CHANGES IN THE STANDARD GIBBS ENERGIES ASSOCIATED WITH THE FORMATION OF DOUBLE SELENATES $(NH_4)_2M(SeO_4)_2.6\,H_2O$ (M = Mn, Co, Ni or Zn) AND $(NH_4)_2Cd(SeO_4)_2.2\,H_2O$

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The energy changes associated with the formation of double selenates of the schoenite type were studied. By using the Filippov eutonic method, the ΔG^0 values were obtained directly for the formation of the $(NH_4)_2M(SeO_4)_2.mH_2O$ salts with M = Mn, Co, Ni, Zn and Cd and $m = 6$ except for Cd, for which $m = 2$. The ΔG^0 values are comparable with those for the analogous potassium salts and they lie within the range of $-13{\cdot}9$ to $-45{\cdot}9$ kJ mol^{-1}. The fact that the final ΔG^0 value is primarily affected by the solubilities of the components and of the compound forming was verified for the examined $(NH_4)_2SeO_4$–$M^{II}SeO_4$–H_2O systems as well.

Previously we demonstrated[1,2] that in systems without significant interactions in the liquid phase, the solubilities of the components and of the forming compound had a dominant effect on the change in the standard Gibbs energy associated with the formation of a compound. In their energy aspects, such systems differ from salt–acid–water systems where strong interactions occur in the liquid phase[3–5]; in systems leading to the formation of acid salts, the polarizing effect of cations has been found to influence networks of hydrogen bonds in the solutions and, consequently, the energy changes during the formation of the acid salts under conditions of heterogeneous equilibrium[3–5].

In the present work, attention was paid to substances of the type of $(NH_4)_2.M(SeO_4)_2.mH_2O$ (M = Mn, Co, Ni or Zn with $m = 6$, and M = Cd with $m = 2$), which are formed in systems where liquid phase interactions can be assumed to be negligible. The ΔG^0 values were determined by the Filippov eutonic method[6–8] whose principle and application have been described, e.g., in ref.[3].

EXPERIMENTAL

$(NH_4)_2SeO_4$ was prepared by neutralization of selenic acid (BDH, Lab. Chemicals Div.) with aqueous ammonia followed by crystallization[9]. The selenates $MSeO_4.nH_2O$ were prepared as described previously[1,10]. The compounds prepared and the phases of heterogeneous mixtures were analyzed titrimetrically[11,12] as in our previous work[1,2]. The procedure included preparation of suitable saturated solutions, whose compositions covered uniformly the solubility curve

(7 to 14 points), sampling of the liquid phase, measurement of the activity of water a_w, and analysis of the liquid phase sample. Complete solubility diagrams have been published[9,10,13].

Activity of water was measured as described previously[14] using a Knauer VP osmometer. The standard Gibbs energies were calculated on a Hewlett-Packard 9845B computer.

RESULTS AND DISCUSSION

The change in the standard Gibbs energy ΔG^0 in the heterogeneous reaction of two components according to the equation

$$(NH_4)_2SeO_4 + MSeO_4.nH_2O \rightarrow (NH_4)_2M(SeO_4)_2.mH_2O + (n - m)\,H_2O \qquad (A)$$

is given by the relationship

$$\Delta G^0 = (m - n)(\mu_3^B - \mu_3^0) + \int_A^B [(x_3 - mx_2)/(x_2 - x_1)]\,(\partial\mu_3/\partial x_1)\,dx_1\,, \qquad (1)$$

where x_i and μ_i are the mole percent and chemical potential values, respectively,

TABLE I

Physico-chemical data of the $(NH_4)_2SeO_4$–$MnSeO_4$–H_2O system at 298 K

Liquid phase composition mole %			a_w[a]	μ_w[b] kJ mol^{-1}	Solid phase
$(NH_4)_2SeO_4$	MnSeO	H_2O			
11·66	0·11	88·23	0·7030	−0·874	[c]
11·20	0·46	88·34	0·7101	−0·849	[d]
8·44	0·53	91·03	0·7835	−0·605	[d]
7·94	0·61	91·46	0·7954	−0·567	[d]
6·40	0·74	92·85	0·8381	−0·438	[d]
5·01	0·76	94·23	0·8733	−0·336	[d]
3·83	1·24	94·92	0·8987	−0·265	[d]
2·54	2·54	94·93	0·9074	−0·241	[d]
2·23	3·44	94·33	0·8903	−0·288	[d]
1·63	4·60	93·77	0·8739	−0·334	[d]
1·59	5·11	93·30	0·8591	−0·376	[d]
1·31	5·62	93·07	0·8513	−0·399	[e]

[a] Activity of water; [b] chemical potential of water; [c] $(NH_4)_2SeO_4 + (NH_4)_2Mn(SeO_4)_2.6\,H_2O$ (invariant point A); [d] $(NH_4)_2Mn(SeO_4)_2.6\,H_2O$; [e] $(NH_4)_2Mn(SeO_4)_2.6\,H_2O + MnSeO_4.5\,H_2O$ (invariant point B).

of the i-th component ($i = 1$ refers to $(NH_4)_2SeO_4$), A and B are the invariable points in the solubility curve, and superscripts B and 0 refer to point B and to the pure solvent, respectively.

