The Electrical Conductivity and Density of the Molten Systems $Li_2SO_4-ZnSO_4$ and $Na_2SO_4-ZnSO_4$

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Zinc sulphate decomposes upon melting. Molten $Li_2SO_4-ZnSO_4$ and $Na_2SO_4-ZnSO_4$ are thermally stable with up to 80 mole% of $ZnSO_4$. We have measured the density and electrical conductivity of these melts. By extrapolation we have calculated the density (ϱ) and molar electrical conductivity (Λ) of pure molten zinc sulphate and we have obtained (t in °C)

$$\varrho_{ZnSO_4}=3.463-0.470\times10^{-3}\,t \quad (g/cm^3),$$
$$\Lambda_{ZnSO_4}=0.0950\,t-35.4 \quad (cm^2/ohm, mole).$$

Many divalent sulphates are, in contrast to the univalent sulphates, not thermally stable upon melting [1], and for some divalent sulphates the decomposition starts already several hundred degrees below the melting point. However, mixtures between univalent and divalent sulphates are often thermally stable in the melt.

The melting point of zinc sulphate is about 750 °C [2], but this melting point has not been measured directly and probably cannot be because of decomposition, which starts at about 600 °C. We have found that molten $Li_2SO_4-ZnSO_4$ and $Na_2SO_4-ZnSO_4$ are thermally stable with up to about 80 mole% of zinc sulphate in the melt and we have measured the density and specific electrical conductivity in this concentration range. From the results of these measurements we have then by extrapolation calculated the density and molar electrical conductivity of pure molten zinc sulphate.

Experimental

The density and conductivity measurements were performed with the same experimental technique as has been used for our previous measurements in molten univalent sulphates [3–11].

For the density measurements a platinum bob with a weight of about 20 g was used and the electrical conductivities were measured in cells of pure quartz. For further details of the experimental technique we refer to some previous papers [7, 10].

All salts were of reagent quality and were used without further purification. The salts were well dried before use.

Measurements were performed from the melting point of the mixtures up to about 100 °C above the melting point. The liquidus lines of the two studied systems were taken from phase diagrams given by EVSEEVA and BERGMAN [12] ($Li_2SO_4-ZnSO_4$) and EVSEEVA [13] ($Na_2SO_4-ZnSO_4$).

Results

Density measurements were performed in pure Li_2SO_4, pure Na_2SO_4 and in the equimolar mixtures of $Li_2SO_4-ZnSO_4$ and $Na_2SO_4-ZnSO_4$. The obtained results are given in Table 1. In Table 2 we have summarized the densities by simple linear relations.

The electrical conductivities were measured on six different compositions for each system (Table 3 and Table 4).

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t(°C)	ϱ(g/cm³)	t(°C)	ϱ(g/cm³)
Equimolar Li_2SO_4-$ZnSO_4$		Equimolar Na_2SO_4-$ZnSO_4$	
694	2.588	660	2.604
691	2.590	647	2.680
685	2.591	634	2.616
666	2.599	618	2.622
643	2.609	607	2.630
629	2.616	589	2.638
601	2.627	556	2.655
593	2.631	542	2.664

Table 1. Obtained densities. The densities of pure lithium sulphate and sodium sulphate have been published previously [10].

Salt	a	$-b \cdot 10^3$	Temp. interval (°C)
Li_2SO_4	2.384	0.462	890— 950
Na_2SO_4	2.445	0.425	903—1047
$LiZnSO_4$	2.882	0.425	590— 690
$NaZnSO_4$	2.940	0.512	540— 660
$ZnSO_4$ (extrapolated mean value)	3.463	0.470	600—1000

Table 2. Coefficients by the relation $\varrho = a + b\,t$ (g/cm³), where t is the temperature in °C.

