The Phase Diagrams of the Binary Systems Li_2SO_4–Na_2SO_4, Li_2SO_4–Rb_2SO_4, and Li_2SO_4–Cs_2SO_4

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The phase diagrams of the systems Li_2SO_4–Rb_2SO_4 and Li_2SO_4–Cs_2SO_4 have been determined by means of differential thermal analyses and electrical conductivity measurements. We have also modified our previously published phase diagram of the system Li_2SO_4–Na_2SO_4, especially in the region near the equimolar mixture.

Pure lithium sulphate forms a face-centered cubic high temperature modification, and nearly equimolar $Li_2SO_4-Na_2SO_4$ and $Li_2SO_4-Ag_2SO_4$ form high temperature modification *. Preliminary measurements indicate that other binary sulphates might form similar phases [2]. All these phases are characterized by an extremely high mobility of the cations in a lattice which is built up by the sulphate ions [2–5]. In other pure salts and salt systems too, high conductivity phases have been investigated [6–9]. The high temperature modifications can, due to their low electrical resistance and often purely ionic conductivity be used as solid electrolytes in electrochemical devices. BUZZELLI [10–12] has recently proposed lithium sulphate and mixtures of lithium sulphate with some other salts as electrolytes for high temperature batteries.

The phase diagram of $Li_2SO_4-Ag_2SO_4$ has been investigated by ØYE [1, 13]. The phase diagram of $Li_2SO_4-Na_2SO_4$, however, is much more complicated, especially in the nearly equimolar region. Since the sensitivity of our DTA apparatus has been improved considerably, it has been possible for us to detect some new transitions in $Li_2SO_4-Na_2SO_4$ and to correct our previously published phase diagram [14]. At several concentrations we have also been able to confirm the results by measurements of the electrical conductivity.

We have previously also investigated the phase diagram of the system $Li_2SO_4-K_2SO_4$. No high conductivity phase is formed in this system, except for the f.c.c. phase in the lithium sulphate rich region [15].

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* In the nearly equimolar mixture [1].

Experimental

The salts were all of reagent quality and were used without further purification.

The experimental technique has been described in detail in some previous papers [15, 16]. Since our first measurements in the $Li_2SO_4-Na_2SO_4$ system the DTA apparatus has been considerably modified and we have, by using Platinel thermocouples [17] in direct contact with the samples increased the sensitivity. We have now found it possible to distinguish between transitions that are as narrow as 2 or 3 °C. In some concentration ranges it is impossible to determine the liquidus curves from the DTA curves and we have in these cases measured the electrical conductivity of the salts, a technique that we previously have found very useful for the $Li_2SO_4-K_2SO_4$ system [15].

Results

The System $Li_2SO_4-Na_2SO_4$

The transitions obtained from the DTA and electrical conductivity measurements are given in Table 1. The constructed phase diagram is shown in Figure 1.

The solubility of sodium sulphate in f.c.c. lithium sulphate is about 30 mole % at 600 °C, but below 575 °C, where lithium sulphate forms a low conductivity monoclinic phase, the sodium sulphate solubility is negligible.

Sodium sulphate is hexagonal between the melting point and 240 °C. At 570 – 600 °C KHLAPOVA [18] has reported a second order transition which is characterized by a change in the lattice parameters of the hexagonal lattice. Also EVSEEVA [19] and COOK et al. [20] have reported a phase transition in the same temperature region. In spite of repeated DTA experiments it has not been possible for us to confirm the transition in pure sodium sulphate. However, the DTA curves for $0.8\,Na_2SO_4 \cdot 0.2\,Li_2SO_4$ and $0.85\,Na_2SO_4 \cdot 0.15\,Li_2SO_4$ show a transition which

Table 1. The transitions in $Li_2SO_4-Na_2SO_4$. The values within brackets were obtained from conductivity measurements.

