selenite ion taken into account. This would give rise to errors, since, for example, in a 0.001 M solution, [SeO₃⁻²] = 0.0000955 M, [HSSeO₃] = 0.0000045 M and [OH⁻] = 0.0000045 M. and hydroxide and hydrogen selenite have different ionic conductivities from selenite. If the ionic conductivity of hydrogen selenite were known, the experimental results could have been interpreted correctly (cf. ref. 2), but this value does not seem to be available.

However, because the calibration and sample solutions had concentrations of about the same order of magnitude, the errors would cancel to some extent, but the Kₐ₀ value cannot be regarded as reliable.

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:
The ionic conductivity of the selenite ion in water was determined by measuring the mean molar conductivities of a series of aqueous solutions of lithium selenite with concentrations below 2 x 10⁻³ mol dm⁻³. The mean molar conductivity at infinite dilution was found by extrapolation to be 172 ± 2.9 Ω⁻¹ cm² mol⁻¹ at 18°C. At that temperature, the ionic conductivity of the lithium ion is 33.4 Ω⁻¹ cm² mol⁻¹, so the ionic conductivity of the selenite ion is 105.2 Ω⁻¹ cm² mol⁻¹. The well washed calcium selenite was mixed with 150 ml of water and agitated intermittently for 1 hr. From this, 10-20 ml was taken in the conductivity cell and the conductivity measured. The sampling and measurement were repeated until a constant value for the conductivity was obtained.

The value of \( \Lambda^0 = (\Lambda_+ + \Lambda_-) \), the molar conductivity, was calculated with \( \Lambda_+ = 105.2 \) and \( \Lambda_- = 102 \) Ω⁻¹ cm² mol⁻¹.

SOURCE AND PURITY OF MATERIALS:
Lithium selenite was prepared from sublimed selenium dioxide by neutralization with lithium hydroxide. An approximately 0.05 M solution was standardized gravimetrically, and this was used to prepare the various dilutions. The composition of the selenite was checked by analysis.

ESTIMATED ERROR:
Temperature: ±0.5 K
Error in \( K_{a0} \) (2s) = 1.1 x 10⁻⁶ (compiler)

REFERENCES:
1. Landolt-Bornstein Physicalisch-Chemische Tabellen II 1923, p. 1105.
**COMPONENTS:**

1. Calcium selenite: CaSeO$_3$; [13780-18-2]
2a. Hydrochloric acid: HCl; [7647-01-0]
2b. Nitric acid: HNO$_3$; [7697-37-2]
3. Water: H$_2$O; [7732-18-5]

**ORIGINAL MEASUREMENTS:**

Chukhlantsev, V.G.

**VARIABLES:**

HCl and HNO$_3$ concentrations
One temperature: 293 K

**EXPERIMENTAL VALUES:**

All concentrations are expressed in units of mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Soln.</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>[Ca$^{2+}$]</th>
<th>pCa</th>
<th>log a$_L$(H)</th>
<th>p[SeO$_3^{2-}$]</th>
<th>$K_{SO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>3.12</td>
<td>8.39</td>
<td>$1.72 \times 10^{-3}$</td>
<td>2.77</td>
<td>0.17</td>
<td>2.94</td>
<td>5.71</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>7.96</td>
<td>$3.1 \times 10^{-3}$</td>
<td>2.51</td>
<td>0.30</td>
<td>2.81</td>
<td>5.32</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
<td>5.89</td>
<td>$1.92 \times 10^{-2}$</td>
<td>1.72</td>
<td>2.10</td>
<td>3.82</td>
<td>5.54</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>2.88</td>
<td>7.87</td>
<td>$2.54 \times 10^{-3}$</td>
<td>2.60</td>
<td>0.38</td>
<td>2.98</td>
<td>5.58</td>
</tr>
<tr>
<td></td>
<td>1.98</td>
<td>5.56</td>
<td>$3.14 \times 10^{-2}$</td>
<td>1.50</td>
<td>2.40</td>
<td>3.90</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>2.42</td>
<td>6.64</td>
<td>$7.09 \times 10^{-2}$</td>
<td>2.15</td>
<td>1.35</td>
<td>3.50</td>
<td>5.65</td>
</tr>
</tbody>
</table>

The average value for $K_{SO}$ is $2.96 \times 10^{-6}$ mol$^2$dm$^{-6}$.

(p$K_{SO}$ = 5.53)

**Notes.**

$[Se_{tot}] = [Ca^{2+}]$ and $[SeO_3^{2-}] = [Se_{tot}] / a_L(H)$

where $a_L(H) = (1 + [H^+] / K_2 + [H^+]^2 / K_2 K_1)$

and the acid dissociation constants have the values $K_1 = 4 \times 10^{-3}$ and $K_2 = 1.0 \times 10^{-8}$ (ref. 1).

**AUXILIARY INFORMATION**

**METHOD APPARATUS/PROCEDURE:**

Solutions of hydrochloric and nitric acids were saturated with calcium 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 calcium concentration was measured (method not stated).

**SOURCE AND PURITY OF MATERIALS:**

C.P.-grade reagents were used. Calcium selenite was precipitated when 0.1N calcium chloride was mixed with a stoichiometric amount of sodium selenite, at 50 - 60°C. The precipitate was washed with water and dried at 40°C. Calcium was determined by precipitating the oxalate, then titrating with permanganate, and selenium gravimetrically as the element, after precipitation with hydrazine.

**ESTIMATED ERROR:**

The spread in the results is 0.31 of a log unit.

Temperature: probably ±0.05 K

**REFERENCES:**