THE CHANGE IN THE STANDARD GIBBS ENERGY $\Delta G°$ IN THE FORMATION OF DOUBLE SELENATES $K_2M^{II}(SeO_4)_2 \cdot x\,H_2O$ (M^{II} = Mn, Co, Ni, Cu, Zn; x = 6 or 2)

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The heterogeneous K_2SeO_4–$M^{II}SeO_4$–H_2O system (M^{II} = Mn, Co, Ni, Cu, Zn) at 298 K was studied using the Filippov eutonic method, yielding values for the change in the standard Gibbs energy $\Delta G°$ for the formation of double selenates in the range $16 \cdot 2 - 30 \cdot 3$ kJ/mol. It follows from the $\Delta G°$ values that, in systems without strong interactions in the liquid phase, the formation of poorly soluble double selenates from readily soluble selenates is energetically most favourable.

The Filippov eutonic method[1-3] can be employed to study the energy conditions under which compounds are formed in phase reactions in heterogeneous systems. This method permits calculation of changes in the standard Gibbs energy $\Delta G°$ for heterogeneous reactions and is based on the assumption that, at equilibrium (at the eutonic or peritonic point), the chemical potentials of the reactants and the compounds formed are equal. According to the Gibbs–Duhem relationship, the chemical potentials of the reactants can be replaced in the calculation by the chemical potential of the solvent. This value can be obtained by measuring the solvent activity in a saturated solution. The applications of the Filippov eutonic method and derivation of the basic relationships are described in detail in the work of Lukeš and Ebert[4,5].

The authors[4-6] have used the Filippov eutonic method in earlier works for calculation of $\Delta G°$ for heterogeneous reactions leading to the formation of hydrogen-phosphites[4,5] and hydrogenselenites[6] in saturated aqueous solutions. This work deals with determination of the energy conditions for the formation of double selenates.

EXPERIMENTAL

Chemicals and Methods

The selenates $M^{II}SeO_4 \cdot x\,H_2O$ were prepared by the reaction of an excess of the appropriate carbonate with the mixture formed by the oxidation of Se or SeO_2 by

hydrogen peroxide $(30\%, \text{Se} : H_2O_2 = 1 : 10)$ by refluxing for 30 hours. The precipitate (excess carbonate and selenite) was filtered off and the clear solution was evaporated until crystallization occurred. Potassium selenate was prepared by neutralization of selenic acid (BDH, Lab. Chemicals Div.) by potassium hydroxide. All the substances were doubly recrystallized from water.

The compounds prepared and the heterogeneous phase mixture were analyzed titrimetrically (complexometric determination of the divalent metals[7] and iodometric determination of selenium after previous reduction to Se^{IV} (ref.[8])). The water of crystallization in the compounds was determined by thermal decomposition (Derivatograph, types OD-102 and Q-1500 from MOM Budapest, heating rate 2·5 K/min) or by drying to constant weight.

The water activity a_w was measured by taking samples of the saturated solutions from the heterogeneous mixtures prepared on the basis of the isothermal-isobaric phase diagrams[9−11] so that their compositions corresponded to points evenly distributed along the solubility curves of the compound or to the invariant points

TABLE I

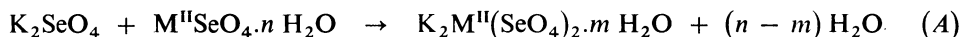Physical data for the K_2SeO_4–$MnSeO_4$–H_2O system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase[a]
K_2SeO_4	$MnSeO_4$	H_2O			
8·47	0·002	91·53	0·7258	−0·795	A k + d
7·85	0·006	92·14	0·7722	−0·641	d
7·00	0·016	92·98	0·8150	−0·507	d
6·26	0·02	93·72	0·8249	−0·477	d
5·19	0·03	94·78	0·8867	−0·298	d
4·02	0·08	95·90	0·9287	−0·183	d
3·04	0·17	96·79	0·9401	−0·153	d
2·56	0·21	97·24	0·9460	−0·138	d
1·97	0·49	97·54	0·9506	−0·126	d
1·39	1·02	97·59	0·9533	−0·119	d
1·04	1·59	97·37	0·9474	−0·134	d
0·68	2·63	96·69	0·9376	−0·160	d
0·45	3·60	95·95	0·9149	−0·221	d
0·26	4·37	95·38	0·8950	−0·275	d
0·25	5·14	94·61	0·8911	−0·286	B d + m

[a] A, B are invariant points; k K_2SeO_4, d $K_2Mn(SeO_4)_2.2\ H_2O$, m $MnSeO_4.5\ H_2O$.

A total of 15 to 18 samples were prepared and about one millilitre of saturated solution was taken.

