

## THE CHANGE IN THE STANDARD GIBBS ENERGY DURING THE FORMATION OF THE ACID SELENITES OF THE ALKALI METALS

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The heterogeneous  $M_2SeO_3-H_2SeO_3-H_2O$  systems ( $M = Li, Na, K, Rb, Cs$ ) were studied at 298 K using the Filippov eutonic method, yielding the values of the change in the standard Gibbs energy of reactions leading to the formation of the acid selenites of these metals. It follows from the  $\Delta G^0$  values that the stability of hydrogenselenites and trihydrogenbis(selenites) increases from lithium to cesium and also, except for cesium salts, on transition from  $MHSeO_3$  to  $MH_3(SeO_3)_2$ .

Filippov's eutonic method<sup>1-3</sup> can be used to study the energy conditions under which compounds are formed by phase reactions in heterogeneous systems. This method, which permits calculation of the change in the standard Gibbs energy of the heterogeneous reaction, is based on the assumption that the chemical potentials of the initial compounds of the system and of the compounds formed are equal at the eutonic point (at equilibrium). Using the Gibbs-Duhem relationship, the chemical potential of the initial components can be replaced in the calculation by the chemical potential of the solvent which can be obtained by measurement of the vapour pressure above the saturated solutions.

Lukeš and Ebert<sup>4,5</sup> used the Filippov eutonic method to calculate the change in the standard Gibbs energy for heterogeneous reactions leading to the formation of acid phosphites in saturated aqueous solutions. In this work, the same procedure is used to measure the energy conditions under which the acid selenites of the alkali metals are formed.

### EXPERIMENTAL

*Chemicals and methods.* Commercially produced chemicals (Lachema, Brno) of *p.a.* purity or pure chemicals were used. The selenites  $Li_2SeO_3 \cdot H_2O$ ,  $K_2SeO_3$ ,  $Rb_2SeO_3$ , and  $Cs_2SeO_3 \cdot H_2O$  were obtained by neutralization of selenious acid using the appropriate carbonate.

The prepared compounds and the phases of the heterogeneous systems were analyzed titrimetrically (iodometric determination of  $Se^{IV}$ )<sup>6</sup>, gravimetrically (selenium, alkali metals)<sup>7,8</sup>, and by the AAS method (alkali metals).

The experimental procedure included preparation of suitable heterogeneous mixtures of selenious acid, the studied selenite and water, checking of the equilibrium established, analysis

of the liquid and solid phases of the sample and the actual measurement of the water vapour pressure above the system.

The preparation of the heterogeneous mixtures was based on the results of study of the isothermic-isobaric phase diagrams<sup>9</sup> so that the amount of liquid phase after equilibrium establishment was at least 25 ml and so that its composition corresponded to the invariant point or to points evenly distributed along the solubility curves. For incongruently soluble compounds, 5–7 samples were prepared for measuring the water vapour pressure by this method, and for congruently soluble compounds, 8–10 samples.

The water vapour pressure above the heterogeneous system was measured psychrometrically<sup>9,10</sup> and by the isopiestic method<sup>11</sup>. The liquid phase was separated from mixtures where the assumed water vapour pressure would be greater than 1.0 kPa above the solution and was measured by the psychrometric method. Mixtures with lower water vapour pressures were measured by the isopiestic method and both phases were used in the measurement.

The change in the standard Gibbs energy in the heterogeneous reaction was calculated using a Hewlett-Packard 9845 B computer.

### THEORETICAL

For incongruently soluble compounds, where the change in the standard Gibbs energy  $\Delta G^0$  of the heterogeneous reaction of two components in a molar ratio of 1 : 1 is given by the relationship

$$\Delta G^0 = (\mu_2^B - \mu_2^A) = \int_A^B [x_3/(x_2 - x_1)] d\mu_3 \quad (1)$$