Mole% Na_2SO_4	(°C)						
0		573					860
5	472	548				804	816
10	474	525				764	785
15	476	501				714	739
20	473	476				681	706
25	474	474				646	672
30	474	487				619	643
32.5	474	495				601	623
35	476	504				591	614
36.5	475	507				592	601
38.5	476	505				592	592
40	476	504		540		595	595
42.5	475	505	509			599	600
45	475	505	513			604	605
47.5			516			611	612
50			518			615	615
52.5			516		541	619	621
55	480		514	531	565	625	625
57.5	481		512	553	590	630	630
60	479		504	570	612	631	631
62.5	481		499	593	635	—	645
65	480		494	610	—	634	667
67.5	478		487			634	689
70	480					649	697
75	478					673	727
80	475				510	706	768
85	463				540		794
90	446					778	824
95						835	859
100					(574)		(884)

must be caused by the change in the lattice parameters of the hexagonal structure. From electrical conductivity measurements in cells with small cell constants it has been possible for us to register the temperature of the second order transition both in pure sodium sulphate and some mixtures with lithium sulphate. Figure 2 shows the specific electrical conductivity of $0.9\,Na_2SO_4 \cdot 0.1\,Li_2SO_4$. The curve is broken at the transition in the hexagonal phase.

KRACEK et al. [21] have thoroughly investigated the polymorphism of sodium sulphate in the temperature interval 160 to 240 °C, where five different modifications have been found.

The structure of nearly equimolar $Li_2SO_4 - Na_2SO_4$ has been investigated by ØYE [1], who found that within a rather small temperature interval a pseudocubic phase is formed. We have previously measured the electrical conductivity [4] of this phase and we have also measured different diffusion coefficients [22].

The liquidus curve obtained by BAKUMSKAYA and BERGMAN [23] is in good agreement with our results,

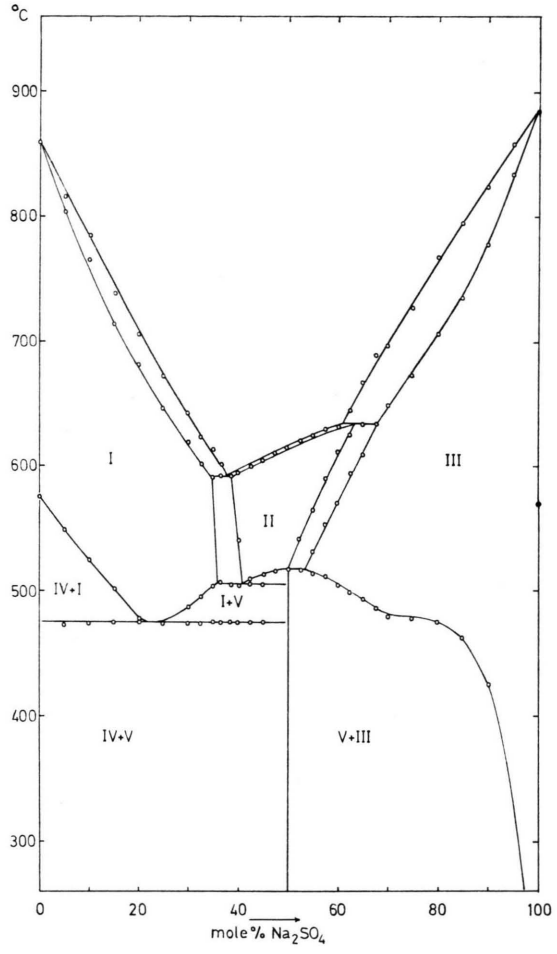

Fig. 1. The phase diagram of $Li_2SO_4-Na_2SO_4$.
○: from DTA, ●: from electrical conductivity measurements.

but they report a transition in sodium sulphate at 758 °C.

The System $Li_2SO_4 - Rb_2SO_4$

The transitions obtained from the DTA and electrical conductivity measurements are given in Table 2. The constructed phase diagram is shown in Figure 3.

The phase diagram of lithium sulphate with 0 – 3 mole % of Rb_2SO_4 has previously been investigated by AUGUSTSSON and GUSTAFSSON [24], who have found a transition between the solidus and the liquidus lines. Similar transitions have been detected also in the $Li_2SO_4 - K_2SO_4$ (l. c. [25]) and $Li_2SO_4 - Cs_2SO_4$ (l. c. [24]). For $Li_2SO_4 - K_2SO_4$, also viscosity and electrical conductiviting measurements have confirmed the existence of the transition.

