COMPONENTS:	EVALUATOR:
1. Potassium selenite; K_2SeO_3; [10431-47-7]	Mary. R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK.
2. Water; H_2O; [7732-18-5]	June 1984.

CRITICAL EVALUATION:

The binary system potassium selenite – water was studied by Janickis (1,2), and data are also available from studies of ternary systems (3,4).

There are three regression equations, corresponding to the equilibria with ice, $K_2SeO_3.4H_2O$ [41292-06-2] and K_2SeO_3. For equation (3), two points had to be eliminated, but otherwise the data were in reasonable agreement.

The equations are (1) for 230 – 273 K, solid phase ice:

$$(T - 273.15) = -0.067 - 0.227y - 0.000154y^3 \qquad\qquad s = 0.44 \text{ (9 pts)}$$

or

$$y = 0.471 - 3.71(T - 293.2) - 0.105(T - 273.2)^2 - 0.00116(T - 273.2)^3$$
$$s = 1.01 \text{ (9 pts)}$$

(2) for 253 – 300 K, solid phase $K_2SeO_3.4H_2O$

$$y = 62.8 + 0.182(T - 273.2) + 0.00198(T - 273.2)^2 \qquad\qquad s = 0.111 \text{ (12 pts)}$$

and (3) for 273 – 353 K, solid phase K_2SeO_3:

$$v = 68.42 + 0.00007494(T - 273.2)^2 \qquad\qquad s = 0.037 \text{ (10 pts)}$$

where $y = 100w$ is the solubility expressed in mass % of K_2SeO_3, T is the temperature in K, and s is the standard deviation of the dependent variable about the regression line.

TENTATIVE SOLUBILITIES

The following tentative solubilities for K_2SeO_3 in water were calculated from equations (2) and (3).

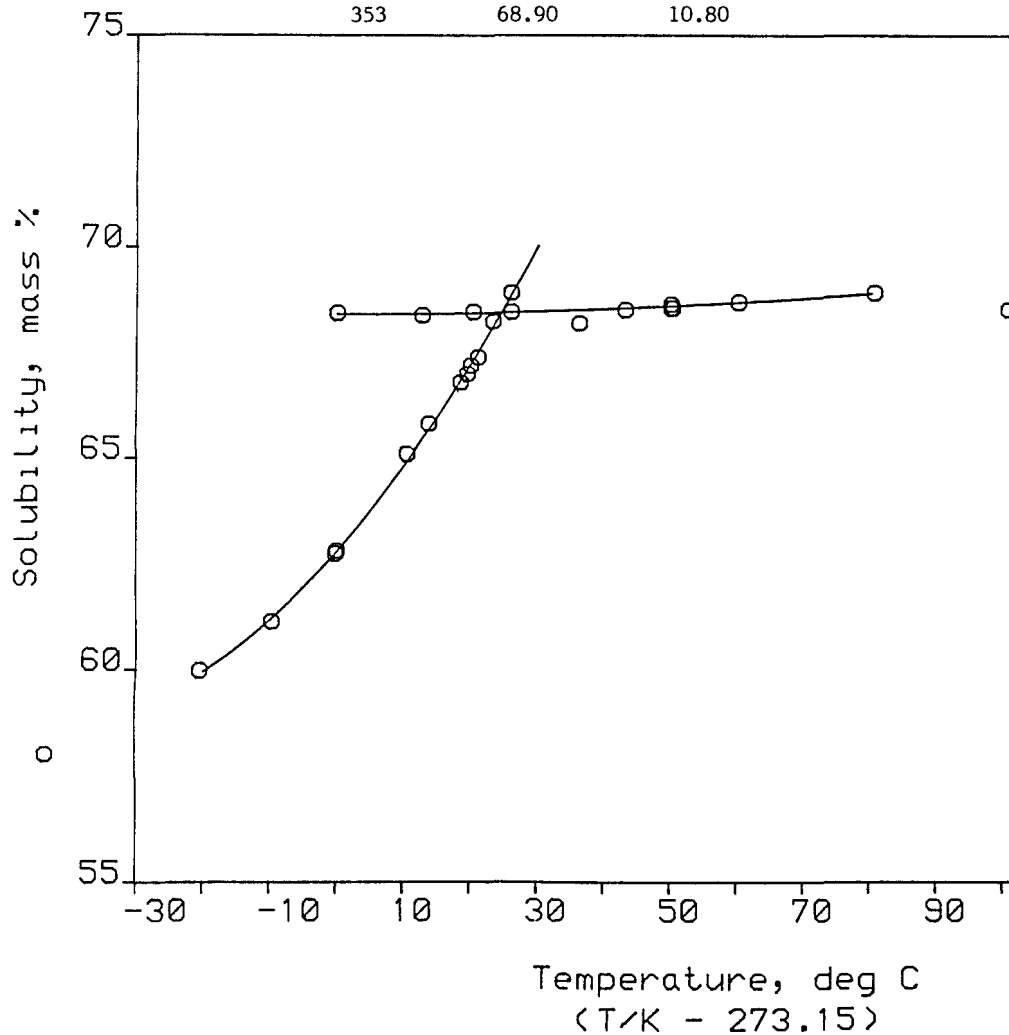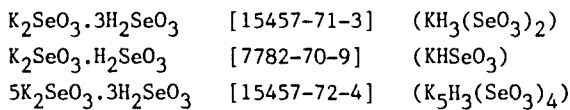| COMPONENTS:	EVALUATOR:
1. Potassium selenite; K_2SeO_3; [10431–47–7] 2. Water; H_2O; [7732–18–5]	Mary. R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK. June 1984.