The water activity a_w was measured using a modified bithermal equilibrium method[11-13] using a VP-Osmometr instrument (1978) from the Knauer company by a previously described method[13]. The changes in the standard Gibbs energy $\Delta G°$ for the heterogeneous reactions were calculated on a Hewlett–Packard 9845 B computer.

The change in the standard Gibbs energy $\Delta G°$ in the heterogeneous reaction of two components according to the equation

$$K_2SeO_4 + M^{II}SeO_4 . n\, H_2O \rightarrow K_2M^{II}(SeO_4)_2 . m\, H_2O + (n - m)\, H_2O \quad (A)$$

is given by the relationship[4]:

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

(x_i, μ_i are the mole percent and chemical potential of the ith component, respectively,

TABLE II

Physical data for the K_2SeO_4–$CoSeO_4$–H_2O system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase[a]
K_2SeO_4	$CoSeO_4$	H_2O			
8·79	0·03	91·18	0·7258	−0·794	A k + d
7·90	0·04	92·06	0·7722	−0·641	d
6·71	0·05	93·24	0·8150	−0·507	d
6·45	0·07	93·48	0·8249	−0·477	d
4·60	0·15	95·25	0·8867	−0·298	d
3·03	0·37	96·60	0·9287	−0·183	d
2·35	0·69	96·96	0·9401	−0·153	d
2·07	0·89	97·03	0·9460	−0·138	d
1·72	1·30	96·98	0·9506	−0·126	d
1·50	1·54	96·96	0·9533	−0·119	d
1·39	2·09	96·60	0·9474	−0·134	d
1·11	2·91	95·97	0·9376	−0·160	d
0·93	3·95	95·11	0·9149	−0·221	d
0·80	4·64	94·55	0·8950	−0·275	d
0·78	4·89	94·33	0·8911	−0·286	B d + c

[a] A, B are invariant points; k K_2SeO_4, d $K_2Co(SeO_4)_2 . 6\, H_2O$, c $CoSeO_4 . 6\, H_2O$.

A and B designate the invariant points on the solubility curve, μ_3^o is the chemical potential of water in the standard state, μ_3^B is the value of μ_3 at point B and index 1 corresponds to K_2SeO_4). The calculation was begun by expressing the dependence $\mu_3 = f(x_1)$ by a polynomial or cubic convergence[14], permitting calculation of the derivation $\partial\mu_3/\partial x_1$ for the appropriate x_1 values. The derivative values were multiplied by the fraction $(x_3 - mx_2)/(x_2 - x_1)$ and plotted against x_1. The curve for the given dependence was obtained using the cubic convergence and the subsequent integration was carried out on the computer.

The relative standard deviation of the measured water activity a_w was less than 0.5% (refs[11,13]) and the relative error in the analysis was not greater than 0.5%. The mathematical procedure for the calculation of ΔG^o also included errors incurred in replacing the function by a polynomial. The fit to the function was expressed by the values of the multiple correlation coefficient R^2, which were[11] above 0.982 in all cases. A further source of error common in older works[4,5] employing the Filippov method and resulting from the graphical integration method was limited by using a computer, similarly as in the work of Mička and Ebert[6]. Repeated calculations

TABLE III

Physical data for the $K_2SeO_4-NiSeO_4-H_2O$ system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase[a]
K_2SeO_4	$NiSeO_4$	H_2O			
8·72	0·02	91·26	0·7290	−0·784	A k + d
8·55	0·03	91·42	0·7366	−0·758	d
7·66	0·03	92·31	0·7791	−0·619	d
6·44	0·04	93·52	0·8223	−0·485	d
4·66	0·05	95·29	0·8814	−0·313	d
3·44	0·06	96·50	0·9146	−0·221	d
2·34	0·14	97·51	0·9446	−0·141	d
1·81	0·26	97·93	0·9565	−0·110	d
1·27	0·39	98·39	0·9685	−0·079	d
0·90	0·61	98·49	0·9728	−0·068	d
0·79	0·79	98·42	0·9751	−0·062	d
0·68	1·18	98·14	0·9731	−0·068	d
0·55	1·73	97·72	0·9693	−0·077	d
0·44	2·28	97·28	0·9617	−0·097	d
0·39	2·82	97·79	0·9536	−0·118	d
0·35	3·39	96·27	0·9417	−0·149	B d + n

[a] A, B are invariant points; k K_2SeO_4, d $K_2Ni(SeO_4)_2.6 H_2O$, n $NiSeO_4.6 H_2O$.

(mainly of the integrals) by various methods (alternative use of various order poly-
nomials and convergences) from a single set of data indicated that the relative error
in the calculated changes in the standard Gibbs energy $\Delta G°$ varied in the range $1 - 3\%$.

