tätskoeffizienten so definiert sind, daß deren Grenzwerte für alle Systeme den Wert 1 annehmen. Bei anderen Definitionen, sofern sich aus diesen für die Logarithmen der Aktivitätskoeffizienten überhaupt noch Reihen entwickeln lassen, überlagern sich diesem Ansatz weitere Terme, die auch die Symmetrie der Funktion beeinflussen.

Für die molare Zusatzentropie erhält man aus Gl. (23) und Gl. (A7)

$$\overline{S}^{\mathrm{E}} = C_0'' + (D_0'' - C_0'')\, x_2 + x_2(1-x_2)\,[a''' + b''' x_2 + c''' x_2^2]. \qquad \text{(A10)}$$

Für die Koeffizienten gelten die Beziehungen

$$C_0'' = -\partial C_0/\partial T, \quad D_0'' = -\partial D_0/\partial T,$$
$$a''' = -\partial a''/\partial T, \; b''' = -\partial b''/\partial T, \; c''' = -\partial c''/\partial T. \qquad \text{(A11)}$$

Für Gl. (A10) gilt das oben Gesagte.

Aus Gl. (24) und (A7) folgt für die molare Zusatzenthalpie

$$\overline{H}^{\mathrm{E}} = x_2(1-x_2)\,[a'''' + b'''' x_2 + c'''' x_2^2] \qquad \text{(A12)}$$

mit

$$a'''' = a'' - T\cdot\partial a''/\partial T,$$
$$b'''' = b'' - T\cdot\partial b''/\partial T \qquad \text{(A13)}$$

und

$$c'''' = c'' - T\cdot\partial c''/\partial T.$$

Man sieht, daß durch die Differentiation die überlagerten Terme mit C_0 und D_0 herausfallen. Gl. (A12) stimmt mit Gl. (31) völlig überein.

Herrn Prof. Dr. R. HAASE danke ich für wertvolle Hinweise und für die freundliche Unterstützung der Arbeit.

The Phase Diagram of the System $Li_2SO_4-K_2SO_4$ from Differential Thermal Analysis

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The phase diagram of Li_2SO_4-K_2SO_4 has been determined by differential thermal analysis. By making use of an improved method, the sensitivity of the measurements has been increased and we have found a number of new transitions, especially in the lithium sulphate rich region. We have also detected a new transition in $LiKSO_4$ at 672 °C. The new transitions have lead to an unusually complicated phase diagram compared with other sulphates. Some of the results have been checked by measuring the electrical conductivities of the phases.
NFA (9014)

About 60 years ago NACKEN[1] determined the phase diagrams of some binary sulphate systems by means of thermal analysis. OYE[2] used concentration cells for the determination of the phase diagram of $Li_2SO_4-Ag_2SO_4$ and we have studied the system $Li_2SO_4-Na_2SO_4$ by means of differential thermal analysis. Except for these investigations only a number of liquidus curves have been studied by Russian authors.

Since both the phase diagrams of $Li_2SO_4-Na_2SO_4$ and $Li_2SO_4-Ag_2SO_4$ given by NACKEN[1] were incorrect and since we in this laboratory have made a number of transport measurements in $Li_2SO_4-K_2SO_4$ (l.c.[3–6]), we decided to check whether also this phase diagram should be corrected. Already some preliminary measurements showed a much greater number of transitions than expected and than NACKEN had found.

In a conventional DTA experiment, the thermocouples are generally not in direct contact with the sample, but shielded with a tube of glass or metal. This is generally necessary due to corrosion, but leads to a comparably low sensitivity, especially if we have several transitions with small temperature differences. We have, however, found that it is possible to use Platinel II thermocouples in direct

[1] R. NACKEN, Neues Jahrb. Mineral. Geol., Beilageband **24**, 23 [1907].
[2] H. OYE, Thesis, Trondheim 1963.
[3] V. LJUBIMOV and A. LUNDÉN, Z. Naturforsch. **21 a** 1592 [1966].
[4] A. LUNDÉN and V. LJUBIMOV, Z. Naturforsch. **23 a**, 1558 [1968].
[5] A. KVIST, Z. Naturforsch. **21 a**, 1221 [1966].
[6] B. AUGUSTSSON and A. KVIST, Z. Naturforsch. **22 a**, 1177 [1967].

contact with a molten sulphate without any corrosion at all. With these thermocouples it is possible to register temperature differences between the two samples, which are smaller than 0.1 °C with samples of about 0.10 g. The experimental technique is discussed further elsewhere[7].