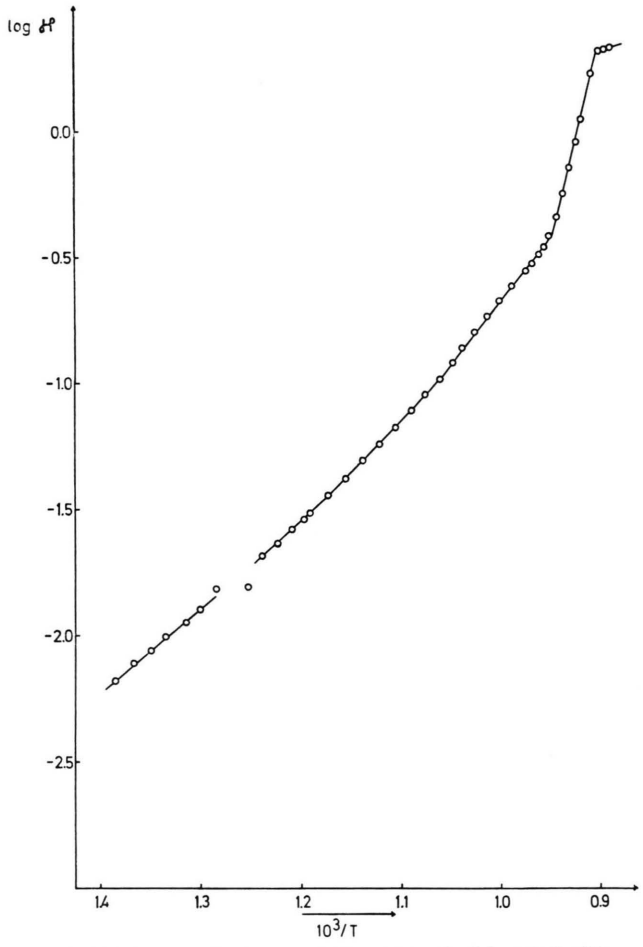

Fig. 2. The electrical conductivity of 0.9 $Na_2SO_4 \cdot 0.1\ Li_2SO_4$.

There are two congruently melting compounds in the $Li_2SO_4 - Rb_2SO_4$ system, $Li_2SO_4 \cdot Rb_2SO_4$ and $4\,Li_2SO_4 \cdot Rb_2SO_4$. According to DIOGENOV and ERMAKOV [26] the latter compound should be $5\,Li_2SO_4 \cdot Rb_2SO_4$, which from our results seems to be impossible.

The liquidus curve reported by DIOGENOV and ERMAKOV [26] is in good agreement with our phase diagram, except for the melting point of the eutecticum on the rubidium rich side of the phase diagram, where they report a melting point, which is about 30 °C lower than ours. The difference is probably caused by super-cooling of their samples.

The liquidus curve around the compound on the lithium rich side was obtained from conductivity measurements, since the heating curve gave no information on the melting point and, from the cooling curve, a too low melting point was obtained due to super-cooling.

Table 2. The transitions in $Li_2SO_4 - Rb_2SO_4$. The values within brackets were obtained from conductivity measurements.

Mole% Rb_2SO_4	(°C)				
0			573		860
2.5		526	573		819
8		526	574	579	694
10	496	526	575	578	663
12	498	528	575	578	(641)
13.5	495	526	576	578	
14					(607)
15	497	527	575		
16					(593)
17.5	498	526		580	580
19					(587)
20	498	524		580	
21	499	526		580	
22.5	498	521		579	597
25	497	525		580	634
27.5	497	525		581	666
30	498	527		581	680
32.5	498	525		581	700
40	498	526		581	728
50					744
60		649		719	729
62.5		650		723	723
70		650		720	804
80		650		719	904
90		650		721	980
100		650			(1071)

The System $Li_2SO_4 - Cs_2SO_4$

The transitions obtained from the DTA measurements are given in Table 3. The constructed phase diagram is shown in Figure 4.

Table 3. The transitions in $Li_2SO_4 - Cs_2SO_4$. The value within brackets was obtained from conductivity measurements.

