

## Calculation of the free Gibbs energy of phase transitions using solubility data.

### 1. The system $\text{Na}_2\text{SO}_4\text{--Na}_2\text{SeO}_4\text{--H}_2\text{O}$ at 15 °C: Stable and metastable equilibria\*

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*Abstract:* The solubility isotherms of the systems  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}\text{--Na}_2\text{SeO}_4\cdot 10\text{H}_2\text{O}\text{--H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\cdot 7\text{H}_2\text{O}\text{--Na}_2\text{SeO}_4\cdot 7\text{H}_2\text{O}\text{--H}_2\text{O}$  have been investigated at 15 °C. It is established that discontinuous series of mixed crystals are formed in both systems. Two methods of calculation of the free Gibbs energy of phase transition at the interruption point of the solubility diagrams are used: (i) on the basis of the composition of the two mixed crystal types, which are in equilibrium with the saturated solution in the eutonic point of the system, and (ii) from the distribution coefficients between each of the mixed crystal phases and their saturated solution, using both experimentally obtained values and calculated distribution coefficients for ideal isomorphic mixing. The data found by the two methods exhibit very good agreement. It is established that the free Gibbs energy of the phase transition in the case of decahydrates is lower than in the case of heptahydrates. This fact is considered as a confirmation of the buffering action of water molecules with respect to the distortion of the crystal structures of the pure salts provoked by the formation of mixed crystals.

## INTRODUCTION

In the systems  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  [1,2] and  $\text{Na}_2\text{SeO}_4\text{--H}_2\text{O}$  [3],  $\text{Na}_2\text{SO}_4\cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{SeO}_4\cdot 7\text{H}_2\text{O}$  appear as metastable phases in addition to the stable crystal phases  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SeO}_4\cdot 10\text{H}_2\text{O}$ . No fields of crystallization of heptahydrates as stable phases are found in the binary systems.

Sodium sulfate and sodium selenate tend to form supersaturated solutions with respect to both the decahydrate and the heptahydrate [2,3]. The supersaturated solutions can be stored for months under suitable conditions: protection from sharp temperature changes and preservation in well-closed vessels with a view to avoiding the penetration of nuclei. Since the dehydrates are isostructural [4,5], the same can be supposed about the heptahydrates. This assumption is based on the analogous compounds type and the analogous solubility diagrams, as well as on the fact that the introduction of crystal seeds of one heptahydrate causes crystallization of the other heptahydrate from the supersaturated solution, which is also valid for the decahydrates [2,3].

It was of interest to study mixed crystal formation in the system sodium sulfate/sodium selenate/water between decahydrates (under equilibrium conditions) and between heptahydrates (metastable solubility in supersaturated solutions). The parallel study of these two systems at the same temperature would permit comparing the co-crystallization of the two pairs of crystal hydrates and drawing some thermodynamic conclusions. For this aim, the temperature 15 °C was chosen.

\*Lecture presented at the 10<sup>th</sup> International Symposium on Solubility Phenomena, Varna, Bulgaria, 22–26 July 2002. Other lectures are published in this issue, pp. 1785–1920.

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## EXPERIMENTAL \*

The system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  was investigated at 20 °C by Collet [6], who found a field of crystallization of  $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$  and a region of mixed crystal formation on the basis of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . This author plotted the solubility diagram without giving numerical data. The system  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  was not at all investigated.

The solubility diagrams of the systems  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  (supersaturated solutions) were studied at 15 °C. Sodium sulfate decahydrate (analytical grade reagent, AR) was used, while sodium selenate was prepared by dissolving sodium carbonate (AR) in selenic acid (AR). The obtained crystals were recrystallized.

