The Electrical Conductivity of Solid and Molten $(Li, K)_2SO_4$ and Solid Li_2SO_4 with Small Quantities of Sodium, Potassium and Rubidium Sulphate

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The electrical conductivity of molten and solid $(Li, K)_2SO_4$ has been measured from 550 to 1086 °C. The electrical conductivity of the high temperature modification of lithium sulphate increases when potassium and rubidium ions are added to the salt, but decreases when sodium ions are added. An explanation of these changes is proposed.

Several investigations of solid and molten $(Li, K)_2SO_4$ have been performed in this institute[1-3]. In connection with these measurements we have now measured the electrical conductivity of solid and molten $(Li, K)_2SO_4$. Since an irregular behavior of the electrical conductivity of solid lithium sulphate with small quantities of potassium sulphate was found, we have also measured the conductivity of solid lithium sulphate with small quantities of sodium sulphate and rubidium sulphate.

The experimental technique is described elsewhere in detail[4]. All chemicals were commercial reagent grade and were used without further purification. Before pouring the salts into the cells of pure quartz, they were dried at 180 °C and mixed mechanically. The measurements were performed in argon atmosphere, but to avoid small gas bubbles in the cells, the pressure was lowered for a few minutes before the measurements started.

A. The Molten State

The specific electrical conductivity of molten $(Li, K)_2SO_4$ is tabulated in Table 1. The conductivity of pure Li_2SO_4 has recently been published by the author[5]. ARNDT[6] has measured the electrical conductivity of pure potassium sulphate and his results are about five per cent higher than the results in this investigation.

It has been found by JAMES and LIU[7] that the deviation from volumetric additivity for the $Li_2SO_4-K_2SO_4$ eutectic is small and it is thus possible to calculate the density over the whole concentration range from the densities of pure lithium sulphate and potassium sulphate measured by JAEGER and KAHN[8].

LJUBIMOV and LUNDÉN[1] have recently in electromigration experiments measured the relative mobility Δb of the lithium and potassium ions in molten and solid $(Li, K)_2SO_4$. From their and our data it is possible to calculate the absolute mobilities of the two cations relative the anion lattice from the relations

$$\Delta b = b_1 - b_2 ,$$
$$\Lambda = F\, b = F(x\, b_1 + (1-x)\; b_2)$$

where F is the FARADAY constant and b_1 and b_2 are the mobilities of the two cations relative the anion lattice.

In Fig. 1 we have plotted b_1, b_2 and Λ/F as functions of the potassium sulphate concentration at

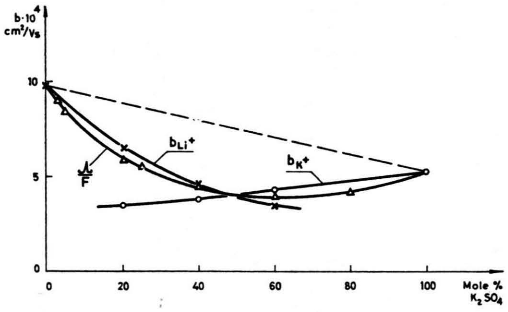

Fig. 1. The mobility of the potassium and the lithium ions and the mean mobility of the cations relative the sulphate ions at 750 °C.

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[1] V. LJUBIMOV and A. LUNDÉN, Z. Naturforschg., to be published.

[2] A. LUNDÉN, B. JONSON, and B. AUGUSTSSON, Z. Naturforschg. **21 a**, 593 [1966].

[3] A. LUNDÉN and J.-E. OLSSON, unpublished.

[4] A. KVIST and A. RANDSALU, Z. Naturforschg., to be published.

[5] A. KVIST, Z. Naturforschg. **21 a**, 487 [1966].

[6] K. ARNDT, Z. Elektrochem. **12**, 337 [1906].

[7] D. W. JAMES and C. H. LIU, J. Chem. Eng. Data **8**, 469 [1963].