CRITICAL EVALUATION: (continued)

T/K	Solubility	
	mass %	molality mol/kg
	$K_2SeO_3 \cdot 4H_2O$	
253	60.0	7.31
263	61.2	7.69
273	62.8	8.23
283	64.8	8.97
293	67.2	9.99
300	69.2	10.95
	K_2SeO_3	
273	68.42	10.56
283	68.43	10.57
293	68.45	10.58
303	68.49	10.59
313	68.54	10.62
323	68.61	10.65
333	68.69	10.69
343	68.79	10.74
353	68.90	10.80

COMPONENTS:	EVALUATOR:
1. Potassium selenite; K_2SeO_3; [10431-47-7] 2. Water; H_2O; [7732-18-5]	Mary. R. Masson, Dept. of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland, UK. June 1984.

CRITICAL EVALUATION: (continued)

TERNARY SYSTEMS

The ternary systems involving potassium sulfite (3) and ethanol (4) are straightforward and the data appear to be reliable. In the system involving selenious acid (5) three double salts are formed.

$$K_2SeO_3.3H_2SeO_3 \quad [15457-71-3] \quad (KH_3(SeO_3)_2)$$
$$K_2SeO_3.H_2SeO_3 \quad [7782-70-9] \quad (KHSeO_3)$$
$$5K_2SeO_3.3H_2SeO_3 \quad [15457-72-4] \quad (K_5H_3(SeO_3)_4)$$

These salts are not identical to the ones formed in the corresponding sodium system.

REFERENCES

1. Janitzki, J. Z. Anorg. Allgem. Chem. 1932, 205, 49.

2. Janickis, J.; Gutmanaite, H. Z. Anorg. Allgem. Chem. 1936, 227, 1.

3. Klebanov, G.S.; Ostapkevich, N.A. Zh. Priklad. Khim. 1966, 39, 2467; *J. Appl. Chem. USSR (Eng. Transl.) 1966, 39, 2315.

4. Klebanov, G.S.; Ostapkevich, N.A. Zh. Priklad. Khim. 1966, 39, 1435; *J. Appl. Chem. USSR (Eng. Transl.) 1966, 39, 1342.

5. Sabbah, R.; Périnet, G. J. Chim. Phys. 1966, 63, 332.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selenite; K_2SeO_3; [10431-47-7] 2. Water; H_2O; [7732-18-5]	Janitzki, J. Z. Anorg. Allgem. Chem. 1932, 205, 49-75.
VARIABLES: Temperature: 253 - 374 K	PREPARED BY: Mary R. Masson

EXPERIMENTAL VALUES:

t/°C	K_2SeO_3 mass %	K_2SeO_3[a] mol/kg	Solid[b] phase
-20.5	59.98	7.305	B
- 9.7	61.14	7.669	B
- 0.2	62.76	8.214	B
+10.5	65.11	9.096	B
13.8	65.83	9.390	B
18.5	66.80	9.807	B
19.5	67.00	9.896	B
21.1	67.40	10.077	B
23.3	68.25	10.478	B
26.0	68.93	10.814	B
0.0	68.45	10.575	A
12.7	68.40	10.551	A
20.3	68.48	10.590	A
26.0	68.48	10.590	A
36.2	68.20	10.454	A
43.1	68.52	10.609	A
50.2	68.56	10.629	A
60.1	68.70	10.698	A
80.5	68.92	10.809	A
100.6	68.53	10.614	A

[a] Molalities calculated by the compiler.