( $x_i$  and  $\mu_i$  are the mole percent and the chemical potential of the  $i$ -th component of the solution and  $A$  and  $B$  are invariant points on the solubility curve of the given compound), the mole percents were originally found using the Gibbs–Duhem relationship and were expressed as a dependence on the chemical potential of water ( $\mu_3$ ). This dependence was obtained using cubic spline interpolation<sup>12</sup>, permitting carrying out the subsequent integration on a computer. In the calculation of  $\Delta G^0$  for reactions leading to the formation of congruently soluble compounds, where it holds that

$$\Delta G^0 = (\mu_2^B - \mu_2^A) = \int_A^B [x_3/(x_2 - x_1)] (\partial\mu_3/\partial x_2) dx_2, \quad (2)$$

the dependence of the chemical potential of water on the mole percent of selenious acid ( $x_2$ ) was expressed using a polynomial of the second to fourth degree. Analytical expression of this dependence permitted calculation of the differential  $\partial\mu_3/\partial x_2$  and the values obtained for the given  $x_2$  values were multiplied by the values of the fraction  $x_3/(x_2 - x_1)$  and plotted against  $x_2$ . The curve for the given dependence was again obtained using cubic spline interpolation and the subsequent integration was carried out using a computer.

The relative standard deviation in the measurement of the water vapour pressure by the psychrometric and isopiestic methods<sup>4,9,11</sup> was less than 0.3%. In addition to the activity of water, the composition of the liquid phase at the selected points along the solubility curve had to be known. Using these analytical methods, the relative error in the analysis was not greater than 0.5%. The mathematical procedure for calculating the  $\Delta G^0$  values for congruently soluble compounds was subject to an error following from the expression of the dependence of the  $\mu_3 = f(x_2)$  polynomial function. The degree of fit to this dependence using the regression polynomial was expressed by the values of the multiple correlation coefficient  $R^2$ , lying in the range

0.976–0.999, corresponding to good fit to the empirical dependence. A further source of error resulting from graphical integration in earlier works<sup>4,5</sup> using the Filippov eutonic method was greatly limited by use of a computer and fitting of points using the cubic spline interpolation method. Repeated calculation of selected integrals indicated that the relative error in the calculated changes in the standard Gibbs energy was not greater than 3%.

## RESULTS AND DISCUSSION

The compositions of the liquid and solid phases and the results of measurement of the water vapour pressure in the study of the  $M_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$  systems ( $M = \text{Li, Na, K, Rb, Cs}$ ) at 298 K are listed in Tables I–V. These values and

TABLE I  
Physical data for the  $\text{Li}_2\text{SeO}_3\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$  system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $\text{kJ mol}^{-1}$	Composition of the solid phase <sup>a</sup>
$\text{Li}_2\text{SeO}_3$	$\text{H}_2\text{SeO}_3$	$\text{H}_2\text{O}$			
—	36.3	63.7			<i>a</i>
1.40	37.1	61.5			<i>a</i>
2.46	39.2	58.3	0.2960	−3.015	<i>A a + b</i>
2.50	38.1	59.4	0.3115	−2.90	<i>b</i>
2.53	31.0	66.5	0.4075	−2.235	<i>b</i>
3.14	23.2	73.7	0.4990	−1.725	<i>b</i>
4.48	15.7	79.8	0.5785	−1.355	<i>b</i>
5.75	13.5	80.8	0.5950	−1.285	<i>b</i>
7.12	12.0	80.9	0.5970	−1.280	<i>b</i>
7.74	12.1	80.2	0.5830	−1.335	<i>b</i>
8.50	12.4	79.1	0.5690	−1.395	<i>B b + c</i>
8.57	11.9	79.5	0.5785	−1.355	<i>c</i>
8.60	11.5	79.9	0.5820	−1.420	<i>c</i>
8.60	11.2	80.2	0.5900	−1.310	<i>c</i>
9.0	10.3	80.7	0.5975	−1.275	<i>c</i>
9.23	10.1	80.7	0.5970	−1.280	<i>c</i>
9.58	9.89	80.5	0.5930	−1.295	<i>C c + d</i>
7.29	6.80	85.9			<i>d</i>
5.20	4.16	90.6			<i>d</i>
4.20	2.80	93.0			<i>d</i>
2.93	8.76	96.20			<i>d</i>
3.34	—	96.7			<i>d</i>

<sup>a</sup> *A, B, C* are invariant points; *a* —  $\text{H}_2\text{SeO}_3$ , *b* —  $\text{LiH}_3(\text{SeO}_3)_2$ , *c* —  $\text{LiHSeO}_3$ , *d* —  $\text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ .

relationships (1) and (2) were employed in the procedure described in the study of acid phosphites<sup>4,5</sup> to calculate the changes in the standard Gibbs energy  $\Delta G^0$  in the heterogeneous reactions leading to the formation of the acid salts present in the given heterogeneous systems. The studied heterogeneous reactions and values of  $\Delta G^0$  obtained are listed in Table VI.