t(°C)	$\varkappa$(ohm⁻¹cm⁻¹)	t(°C)	$\varkappa$(ohm⁻¹cm⁻¹)
25 mole% $ZnSO_4$		67 mole% $ZnSO_4$	
751.8	2.350	700.3	0.667
747.2	2.337	694.8	0.665
725.2	2.225	683.8	0.650
689.2	2.035	655.8	0.584
653.5	1.844		
		75 mole% $ZnSO_4$	
33 mole% $ZnSO_4$		872.8	1.054
787.0	2.133	863.5	0.980
780.8	2.074	839.8	0.908
764.0	2.012	794.8	0,800
737.3	1.881	790.3	0.785
708.6	1.773	773.5	0.751
678.3	1.641	761.5	0.708
642.5	1.482	733.0	0.639
614.0	1.355		
582.8	1.219		
50 mole% $ZnSO_4$			
718.3	0.981		
689.8	0.923		
662.3	0.863		
641.2	0.825		
616.2	0.769		
542.4	0.608		
527.0	0.571		
503.8	0.510		

Table 3. Obtained conductivities for the system Li_2SO_4-$ZnSO_4$. The electrical conductivity of pure Li_2SO_4 has been published previously[1].

t(°C)	$\varkappa$(ohm⁻¹cm⁻¹)	t(°C)	$\varkappa$(ohm⁻¹cm⁻¹)
25 mole% $ZnSO_4$		67 mole% $ZnSO_4$	
847.3	1.492	697.0	0.424
840.8	1.473	693.8	0.420
821.3	1.412	682.0	0.400
783.3	1.299	659.3	0.363
756.3	1.211	640.0	0.332
		616.8	0.297
33 mole% $ZnSO_4$		593.8	0.261
813.3	1.245	569.0	0.224
770.3	1.122		
752.3	1.073	75 mole% $ZnSO_4$	
743.3	1.027	712.5	0.421
693.8	0.903	698.2	0.397
667.5	0.826	679.5	0.366
		647.0	0.315
50 mole% $ZnSO_4$		625.5	0.280
730.2	0.688		
713.5	0.648		
687.5	0.589		
650.0	0.511		
626.0	0.461		
608.3	0.425		
588.8	0.386		

Table 4. Obtained conductivities for the system $NaSO_4$-$ZnSO_4$. The electrical conductivity of pure Na_2SO_4 has been published previously[11].

Discussion

In very accurate measurements POWERS, KATZ, and KLEPPA [14] have for some univalent binary nitrates found a linear relation between the excess molar volumes of the equimolar mixtures and the parameter $[(d_1-d_2)/(d_1+d_2)]^4$, where d_1 and d_2 are the interionic distances characteristic of the two pure salts. This deviation from volumetric additivity, however, is very small and it can in many cases be neglected.

Also in molten sulphates the deviation from volumetric additivity is small; JAMES and LIU [15] have investigated equimolar $Li_2SO_4-K_2SO_4$ and we have more recently measured densities of binary mixtures of Li_2SO_4, Na_2SO_4, K_2SO_4, Ag_2SO_4 and Tl_2SO_4 (l. c. [7, 10]).

Since the excess volumes are a function of the differences in cationic radii, and these differences are small for Li^+, Na^+ and Zn^{++}, negligible excess volumes are expected in such salts as $Li_2SO_4-ZnSO_4$. We have therefore calculated the molar volume of pure $ZnSO_4$ by linear extrapolation and obtain for the density (t in °C).

$$\varrho_{ZnSO_4} = 3.463 - 0.470 \cdot 10^{-3}\,t \quad (g/cm^3).$$

[14] B. F. POWERS, J. L. KATZ, and O. J. KLEPPA, J. Phys. Chem. 66, 103 [1962].

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This result is the mean of the results obtained from $Li_2SO_4 - ZnSO_4$ and $Na_2SO_4 - ZnSO_4$. The extrapolated molar volume for the two systems differ only about 1%.

For the electrical conductivities the situation is somewhat more complicated. In Tables 5 and 6 we have sumarized the temperature dependence of the molar electrical conductivities of the investigated mixtures.