To check the results obtained with our equipment and with other methods, we have made some measurements in the Li_2SO_4—Ag_2SO_4 system. The agreement between our results and those obtained by OYE[2] from concentration cell measurements is good (Table 1). The results generally differ less than 2 °C, but the scattering in OYE's values seems to be somewhat larger than in ours.

Measurements in the $Li_2SO_4 - K_2SO_4$ system were performed at 26 different concentrations and to check the obtained results, we have also measured the electrical conductivities at some concentrations.

The accuracy of the DTA measurements has been estimated to ± 1 °C, but for some transitions, especially where the slope of the lines is large or where several peaks with small temperature intervals have been obtained, the accuracy is of cause lower.

The obtained transitions are tabulated in Table 2 and the phase diagram is shown in Fig. 1.

In the pure salts the transitions are identical with those given in the literature. MAJUMDAR and ROY[8] report for instance 583 °C as transition point in pure potassium sulphate compared with our result 584 ± 1 °C. The melting point of this salt was determined from conductivity measurements. In $LiKSO_4$, however, a new transition was found at 672 °C, while the transition at 436 °C is in good agreement with literature data[9–10].

The phase diagram above 50 mole% K_2SO_4 is quite conventional compared with other binary

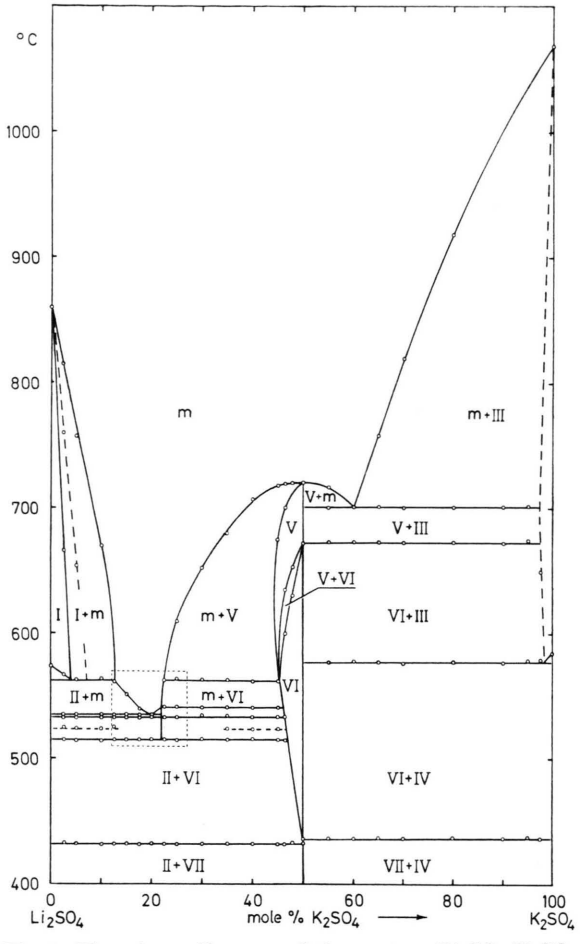

Fig. 1. The phase diagram of the system Li_2SO_4-K_2SO_4. Structures: I: fcc[2], II: monoclinic[2], III: hexagonal[8], IV: orthorombic[8], V: unknown, VI: hexagonal[9], VII: hexagonal[9]. The area inside the dotted square is shown in Fig. 2. The dotted line in m + I has been discussed elsewhere[6].

sulphates. The maximal solubility of Li_2SO_4 in pure potassium sulphate does not exceed 3 mole%, while the potassium sulphate solubility in $LiKSO_4$ is

mole % Ag_2SO_4	Liquidus	Solidus	Other transitions 1	2	3	4
10	775 (774)	732 (724)	545 (541)	517 (515)	421 (417)	392 (393)
28	619 (626)	560 (559)		516 (515)	422 (417)	391 (393)
80	576 (574)	576 (574)	566 (568)	498 (495)	405 (404)	391 (393)

Table 1. Transitions at some concentrations compared with those obtained by OYE[2](within parentheses) for the system Li_2SO_4-Ag_2SO_4 in °C.