The solubilities were studied by the method of isothermal decrease of supersaturation [7]. Saturated solutions containing different sulfate/selenate ratios were prepared at 100 °C for investigating the system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$ . These solutions were transferred to a vessel thermostated at 15 °C and after temperature stabilization, supersaturation was reduced by addition of sodium sulfate or sodium selenate decahydrate seeds. The solubility diagram of the system  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  (supersaturated solutions with respect to the decahydrates) at 15 °C was investigated as follows: at 20 °C (when sodium selenate heptahydrate has its highest solubility [3]) saturated solutions with respect to heptahydrates, containing different sulfate/selenate ratios, were prepared. After filtering, the solutions were placed in a vessel thermostated at 15 °C and the supersaturation was decreased by adding sodium sulfate or sodium selenate heptahydrate seeds. The equilibrium composition of the mixed crystals was achieved by stirring at 15 °C for 48 h. The thermostated vessel and all the glass vessels used were washed carefully with distilled hot water before placing the samples in them. Prior to the withdrawal of samples for determining the composition of the equilibrium solid and liquid phases, a small amount of the liquid phase was taken out and a sodium sulfate decahydrate seed was introduced in it in order to check whether the solution was supersaturated with respect to the decahydrates.

The liquid and solid phases were analyzed by gravimetric determination of the selenate ion content using the method of precipitation of selenium from hydrochloric acid solutions by reduction with hydrazine hydrochloride [8]. After determination of selenates, the filtrate was used for gravimetric determination of the sulfate ions as  $\text{BaSO}_4$  [9]. The accuracy of the analysis methods was 0.1–0.2 %. The composition of the thoroughly suction-dried solid phase was calculated by the variant of Schreinemakers' method for indirect algebraic determination of mixed crystals composition [10].

## RESULTS

Tables 1 and 2 and Figs. 1 and 2 present the results from the investigation of the systems  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  at 15 °C. It is established that in each of both systems, two series of mixed crystals are formed based on sodium sulfate decahydrate (or heptahydrate) and on sodium selenate decahydrate (or heptahydrate), respectively. The distribution coefficients of the components between the solid and liquid phases were calculated (Tables 1 and 2).

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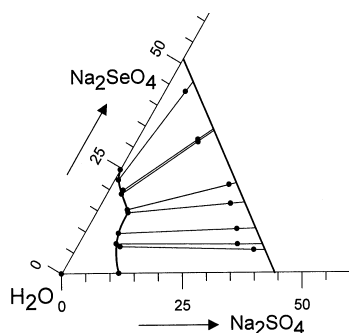
\* The experimental part of this work was carried out by Mrs. Bl. Keremidchieva

**Table 1** Solubility in the system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  at 15.0 °C.

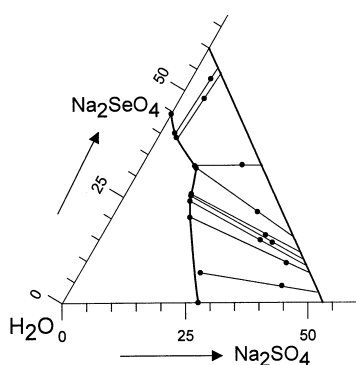
Liquid phase				Wet solid phase		Solid phase composition calculated as ideally suction dried [10]		$D_{\text{SeO}_4^{2-}/\text{SO}_4^{2-}}$	$D_{\text{SO}_4^{2-}/\text{SeO}_4^{2-}}$
$\text{Na}_2\text{SeO}_4$		$\text{Na}_2\text{SO}_4$		$\text{Na}_2\text{SeO}_4$	$\text{Na}_2\text{SO}_4$	$\text{Na}_2\text{SeO}_4$	$\text{Na}_2\text{SO}_4$		
mass %	mol/kg $\text{H}_2\text{O}$	mass %	mol/kg $\text{H}_2\text{O}$	mass %	mass %	mass %	mass %		
–	–	11.83	0.945	–	–	–	–	–	–
6.36	0.397	8.95	0.744	5.46	37.23	5.39	39.44	0.19	–
7.05	0.438	7.81	0.646	6.83	33.13	6.78	38.24	0.20	–
9.52	0.604	7.07	0.597	10.46	31.22	10.60	34.95	0.22	–
14.42	0.967	6.64	0.592	16.49	26.92	16.77	29.64		eutonic
15.12	1.02	6.15	0.550	20.95	24.40	21.36	25.69	–	2.94
18.88	1.28	3.07	0.277	31.09	12.96	33.87	14.92	–	2.70
19.76	1.35	3.00	0.273	31.73	12.59	34.24	14.60	–	2.78
22.21	1.53	0.82	0.075	43.17	4.35	45.65	4.77	–	2.83
24.64	1.73	–	–	–	–	–	–	–	–

