

<p>COMPONENTS: Sparingly soluble selenites</p>	<p>EVALUATOR: Mary R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK.  July 1984.</p>
<p>CRITICAL EVALUATION:</p> <p>Much of the data for the solubilities of sparingly soluble selenites come from three papers (1 - 3) by two groups of workers. None of these data are totally satisfactory because the experimental procedures are deficient in certain respects.</p> <p>Ripan and Vericeanu (1) used the sensitive but unselective conductometric method to determine how much of the sparingly soluble salts had dissolved in water. Also, they neglected to make any correction for the hydrolysis of the selenite ion, or of any hydrolysable metal ion. Few replicates were done.</p> <p>Chukhlantsev (2) and Chukhlantsev and Tomashevsky (3) determined the conditional solubilities in acid solutions, in order to increase the concentrations to be determined. This procedure has the disadvantage that the subsequent calculations to find the solubility in pure water require values for the acid dissociation constants of selenious acid for the relevant temperature and in the same medium, and only estimates of these are available. Again, few replicate determinations were done. In this case, the chemistry was reasonably selective.</p> <p>The other work that has been done does not appear to be of much superior quality (4 - 18). Thus, even where 3 or 4 determinations have been made, it is impossible to make any reasoned choice between them. None of the values can be regarded as RECOMMENDED.</p> <p>The solubilities are usually reported in terms of concentration constants, generally as <math>K_{SO}</math> values. No attempts have been made to calculate the corresponding thermodynamic constants, since the media are not adequately defined to allow calculation of activity coefficients.</p> <p>Silver selenite has been studied by several authors (2, 11-15). The work of Chukhlantsev (2) has been discussed already. Lin and Pan (11) calculated <math>pK_{SO} = 14.74</math> from work on the silver selenite electrode, but they made several errors in their calculation, and attempted recalculations gave nonsensical figures, so this work is rejected (not compiled). Selivanova's work (12) seems careful, but hydrolysis of selenite is neglected, and it is not certain whether equilibrium was really reached. Mehra and Gubeli (13,14) did extensive work, but they made little use of the data collected. The calculations of the compiler have shown that there is a lack of consistency between the results obtained by the different experimental techniques employed. The work of Chao and Cheng (15) gives a value that ought to be reasonably reliable, but it is not certain whether silver-ion activities or concentrations were used to calculate the solubility product. Also, the constant refers to a freshly precipitated solid.</p>	

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CRITICAL EVALUATION: (continued)				
TERNARY SYSTEMS				
<p>The ternary systems barium selenite - selenium dioxide - water (5) and nickel selenite - selenium dioxide - water (9) have been studied. In the first case the solid phase <math>\text{BaSe}_2\text{O}_5</math> [83534-22-9] was observed, and in the second case, <math>\text{Ni}(\text{HSeO}_3)_2 \cdot 2\text{H}_2\text{O}</math> [83753-29-1].</p>				
GENERAL COMMENTS				
<p>My feeling about all the data for the sparingly soluble selenites is that they do little more than give some general guidance as to the solubility behaviour that is to be expected for the various metal selenites. There is certainly scope for much more experimental investigation of these systems.</p>				
NOTE				
<p>The Chemical Abstracts reports of some Russian papers (19 - 23) suggest that these give solubility product data, but there is no original experimental solubility work reported in these papers. They report calculations of 'theoretical' solubility products from other thermodynamic data, and comparison of these with literature values; and also correlations of other thermodynamic parameters.</p>				
REPORTED VALUES				
Ion	$K_{sO}$	$pK_{sO}$	Other constants	Ref.
$\text{Be}^{2+}$	$1.1 \times 10^{-8} \text{ mol}^2\text{dm}^{-6}$	7.96 a		1
$\text{Mg}^{2+}$	$1.9 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.72 a		1
	$1.29 \times 10^{-5} \text{ mol}^2\text{dm}^{-6}$	4.89 b		2
$\text{Ca}^{2+}$	$1.8 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.74 a		1
	$2.96 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.53 b		2
$\text{Sr}^{2+}$	$7.9 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.10 a		1
	$1.82 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.74 b		2
	$8.4 \times 10^{-7} \text{ mol}^2\text{dm}^{-6}$	6.07 b		2 *
	$4.23 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	5.37 c		4
$\text{Ba}^{2+}$	$6.2 \times 10^{-6} \text{ mol}^2\text{dm}^{-6}$	6.21 a		1
	$4.07 \times 10^{-7} \text{ mol}^2\text{dm}^{-6}$	6.39 c		4
	$4.45 \times 10^{-7} \text{ mol}^2\text{dm}^{-6}$	6.35 d		5
$\text{Mn}^{2+}$	$1.2 \times 10^{-7} \text{ mol}^2\text{dm}^{-6}$	6.9 b		3

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Ion	$K_{sO}$	$pK_{sO}$	Other constants	Ref.
Fe <sup>3+</sup>	$2.0 \times 10^{-31} \text{ mol}^5 \text{ dm}^{-15}$	30.7 b		2
	$3.7 \times 10^{-36} \text{ mol}^5 \text{ dm}^{-15}$	35.4 e		7
Co <sup>2+</sup>	$1.2 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$	6.92 a		1
	$1.6 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$	6.8 b		3
	$1.05 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$	7.98		8
	$1.17 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} (I = 0.3)$	5.93 e	$K_{\text{instab}} = 5.3 \times 10^{-4}$	8
	$1.14 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6} (I = 0.01)$	6.94 e	$K_{\text{instab}} = 6.25 \times 10^{-6}$	8
Ni <sup>2+</sup>	$5.1 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$	5.29 a		1
	$1.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$	5.0 b		3
Cu <sup>2+</sup>	$3.2 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$	7.49 a		1
	$2.09 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$	7.68 b		2
	$1.02 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$	7.99 e		10
Ag <sup>+</sup>	$9.7 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.01 b		2
	$2.85 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.55 c		12
	$1.43 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.84 c	recalc. value	
	$2.63 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.58 c	(alk. data) $I = 1$	13,14
	$2.34 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.63 c	(all data) $I = 1$ $\beta_1 = 2.63 \times 10^2 \text{ c}$ $\beta_2 = 5.75 \times 10^3 \text{ c}$	
	$3.55 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$	15.45 b	$I = 0.1$	15
Zn <sup>2+</sup>	$1.9 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$	7.71 a		1
	$2.58 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$	6.59 b		2
Cd <sup>2+</sup>	$6.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$	8.22 a		1
	$1.29 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$	8.89 b		2
	$4.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$	9.40 e		16
Hg <sub>2</sub> <sup>2+</sup>	$2.3 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$	14.64 b		3
	$8.7 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$	???		16

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CRITICAL EVALUATION: (continued)				
Ion	$K_{s0}$	$pK_{s0}$	Other constants	Ref.
Hg <sup>2+</sup>	$5.76 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$	14.24 e		16
	-	c	$K_{s2} = 4.42 \times 10^{-2}$	17
			( $pK_{s2} = 1.35$ )	
	$2.16 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$	14.67 c	$K_f \text{ for } \text{Hg}(\text{SeO}_3)_2^-$	18
			$= 10^{12.48} \text{ mol}^{-2} \text{ dm}^6$	
			$K_{s2} = 10^{-1.36}$	
Pb <sup>2+</sup>	$3.4 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$	11.5 b		3
	$3.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$	6.52 d		5
Temperatures: a - 291.2 K, b - 293.2 K, c - 298.2 K, d - 283.2 K, e - not stated, presumably ambient (293.2 - 298.2 K, usually)				
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CRITICAL EVALUATION: (continued)

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