

THE CHANGE IN THE STANDARD GIBBS ENERGY ΔG° DURING THE FORMATION OF THE DOUBLE SELENATES

$M_2Mg(SeO_4)_2 \cdot 6 H_2O$ ($M = K, NH_4, Rb, Cs$)

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The energy conditions for the formation of the compounds under the conditions of heterogeneous equilibrium were studied using the Filippov eutonic method, permitting the ΔG° values for the reactions leading to the formation of the above double selenates to be obtained directly. The values obtained, which varied in the range -17.8 to $-24.4 \text{ kJ mol}^{-1}$, were correlated with the solubilities of the compounds formed and the selenates M_2SeO_4 . The interaction M_2SeO_4 - $MgSeO_4$ in the liquid phase was also studied.

The Filippov eutonic method¹⁻³ is based on the assumption that the chemical potentials of the initial components and of the products formed are equal in the invariant points. The whole calculation is described in greater detail, e.g. in the works of Lukeš and Ebert^{4,5}.

The authors used the Filippov method in earlier works⁴⁻⁷ both in systems with the formation of hydrogen salts^{4,5,7} and to study systems with formation of double selenates⁶. In the first type of system containing phosphites^{4,5} and selenites⁷, it was demonstrated that the cations M^+ ($M = Li-Cs$) affect the ΔG° value for the formation of the compound. This work was carried out to study the effect of the cations of the alkali metals and ammonium cation on the energy conditions for the formation of compounds in the various systems M_2SeO_4 - $MgSeO_4$ - H_2O ($M = K, NH_4, Rb, Cs$). In systems with $M = Li$ and Na , no double compounds are formed at 298 K (refs^{8,9}).

EXPERIMENTAL

Chemicals

$MgSeO_4 \cdot 6 H_2O$ was prepared in the same way as other selenates $M^IISeO_4 \cdot 6 H_2O$, as described earlier⁶. The selenates M_2SeO_4 ($M = K, NH_4, Rb, Cs$) were prepared by neutralization of H_2SeO_4 (BDH, Lab. Chemicals Div.) with the corresponding hydroxide or carbonate (or an aqueous solution of NH_3) in aqueous solution. All the substances prepared were twice recrystallized from water. Analyses for Se and water of crystallization were carried out by the method

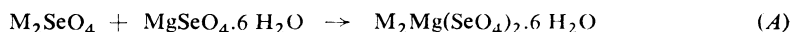
already described⁶; the Mg content was found complexometrically¹⁰. The results of the analyses indicated that the compounds had the expected compositions.

Methods

An analogous experimental procedure to that employed previously⁶ was employed and included the preparation of suitably saturated solutions according to the already published solubility diagrams^{8,11,12}, with composition that evenly covered 15 to 16 points on the solubility curve defining the crystallization field of the compound.

The water activity was measured on the VP-Osmometr (1978) instrument¹² from the Knauer Co. (F.R.G.). The changes of the standard Gibbs energy in the heterogeneous reactions ΔG° were calculated using the Hewlett-Packard 9845B computer.

It holds for the change in the standard Gibbs energy ΔG° for a heterogeneous reaction of two components according to the equation



for congruently soluble compounds that

$$\Delta G^\circ = \int_B^A [(x_3 - 6x_2)/(x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1,$$

where x_i , μ_i are the molar percent or chemical potentials of the i -th component in solution; A and B are the invariant points on the solubility curve and index 1 always refers to M_2SeO_4 .

The calculation was carried out using the procedure described previously⁶, including fitting polynomials or cubic splines to the functions $\mu_3 = f(x_1)$ and $V = f(x_1)$ (where $V = (\partial\mu_3/\partial x_1) \cdot (x_3 - 6x_2)/(x_2 - x_1)$). The multiple correlation coefficient values varied above 0.9958. Repeated calculations by various methods (alternative use of polynomials and splines in calculating the derivatives and integrals) demonstrated that the error in the calculated changes in the standard Gibbs energy ΔG° varied in the range 1.0–2.5%.

RESULTS

The compositions of the liquid phases and the results obtained from measurement of the water activity in the heterogeneous systems M_2SeO_4 – $MgSeO_4$ – H_2O ($M = K, NH_4, Rb, Cs$) are given in Tables I–IV. These values are valid for that part of the solubility curve defining the crystallization field of the double selenate being formed, $M_2Mg(SeO_4)_2 \cdot 6 H_2O$ ($M = K, NH_4, Rb, Cs$). The calculated changes in the standard Gibbs energy ΔG° and the solubility values for the initial selenates and the double salts formed are listed in Table V.