In the calculations, the functions $\mu_3 = f(x_1)$ and $V = f(x_1)$, where

$$V = [(x_3 - mx_2)/(x_2 - x_1)]\, \partial\mu_1/\partial x_1 \tag{2}$$

were expressed via polynomials or cubic splines[1]. The multiple correlation coefficients R^2 for the polynomials were invariably higher than 0·9986. Modified calculations using alternative polynomials or splines for obtaining $\partial\mu_1/\partial x_1$ and integrals indicated that the relative error of ΔG^0 values was less than 2%.

The liquid phase compositions and water activities and chemical potentials for the $(NH_4)_2SeO_4$–$MSeO_4$–H_2O heterogeneous systems at 298 K are given in Tables I–V. These values are related to the part of the solubility curve defining the crystallization field of the double selenate formed. The calculated changes in the standard Gibbs energy ΔG^0 associated with the heterogeneous reactions (A) at 298 K and the solubilities of the initial product selenates are given in Table VI.

The $-\Delta G^0$ values increase in order Cd < Mn < Co < Zn < Ni, which is also the order of decrease in the double salt solubilities. The solubility differences are

TABLE II

Physico-chemical data of the $(NH_4)_2SeO_4$–$CoSeO_4$–H_2O system at 298 K

Liquid phase composition mole %			a_w[a]	μ_w[b] kJ mol^{-1}	Solid phase
$(NH_4)_2SeO_4$	$CoSeO_4$	H_2O			
10·62	0·05	89·34	0·8090	−0·525	[c]
4·43	0·15	95·42	0·9320	−0·174	[d]
3·36	0·40	96·24	0·9497	−0·128	[d]
2·93	0·40	96·68	0·9563	−0·111	[d]
2·68	0·70	96·62	0·9626	−0·095	[d]
2·14	1·29	96·57	0·9649	−0·089	[d]
1·62	1·92	96·46	0·9627	−0·094	[d]
1·00	3·07	95·93	0·9521	−0·122	[d]
0·69	4·43	94·88	0·9086	−0·238	[e]

[a] Activity of water; [b] chemical potential of water; [c] $(NH_4)_2SeO_4 + (NH_4)_2Co(SeO_4)_2.6\,H_2O$ (invariant point A); [d] $(NH_4)_2Co(SeO_4)_2.6\,H_2O$; [e] $(NH_4)_2Co(SeO_4)_2.6\,H_2O + CoSeO_4.6\,H_2O$ (invariant point B).

higher than in the case of the analogous potassium salts[1], and so the differences among the ΔG^0 values are less affected by the solubilities of the initial selenates $MSeO_4.nH_2O$.

The cadmium salt, $(NH_4)_2Cd(SeO_4)_2.2\,H_2O$, for which the $-\Delta G^0$ value is lowest, is the only one of the fourteen double salts of the type $M^IM^{II}(SeO_4)_2.mH_2O$ studied by us that is incongruently soluble[9,10], and the value of $-\Delta G^0 = 13{\cdot}9$ kJ mol^{-1}is the lowest not only in the group of double selenates $(NH_4)_2M^{II}(SeO_4)_2.mH_2O$ studied in this work but in the whole series of fourteen double salts investigated by us[1,2]. Similarly, the value of $-\Delta G^0 = 45{\cdot}9$ kJ mol^{-1} for $(NH_4)_2Ni(SeO_4)_2.6\,H_2O$ is the highest in the entire group of the fourteen double selenates examined; this compound is also the least soluble of them, and so its formation from ions present in the liquid phase under the conditions of heterogeneous equilibrium is most preferred.

Overall , the results obtained corroborate the conclusion that the effect of solubility as the principal factor controlling the energy changes in the formation of double salts in systems without significant interactions in the liquid phase is a general feature of systems of this type.

TABLE III

Physico-chemical data of the $(NH_4)_2SeO_4$–$NiSeO_4$–H_2O system at 298 K

Liquid phase composition mole %			a_w[a]	μ_w[b] kJ mol^{-1}	Solid phase
$(NH_4)_2SeO_4$	$NiSeO_4$	H_2O			
7·68	0·024	92·29	0·7783	−0·621	c
4·90	0·027	95·07	0·7937	−0·572	d
3·23	0·05	96·72	0·8718	−0·340	d
2·86	0·12	97·02	0·9569	−0·109	d
1·27	0·21	98·52	0·9681	−0·080	d
1·16	0·31	98·54	0·9726	−0·0689	d
0·91	0·46	98·63	0·9764	−0·0592	d
0·80	0·57	98·63	0·9780	−0·0552	d
0·71	0·66	98·63	0·9785	−0·0539	d
0·49	0·96	98·55	0·9784	−0·0541	d
0·45	1·08	98·47	0·9770	−0·0577	d
0·31	1·60	98·08	0·9754	−0·0618	d
0·23	1·98	97·79	0·9686	−0·079	d
0·16	3·25	96·59	0·9447	−0·141	e

