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ENTHALPIES OF CRYSTALLIZATION OF EQUILIBRIUM SOLID PHASES OCCURRING IN THE SYSTEM $K_2SO_4 - (NH_4)_2SO_4 - H_2O$ at 298.15 K

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The concentration dependences of the differential enthalpies of solution were measured along several crystallization paths in the above-mentioned system, and the enthalpies of crystallization of mixed crystals occurring as a stable solid phase in the system were calculated on this basis. The obtained results confirmed the existence of a region of breaking continuity in the equilibrium solid phases.

Keywords: crystallization, $K_2SO_4 - (NH_4)_2SO_4 - H_2O$ system

Introduction

Equilibrium investigations of the system $K_2SO_4 - (NH_4)_2SO_4 - H_2O$ at 298.15 K have revealed that mixed crystals of $(K, NH_4)_2SO_4$ form a stable solid phase. Some investigators [1–4] reported that these crystals occur within the whole range of concentration, but others [5–8] found a point of discontinuity of peritonic type. The X-ray diffraction patterns [9] of the equilibrium solid phases also suggest the existence of a region of breaking continuity. However, this fact should be verified by other investigation methods.

To achieve this, it was decided to test the enthalpies of crystallization, $\Delta_{\mathrm{cryst}}H_{\mathrm{m}}$ of mixed crystals in both the continuity region and the presumed discontinuity region. To pinpoint these measurements were made of the concentration dependences of the differential enthalpies of solution, $\Delta_{\mathrm{sol}}H_2$, along several crystallization paths. This allowed calculation of the last differential enthalpies of solution, $\Delta_{\mathrm{sol}}H_2^{\mathrm{sat}}$, and also of the enthalpies of crystallization, according to the dependence:

$$|\Delta_{\mathrm{sol}}H_2^{\mathrm{sat}}| = |\Delta_{\mathrm{cryst}}H_{\mathrm{m}}| \tag{1}$$

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Experimental

The experiments were carried out with a home-made calorimeter of isoperibol type, a detailed description of which was given in a recent paper [10].

In order to obtain appropriate solid phases, the equilibrium data of Dejewska [11] were used. In the prepared solutions and solid phases, the potassium ion content was determined by means of sodium tetraphenylborate, that of ammonium ion through decomposition with sodium hydroxide in a Parnas apparatus, and that of sulphate by means of gravimetric analysis.

Solid phases, after drying, were crushed in a ball vibrating grinder. For every sample, the mother liquor content was determined.

All solutions used in calorimetric experiments were prepared by weighing. Double distilled water was used throughout the experiments. Analytical grade salts (POCh. Gliwice, Poland) were used.

The calculations were performed with an IBM PC/AT microcomputer, using the program Statgraphics (Statistical Graphics System by Statistical Graphics Corporation, vers. 2.6).

Results and discussion

For the calorimetric work, a knowledge of the equilibrium data was essential, i.e. the solubility isotherm data and the compositions relating to its solid phases. Research performed earlier in our Institute [11] was therefore utilized and suitable equilibrium phases were obtained. The time necessary for the system to reach the equilibrium state from supersaturated solution was 24 h.

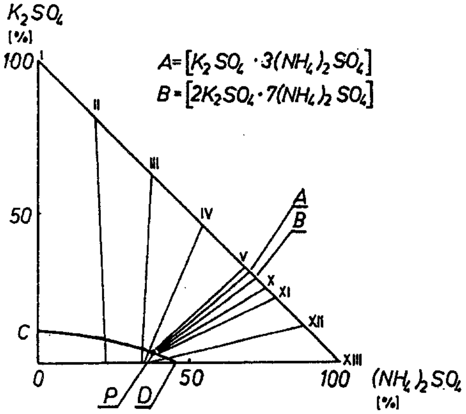

Fig. 1 The system K_2SO_4 – $(NH_4)_2SO_4$ – H_2O at 298.15 K

Figure 1 shows the investigated system at 298.15 K. In the section K_2SO_4 – $(NH_4)_2SO_4$, mixed crystals of $(K, NH_4)_2SO_4$ occur; curve C–D represents the solubility isotherm. Section A–B is the presumed discontinuity region, and point P is the peritonic point. The compositions of the mixed crystals at points A and B were calculated stoichiometrically on the basis of the analytical data for point A: K_2SO_4=30.50% and $(NH_4)_2SO_4$=69.50%; and for point B: K_2SO_4=27.50% and $(NH_4)_2SO_4$=72.50%. The compositions of the solid phases established on this basis are $K_2SO_4\cdot 3(NH_4)_2SO_4$ for point A and $2K_2SO_4\cdot 7(NH_4)_2SO_4$ for point B.