Mole% Cs_2SO_4	(°C)				
0		573			860
5	529	577	622		750
7.5	530	578	624		686
10	530	578	623		623
12.5	530	580	624		632
15	530	579	623		641
17.5	530			633	643
20	530			633	640
25	530			633	656
30	529			631	692
40	529			631	725
47.5	530			633	738
50					740
52.5				711	737
60				711	725
65				710	710
70				712	745
80				712	858
90				713	—
97.5				714	—
100					(1010)

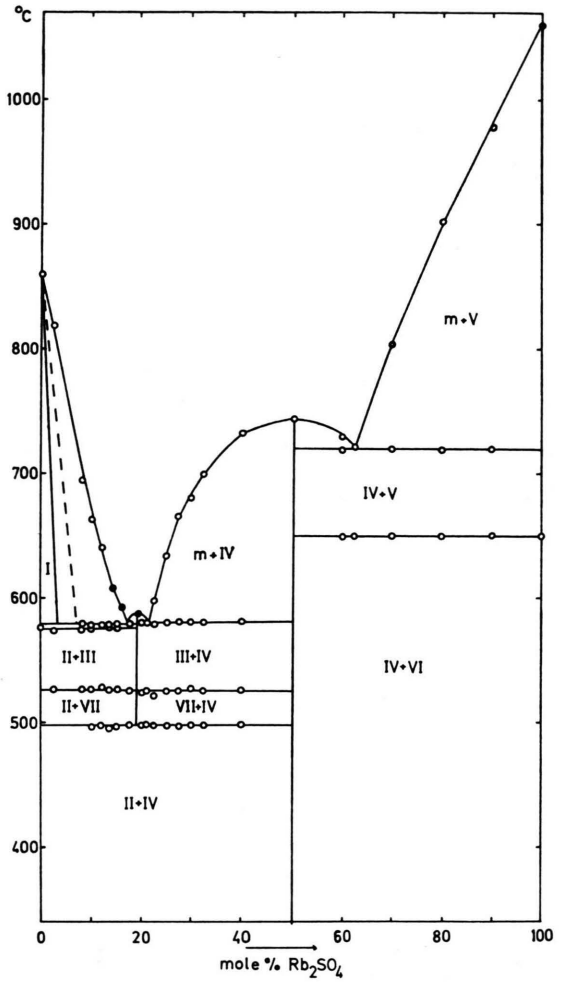

Fig. 3. The phase diagram of $Li_2SO_4-Rb_2SO_4$.
o: from DTA, ●: from electrical conductivity measurements.

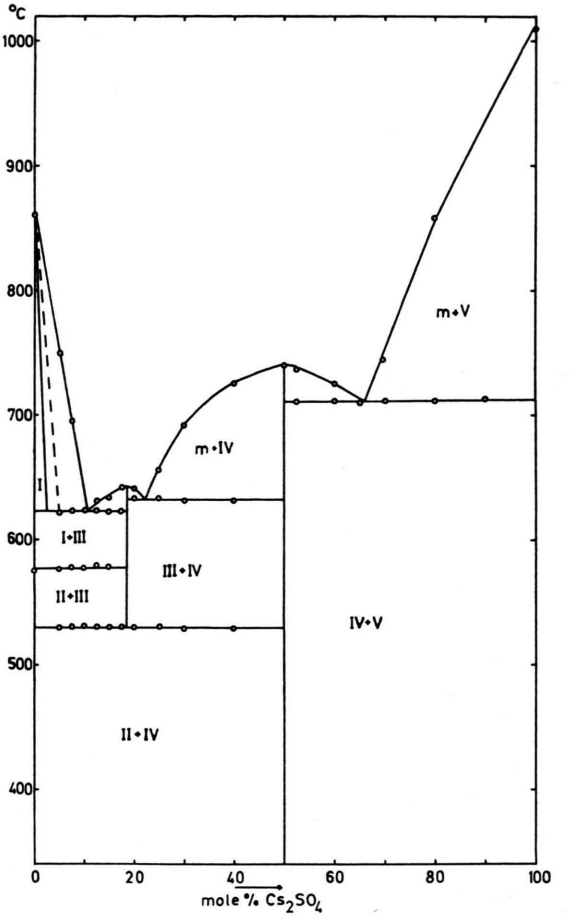

Fig. 4. The phase diagram of $Li_2SO_4-Cs_2SO_4$.

The phase diagram of lithium sulphate with 0 to 3 mole % of Cs_2SO_4 has previously been investigated by AUGUSTSSON and GUSTAFSSON [24].

There are two congruently melting compounds in the $Li_2SO_4-Cs_2SO_4$ system, $Li_2SO_4 \cdot Cs_2SO_4$ and $5\,Li_2SO_4 \cdot Cs_2SO_4$. According to DERGUNOV [27] the latter compound should be $4\,Li_2SO_4 \cdot Cs_2SO_4$, but DIOGENOV and ERMAKOV [26] report $5\,Li_2SO_4 \cdot Cs_2SO_4$.