[b] Solid phases: A - K_2SeO_3, B - $K_2SeO_3 \cdot 4H_2O$

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
For each temperature, a saturated solution was prepared by stirring the salt in water inside a stoppered 4-cm diameter test-tube. Small samples of solution were removed at intervals for analysis, in order to test for attainment of equilibrium. The time required varied between 3 and 23 hr. The solutions were analysed for SeO_2 by the method of Norris and Fay (1). The solid phases were identified by analysis.	

ESTIMATED ERROR:
Temperature: -20 - 0°C ±0.2°C, 0 - 60°C ±0.1°C, 60 - 110°C ±0.3°C Analyses: no estimate possible.

REFERENCES.
1. Norris, J.F.; Fay, H. Amer. Chem. J. 1896, 18, 703; 1900, 23, 119.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selenite; K_2SeO_3; [10431-47-7] 2. Water; H_2O; [7732-18-5]	Janickis, J.; Gutmanaite, H. *Z. Anorg. Allgem. Chem.* 1936, 227, 1-16.

VARIABLES:	PREPARED BY:
Temperature: 230 - 273 K Composition	Mary R. Masson

EXPERIMENTAL VALUES:

Compositions of equilibrium solutions

$t/°C$	K_2SeO_3 mol/dm^3	K_2SeO_3 mass %	K_2SeO_3[a] mol/kg	Solid phase
- 0.262	0.05	1.019	0.0502	ice
- 0.500	0.1	2.021	0.1006	"
- 0.970	0.2	3.987	0.2024	"
- 2.375	0.5	9.54	0.514	"
- 5.03	1	17.87	1.060	"
-13.0	2	32.01	2.294	"
-23.6	3.194	45.13	4.01	"
-43.5	satd.	58.0	6.74	ice + K_2SeO_3

[a] Molalities calculated by the compiler.

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Freezing points of prepared solutions were measured by use of a Beckman-type apparatus (1). Determinations were repeated until the desired reproducibility was attained. Each reported value is the mean of at least three determinations.	Potasium selenite was prepared by neutralization of selenious acid with potassium hydroxide.

ESTIMATED ERROR:

Temperature reproducibility 0.5%

REFERENCES:
1. Ostwald, W.; Luther, R. *Hand- und Hilfsbuch zur Ausfuhrung physikochem- ischer Messungen*, 5th Ed., Akademische Verlag., Leipzig, 1931.

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selente; K_2SeO_3; [10431-47-7] 2. Potassium sulfite; K_2SO_3; [10117-38-1] 3. Water; H_2O; [7732-18-5]	Klebanov, G.S.; Ostapkevich, N.A. *Zh. Prikl. Khim.* 1966, *39*, 2467-2470; *J. Appl. Chem. USSR (Eng. Transl)* 1966, *39*, 2315-8.

VARIABLES:	PREPARED BY:
Two temperatures: 273 and 333 K Potassium selenite and potassium sulfite concentrations.	Mary R. Masson

EXPERIMENTAL VALUES:

Composition of equilibrium solutions

K_2SeO_3 mass %	K_2SO_3 mass %	K_2SeO_3[a] mol/kg	K_2SO_3[a] mol/kg	Solid[b] phase
Temperature = 0°C				
62.83	–	8.239	0.	B
56.02	3.97	6.825	0.627	B
50.64	8.00	5.968	1.222	B
49.51	10.50	6.035	1.659	B + C
45.10	12.03	5.128	1.773	C
35.21	20.25	3.853	2.873	C
20.30	32.50	2.096	4.351	C
12.86	38.51	1.289	5.004	C
–	51.40	0.	6.683	C
Temperature = 50°C				
68.56	–	10.629	0.	A
59.50	5.50	8.286	0.993	A
52.80	10.90	7.090	1.897	A
51.30	13.70	7.144	2.473	A + C
46.00	15.20	5.779	2.475	C
32.50	24.11	3.651	3.511	C
23.31	32.74	2.585	4.707	C
17.10	38.00	1.856	5.348	C
12.50	42.01	1.339	5.835	C
–	52.00	0.	6.845	C

[a] Molalities calculated by the compiler.