[7] K. SCHROEDER and A. KVIST, Z. Naturforsch. **23 a**, 773 [1968].
[8] A. J. MAJUMDAR and R. ROY, J. Phys. Chem. **69**, 1684 [1965].
[9] H. F. FISCHMEISTER and A. RÖNNQUIST, Arkiv Kemi **15**, 393 [1960].
[10] A. J. BRADLEY, Phil. Mag. **49**, 1225 [1925].

mole % K_2SO_4	1	2	3	4	5	6	7	8	9	10	Liquidus
0.0							574				860
2.5	433	515	525	533	535		567		666	760	815
5.0	432	514	524	533	534		563			654	757
10.0	431	514	524	533	535		564				670
12.5	432	515	526	533	535						561
15.0	432	515		533	535						551
17.5	432	515		533	535						540
20.0	432	515		533							535
22.5	432	515		533		541					562
25.0	431	514		534		542	564				610
30.0	431	516		535		541	563				653
35.0	432	515	524	535		541	563				680
40.0	432	516	523	533		541	561				708
45.0	432	515	524	534		541	562			675	718
46.5	432	515		534				600	635	701	720
48.0	433							630	653		720
50.0	432	436							672		720
55.0		437						577	673	700	717
60.0		436						578	673		702
65.0		437						577	673	701	758
70.0		436						576	672	700	819
80.0		437						577	673	701	918
90.0		436						576	672	701	
95.0		437						579	675	702	
97.5		436						579	649		
100.0								584			1068

Table 2. The obtained transitions in the system Li_2SO_4-K_2SO_4 in °C. The melting point of pure potassium sulphate was obtained from conductivity measurements.

much smaller. In the lithium sulphate rich region we have found a larger number of transitions than expected. Some of these transitions could not be seperated when the thermocouple was shielded with a glass tube[6].

The liquidus curve of Li_2SO_4—K_2SO_4 has been studied at least ten times by BERGMAN and coworkers[11], but the disagreement between their different papers is remarkably great. If we for instance consider $LiKSO_4$, the melting point varies between 724 and 736 °C in papers published within a few years[11]. Our melting point (720 °C) is even lower than 724 °C and is in better agreement with the one obtained by NACKEN[1]. The eutectica are situated at about 20 and 60 mole% K_2SO_4 and here the melting points are in better agreement with BERGMAN and coworkers.

Fig. 2 shows the different phases in the lithium sulphate rich region near the eutectic. The appearance of the phase diagram resembles for instance that of Mn_3O_4—SiO_2 (l.c.[12]).

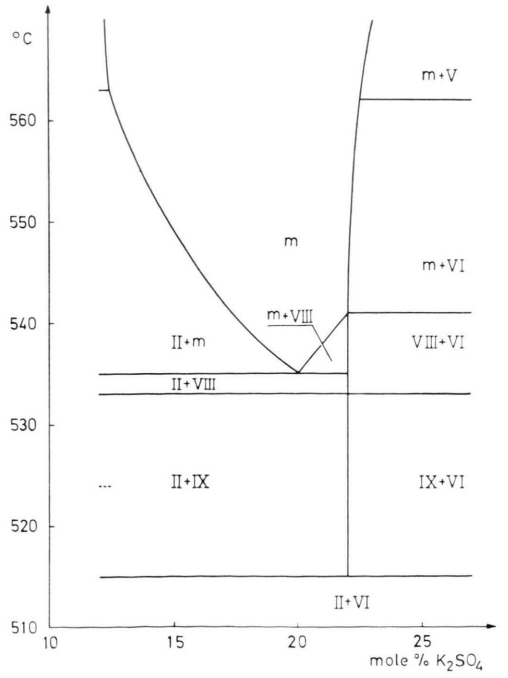

Fig. 2. The phase diagram of the system Li_2SO_4-K_2SO_4 around the eutectic at 20 mole% K_2SO_4. The structures of the phases VIII and IX are unknown.