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T °C	$\varkappa$ Ω^{-1} cm^{-1}
3.00 mole% K_2SO_4	
903.8	4.076
876.3	3.936
851.5	3.804
824.8	3.655
803.5	3.533
4.89 mole% K_2SO_4	
911.3	3.931
898.3	3.871
874.0	3.750
852.0	3.636
828.0	3.504
807.5	3.392
799.3	3.349
792.3	3.309
787.3	3.276
780.0	3.238
774.3	3.207
769.8	3.176
20.00 mole% K_2SO_4	
902.3	2.565
888.0	2.506
878.0	2.460
873.3	2.447
863.5	2.399
847.5	2.334
841.2	2.301
837.0	2.297
818.8	2.219
806.4	2.165
781.3	2.045
774.0	2.010
762.3	1.956
750.3	1.899
738.8	1.849
724.8	1.783
704.8	1.688
687.5	1.603
674.3	1.539
629.0	1.304
622.5	1.269
607.8	1.193
596.5	1.138
580.0	1.054
562.0	0.958
552.8	0.913
25.00 mole% K_2SO_4	
848.0	2.155
873.8	2.250
907.3	2.400
938.3	2.504
859.5	2.200
834.5	2.095
815.8	2.014
791.0	1.912
25.00 mole% K_2SO_4	
767.3	1.812
737.5	1.679
714.6	1.571
677.0	1.397
659.3	1.316
635.0	1.202
610.0	1.085
586.8	0.929
569.8	0.808
560.4	0.744
40.00 mole% K_2SO_4	
813.3	1.561
825.5	1.607
842.5	1.672
874.5	1.794
889.3	1.845
906.3	1.909
852.0	1.709
841.6	1.668
808.5	1.541
795.5	1.500
784.5	1.458
770.3	1.399
751.3	1.329
736.0	1.264
721.3	1.205
716.8	1.190
60.00 mole% K_2SO_4	
903.8	1.551
890.3	1.505
878.5	1.469
860.0	1.411
841.4	1.356
822.0	1.299
799.0	1.221
782.8	1.169
765.8	1.118
749.5	1.064
726.3	0.990
708.8	0.927
80.00 mole% K_2SO_4	
961.0	1.617
943.0	1.573
950.0	1.591
100.00 mole% K_2SO_4	
1086.4	1.926
1084.5	1.922
1081.3	1.917
1078.5	1.912
1074.8	1.908
1072.0	1.899
1068.3	1.887

Table 1. The specific electrical conductivity of molten $(Li, K)_2SO_4$. The conductivity of pure lithium sulphate has recently been published by the author [5].

approximately 750 °C. The three curves intersect at about 45 mole per cent potassium sulphate.

Since the melting point of potassium sulphate is 1068 °C, the conductivity of this salt was extrapolated to 750 °C.

The excess conductivity $\Delta\Lambda$ is defined from

$$\Delta\Lambda = \Lambda_{\text{ideal}} - \Lambda ,$$

where $$\Lambda_{\text{ideal}} = x\,\Lambda_1 + (1-x)\,\Lambda_2 .$$

x is the equivalent fraction of component 1 and Λ_i is the conductivity of the pure salt.

The relative excess conductivity of $(Li, K)_2SO_4$ is almost ten times the relative excess conductivity of $(Li, K)NO_3$ (l. c. [9]), but most salt mixtures containing lithium ions show definite deviations from additivity [10].

B. The Solid State

X-ray measurements have shown that the structure of α-Li_2SO_4 is cubic face-centered with unit cell edge 7.07 Å [11]. The cations can move rather freely in the lattice and the electrical conductivity of the high temperature modification is almost the same as the conductivity of the melt [5, 12].

In Fig. 2 we have plotted the specific electrical conductivity $\varkappa$ of α-Li_2SO_4 with 3.00 mole per cent potassium sulphate. In the melt the conductivity

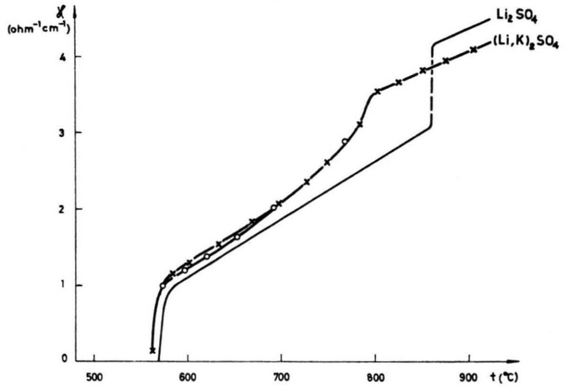

Fig. 2. The specific electrical conductivity of solid and molten Li_2SO_4 with 3.00 mole per cent K_2SO_4. ×: decreasing temperature; o: increasing temperature.

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[9] B. DE NOOIJER, Theses, Amsterdam 1965.

[10] E. R. VAN ARTSDALEN and I. S. YAFFE, J. Phys. Chem. **59**, 118 [1955].

[11] T. FØRLAND and J. KROGH-MOE, Acta Chem. Scand. **11**, 565 [1957].

