

## Sub-solid equilibria in the systems $\text{Li}_2\text{SO}_4\text{--Na}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$

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### Abstract

Sub-solid regions of the phase diagrams of the systems  $\text{Li}_2\text{SO}_4\text{--Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$  were investigated in the concentration range 0–50 mol.%  $\text{Na}_2\text{SO}_4$  and 0–100 mol.%  $\text{K}_2\text{SO}_4$ , respectively. All components of these systems exist in the high- and low-temperature polymorphic forms. Experimental results are compared with calculated curves describing the equilibrium between the solid solution of the high-temperature phase and the pure low-temperature form of  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ , respectively. The systems in question can be used for storage of thermal energy.

### INTRODUCTION

The systems  $\text{Li}_2\text{SO}_4\text{--Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4\text{--K}_2\text{SO}_4$  belong to the class of systems whose components can exist in several polymorphic forms. Equimolar compounds,  $\text{LiNaSO}_4$  and  $\text{NaKSO}_4$ , are formed in both systems. As the enthalpy of the sub-solid transformation is rather high ( $25.0 \text{ kJ mol}^{-1}$  for  $\text{Li}_2\text{SO}_4$  [1]) these systems can be applicable to the storage of thermal energy.

In this work we will present experimental data on the phase equilibria in the sub-solid region of these systems and compare these with calculated equilibrium curves.

### EXPERIMENTAL

The phase equilibria were investigated by the classical “cooling curves” method. The decrease in temperature was measured by a Pt/Rh10–Pt thermocouple. The thermoelectric voltage of the thermocouple was measured by a digital voltmeter connected on-line with a computer. The “temperature” was measured in 5 s intervals, and the cooling rate was  $0.5\text{--}2.0 \text{ K min}^{-1}$ . The “cooling curves” obtained were treated numerically. The reproducibility of the determination of the equilibrium temperatures was  $\pm 0.2 \text{ K}$ . The thermocouple was calibrated using the temperatures of melting of pure

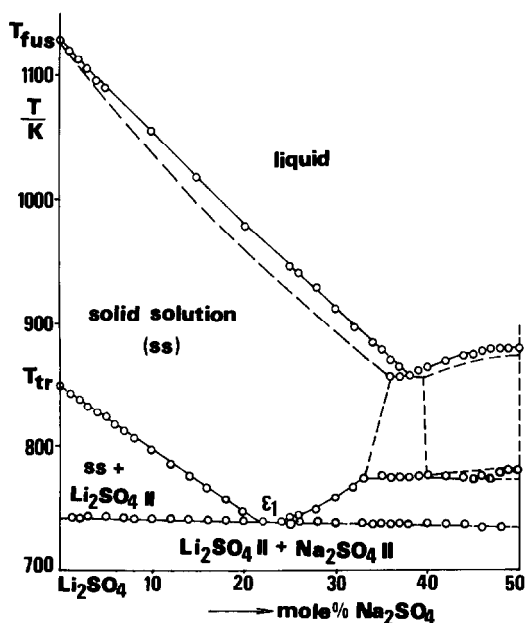


Fig. 1. Experimental phase diagram of the system  $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$  (0–50 mol.%  $\text{Na}_2\text{SO}_4$ ): full line and points, experimental; dashed line, predicted.

salts [2]. The uncertainty of the experimental data was estimated to be  $\pm 1$  K.

## RESULTS

Forty mixtures were investigated in the sub-system  $\text{Li}_2\text{SO}_4\text{-LiNaSO}_4$ . From the point of view of this work, the sub-system  $\text{LiNaSO}_4\text{-Na}_2\text{SO}_4$  is of less interest. Moreover, it is described sufficiently in the literature [3–6]. The experimental results are presented in Fig. 1.

In the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ , 38 mixtures were investigated. The experimental phase diagram is presented in Fig. 2. (The tabulated data can be supplied by the authors on request.)

## DISCUSSION

In the systems studied, the high-temperature phases form solid solutions while the low-temperature phases, with the exception of  $\text{K}_2\text{SO}_4$ , are immiscible. When the solid solution of the high-temperature phase is in equilibrium with the pure component of the low-temperature phase, it follows the equation [7]

$$\ln a_s(B_1) = \frac{\Delta H_{tr}}{R} \left( \frac{1}{T_{tr}(B_1/B_2)} - \frac{1}{T} \right) \quad (1)$$

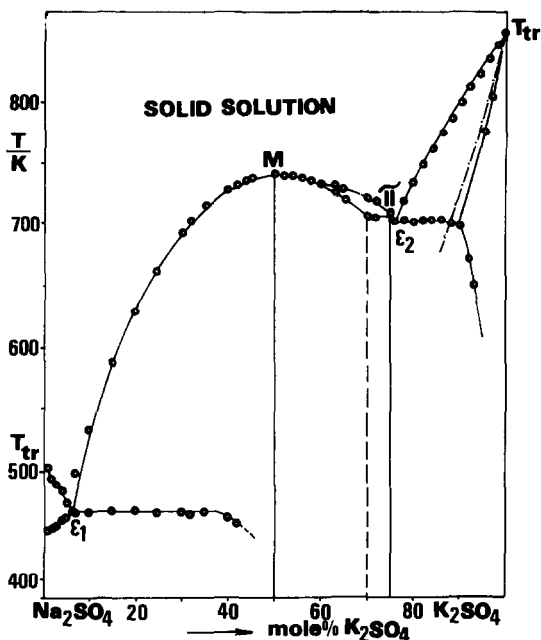


Fig. 2. Sub-solid part of the phase diagram of the system  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ : full line and points, experimental; dashed and dotted line calculated; dashed line, predicted.