[11] a) A. G. BERGMAN and E. L. BAKUMSKAYA, Zh. Neorg. Khim. **1**, 2091 [1956]. — b) A. G. BERGMAN, A. I. KISLOVA and E. I. KOROBKA, Zh. Obshchei Khim. **24**, 1133 [1954].

[12] A. MUAN, Am. J. Sci. **257**, 300 [1959].

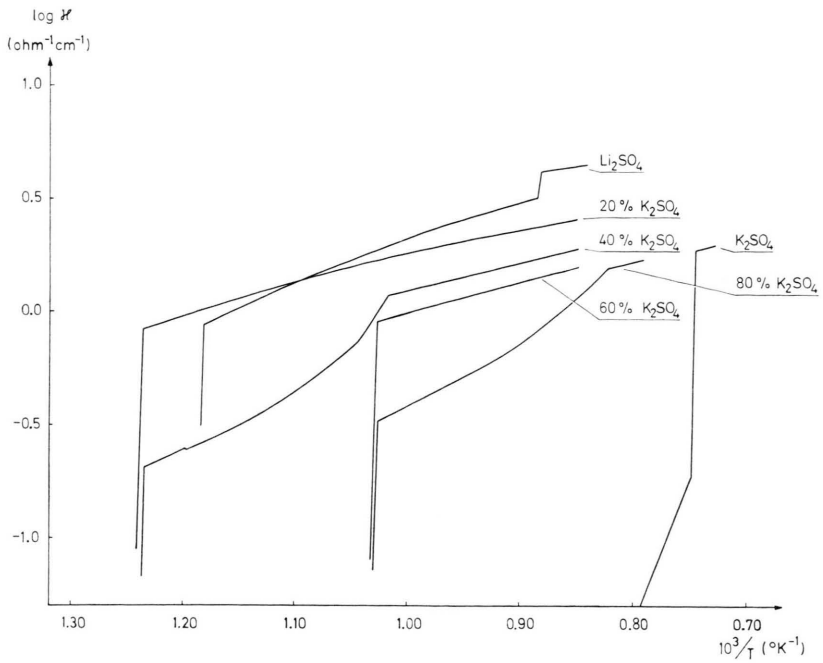

Fig. 3. The log of the specific electrical conductivity of some mixtures between Li_2SO_4 and K_2SO_4 as a function of the inverse temperature in °K.

A compound exists in $(Li, K)_2SO_4$ at about 22 mole% potassium sulphate between 515 and 541 °C. It has been rather difficult to determine the temperatures of the different transitions on both sides of this compound due to the small temperature difference, about 2 °C, between the eutectic line and a transition in the compound at about 533 °C. The corresponding two peaks on the DTA curves, however, are well separated, especially when the temperature is increased slowly.

Between 2.5 and 12.5, and between 35 and 45 mole% K_2SO_4 a small peak is obtained at about 524 °C which has not been possible to explain. Since the sulphate ion is not completely spherical it might be caused by changes in the rotational properties of the sulphate ions. It seems improbable that the peak is caused by impurities in the salt.

The temperature differences between the different peaks in the lithium sulphate rich region are too small for X-ray investigations and it is also difficult to find a method for making more accurate investigations of the phases.

We have previously found it useful to combine DTA experiments with measurements of the electrical conductivities of the salt[6], especially when the conductivity of the salt is high. In the system $Li_2SO_4-K_2SO_4$ this is the case only for a few of the phases (Fig. 3), but some conclusions can be drawn. If we for instance have a pure phase as in pure lithium sulphate, a sudden change in the conductivity is obtained at the melting point, but for a phase mixture the log $\varkappa$-curve (as a function of $1/T$) is slightly concave. The curve is also continous at the melting point and this can be seen for Li_2SO_4 with 40 and 80 mole% Li_2SO_4. The transition points obtained from the conductivity measurements are in good agreement with the DTA values.

It has generally been accepted that the binary sulphates form comparably simple phase diagrams, but the three systems $Li_2SO_4-K_2SO_4$, $Li_2SO_4-Ag_2SO_4$ and $Li_2SO_4-Na_2SO_4$ can hardly be considered simple. Investigations of lithium sulphate with small quantities of other divalent sulphates also indicate that other systems are rather complex[13].

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[13] K. Schroeder and A. Kvist, unpublished.