The differential enthalpies of solution were measured along the crystallization paths, from binary solutions of $(NH_4)SO_4$ – H_2O to the solubility isotherm, i.e. as in the case of binary systems, but now with binary and ternary solutions as solvent, not water and binary solutions.

The crystallization paths II–V and X–XII represent mixed crystals from the continuity region; paths VI–IX mixtures of crystals A and B; and paths I and XIII potassium and ammonium sulphates, respectively.

The paths were described by the equation

$$c_2 = c_2^0 + k \cdot c_1 \tag{2}$$

where c_1 and c_2 are the concentrations of K_2SO_4 and $(NH_4)_2SO_4$ (in %), respectively, c_2^0 is the concentration of the binary solution of $(NH_4)_2SO_4$ (in %), and k is a constant.

The coefficients in Eq. (2) are given in Table 1, together with data relating to the equilibrium phases occurring along the crystallization paths.

Table 1 Coefficients of Eq. (2) and compositions of equilibrium phases along the crystallization paths; M_{cr} denotes the molar mass of mixed crystals

Cristallization path	Coefficients of Eq. (2)		Satur. solns	Mixed crystals		
	c_2^0 %	k	c_1^{sat} %	K_2SO_4 %	K_2SO_4 mol %	M_{cr} $g\cdot mol^{-1}$
II	22.77	–0.0422	7.60	80.63	75.94	164.14
III	33.57	0.0707	5.02	62.04	55.34	155.45
IV	34.80	0.4238	4.25	45.79	39.05	148.59
V	34.31	1.0796	3.60	31.60	25.94	143.07
VI	34.56	1.2332	3.32	29.30	23.91	142.21
VII	34.36	1.2945	3.32	28.61	23.30	141.96
VIII	34.31	1.3115	3.32	28.43	23.15	141.89
IX	34.02	1.3996	3.32	27.50	22.34	141.55
X	33.72	1.6817	3.18	24.71	19.93	140.54
XI	33.48	2.0000	2.97	22.17	17.76	139.62
XII	32.46	4.8426	1.79	11.56	9.02	135.94

As already mentioned, the differential enthalpies of solution of mixed crystals were measured along the crystallization paths. As concerns both the measured $\Delta_{sol}H_2$ values and the compositions of mixed crystals, corrections were made for the mother liquor content, amounting to 2–7% of the dry mass of the crystals. The obtained concentration dependences of $\Delta_{sol}H_2$ were described by the equation

$$\Delta_{sol}H_2=\sum_{i=0}^{2} a_i \cdot m_2^i \tag{3}$$

where a_i is an adjustable parameter, and m_2 is the molality of ammonium sulphate.

From these dependences and the known compositions of the saturated solutions, the last differential enthalpies of solution were calculated and hence from Eq. (1) the molar enthalpies of crystallization of mixed crystals.

Those data and also the coefficients in Eq. (3) are listed in Table 2, together with the number of experimental points used in each fit.

The obtained results permit calculation of the excess enthalpies of crystallization, $\Delta_{cryst}H_m^E$, which were taken as the measure of interactions between the components of mixed crystals. These values were determined as the difference between the enthalpy of crystallization, $\Delta_{cryst}H_m$, per mole of mixed crystals, $(K, NH_4)_2SO_4$, and the sum of the enthalpies of crystallization of a molar mixture of K_2SO_4 and $(NH_4)_2SO_4$, corresponding to the mixed crystals, according to the following equation:

$$\Delta_{cryst}H_m^E = \Delta_{cryst}H_m - (x_1 \cdot \Delta_{cryst}H_{m(1)} + x_2 \cdot \Delta_{cryst}H_{m(2)}) \tag{4}$$

where $\Delta_{cryst}H_{m(1)}$ and $\Delta_{cryst}H_{m(2)}$ are the crystallization enthalpies of K_2SO_4 and $(NH_4)_2SO_4$, respectively; and x_1 and x_2 are the mole fractions of K_2SO_4 and $(NH_4)_2SO_4$ in the mixed crystals, respectively. The calculations yielded $\Delta_{cryst}H_{m(1)}=-20167\pm349\ \mathrm{J\cdot mol^{-1}}$ and $\Delta_{cryst}H_{m(2)}=-7954\pm257\ \mathrm{J\cdot mol^{-1}}$ [12].