The liquidus curve is in good agreement both with DERGUNOV [27] and DIOGENOV and ERMAKOV [26], except for the melting point of the eutecticum on the cesium sulphate rich side, where we, like in the system $Li_2SO_4-Rb_2SO_4$, obtain a higher value.

Except for the f.c.c. phase in lithium sulphate, there is no high conductivity phase neither in $Li_2SO_4-Rb_2SO_4$ nor $Li_2SO_4-Cs_2SO_4$.

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Altersbestimmung nach der K-Ca-Methode an Sylvin des Oberen Zechsteines des Werragebietes

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Potassium-Calcium Age Determination of Sylvite of the Upper Zechstein Salinar Deposit of the Werra Region, Western Germany

The potassium-calcium age determination method was applied to two sylvite samples from the upper Zechstein salinar deposit of the Werra region, Germany. Age values were obtained of 133 million years for one sample and of 40.5 million years for the other one, a recrystallised sample.

1. Die K-Ca-Methode zur Altersbestimmung an Mineralien und Gesteinen

Unter den für eine Altersbestimmungsmethode geeigneten natürlich radioaktiven Isotopen erscheint das ^{40}K in zweierlei Hinsicht besonders günstig. Die Häufigkeit des Elementes Kalium in der Erdkruste [1] mit 2,59% ist sehr hoch. Der Zerfall des ^{40}K in ^{40}Ca ist mit einer relativen Wahrscheinlichkeit von 0,875 stark bevorzugt vor dem K-Einfang, der zum ^{40}Ar führt. Das natürliche Element Calcium ist allerdings noch häufiger als Kalium (3.63%) und erschwert die Bestimmung des akkumulierten radiogenen Calciums. Als geeignete Mineralien wurden von AHRENS [2] Lepidolith und Muskovit vorgeschlagen und von BACKUS [3] gemessen. Diese Mineralien enthalten etwa 10% Kalium.

Wir haben Sylvinproben (KCl) aus der Grube Hadtorf der Salzdetfurth AG verwendet. Dieses Mineral enthielt nach der Schweretrennung zwischen 70% und 90% reines KCl. An zwei Proben wurde das K/Ca-Alter bestimmt.

2. Aufbereitung der Proben

Mechanische Aufbereitung

Von den 2 bis 5 kg schweren Proben wurden Sylvinstücke mit 2 – 4 cm Durchmesser abgeschlagen, in einem Achatmörser zerkleinert und mit Schüttelsieben die Körnung 1 – 2 mm abgetrennt. Anschließend wurde die Probe in einen Scheidetrichter mit Benzol-Bromoform-Gemisch zur Schweretrennung gegeben. Die Dichte der Trennmischung liegt zwischen der des Sylvins (1,99 g pro cm^3) und der von Kochsalz (2,14 g/cm^3), das bis zu 40% in der Rohprobe enthalten war. Im Trichter schwammen die Sylvinkristalle auf, während die dichteren Kochsalzteilchen absanken. So konnte das beigemischte NaCl zu mehr als 80% abgetrennt werden.

Chemische Aufbereitung

Etwa 20 g der Substanz wurden in 60 ml bidestilliertem Wasser gelöst und mit Ammoniak ein p_H-Wert von 7 bis 7,5 eingestellt. Die noch heiße Lösung wurde mit Ammoniumoxalat im Überschuß versetzt und etwa 10 Stunden stehen gelassen.

3. Ionenaustauschchromatographie

Zur Feinabtrennung des Calciums wurde das ausgefällte Calciumoxalat mit HCl aufgenommen und auf eine Ionenaustauschersäule [4] gegeben. Die Austauschersäule war mit einer automatischen Niveauregulierung für das Elutionsmittel versehen. Außerdem war am Auslauf ein Kapillarabzweig vorhanden, über den ständig ein kleiner Teil des Eluats in einem Flammenphotometer analysiert wurde. Dadurch konnte die Trennung des Kaliumpeaks vom Calciumpeak überwacht werden. Die Gesamtdauer der Trennung betrug etwa 5 Stunden. Die Calciumfraktion war in 265 cm^3 Eluat enthalten.