[a] Activity of water; [b] chemical potential of water; [c] $(NH_4)_2SeO_4 + (NH_4)_2Ni(SeO_4)_2.6\,H_2O$ (invariant point A); [d] $(NH_4)_2Ni(SeO_4)_2.6\,H_2O$; [e] $(NH_4)_2Ni(SeO_4)_2.6\,H_2O + NiSeO_4.6\,H_2O$ (invariant point B).

TABLE IV

Physico-chemical data of the $(NH_4)_2SeO_4$–$ZnSeO_4$–H_2O system at 298 K

Liquid phase composition mole %			a_w[a]	μ_w[b] kJ mol^{-1}	Solid phase
$(NH_4)_2SeO_4$	$ZnSeO_4$	H_2O			
8·99	0·008	91·00	0·7299	−0·780	[c]
6·62	0·021	93·36	0·7390	−0·749	[d]
3·59	0·04	96·37	0·8953	−0·274	[d]
2·73	0·12	97·15	0·9152	−0·220	[d]
2·02	0·26	97·72	0·9452	−0·140	[d]
1·88	0·37	97·75	0·9512	−0·124	[d]
1·41	0·59	97·99	0·9621	−0·096	[d]
1·09	0·91	98·01	0·9669	−0·084	[d]
0·75	1·48	97·77	0·9695	−0·077	[d]
0·48	2·19	97·33	0·9663	−0·085	[d]
0·36	2·99	96·65	0·9583	−0·106	[d]
0·21	3·13	96·66	0·9271	−0·188	[d]
0·14	5·41	94·45	0·8848	−0·303	[e]

[a] Activity of water; [b] chemical potential of water; [c] $(NH_4)_2SeO_4 + (NH_4)_2Zn(SeO_4)_2.6\ H_2O$ (invariant point A); [d] $(NH_4)_2Zn(SeO_4)_2.6\ H_2O$; [e] $(NH_4)_2ZnSeO_4)_2.6\ H_2O + ZnSeO_4.6\ H_2O$ (invariant point B).

TABLE V

Physico-chemical data of the $(NH_4)_2SeO_4$–$CdSeO_4$–H_2O system at 298 K

Liquid phase composition mole %			a_w[a]	μ_w[b] kJ mol^{-1}	Solid phase
$(NH_4)_2SeO_4$	$CdSeO_4$	H_2O			
10·39	0·54	89·07	0·7175	−0·823	[c]
9·59	0·67	89·74	0·7708	−0·645	[d]
6·02	0·91	93·07	0·7983	−0·558	[d]
5·35	1·18	96·47	0·8317	−0·457	[d]
4·90	1·58	93·52	0·8636	−0·363	[d]
4·34	2·03	93·64	0·8690	−0·348	[d]
3·73	2·76	93·50	0·8975	−0·268	[e]

[a] Activity of water; [b] chemical potential of water; [c] $(NH_4)_2SeO_4 + (NH_4)_2Cd(SeO_4)_2.2\ H_2O$ (invariant point A); [d] $(NH_4)_2Cd(SeO_4)_2.2\ H_2O$; [e] $(NH_4)_2Cd(SeO_4)_2.2\ H_2O + CdSeO_4.2\ H_2O$ (invariant point B).

TABLE VI

Changes in the standard Gibbs energy $-\Delta G^0$ for the formation of double selenates under conditions of heterogeneous equilibrium, and solubilities of the double salts $(m_s)_D$ and of the selenates $MSeO_4.nH_2O$, $(m_s)_M$ ($n = 6$ for Co, Ni and Zn; $n = 5$ for Mn; and $n = 2$ for Cd). Solubility of $(NH_4)_2SeO_4$ is 6·71 mol kg^{-1}; 298 K

Compound	$-\Delta G^0$ kJ mol^{-1}	$(m_s)_D$ mol kg^{-1}	$(m_s)_M$ mol kg^{-1}
$(NH_4)_2Mn(SeO_4)_2.6\,H_2O$	16·9	1·48	2·95
$(NH_4)_2Co(SeO_4)_2.6\,H_2O$	18·3	0·796	2·83
$(NH_4)_2Ni(SeO_4)_2.6\,H_2O$	45·9	0·306	1·93
$(NH_4)_2Zn(SeO_4)_2.6\,H_2O$	29·9	0·458	3·26
$(NH_4)_2Cd(SeO_4)_2.2\,H_2O$	13·9	4·01[a]	2·56

[a] Since the compound is incongruently soluble, this value was obtained graphically.

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