DISCUSSION

It follows from Table V that, similar to the K_2SeO_4 – $M^{II}SeO_4$ – H_2O ($M^{II} = Mn, Co, Ni, Cu, Zn$)⁶, the solubilities of the components and double salts have a decisive effect on the ΔG° value. The lowest $|\Delta G^\circ|$ value was obtained for $K_2Mg(SeO_4)_2 \cdot 6 H_2O$. Although the solubility of $Cs_2Mg(SeO_4)_2 \cdot 6 H_2O$ is almost the same (see

Table V), the $|\Delta G^\circ|$ value for the formation of this compound is much higher (Table V). This difference is a result of the greater solubility of Cs_2SeO_4 . On the other hand, the solubilities of K_2SeO_4 and Rb_2SeO_4 are very similar (Table V). However, because the solubility of the compound $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ is much lower than that for the corresponding potassium salt (Table V), a much higher $|\Delta G^\circ|$ value was found for the formation of $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ than for the formation of $\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (see Table V). Similar results are obtained from comparison of the ΔG° values for the formation of $\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ($\Delta G^\circ = -17.8 \text{ kJ mol}^{-1}$) and $\text{K}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ($\Delta G^\circ = -30.3 \text{ kJ mol}^{-1}$)⁶. The solubilities of the two initial selenates are almost identical (3.26 mol kg^{-1} for $\text{ZnSeO}_4 \cdot 6 \text{H}_2\text{O}$ (ref.⁶) and 3.24 mol kg^{-1} for $\text{MgSeO}_4 \cdot 6 \text{H}_2\text{O}$), but the solubility of $\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ is almost double ($(m_s)_D = 1.24 \text{ mol kg}^{-1}$) that of $\text{K}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$ ($(m_s)_D = 0.721 \text{ mol kg}^{-1}$)⁶.

As it was assumed that there is negligible interaction of the components in solution, the water activities in solutions of $\text{M}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$, where $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and NH_4 , were compared with the a_w values calculated assuming addi-

TABLE I
Physical data for the K_2SeO_4 - MgSeO_4 - H_2O system at 298 K

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase ^a
K_2SeO_4	MgSeO_4	H_2O			
9.08	0.092	90.83	0.7343	-0.766	A k + d
8.95	0.090	90.96	0.7358	-0.761	d
8.03	0.096	91.88	0.7650	-0.664	d
7.57	0.139	92.29	0.7841	-0.603	d
6.50	0.288	93.21	0.8206	-0.490	d
5.04	0.493	94.47	0.8700	-0.345	d
4.09	0.832	95.08	0.8941	-0.278	d
3.15	1.24	95.61	0.9102	-0.233	d
2.68	1.60	95.73	0.9164	-0.216	d
2.16	2.11	95.74	0.9165	-0.216	d
1.746	2.78	95.48	0.9161	-0.217	d
1.38	3.45	95.17	0.9101	-0.234	d
0.754	4.81	94.43	0.8766	-0.327	d
0.617	5.27	94.11	0.8649	-0.360	d
0.526	5.81	93.67	0.8522	0.397	B d + m

^a A, B are invariant points, k K_2SeO_4 , d $\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$, m $\text{MgSeO}_4 \cdot 6 \text{H}_2\text{O}$.

vity of the values for MgSeO_4 and M_2SeO_4 solutions (ref.¹³). The older Stachanova and Vasilev relationships¹³ were modified for valence unsymmetrical electrolytes¹¹ to give

$$a_w^T = (a_w^B)_1 m_1 \bar{m}_1^{-1} + (a_w^B)_2 m_2 \bar{m}_2^{-1}, \quad (2)$$

where a_w^T is the water activity in a ternary solution, and $(a_w^B)_1$ and $(a_w^B)_2$ are the water activities in binary solutions of salts 1 and 2 at molar concentrations of \bar{m}_1 and \bar{m}_2 . The \bar{m}_1 and \bar{m}_2 values are given by the relationships:

$$\bar{m}_1 = m_1 + (z_{K2} + z_A)(z_{K1} + z_A)^{-1} m_2 \quad (3)$$

and

$$\bar{m}_2 = m_2 + (z_{K1} + z_A)(z_{K2} + z_A)^{-1} m_1, \quad (4)$$

where m_1 and m_2 are the molalities of the salts in the ternary solution. z_{K1} , z_{K2} and z_A are the values of the absolute charges on the cation in salt 1, the cation in