RESULTS

The compositions of the liquid phases and the measured water activity values a_w
obtained in the study of the heterogeneous systems $K_2SeO_4-M^{II}SeO_4-H_2O$ $(M^{II} =$
$=$ Mn, Co, Ni, Cu, Zn) at 298 K are listed in Tables I to V. These values are related
to that part of the solubility curve defining the crystallization field of the double selen-
ates formed $K_2M^{II}(SeO_4)_2.x H_2O$ $(x = 2$ for Mn, $x = 6$ for Co, Ni, Cu, Zn). The
calculated changes in the standard Gibbs energy $\Delta G°$ for the heterogeneous reactions
leading to the formation of the double salts and the solubility values for the initial
reactants and compounds at 298 K are listed in Table VI.

DISCUSSION

Earlier studies[4−6] dealing with study of energy conditions for the formation of acid
salts interpreted changes in the $\Delta G°$ values for the formation of the compounds on

TABLE IV
Physical data for the $K_2SeO_4-CuSeO_4-H_2O$ system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water kJ mol^{-1}	Composition of the solid phase^a
K_2SeO_4	$CuSeO_4$	H_2O			
8·49	0·015	01·49	0·7381	−0·753	A k + d
7·67	0·018	92·34	0·7798	−0·617	d
6·46	0·03	93·51	0·8220	−0·486	d
4·57	0·06	95·37	0·8889	−0·292	d
3·56	0·10	96·34	0·9189	−0·210	d
2·79	0·18	97·02	0·9399	−0·154	d
2·45	0·24	97·31	0·9479	−0·132	d
1·74	0·39	97·86	0·9624	−0·095	d
1·38	0·58	98·04	0·9664	−0·085	d
1·10	0·75	98·16	0·9678	−0·081	d
0·71	1·19	98·10	0·9723	−0·070	d
0·65	1·32	98·03	0·9721	−0·070	d
0·57	1·44	97·99	0·9719	−0·071	d
0·47	1·57	97·95	0·9715	−0·072	B d + c

^{a} A, B are invariant points; k K_2SeO_4, d $K_2Cu(SeO_4)_2.6 H_2O$, c $CuSeO_4.5 H_2O$.

TABLE V

Physical data for the K_2SeO_4–$ZnSeO_4$–H_2O system

Composition of the liquid phase, mole %			Water activity	Chemical potential of water $kJ\,mol^{-1}$	Composition of the solid phase[a]
K_2SeO_4	$ZnSeO_4$	H_2O			
8·77	0·03	91·20	0·7261	−0·794	A k + d
8·19	0·03	91·78	0·7500	−0·713	d
7·51	0·04	92·45	0·7787	−0·620	d
6·76	0·11	93·14	0·8030	−0·528	d
5·35	0·17	94·48	0·8575	−0·318	d
4·11	0·26	95·63	0·8960	−0·272	d
3·33	0·31	96·37	0·9165	−0·216	d
2·31	0·48	97·21	0·9406	−0·152	d
1·74	0·82	97·44	0·9542	−0·116	d
1·12	1·44	97·44	0·9583	−0·106	d
0·97	1·79	97·24	0·9594	−0·103	d
0·74	2·68	96·58	0·9513	−0·124	d
0·58	3·35	96·07	0·9432	−0·145	d
0·46	4·02	95·52	0·9265	−0·189	d
0·42	4·99	94·59	0·9021	−0·255	d
0·41	5·62	93·97	0·8748	−0·332	d
0·39	5·68	93·93	0·8724	−0·338	B d + z

[a] A, B are invariant points; k K_2SeO_4, d $K_2Zn(SeO_4)_2.6\,H_2O$, z $ZnSeO_4.6\,H_2O$.

TABLE VI

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 $MSeO_4.x\,H_2O$ ($x = 5$ for Mn, Cu; $x = 6$ for Co, Ni, Zn); solubility of $K_2SeO_4 = 5·13$ mol . . kg^{-1}

Compound	$-\Delta G^o$	$(m_s)_D{}^a$	$(m_s)_M{}^b$
$K_2Mn(SeO_4)_2.2\,H_2O$	21·1	0·712	2·95
$K_2CO(SeO_4)_2.6\,H_2O$	24·1	0·864	2·83
$K_2Ni(SeO_4)_2.6\,H_2O$	23·8	0·446	1·93
$K_2Cu(SeO_4)_2.6\,H_2O$	16·2	0·525	0·999
$K_2Zn(SeO_4)_2.6\,H_2O$	30·3	0·721	3·26

[a] $(m_s)_D$ solubility of double salt, [b] $(m_s)_M$ solubility of $MSeO_4.x\,H_2O$.