Mole% $ZnSO_4$	a	$-b$	Temp. interval (°C)
0	0.34924	71.4	866–930
25	0.29788	98.0	653–752
33	0.24848	82.3	583–787
50	0.11886	33.6	504–718
67	0.10668	39.6	656–700
75	0.15556	81.1	733–873

Table 5. Coefficients of the relation $\Lambda = a\,t + b$ (cm²/ohm mole) for molten $Li_2SO_4 - ZnSO_4$, where t is the temperature in °C. The standard deviation of Λ is about 0.4 cm²/ohm mole.

Mole% $ZnSO_4$	a	$-b$	Temp. interval (°C)
0	0.25851	73.4	916–959
25	0.21240	84.1	756–847
33	0.18909	75.8	667–813
50	0.13023	54.7	588–730
67	0.09067	39.4	569–697
75	0.09172	42.1	625–712

Table 6. Coefficients of the relation $\Lambda = a\,t + b$ (cm²/ohm mole) for molten $Na_2SO_4 - ZnSO_4$, where t is the temperature in °C. The standard deviation of Λ is about 0.4 cm²/ohm mole.

The excess molar conductivities of molten salts can in contrast to the excess molar volumes not be neglected. The shapes of the conductivit isoterms have been studied in several papers [5, 7, 8, 16, 17] and by making use of our previous experience from other conductivity measurements, we have extrapolated the conductivity isotherms to pure zinc sulphate (Fig. 1 and 2) and we have then calculated the temperature dependence of the electrical conductivity of the pure salt:

$$\Lambda_{ZnSO_4} = 0.0950\, t - 35.4 \quad (\text{cm}^2/\text{ohm, mole}).$$

[16] B. de Nooijer, Thesis, Amsterdam 1965.

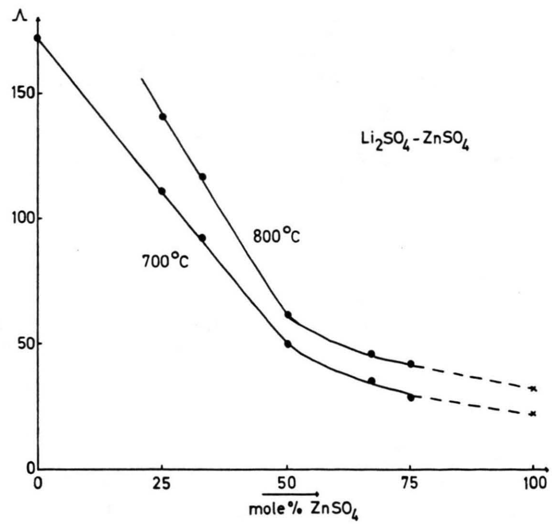

Fig. 1. The molar electrical conductivity in cm²/ohm mole for molten $Li_2SO_4 - ZnSO_4$.

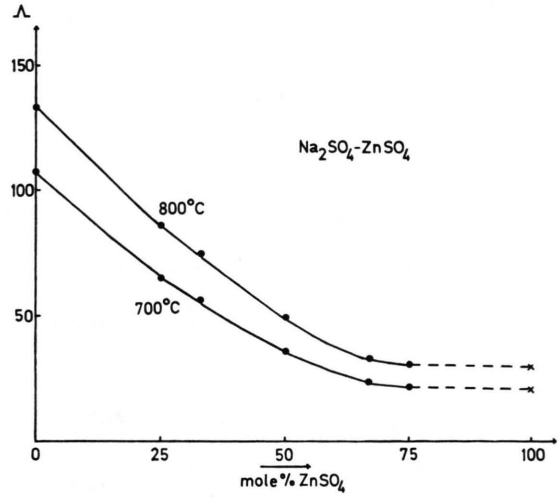

Fig. 2. The molar electrical conductivity in cm²/ohm mole for molten $Na_2SO_4 - ZnSO_4$.

It should be possible to use the method which we have described here to determine the density and the electrical conductivity of many other salts, where the thermal stability is low in the melt.

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