[b] Solid phases: A – K_2SeO_3, B – $K_2SeO_3.4H_2O$, C – K_2SO_3

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:

Mixtures of K_2SeO_3 and K_2SO_3 were dissolved isothermally in water contained in glass vessels with stirrers fitted with hydraulic seals. Trace amounts of p-phenylenediamine were added to the solutions to prevent aerial oxidation of the sulfite. 0°C was maintained by melting ice, and 50°C with the aid of a contact thermometer and electromagnetic relay. Equilibrium was reached after 2 days at 0°C and 30-35 hr at 50°C.
    The solutions were analysed for selenite and sulfite as follows. For sulfite, sodium bicarbonate and excess of 0.1N iodine solution were added, then the solution was acidified with acetic acid, and the excess of iodine was titrated with thiosulfate. For selenite, sulfite was bound with formaldehyde, the solution was acidified with HCl, and KI was added. The iodine liberated was titrated with thiosulfate.
    The solid residues were also analysed. The compositions of the solid phases were determined by Schreinemakers' remainder method.
	Potassium selenite was of reagent-grade quality, and potassium sulfite was prepared from "pure" grade potassium sulfite by salting out with alcohol (99.8% salt content).

	ESTIMATED ERROR: Temperature: ±0.1 K Analyses: no estimate possible.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selenite; K_2SeO_3; [10431-47-7] 2. Ethanol; C_2H_5OH; [64-17-5] 3. Water; H_2O; [7732-18-5]	Klebanov, G.S.; Ostapkevich, N.A. *Zh. Priklad. Khim.* 1966, 39, 1435-7; **J. Appl. Chem. USSR (Eng. Transl.)* 1966, 39, 1342-4.

VARIABLES:	PREPARED BY:
Two temperatures: 293 and 323 K Ethanol concentration	Mary R. Masson

EXPERIMENTAL VALUES:

Initial C_2H_5OH mass %	K_2SeO_3 mass %	Upper layer C_2H_5OH mass %	K_2SeO_3[a] mol/kg	C_2H_5OH[a] mol/kg	K_2SeO_3 mass %	Lower layer C_2H_5OH mass %	K_2SeO_3[a] mol/kg	C_2H_5OH[a] mol/kg	Solid[b] phase
Temperature = 20°C									
0.0	–	–	–	–	67.2	–	9.986	–	B
2.0		not enough sample			64.37	1.85	9.288	1.189	B
10.0	0.44	77.16	0.096	74.770	63.79	1.33	8.914	0.828	B
30.0	0.45	77.15	0.098	74.760	63.63	1.32	8.849	0.817	B
50.0	0.46	77.21	0.096	75.053	63.53	1.31	8.807	0.809	B
70.0	0.44	77.21	0.096	74.986	63.45	1.30	8.774	0.801	B
80.0	0.42	78.05	0.095	78.688	–	–	–	–	A
90.0	0.39	86.23	0.142	139.889	–	–	–	–	A
Temperature = 50°C									
0.0	–	–	–	–	68.65	–	10.674	–	A
10.0	0.53	75.32	0.107	67.698	65.01	1.65	9.504	1.074	A
30.0	0.53	75.33	0.107	67.735	64.91	1.64	9.459	1.064	A
50.0	0.53	75.41	0.107	68.032	65.00	1.63	9.494	1.060	A
70.0	0.52	75.34	0.105	67.744	65.02	1.64	9.506	1.068	A
80.0	0.45	78.48	0.104	80.849	–	–	–	–	A
90.0	0.35	85.81	0.123	134.581	–	–	–	–	A

[a] Molalities calculated by the compiler.

[b] Solid phases: A – K_2SeO_3, B – $K_2SeO_3 \cdot 4H_2O$

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Aqueous ethanolic solutions were saturated with potassium selenite at 20 and 50°C in glass vessels (100-150 ml), fitted with hydraulic seals at 20°C and with reflux condensers at 50°C. Equilibrium was reached after 16-28 hr. Selenite in the solutions and moist solids was determined iodometrically, and ethanol iodometrically after distillation from the samples.	Reagent-grade potassium selenite was used. Ethanol and water were distilled twice.
	ESTIMATED ERROR: Temperature: ±0.1 K Analyses: no estimate possible.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selenite; K_2SeO_3; [10431-47-7]	Sabbah, R.; Périnet, G.
2. Selenious acid; H_2SeO_3; [7783-00-8]	*J. Chim. Phys.* 1966, *63*, 332-6.
3. Water; H_2O; [7732-18-5]	

VARIABLES:	PREPARED BY:
Temperature: 298 K Concentrations of the components	Mary R. Masson

EXPERIMENTAL VALUES:

Composition of equilibrium solutions, mol/1000 g of solution, at 25°C.