the basis of the polarization influence of the cations on the hydrogen bond system in the solution. This effect has been demonstrated both for the alkali metal phosphites, alkaline earth phosphites and alkali metal selenites. The systems studied here are very different from earlier systems. It can be assumed that the interactions in the liquid phase in the K_2SeO_4–$M^{II}SeO_4$–H_2O systems are much weaker than those in acid salt systems[4−6], where association through hydrogen bond formation is important in the formation of hydrogenpolyanions. Hydrogenphosphites[4,5] and hydrogenselenites[6] have very different stoichiometries in the solid phase[4−6]. The stoichiometry of the double selenates is always the same $(K_2SeO_4 : M^{II}SeO_4 : H_2O =$ $= 1 : 1 : 6)$, except for the manganese salt, which crystallizes as the dihydrate $(1 : 1 : 2)$. The $K_2M^{II}(SeO_4)_2 . 6\,H_2O$ compounds $(M^{II} = Co, Ni, Cu, Zn)$ are called Tutton salts[15,16] and are isostructural.

The structure of the solid state in double selenates of the Tutton salt type contains primarily tetrahedral anions $SeO_4^{2−}$ and deformed octahedral cations $[M^{II}(H_2O)_6]^{2+}$ $(refs^{17−19})$. It can be assumed that these species are present in solution (e.g. ref.[20]) and are retained in the transition from the liquid to the solid phase.

The deviation for $K_2Mn(SeO_4)_2.2\,H_2O$ can be attributed most probably to the fact that this double salt is not a Tutton salt and has different stoichiometry from these salts (dihydrate rather than a hexahydrate).

It follows from Table VI that the $\Delta G°$ value in this type of system is primarily affected by the solubility of the initial selenates and of the double selenate formed. The results obtained (Table VI) indicate that the formation of the compound becomes energetically more favourable as its solubility decreases and that of the reactant increases. A large value of $|\Delta G°|$ was found for $K_2Zn(SeO_4)_2.6\,H_2O$, where the solubility of $ZnSeO_4 . 6\,H_2O$ is high. The lowest $|\Delta G°|$ value was found for $K_2Cu(SeO_4)_2.6\,H_2O$. The solubility of $CuSeO_4.5\,H_2O$ is very different from that of the other selenates $M^{II}SeO_4.x\,H_2O$ and it has the most marked field in the solubility diagram. The field for the double selenate $K_2Cu(SeO_4)_2.6\,H_2O$ is less marked. Thus, the overall character of the solubility diagram corresponds to energetically less favourable formation of the double salt. Almost identical $\Delta G°$ values were found for the compounds $K_2Ni(SeO_4)_2.6\,H_2O$ and $K_2Co(SeO_4)_2.6\,H_2O$. While the solubility of the nickel double salt is much lower than that of the corresponding cobalt salt, the nickel selenate is less soluble than the cobalt selenate.

REFERENCES

1. Filippov V. K.: Radiokhimiya 7, 449 (1965).
2. Filippov V. K. in: *Problemy Sovremennoi khimii koordinatsionnykh soedineii*, p. 41. Izd. LGU, Leningrad 1969.
3. Filippov V. K.: Zh. Neorg. Khim. *17*, 1590 (1972).
4. Lukeš I., Ebert M.: Collect. Czech. Chem. Commun. *45*, 2283 (1980).
5. Lukeš I., Ebert M.: Collect. Czech. Chem. Commun. *45*, 3069 (1980).

6. Mička Z., Ebert M.: Collect. Czech. Chem. Commun. *51*, 1933 (1986).
7. Přibil R.: *Komplexometrie*. SNTL, Prague 1977.
8. Blanka B., Hudec P., Toužín J.: Collect. Czech. Chem. Commun. *28*, 3434 (1963).
9. Vojtíšek P., Ebert M.: Z. Chem. *25*, 414 (1985).
10. Vojtíšek P., Ebert M.: Z. Chem. *27*, 229 (1987).
11. Vojtíšek P.: *Thesis*. Charles University, Prague 1984.
12. Robinson N. A., Stokes R₁ H. in: *Electrolyte Solutions*, IInd. ed. Butterworth, London 1959.
13. Vojtíšek P., Ebert M.: Chem. Listy, in press.
14. Ahlberg J. H., Nilson E. N., Welsh J. L. in: *The Theory of Splines and Their Application*, p.74. Academic Press, New York 1967.
15. Tutton A. E. H.: J. Chem. Soc. *89*, 1059 (1906).
16. Whitnall J. M., Kennard C. H. L.: J. Solid State Chem. *22*, 379 (1977).
17. Monge A., Gutierrez-Puebla C.: Acta Crystallogr., B *37*, 427 (1981).
18. Montgomery H.: Acta Crystallogr., B *36*, 440 (1980).
19. Whitnall J. M., Kennard C. H. L., Nimmo J. K., Moore F. H.: Cryst. Struct. Commun. *4*, 709 (1975).
20. Eigen M.: Pure Appl. Chem. *6*, 105 (1963).

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