TABLE II  
Physical data for the  $\text{Na}_2\text{SeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$  system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $\text{kJ mol}^{-1}$	Composition of the solid phase <sup>a</sup>
$\text{Na}_2\text{SeO}_3$	$\text{H}_2\text{SeO}_3$	$\text{H}_2\text{O}$			
—	36.3	63.7			<i>a</i>
0.70	37.2	62.1			<i>a</i>
1.54	39.9	58.5	0.3345	-2.715	<i>A</i> <i>a</i> + <i>b</i>
1.54	38.4	60.1	0.3495	-2.605	<i>b</i>
1.75	36.0	62.3	0.3690	-2.470	<i>b</i>
2.17	33.4	64.5	0.3975	-2.285	<i>b</i>
2.51	32.6	64.9	0.4030	-2.255	<i>b</i>
2.53	30.9	66.6	0.4150	-2.180	<i>B</i> <i>b</i> + <i>c</i>
2.55	29.8	67.7	0.4370	-2.050	<i>c</i>
2.66	28.7	68.6	0.4500	-1.980	<i>c</i>
2.70	26.9	70.4	0.4730	-1.855	<i>c</i>
3.35	10.7	85.9	0.6725	-0.985	<i>c</i>
6.33	8.26	85.4	0.6660	-1.010	<i>c</i>
7.15	8.84	84.0	0.6425	-1.095	<i>c</i>
7.85	9.34	82.8	0.6295	-1.150	<i>c</i>
8.81	10.5	80.7	0.6040	-1.250	<i>C</i> <i>c</i> + <i>d</i>
8.97	10.2	80.8	0.6065	-1.240	<i>d</i>
9.04	9.95	81.0	0.6080	-1.235	<i>d</i>
9.95	7.59	82.5	0.6280	-1.155	<i>d</i>
11.4	6.69	81.9	0.6195	-1.190	<i>d</i>
12.1	6.49	81.4	0.6115	-1.220	<i>d</i>
12.6	6.25	81.1	0.6080	-1.235	<i>D</i> <i>d</i> + <i>e</i>
11.7	5.03	83.3			<i>e</i>
10.9	3.66	85.4			<i>e</i>
10.5	2.62	86.9			<i>E</i> <i>e</i> + <i>f</i>
9.58	1.83	88.6			<i>f</i>
8.47	—	91.5			<i>f</i>

<sup>a</sup> *A*, *B*, *C*, *D*, *E* are invariant points; *a* —  $\text{H}_2\text{SeO}_3$ , *b* —  $\text{NaH}_7(\text{SeO}_3)_4$ , *c* —  $\text{NaH}_3(\text{SeO}_3)_2$ , *d* —  $\text{NaHSeO}_3$ , *e* —  $\text{Na}_2\text{SeO}_3$ , *f* —  $\text{Na}_2\text{SeO}_3 \cdot 5 \text{H}_2\text{O}$ .

TABLE III  
Physical data for the  $K_2SeO_3-H_2SeO_3-H_2O$  system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $kJ\ mol^{-1}$	Composition of the solid phase <sup>a</sup>
$K_2SeO_3$	$H_2SeO_3$	$H_2O$			
—	36.3	63.7			<i>a</i>
1.69	43.4	54.9			<i>a</i>
5.64	63.0	31.4			<i>a</i>
8.7	91.3	—			<i>A</i> <i>a</i> — <i>b</i>
					melt
7.31	48.7	44.0			<i>b</i>
6.54	38.4	55.0			<i>b</i>
5.41	25.9	68.7			<i>b</i>
5.14	20.3	74.5			<i>b</i>
4.50	15.1	80.4			<i>b</i>
11.0	19.2	69.8			<i>b</i>
18.0	25.4	56.7	0.3510	—2.595	<i>B</i> <i>b</i> + <i>c</i>
18.0	23.6	58.4	0.3765	—2.420	<i>c</i>
15.0	18.9	66.1	0.4675	—1.85	<i>c</i>
14.2	16.9	68.9	0.5040	—1.700	<i>c</i>
13.8	15.0	71.2	0.5305	—1.570	<i>c</i>
13.7	13.3	73.0	0.5565	—1.455	<i>c</i>
14.4	12.6	73.0	0.5540	—1.465	<i>c</i>
15.3	12.4	72.2	0.5450	—1.505	<i>c</i>
16.0	11.5	72.2	0.5400	—1.525	<i>c</i>
17.1	11.0	71.8	0.5375	—1.540	<i>c</i>
17.8	10.1	72.1	0.5405	—1.525	<i>C</i> <i>c</i> + <i>d</i>
18.2	9.18	72.6	0.5510	—1.475	<i>d</i>
18.3	8.34	73.4	0.5600	—1.495	<i>d</i>
18.6	7.88	73.5	0.5635	—1.420	<i>d</i>
18.9	7.53	73.6	0.5635	—1.420	<i>d</i>
20.0	7.41	72.5	0.5495	—1.485	<i>d</i>
21.1	6.80	72.1	0.5410	—1.525	<i>d</i>
21.8	6.67	71.6	0.5395	—1.530	<i>D</i> <i>d</i> + <i>e</i>
18.7	3.06	78.2			<i>e</i>
17.1	1.40	81.5			<i>e</i>
16.1	—	83.9			<i>e</i>