TABLE II
Physical data for the Rb_2SeO_4 - MgSeO_4 - H_2O system at 298 K

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase ^a
Rb_2SeO_4	MgSeO_4	H_2O			
8.38	0.057	91.57	0.7347	-0.764	A r + d
7.36	0.065	92.58	0.7850	-0.600	d
6.33	0.071	93.60	0.8320	-0.456	d
4.76	0.097	95.15	0.8770	-0.321	d
4.19	0.147	95.66	0.8963	-0.271	d
3.48	0.240	96.28	0.9169	-0.215	d
2.83	0.360	96.82	0.9324	-0.174	d
2.05	0.716	97.24	0.9471	-0.135	d
1.43	1.20	97.37	0.9559	-0.111	d
1.06	1.86	97.08	0.9558	-0.112	d
0.828	2.45	96.72	0.9476	-0.134	d
0.632	3.15	96.22	0.9366	-0.162	d
0.530	3.76	95.71	0.9254	-0.192	d
0.424	5.08	94.49	0.8919	-0.284	d
0.390	5.85	93.76	0.8598	-0.375	B d + m

^a A, B are invariant points, r Rb_2SeO_4 , d $\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$, m $\text{MgSeO}_4 \cdot 6 \text{H}_2\text{O}$.

salt 2 and the common anion, respectively. A more detailed description of the calculation is given in the work of Vojtíšek¹¹. The relative differences between the measured and "additive" values (in per cent) are given by the relationship:

$$\Delta = (a_w^E - a_w^T) (a_w^E)^{-1} \cdot 100, \quad (5)$$

where a_w^E is the measured activity value. Table VI lists the results of comparison of the calculated and measured values of a_w^T and a_w^E for solutions of $M_2Mg(SeO_4)_2$ ($M = K, Rb, Cs, NH_4$) at various concentrations. Table VI also lists the results obtained for solutions of $Li_2SeO_4 + MgSeO_4$ and $Na_2SeO_4 + MgSeO_4$. The double salt is not crystallized out of these two solutions at 298 K (refs^{8,9}).

It follows from Table VI that the deviations from "additivity" are small, less than 1.8%. The deviations increase with increasing concentration. Although it follows from Table VI that the deviations are systematic and that they have a different sign for $M = Li$ and Na (i.e. systems without the double compound^{8,9}), the measurement

TABLE III
Physical data for the Cs_2SeO_4 - $MgSeO_4$ - H_2O system at 298 K

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase ^a
Cs_2SeO_4	$MgSeO_4$	H_2O			
10.29	0.019	89.69	0.6431	-1.09	A c + d
9.70	0.033	90.27	0.6861	-0.934	d
8.84	0.045	91.12	0.7077	-0.857	d
7.84	0.127	92.04	0.7512	-0.709	d
5.96	0.270	93.77	0.8160	-0.504	d
4.75	0.277	94.97	0.8644	-0.361	d
4.40	0.520	95.08	0.8761	-0.328	d
3.20	1.01	95.79	0.9051	-0.247	d
2.36	1.81	95.83	0.9224	-0.200	d
2.03	2.09	95.88	0.9248	-0.194	d
1.69	2.82	95.49	0.9188	-0.210	d
1.10	4.08	94.82	0.9002	-0.261	d
0.992	4.60	94.41	0.8896	-0.290	d
0.816	5.42	93.77	0.8614	-0.370	d
0.771	5.57	93.66	0.8576	-0.381	d
0.722	5.84	93.44	0.8493	-0.405	B d + m

^a A, B are invariant points, c Cs_2SeO_4 , d $Cs_2Mg(SeO_4)_2 \cdot 6 H_2O$, m $MgSeO_4 \cdot 6 H_2O$.