The values of $\Delta_{cryst}H_m^E$, calculated in this way, as a function of mixed crystal composition (expressed in mol%), are presented in Fig. 2. Because of the very small differences in their contents, the values representing solid phases in the discontinuity region (points VI–IX) are shown in the window on an enlarged concentration scale. Segment A–B is the presumed discontinuity region.

It can be seen from the graph that the values of $\Delta_{cryst}H_m^E$, representing the continuity region (points II–V and X–XII) lie on a parabola. However, the values representing the discontinuity region vary in the range $3710\pm278\ \mathrm{J\cdot mol^{-1}}$ (point IX) and $4013\pm278\ \mathrm{J\cdot mol^{-1}}$ (point VII) and lie distinctly outside the curve. Moreover, the points representing solid phases occurring near the discontinuity region, i.e. points V and XI, are also outside the curve.

Table 2 Coefficients of Eq. (3) and values of crystallization enthalpies of mixed crystals; N – number of experimental points used in each fit, R – correlation coefficient

Crystallization path	N	a_o / $\mathrm{J \cdot mol^{-1}}$	a_1 / $\mathrm{J \cdot kg \cdot mol^{-2}}$	a_2 / $\mathrm{J \cdot kg^2 \cdot mol^{-3}}$	R	$-\Delta_{crys}H_m$ / $\mathrm{J \cdot mol^{-1}}$
II	14	−1.76107E5	1.25523E5	−2.43212E4	0.8310	14711±184
III	16	−9.58512E4	3.79332E4	−4.21768E3	0.8352	10916±178
IV	17	−4.44373E4	1.36324E4	−1.29741E3	0.8411	9050±168
V	19	−3.38335E4	9.28372E3	−8.41158E2	0.8671	8473±137
VI	21	−5.89056E3	−3.09523E3	5.64302E2	0.8300	7150±181
VII	22	1.58199E3	−5.58135E3	7.77733E2	0.8655	6787±146
VIII	24	3.00972E4	−1.77719E4	2.07308E3	0.8004	6806±207
IX	25	2.28575E4	−1.41337E4	1.62977E3	0.8003	6972±208
X	27	4.87444E3	−5.29012E3	5.62103E2	0.8750	7475±109
XI	26	2.57333E3	−4.02010E3	4.19193E2	0.8677	6986±135
XII	25	2.47286E3	−3.60899E3	3.42592E2	0.8710	7020±118

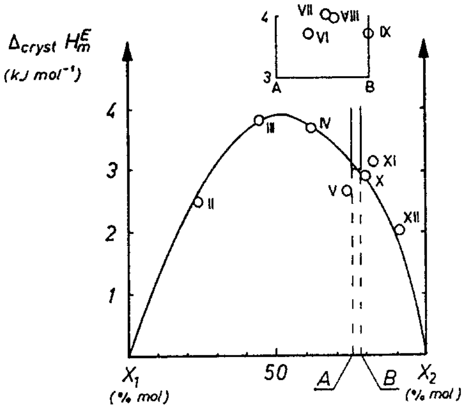

Fig. 2 The excess molar enthalpies of crystallization of mixed crystals, $\Delta_{cryst}H^E_m$, as a function of their contents; x_1 and x_2 are the molar fractions of K_2SO_4 and $(NH_4)_2SO_4$, respectively

The presented eesults point to the region of presumed discontinuity different interactions between the components of mixed crystals occur than in the continuity region. They also confirm the fact of the existence of two such regions.

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Zusammenfassung — Für die obengenannten Systeme wurden, mehrere Kristallisationsradien entlang, die Messungen der Konzentrationsabhängigkeiten durchgeführt, die es unter differentiellen Lösungsenthalpien gibt. Auf dieses Grundlage wurden die Kristallisationenthalpien von Mischkristallen, die als stabile feste Phase vorkommen, bestimmt.
Die erreichten Ergebnisse bestätigen die Tatsache, daß ein unterbrochenes Gebiet in den gleichgewichten festen Phasen vorkommt.