<sup>a</sup> *A*, *B*, *C*, *D* are invariant points; *a* —  $H_2SeO_3$ , *b* —  $KH_3(SeO_3)_2$ , *c* —  $KHSeO_3$ , *d* —  $K_5H_3(SeO_3)_4$ , *e* —  $K_2SeO_3$ .

Study of the  $M_2SeO_3-H_2SeO_3-H_2O$  heterogeneous systems ( $M = Li, Na, K, Rb, Cs$ ) at 298 K on the basis of measurement of the water vapour pressure indicated the presence of hydrogenselenite  $MHSeO_3$  and trihydrogenbis(selenite)  $MH_3(SeO_3)_2$  for all the alkali metals and also the compounds  $NaH_7(SeO_3)_4$ ,  $K_5H_3(SeO_3)_4$ , and  $CsH_5(SeO_3)_3$ . The measured water vapour pressure measurements were then used to calculate the changes in the standard Gibbs energy  $\Delta G^0$  for the formation of the given acid salts. As the solubility diagrams for potassium and rubidium selenites contain a melt region and the change in the standard Gibbs energy can not be calculated for the reaction of selenious acid with selenites or with hydrogenselenites, the reaction

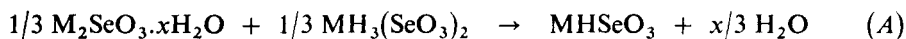


TABLE IV  
Physical data for the  $Rb_2SeO_3-H_2SeO_3-H_2O$  system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $\text{kJ mol}^{-1}$	Composition of the solid phase <sup>a</sup>
$Rb_2SeO_3$	$H_2SeO_3$	$H_2O$			
—	36.3	63.7			<i>a</i>
1.16	38.7	60.1			<i>a</i>
2.23	42.9	54.9			<i>a</i>
9.52	47.9	42.6			<i>b</i>
11.7 — 17.2	88.3 — 82.8	—			melt
7.51	31.2	61.3			<i>b</i>
7.05	22.1	70.9			<i>b</i>
8.90	20.7	70.4			<i>b</i>
12.2	21.5	66.3			<i>b</i>
16.6	23.2	60.1	0.3535	2.580	<i>A</i> <i>b</i> + <i>c</i>
15.5	20.5	64.0	0.4035	2.250	<i>c</i>
14.9	18.3	66.8	0.4375	2.050	<i>c</i>
14.5	15.7	69.8	0.4710	1.865	<i>c</i>
14.8	14.4	70.8	0.4855	1.790	<i>c</i>
18.3	11.5	70.2	0.4810	1.815	<i>c</i>
21.0	11.1	67.9	0.4510	1.975	<i>c</i>
21.6	10.7	67.7	0.4470	1.995	<i>B</i> <i>c</i> + <i>d</i>
16.8	5.45	77.8			<i>d</i>
14.0	2.20	83.8			<i>d</i>
12.4	—	87.6			<i>d</i>

<sup>a</sup> *A, B* are invariant points; *a* —  $H_2SeO_3$ , *b* —  $RbH_3(SeO_3)_2$ , *c* —  $RbHSeO_3$ , *d* —  $Rb_2SeO_3$ .