**Table 2** Solubility in the system  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  at 15.0 °C.

Liquid phase				Wet solid phase		Solid phase composition calculated as ideally suction dried [10]		$D_{\text{SeO}_4^{2-}/\text{SO}_4^{2-}}$	$D_{\text{SO}_4^{2-}/\text{SeO}_4^{2-}}$
$\text{Na}_2\text{SeO}_4$		$\text{Na}_2\text{SO}_4$		$\text{Na}_2\text{SeO}_4$	$\text{Na}_2\text{SO}_4$	$\text{Na}_2\text{SeO}_4$	$\text{Na}_2\text{SO}_4$		
mass %	mol/kg $\text{H}_2\text{O}$	mass %	mol/kg $\text{H}_2\text{O}$	mass %	mass %	mass %	mass %		
–	–	27.58	2.68	–	–	–	52.97	–	–
7.04	0.545	24.54	2.52	3.94	42.75	2.58	50.79	0.18	–
20.14	1.67	15.89	1.75	9.35	40.98	6.70	47.14	0.11	–
23.98	2.05	14.02	1.59	14.77	32.96	8.76	45.32	0.11	–
25.24	2.18	13.57	1.56	14.18	35.72	9.90	44.31	0.12	–
25.70	2.24	13.43	1.55	15.97	33.44	11.29	43.08	0.14	–
31.74	2.96	11.43	1.42	21.42	29.07	15.30	39.53	0.14	–
32.23	3.00	10.87	1.34	32.48	20.45	32.58	24.24		eutonic
38.92	3.60	3.84	0.472	48.08	4.93	53.65	5.60	–	1.06
39.98	3.71	2.95	0.364	52.71	3.99	55.23	4.19	–	1.03
44.49	4.24	–	–	–	–	59.97	–	–	–



**Fig. 1** Solubility diagram of the system  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  at  $15^\circ\text{C}$ .



**Fig. 2** Solubility diagram of the system  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  at  $15^\circ\text{C}$ .

### CALCULATION OF THE FREE GIBBS ENERGY OF PHASE TRANSITIONS

It is known that there are isostructural salt pairs such as  $\text{Mg}(\text{HCOO})_2 - \text{Cd}(\text{HCOO})_2 - \text{H}_2\text{O}$  [11] or  $\text{MeMgCl}_3 \cdot 6\text{H}_2\text{O} - \text{MeMgBr}_3 \cdot 6\text{H}_2\text{O} - \text{H}_2\text{O}$  ( $\text{Me} = \text{NH}_4, \text{Rb}, \text{Cs}$ ), which form discontinuous series of mixed crystals, due to essential differences in the crystal lattice parameters. The same behavior is observed in the systems  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$ . The interruption in the mixed crystal series represents, in fact, a phase transition.

The free Gibbs energies of the phase transitions at the interruption points in the diagrams of the systems  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O} - \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O} - \text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O} - \text{H}_2\text{O}$  were calculated on the basis of the compositions of the two kinds of mixed crystals coexisting in equilibrium with the liquid phase. The condition needed for equilibrium of the component  $i$  between the solid phases I and II is:  $\mu_i^{\text{I}} = \mu_i^{\text{II}}$  Then

$$\mu_i^{0\text{I}} + RT \ln x_i^{\text{I}} \cdot f_i^{\text{I}} = \mu_i^{0\text{II}} + RT \ln x_i^{\text{II}} \cdot f_i^{\text{II}} \quad (1)$$

$$\mu_i^{0\text{II}} - \mu_i^{0\text{I}} = \Delta G_i^{\text{I} \rightarrow \text{II}} = -RT \ln \frac{x_i^{\text{II}} \cdot f_i^{\text{II}}}{x_i^{\text{I}} \cdot f_i^{\text{I}}} \quad (2)$$

Here  $x_i$  stands for the molar part and  $f_i$  for the rational activity coefficient of the component  $i$  in the mixed crystals, while the mixed crystal phases with sodium sulfate or sodium selenate structures are denoted by I and II, respectively.