[12] A. KVIST and A. LUNDÉN, Z. Naturforschg. **20 a**, 235 [1965].

($\varkappa_l$) is lower in the mixture than in the pure salt, but in the solid high temperature modification it ($\varkappa_s$) is highest in the mixture. $\varkappa_s$ is however higher when the temperature is lowered than when it is raised. This effect seems to increase with increasing concentration of potassium ions. A slight time dependence of $\varkappa_s$ at constant temperature was also found.

Lundén, Jonson, and Augustsson[2] have found that also the rheological properties of solid (Li, K)$_2$SO$_4$ are dependent on the pretreatment of the salt.

In order to investigate the influence on the electrical conductivity from foreign univalent ions we have also used sodium and rubidium ions as impurities. The radius of the sodium ion is only 0.98 Å, but the rubidium ion is somewhat greater than the potassium ion.

Fig. 3 shows the electrical conductivity of (Li, Na)$_2$SO$_4$ with 4.89 mole per cent sodium sulphate. The conductivity is lower in the mixture than in the pure salt and it is not affected by the pretreatment. (Li, Rb)$_2$SO$_4$ with 2.00 mole per cent rubidium sulphate behaves almost like (Li, K)$_2$SO$_4$ (Fig. 4).

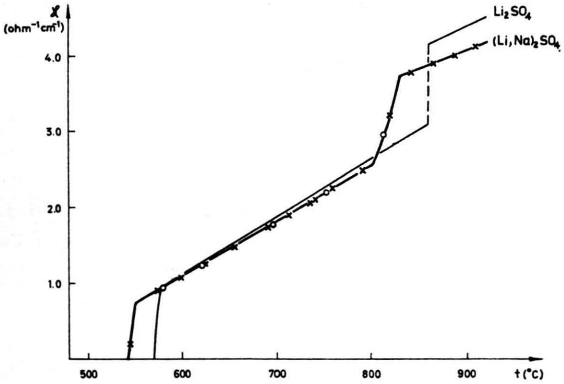

Fig. 3. The specific electrical conductivity of solid and molten Li$_2$SO$_4$ with 4.89 mole per cent Na$_2$SO$_4$. ×: decreasing temperature; o: increasing temperature.

Lundén and Olsson[3] have in thermal diffusion experiments found a considerable enrichment of the heavy cations in solid (Li, K)$_2$SO$_4$ and (Li, Rb)$_2$SO$_4$ at the hot side, but in solid (Li, Na)$_2$SO$_4$ the enrichment was insignificant.

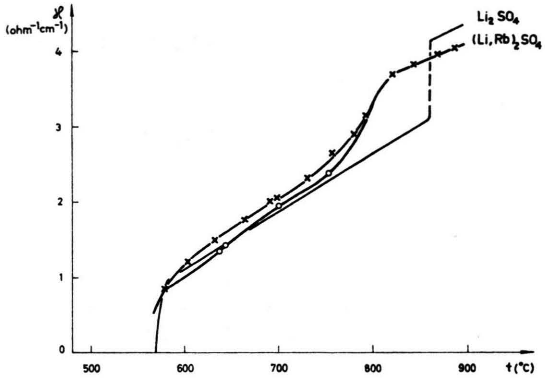

Fig. 4. The specific electrical conductivity of solid and molten Li$_2$SO$_4$ with 2.00 mole per cent rubidium sulphate. ×: decreasing temperature; o: increasing temperature.

In the sulphate lattice there are two positions with different sizes for the cations. The free spaces of these positions are 1.42 Å and 2.76 Å, respectively[13]. Both positions are however too small for a potassium or a rubidium ion and it is therefore probable that these ions are attracted by dislocations in the salt. They will then be very mobile along the grain boundaries and electromigration experiments have shown[1] that the mobility of the potassium ion even exceeds the mobility of the lithium ion.

According to the X-ray measurements[13] the sodium ions are small enough to replace lithium ions in the lattice, but since only the positions with the biggest free space are available for them, their mobility should be lower than the mobility of the lithium ions and this will cause the observed decrease in the conductivity.

In solid (Li, Ag)$_2$SO$_4$ with small quantities of silver sulphate an X-ray reflection which should not appear for a cubic face-centered structure has been found by Øye[13] and he has suggested as a possible explanation that the formation of the cubic lattice is incomplete.

It was not possible to measure the electrical conductivity of solid potassium sulphate in this investigation since its structure is hexagonal and thus does not exhibit rotational symmetry.

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[13] H. A. Øye, Theses, Trondheim 1963.