where  $a_s(B_1)$  is the activity of the component  $B_1$  in the high-temperature solid solution,  $\Delta H_{tr}(B_1/B_2)$  is the enthalpy of transition of pure component B and  $T_{tr}$  is the temperature of the phase transition for the pure component. In eqn. (1), it is assumed that  $\Delta H_{tr}$  does not depend on temperature. This is an acceptable approximation provided  $T_{tr} - T < 100$  K. In the calculation of the equilibrium temperature, we may assume in the first approximation that the solid solution is thermodynamically ideal and that this ideal behaviour can be defined in the same way as in molten electrolytes [8]. Then, for the activity of component  $B_1$  in a binary mixture of the type  $M_2\text{SO}_4\text{-N}_2\text{SO}_4$  (M, N being univalent cations), it follows that

$$a_s(B_1) = x_B^2 \quad (2)$$

where  $x_B$  is the mole fraction of component B in the mixture.

#### The system $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$

As can be seen from Fig. 3, the experimental and calculated curves of the sub-solid equilibrium of  $\text{Li}_2\text{SO}_4$  in the system  $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$  are in good agreement. The value  $\Delta H_{tr}(\text{Li}_2\text{SO}_4) = 25.0 \text{ kJ mol}^{-1}$  [1] was used in this calculation. This supports the assumption that the solid solution of  $\text{Li}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$  behaves almost ideally. The equilibrium data presented in this work (see Fig. 1) are in good agreement with the results published by Schroeder [6].

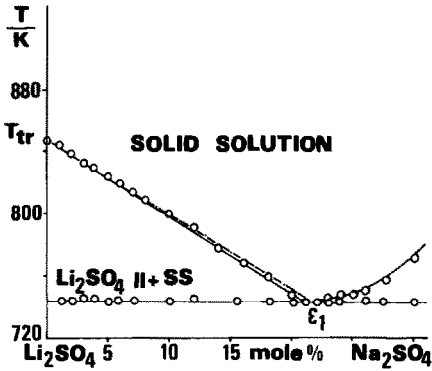


Fig. 3. Detail of sub-solid region of  $\text{Li}_2\text{SO}_4$ -rich corner of the phase diagram of the system  $\text{Li}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ : full line and points, experimental; dashed and dotted line, calculated.

#### The system $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$

The phase diagram of the system  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  has been studied rather extensively [3,4,9-18]. There are, however, striking differences in the cited papers, especially as far as the sub-solid region of the phase diagram is concerned. Nacken [4], for example, has assumed the existence of  $\text{NaKSO}_4$  in this system but does not report any formation of solid solution of the low-temperature form of  $\text{K}_2\text{SO}_4$ . Jänecke [11] assumes a peritectoid decomposition of the solid solution formed on the basis of the low-temperature phase of  $\text{K}_2\text{SO}_4$ . Bellanca [16] has reported mutual solubility of the low-temperature phases of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  and the existence of  $\text{NaKSO}_4$ . As in the previous case, we tried to find out the most probable equilibrium data by combination of the experimental investigation and the calculation of sub-solid equilibrium curves.

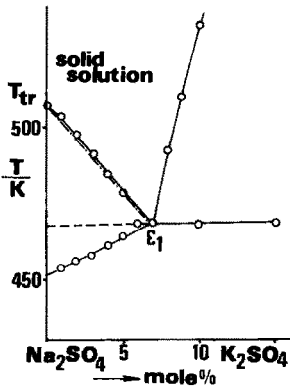


Fig. 4. Detail of sub-solid region of  $\text{Na}_2\text{SO}_4$ -rich corner of the phase diagram of the system  $\text{Na}_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$ : full line and points, experimental; dashed and dotted line, calculated; dashed line, predicted.

As can be seen from Fig. 4, the calculated data for  $\text{Na}_2\text{SO}_4$  are in good agreement with our experimental data. In these calculations,  $\Delta H_{\text{tr}}(\text{Na}_2\text{SO}_4) = 7.48 \text{ kJ mol}^{-1}$  [19]. The same assumptions were made as in the former case. It was assumed in the calculations that  $a(\text{Na}_2\text{SO}_4, \text{low-temperature form}) = 1$ . Thus it follows that the experimentally observed change in the temperature of the end of the decomposition of the solid solution  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$  in the  $\text{Na}_2\text{SO}_4$ -rich region is an "artefact", probably caused by the non-equilibrium conditions of the eutectoid reaction.

On the  $\text{K}_2\text{SO}_4$  side (Fig. 2), the sub-solid equilibrium curve of  $\text{K}_2\text{SO}_4$ , calculated assuming that  $a(\text{K}_2\text{SO}_4, \text{low-temperature form}) = 1$ , disagrees considerably with the experimental results ( $\Delta H_{\text{tr}}(\text{K}_2\text{SO}_4) = 8.95 \text{ kJ mol}^{-1}$  [19]). Thus we may assume that in this case the solid solutions are formed on the basis of both the high-temperature and the low-temperature form of  $\text{K}_2\text{SO}_4$ . The experiment confirms this conclusion.

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