In the case of nonideal mixed crystals, the ratio  $f_1/f_2$  will change with the composition of the system, which will be observed as a monotonic variation of the distribution coefficient  $D$  of the components between the mixed crystals and the solution with increasing amount of the salt admixture content in the system. The constancy of the distribution coefficients for all concentration ratios provides evidence for a relative constancy of the ratio  $f_1/f_2$ . In the case of ideal mixed crystals,  $f_1 = f_2 = 1$ .

In the system  $\text{Na}_2\text{SO}_4\text{--Na}_2\text{SeO}_4\text{--H}_2\text{O}$ , the formation of  $\text{Na}_2(\text{SO}_4, \text{SeO}_4)\cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2(\text{SO}_4, \text{SeO}_4)\cdot 7\text{H}_2\text{O}$  mixed crystals showing constant values of the distribution coefficients between the mixed crystals and the solution can be explained by a "buffering and screening effect" of the high number of water molecules in the mixed crystal phases [12]. In earlier papers [13–15], we have shown that such a constant value of the distribution coefficient actually corresponds to the formation of close to ideal mixed crystals. On the basis of this assumption from eq. 2, we obtain

$$\Delta G_1^{\text{I} \rightarrow \text{II}} = -RT \ln \frac{x_1^{\text{II}}}{x_1^{\text{I}}}; \Delta G_2^{\text{II} \rightarrow \text{I}} = -RT \ln \frac{x_2^{\text{I}}}{x_2^{\text{II}}} \quad (3)$$

Here, the indices 1 and 2 designate the two salt components: sodium sulfate and sodium selenate, respectively.

The compositions of each of the two mixed crystal phases coexisting at the eutonic point were calculated using the equations [14]:

$$D_{2/\text{II}} = \frac{x_2^{\text{I}}}{x_1^{\text{I}}} \cdot \frac{m_1}{m_2}; D_{1/2\text{II}} = \frac{x_1^{\text{II}}}{x_2^{\text{II}}} \cdot \frac{m_2}{m_1} \quad (4)$$

Here  $D_{2/\text{II}}$  refers to the distribution coefficient of component 2 between the solid phase of component 1 with structure I and the solution. Analogously,  $D_{1/2\text{II}}$  refers to the distribution coefficient of component 1 between a solid phase of component 2 with structure II and the solution. The distribution coefficients data calculated from the experimentally obtained compositions of the solid and liquid phases lying in the closest proximity to the eutonic point, the molalities  $m_1$  and  $m_2$  of salts 1 and 2 in the solution at the eutonic point, and the equation  $x_1 + x_2 + x_3 = 1$  were used. On the basis of the calculated compositions and eqs. 3, the free Gibbs energies for the respective phase transitions were found. The data are presented in Table 3.

**Table 3** Free Gibbs energies of phase transitions calculated according to eq. 3.

Experimental distribution coefficients values	Molar ratio of the components in the eutonic solution	Calculated molar parts of the components in the mixed crystals coexisting in the eutonic point			Molar part ratio of the components in the mixed crystals	Free Gibbs energies of phase transitions kJ/mol
Mixed crystals $\text{Na}_2\text{SO}_4\text{--Na}_2\text{SeO}_4$ decahydrates						
$D_{1/2\text{II}}^{\text{exp}} = 2.94$	$m_2/m_1 = 1.63$	$x_1^{\text{II}} = 0.0585$	$x_2^{\text{II}} = 0.0325$	$x_3^{\text{II}} = 0.909$	$x_1^{\text{II}}/x_2^{\text{II}} = 1.80$	$\Delta G_1^{\text{I} \rightarrow \text{II}} = 0.32$
$D_{2/\text{II}}^{\text{exp}} = 0.22$	$m_1/m_2 = 0.613$	$x_1^{\text{I}} = 0.067$	$x_2^{\text{I}} = 0.024$	$x_3^{\text{I}} = 0.909$	$x_2^{\text{I}}/x_1^{\text{I}} = 0.359$	$\Delta G_2^{\text{II} \rightarrow \text{I}} = 0.73$
Mixed crystals $\text{Na}_2\text{SO}_4\text{--Na}_2\text{SeO}_4$ heptahydrates						
$D_{1/2\text{II}}^{\text{exp}} = 1.06$	$m_2/m_1 = 2.23$	$x_1^{\text{II}} = 0.0403$	$x_2^{\text{II}} = 0.0847$	$x_3^{\text{II}} = 0.875$	$x_1^{\text{II}}/x_2^{\text{II}} = 0.475$	$\Delta G_1^{\text{I} \rightarrow \text{II}} = 2.06$
$D_{2/\text{II}}^{\text{exp}} = 0.14$	$m_1/m_2 = 0.449$	$x_1^{\text{I}} = 0.0953$	$x_2^{\text{I}} = 0.0297$	$x_3^{\text{I}} = 0.875$	$x_2^{\text{I}}/x_1^{\text{I}} = 0.312$	$\Delta G_2^{\text{II} \rightarrow \text{I}} = 2.51$