TABLE IV
Physical data for the $(\text{NH}_4)_2\text{SeO}_4$ - MgSeO_4 - H_2O system at 298 K

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase ^a
$(\text{NH}_4)_2\text{SeO}_4$	MgSeO_4	H_2O			
10.78	0.039	89.19	0.7347	-0.764	A n + d
9.13	0.041	90.83	0.7850	-0.600	d
7.04	0.075	92.89	0.8320	-0.456	d
5.51	0.101	94.39	0.8770	-0.321	d
4.44	0.200	95.36	0.8963	-0.271	d
3.57	0.381	96.05	0.9169	-0.215	d
2.74	0.635	96.63	0.9324	-0.174	d
1.89	0.955	97.16	0.9471	-0.135	d
1.68	1.22	97.10	0.9559	-0.112	d
1.31	1.82	96.87	0.9558	-0.112	d
0.860	2.99	96.15	0.9476	-0.134	d
0.526	4.07	95.41	0.9366	-0.162	d
0.391	4.60	95.01	0.9254	-0.192	d
0.251	5.23	94.52	0.8919	-0.284	d
0.212	5.76	94.03	0.8598	-0.375	B d + m

^a A, B are invariant points, n $(\text{NH}_4)_2\text{SeO}_4$, d $(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$, m $\text{MgSeO}_4 \cdot 6 \text{H}_2\text{O}$.

TABLE V
Changes in the standard Gibbs energy (kJ mol^{-1}) for the formation of double selenates under conditions of heterogeneous equilibrium and solubilities of double salts (mol kg^{-1}) and selenates M_2SeO_4 (M = K, Rb, Cs, NH_4) at 298 K

Compound	$-\Delta G^0$	$(m_s)_D$	$(m_s)_M$
$\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$	17.8	1.223	5.13
$\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$	24.4	0.768	5.20
$\text{Cs}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$	23.7	1.200	6.34
$(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6 \text{H}_2\text{O}$	20.1	0.853	6.71

Solubility of $\text{MgSeO}_4 \cdot 6 \text{H}_2\text{O} = 3.24 \text{ mol kg}^{-1}$; $(m_s)_D$, $(m_s)_M$ solubility of double salts and selenates M_2SeO_4 (at 298 K).

TABLE VI
Values of a_w^T and a_w^E in $M_2Mg(SeO_4)$ solutions at 298 K

$m, \text{ mol kg}^{-1}$	a_w^E	a_w^T	$\Delta, \%$
$Li_2SeO_4 + MgSeO_4 (1:1)$			
0.302	0.9799	0.9809	-0.10
0.589	0.9572	0.9599	-0.28
0.983	0.9178	0.9235	-0.62
1.307	0.8784	0.8860	-0.87
1.603	0.8384	0.8453	-0.82
$Na_2SeO_4 + MgSeO_4 (1:1)$			
0.295	0.9818	0.9822	-0.04
0.595	0.9622	0.9634	-0.13
0.965	0.9345	0.9364	-0.20
1.307	0.8984	0.9049	-0.72
1.603	0.8613	0.8709	-1.11
$K_2Mg(SeO_4)_2$			
0.304	0.9814	0.9821	-0.07
0.604	0.9631	0.9636	-0.05
0.993	0.9388	0.9351	+0.39
1.223	0.9238	0.9147	+0.99
1.320 ^a	0.9169	0.9051	+1.29
$Rb_2Mg(SeO_4)_2$			
0.196	0.9884	0.9882	+0.02
0.410	0.9760	0.9756	+0.04
0.601	0.9653	0.9631	+0.23
0.768	0.9561	0.9509	+0.54
$Cs_2Mg(SeO_4)_2$			
0.204	0.9883	0.9889	-0.06
0.388	0.9780	0.9784	-0.04
0.630	0.9644	0.9605	+0.40
0.803	0.9540	0.9464	+0.80
0.970	0.9431	0.9315	+1.23
1.180	0.9267	0.9108	+1.72
1.200	0.9250	0.9087	+1.76
$(NH_4)_2Mg(SeO_4)_2$			
0.154	0.9908	0.9907	+0.01
0.338	0.9798	0.9802	-0.04
0.647	0.9619	0.9616	+0.03
0.846	0.9508	0.9483	+0.26
0.854	0.9505	0.9477	+0.29

^a Supersaturated solution.

demonstrated that the assumption of negligible interaction in the liquid phase in the M_2SeO_4 - $MgSeO_4$ - H_2O systems is basically acceptable.

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