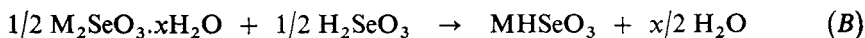
was selected for calculation of  $\Delta G^0$  for selenites of the  $MHSeO_3$  type. The values of  $\Delta G^0$  obtained then permitted evaluation of the effects of the cations of all the alkali

TABLE V  
Physical data for the  $Cs_2SeO_3-H_2SeO_3-H_2O$  system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $\text{kJ mol}^{-1}$	Composition of the solid phase <sup>a</sup>
$Cs_2SeO_3$	$H_2SeO_3$	$H_2O$			
—	36.3	63.7			<i>a</i>
0.493	35.8	63.7			<i>a</i>
1.59	40.8	57.6			<i>a</i>
2.87	45.5	51.7			<i>a</i>
4.83	57.5	37.7	0.1040	-5.610	<i>A a + b</i>
4.53	49.9	45.6	0.1750	-4.320	<i>b</i>
4.21	43.7	52.1	0.2465	-3.470	<i>b</i>
4.07	39.0	56.9	0.3075	-2.925	<i>b</i>
4.01	36.9	59.1	0.3320	-2.735	<i>b</i>
3.98	34.6	61.4	0.3560	-2.560	<i>b</i>
4.09	26.7	69.2	0.4555	-1.950	<i>b</i>
4.27	26.1	69.6	0.4600	-1.925	<i>b</i>
4.49	25.2	70.4	0.4680	-1.880	<i>b</i>
4.96	23.6	71.4	0.4820	-1.810	<i>B b + c</i>
4.75	18.8	76.4	0.5370	-1.540	<i>c</i>
4.79	16.8	78.4	0.5615	-1.430	<i>c</i>
4.88	15.8	79.4	0.5720	-1.385	<i>c</i>
5.33	14.5	80.2	0.5850	-1.330	<i>c</i>
6.47	13.7	79.8	0.5815	-1.345	<i>c</i>
7.80	13.3	78.9	0.5665	-1.410	<i>c</i>
9.60	13.1	77.3	0.5165	-1.640	<i>c</i>
11.5	13.0	75.5	0.5050	-1.695	<i>C c + d</i>
11.6	12.3	76.1	0.5155	-1.645	<i>d</i>
11.6	11.8	76.6	0.5220	-1.610	<i>d</i>
14.2	9.30	76.5	0.5185	-1.630	<i>d</i>
15.4	8.23	76.4	0.5180	-1.630	<i>d</i>
16.9	8.04	75.1	0.5000	-1.720	<i>d</i>
18.5	7.20	74.3	0.4890	-1.775	<i>d</i>
20.4	6.32	73.2	0.4735	-1.855	<i>D d + e</i>
17.1	2.37	80.5			<i>e</i>
15.1	—	84.9			<i>e</i>

<sup>a</sup> *A, B, C, D* are invariant points; *a* —  $H_2SeO_3$ , *b* —  $CsH_5(SeO_3)_3$ , *c* —  $CsH_3(SeO_3)_2$ , *d* —  $CsHSeO_3$ , *e* —  $Cs_2SeO_3 \cdot H_2O$ .

metals on the formation of the given type of acid selenites and thus also on the formation of hydrogen bonds in these systems. From the point of view of this effect, the studied cations assume the following order:  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ \approx \text{Na}^+ > \text{Li}^+$ . The larger the cation, the more readily it disturbs the structure of solutions of tetrameric hydrogenselenite anions<sup>13-15</sup> in favour of simple and more easily formed hydrogenselenites of the  $\text{MHSeO}_3$  type. The smaller size of the sodium cation compared to the potassium cation is compensated by its stronger polarization action on the  $\text{H}_2\text{O}$  molecule, leading to an increase in its effective radius and the effects of the two cations become equal. The size of the lithium cation has a negligible effect even during hydration and its polarization effect in destruction of the structure of the polymeric hydrogenselenite anions is small compared to its hydration. Although the values of the changes in the standard Gibbs energy in the heterogeneous reactions



leading to formation of acid salts of the  $\text{MHSeO}_3$  and  $\text{MH}_3(\text{SeO}_3)_2$  types for the  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Cs}^+$  cations are much larger than the values found for reaction (A), the order of cation effects remains the same,  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ . The overall higher