(1) Component  $\text{Na}_2\text{SO}_4$

(2) Component  $\text{Na}_2\text{SeO}_4$

(3) Component  $\text{H}_2\text{O}$

(I)  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{SO}_4\cdot 7\text{H}_2\text{O}$  structures, respectively

(II)  $\text{Na}_2\text{SeO}_4\cdot 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{SeO}_4\cdot 7\text{H}_2\text{O}$  structures, respectively

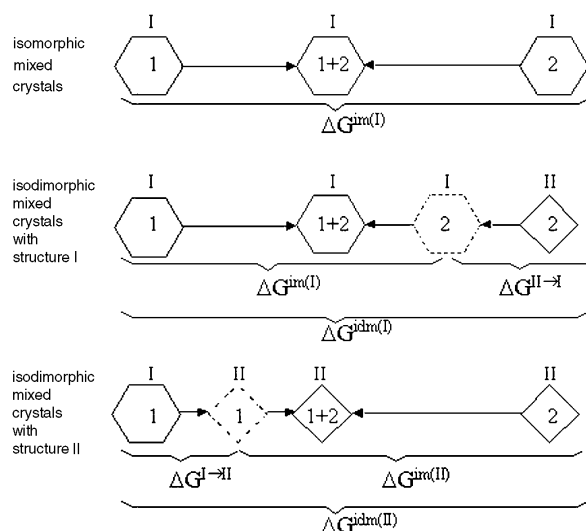


Fig. 3 Scheme for isomorphous and isodimorphous mixing [13,14].

Applying the theory for isomorphous and isodimorphous co-crystallization and using experimental data for the distribution coefficients  $D^{\text{exp}}$ , a second method was also developed for calculation of the free Gibbs energy  $\Delta G$  of the phase transition at the interruption point in the mixed crystals series. From the scheme of isodimorphous co-crystallization (Fig. 3) it follows [13,14]:

$$\Delta G_1^{\text{I} \rightarrow \text{II}} = \Delta G_{1/2}^{\text{idm}} - \Delta G_{1/2}^{\text{im}} = -RT \ln \frac{D_{1/2}^{\text{exp}}}{D_{1/2}^{\text{im}}}; \quad (5)$$

$$\Delta G_2^{\text{II} \rightarrow \text{I}} = \Delta G_{2/1}^{\text{idm}} - \Delta G_{2/1}^{\text{im}} = -RT \ln \frac{D_{2/1}^{\text{exp}}}{D_{2/1}^{\text{im}}}$$

Indices idm and im denote isodimorphous or isomorphous mixing. On the assumption of ideal isomorphous mixing, the distribution coefficients of the components between the mixed crystals and the solution  $D^{\text{im}}$  were calculated from the solubilities  $M_1$  and  $M_2$  (in molalities) of both components in their binary aqueous solutions [14,15]:

$$D_{2/1}^{\text{im}} = \left[ \frac{M_1}{M_2} \right]^2; \quad D_{1/2}^{\text{im}} = \left[ \frac{M_2}{M_1} \right]^2 \quad (6)$$

Using the experimental data on  $D_{2/1}^{\text{idm}} \equiv D^{\text{exp}}$  and the calculated data on  $D_{2/1}^{\text{im}}$  (assuming formation of a continuous mixed crystal series), one can find the free Gibbs energy of phase transition according to eqs. 5. The results obtained are given in Table 4. The data in Tables 3 and 4 display very good agreement with respect to the values of the free Gibbs energies of phase transitions calculated by the two independent methods.