Na/Se	$[H_2SeO_3]$ total	$[H_2SeO_3]$ free	$[K_2SeO_3]$	Solid[a] phase
0.0	6.23	6.23	0.0	A
0.093	6.60	6.29	0.309	A
0.147[6]	6.86	6.35	0.505	A
0.174	6.99	6.38	0.607	A
0.220	7.32	6.51	0.808	A
0.254	7.03	6.14	0.890	B
0.274	6.32	5.46	0.864	B
0.378	5.45	4.42	1.03	B
0.502	4.75	3.56	1.19	B
0.696	4.57	2.98	1.59	B
0.728	4.56	2.90	1.66	B
0.868	5.42	3.07	2.35	B + C
0.968	5.12	2.64	2.48	C
1.04	4.94	2.38	2.56	C
1.10	4.75	2.13	2.62	C
1.20	4.62	1.84	2.78	C
1.28	4.52	1.62	2.90	C + D
1.33	4.36	1.45	2.91	D
1.43	4.19	1.20	2.99	D
1.53	4.03	0.941	3.09	D
1.60	4.08	0.815	3.26	D
1.64	3.98	0.710	3.27	E
1.74	3.83	0.489	3.34	E
1.86	3.61	0.248	3.36	E
2.00	3.40	0.0	3.40	E

[a]Solid phases:

A – H_2SeO_3

B – $K_2SeO_3 \cdot 3H_2SeO_3$

C – $K_2SeO_3 \cdot H_2SeO_3$

D – $5K_2SeO_3 \cdot 3H_2SeO_3$

E – K_2SeO_3

AUXILIARY INFORMATION

METHOD APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
A series of solutions of differing extents of neutralization of selenious acid were kept until crystals formed. The mixture of crystals and saturated solution was placed in a conical flask, which was sealed and then agitated in a thermostat at 25°C for up to a week. The solutions were analysed by potentiometric titration with hydrochloric acid or sodium hydroxide solution. Crystals could not be obtained from solutions with Na/Se between 0.22 and 0.25. The solids were identified and characterized by thermogravimetry, differential thermal analysis, and X-ray diffraction; but some difficulties were encountered, owing to the deliquescence and hygroscopicity of some of the solid phases.	Water was distilled and demineralized. Its final conductivity at 25°C was about 2×10^{-5} $ohm^{-1}m^{-1}$. Selenious acid (Fluka) was found by analysis to be 99.6% pure.
	ESTIMATED ERROR: Temperature: ± 0.05 K
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
1. Potassium selenite; K_2SeO_3; [10431-47-7]	Sabbah, R.; Périnet, G.
2. Selenious acid; H_2SeO_3; [7783-00-8]	*J. Chim. Phys.* <u>1966</u>, *63*, 332-6.
3. Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES (continued):

Composition of solutions expressed in units of mass % and mol/kg

H_2SeO_3[b] mass %	K_2SeO_3[b] mass %	H_2SeO_3[c] mol/kg	K_2SeO_3[c] mol/kg
80.355	0.	31.712	0.
81.128	6.339	50.191	2.466
81.902	10.361	82.072	6.527
82.289	12.453	121.349	11.545
83.966	16.577	–	–
79.194	18.259	241.064	34.943
70.423	17.726	46.072	7.290
57.009	21.131	20.220	4.712
45.917	24.414	11.999	4.011
38.436	32.620	10.296	5.493
37.404	34.057	10.161	5.817
39.597	48.213	25.183	19.277
34.051	50.880	17.519	16.457
30.697	52.521	14.182	15.255
27.473	53.752	11.345	13.954
23.732	57.034	9.567	14.454
20.895	59.496	8.626	14.789
18.702	59.702	6.714	13.475
15.478	61.343	5.177	12.899
12.137	63.394	3.846	12.628
10.512	66.882	3.605	14.421
9.158	67.087	2.989	13.765
6.307	68.523	1.943	13.270
3.199	68.934	0.890	12.057
0.	69.754	0.	11.241

[b] Mass % values calculated by the compiler.
[c] Molalities calculated by the compiler.