TABLE VI

Changes in the standard Gibbs energy ( $\text{kJ mol}^{-1}$ ) in the heterogeneous reactions for the formation of acid selenites

Reaction	$\Delta G^0$
$\text{LiHSeO}_3 + \text{H}_2\text{SeO}_3 \rightarrow \text{LiH}_3(\text{SeO}_3)_2$	-15.35
$1/2 \text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O} + 1/2 \text{H}_2\text{SeO}_3 \rightarrow \text{LiHSeO}_3 + 1/2 \text{H}_2\text{O}$	- 8.85
$1/3 \text{Li}_2\text{SeO}_3 \cdot \text{H}_2\text{O} + 1/3 \text{LiH}_3(\text{SeO}_3)_2 \rightarrow \text{LiHSeO}_3 + 1/3 \text{H}_2\text{O}$	- 0.31
$\text{NaH}_3(\text{SeO}_3)_2 + 2 \text{H}_2\text{SeO}_3 \rightarrow \text{NaH}_7(\text{SeO}_3)_4$	- 6.20
$\text{NaHSeO}_3 + \text{H}_2\text{SeO}_3 \rightarrow \text{NaH}_3(\text{SeO}_3)_2$	-18.05
$1/2 \text{Na}_2\text{SeO}_3 + 1/2 \text{H}_2\text{SeO}_3 \rightarrow \text{NaHSeO}_3$	-12.20
$1/3 \text{Na}_2\text{SeO}_3 + 1/3 \text{NaH}_3(\text{SeO}_3)_2 \rightarrow \text{NaHSeO}_3$	- 2.11
$1/3 \text{K}_2\text{SeO}_3 + 1/3 \text{KH}_3(\text{SeO}_3)_2 \rightarrow \text{KHSeO}_3$	- 2.08
$1/3 \text{Rb}_2\text{SeO}_3 + 1/3 \text{RbH}_3(\text{SeO}_3)_2 \rightarrow \text{RbHSeO}_3$	- 2.85
$\text{CsH}_3(\text{SeO}_3)_2 + \text{H}_2\text{SeO}_3 \rightarrow \text{CsH}_5(\text{SeO}_3)_3$	- 7.70
$\text{CsHSeO}_3 + \text{H}_2\text{SeO}_3 \rightarrow \text{CsH}_3(\text{SeO}_3)_2$	-19.25
$1/2 \text{Cs}_2\text{SeO}_3 \cdot \text{H}_2\text{O} + 1/2 \text{H}_2\text{SeO}_3 \rightarrow \text{CsHSeO}_3 + 1/2 \text{H}_2\text{O}$	-17.71
$1/3 \text{Cs}_2\text{SeO}_3 \cdot \text{H}_2\text{O} + 1/3 \text{CsH}_3(\text{SeO}_3)_2 \rightarrow \text{CsHSeO}_3 + 1/3 \text{H}_2\text{O}$	- 4.82



value of  $\Delta G^0$  can be explained as characterizing the far more complex structural changes in solution than those occurring in reaction (A).

Of the energetic conditions in the heterogeneous reactions that lead to the formation of various types of acid salts for the individual cations, the effect of the cation size is again decisive, determining its depolymerization effect on the anion and the ability to form simpler anions,  $\text{H}_3(\text{SeO}_3)_2^-$  and  $\text{HSeO}_3^-$ . Acid salts of the studied cation of the  $\text{MH}_3(\text{SeO}_3)_2$  type are most stable and only for the large cesium cation are the conditions for the formation of  $\text{CsH}_3(\text{SeO}_3)_2$  and  $\text{CsHSeO}_3$  practically identical.

When reactions of type (A) are neglected, the energetic conditions for the formation of the  $\text{NaH}_7(\text{SeO}_3)_4$  and  $\text{CsH}_5(\text{SeO}_3)_3$  salts are characterized by low  $\Delta G^0$  values. These compounds are formed in very concentrated solutions with large selenious acid contents. Because of the low number of cations, their stabilization effect on the system of hydrogen bonds will be smaller. The energetic conditions characterizing the formation of the compound  $\text{K}_5\text{H}_3(\text{SeO}_3)_4$  can not be compared with those for the formation of the other acid salts because of the different starting compounds in the heterogeneous reactions.

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