From these data on the phase transitions of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  to the structures of  $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{SeO}_4 \cdot 7\text{H}_2\text{O}$ , respectively, and vice versa, the free Gibbs energies for the phase transitions from one type of mixed crystals to another type of mixed crystals  $\Delta G_{\text{mix}}$  can be calculated:

$$\Delta G_{\text{mix}}^{\text{I} \rightarrow \text{II}} = x_1^{\text{II}} \Delta G_1^{\text{I} \rightarrow \text{II}} + x_2^{\text{II}} \Delta G_2^{\text{I} \rightarrow \text{II}}; \quad \Delta G_{\text{mix}}^{\text{II} \rightarrow \text{I}} = x_1^{\text{I}} \Delta G_1^{\text{II} \rightarrow \text{I}} + x_2^{\text{I}} \Delta G_2^{\text{II} \rightarrow \text{I}} \quad (7)$$

**Table 4** Free Gibbs energies of phase transitions calculated according to eq. 5.

Mixed crystals Na <sub>2</sub> SO <sub>4</sub> -Na <sub>2</sub> SeO <sub>4</sub>	Experimentally obtained distribution coefficients	Calculated distribution coefficients eq. 6	Free Gibbs energy of phase transitions kJ·mol <sup>-1</sup>
decahydrates	$D_{1/2\text{II}}^{\text{exp}} = 2.94$ $D_{2/1\text{I}}^{\text{exp}} = 0.22$	$D_{1/2}^{\text{im}} = 3.356$ $D_{2/1}^{\text{im}} = 0.298$	$\Delta G_1^{\text{I} \rightarrow \text{II}} = 0.32$ $\Delta G_2^{\text{II} \rightarrow \text{I}} = 0.73$
heptahydrates	$D_{1/2\text{II}}^{\text{exp}} = 1.06$ $D_{2/1\text{I}}^{\text{exp}} = 0.14$	$D_{1/2}^{\text{im}} = 2.5$ $D_{2/1}^{\text{im}} = 0.40$	$\Delta G_1^{\text{I} \rightarrow \text{II}} = 2.05$ $\Delta G_2^{\text{II} \rightarrow \text{I}} = 2.51$

(1) Component Na<sub>2</sub>SO<sub>4</sub>(2) Component Na<sub>2</sub>SeO<sub>4</sub>(I) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O or Na<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O structures, respectively(II) Na<sub>2</sub>SeO<sub>4</sub>·10H<sub>2</sub>O or Na<sub>2</sub>SeO<sub>4</sub>·7H<sub>2</sub>O structures, respectively**Table 5** Free Gibbs energies of phase transitions of the mixed crystals calculated according to eq. 7.

	Molar parts of the hydrated salts in the mixed crystals at the eutonic point				$\Delta G_{\text{mix}}^{\text{I} \rightarrow \text{II}}$ kJ/mol	$\Delta G_{\text{mix}}^{\text{II} \rightarrow \text{I}}$ kJ/mol
	$x_{1*}^{\text{I}}$	$x_{2*}^{\text{I}}$	$x_{1*}^{\text{II}}$	$x_{2*}^{\text{II}}$		
decahydrates	0.736	0.264	0.643	0.357	-0.0048	-0.0050
heptahydrates	0.762	0.238	0.322	0.678	-1.04	-0.97

Here,  $x_{1*}$  and  $x_{2*}$  stand for the molar parts of the respective hydrated salts in the mixed crystals,  $x_{1*} + x_{2*} = 1$ . The results obtained are given in Table 5.

The values found for the free Gibbs energy of phase transitions indicate that the phase transitions from one to another kind of mixed crystals of decahydrates proceed with a smaller change in the free Gibbs energy than is the case of the corresponding phase transitions for heptahydrates. This result confirms the buffering action of water molecules with respect to the distortions of the crystal structures provoked by the formation of mixed crystals. A larger number of water molecules in the crystal structure favors mixed crystals formation.

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