The Electrical Conductivity and Density of Solid and Molten $Li_2SO_4-Ag_2SO_4$

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The electrical conductivity of solid and molten $Li_2SO_4-Ag_2SO_4$ has been measured for different concentration values. Density measurements of molten Li_2SO_4, Ag_2SO_4 and equimolar $(Li, Ag)_2SO_4$ show that the system can be considered ideal. The equivalent conductivity of molten $(Li, Ag)_2SO_4$ can be calculated from the conductivities of the pure salts by assuming that the cations are moving in groups, each group containing about four cations.

In a recent paper [1] we have proposed that the cations in molten lithium sulphate are moving in groups, each group containing k cations, and that it is possible to calculate k when foreign univalent cations of molar fraction x are added, from the relation

$$k = \frac{1}{x} \frac{\Delta\Lambda}{\Lambda} \frac{b}{\Delta b} \tag{1}$$

where $\Delta b/b$ is the relative difference in mobility between the lithium ion and the foreign cation and $\Delta\Lambda/\Lambda$ the relative difference in equivalent conductivity between pure lithium sulphate and the mixture.

From Eq. (1) it was found that $k = 2.7$ for the system $Li_2SO_4-K_2SO_4$.

Eq. (1) is, however, only valid in dilute mixtures and we decided to investigate if it is possible in favourable cases to find a similiar relation which is valid at all concentrations.

An interesting system is $Ag_2SO_4-Li_2SO_4$. The anion is large compared with the cations and the mass of the silver ion is much larger than that of the lithium ion.

According to an obvious model we have made the following assumptions for the system $Li_2SO_4-Ag_2SO_4$:

- the cations are moving in groups, each group containing the same number k of cations,
- the cations are randomly distributed,
- all groups containing silver ions have the same mobility b_{Ag},
- groups containing only lithium ions have the mobility b_1.

Then, in a mixture with molar fraction a of Li_2SO_4, the probability of a group to contain k lithium ions will be a^k, and therefore

$$\Lambda/F = a^k b_1 + (1-a^k)\, b_{Ag}\,. \tag{2}$$

Since by definition

$$\Lambda/F = a\, b_{Li} + (1-a)\, b_{Ag}$$

it follows from Eq. (2) that

$$b_{Li} - b_{Ag} = a^{k-1}(b_1 - b_{Ag})\,. \tag{3}$$

For the case $1-a = x \ll 1$, one has

$$b_1 = \Lambda_{Li_2SO_4}/F \approx b_{Li}$$

and Eq. (2) yields

$$\Lambda/F = (\Lambda_{Li_2SO_4}/F) - x\,k\,(b_{Li} - b_{Ag})\,,$$

which is identical with Eq. (1).

If in the model the further assumption is made that at all concentrations

$$b_1 = \Lambda_{Li_2SO_4}/F \quad \text{and} \quad b_{Ag} = \Lambda_{Ag_2SO_4}/F\,,$$

one gets from Eq. (2)

$$\Lambda = a^k\, \Lambda_{Li_2SO_4} + (1-a^k)\, \Lambda_{Ag_2SO_4} \tag{4}$$

and from Eq. (3)

$$b_{Li} - b_{Ag} = a^{k-1}(\Lambda_{Li_2SO_4} - \Lambda_{Ag_2SO_4})/F\,. \tag{5}$$

The model can be tested by measuring Λ and $b_{Li} - b_{Ag}$ as functions of a and looking if the parameter k can be so adjusted that the Eqs. (4) and (5) reproduce the experimental curves.

As a first step we have measured the electrical conductivity of molten and also solid $Li_2SO_4-Ag_2SO_4$ at different concentrations, and the density of molten Li_2SO_4, Ag_2SO_4 and equimolar $(Li, Ag)_2SO_4$.

Experimental

In all experiments reagent grade silver sulphate (Mallinckrodt) and lithium sulphate (Hopkin & Williams AnalaR) was used without further purification. The salts were dried over night at 180 °C

[1] A. KVIST, Z. Naturforschg. **21 a**, 1601 [1966].

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before use and mixed mechanically. All measurements were performed in air.

Conductivity measurements: Two not fully understood processes are taking place when glass is in contact with a salt melt; ion exchange and diffusion of ions from the melt into the glass. The charges are generally transported by ions in silica glasses [2]. Since it is possible to construct conductivity cells in several different ways, we decided to measure the electrical conductivity of silica glass immersed in lithium sulphate up to 1000 °C. Electrical conduction in silica glasses immersed in various salt mixtures has recently been studied by STERN [3].

U-cells were used for the measurements of the electrical conductivity of Vycor and quartz. The legs, 12 mm in diameter, were separated by a glass partition, 1 – 4.2 mm thick, and in each leg a bright platinum electrode was placed near the partition. Since the electrical conductivity of the salt is very high compared with the conductivity of the glass, the positions of the electrodes did not influence the results. The measurements were performed in argon atmosphere.

The cell was placed in an air thermostate in a big furnace. The temperature was measured with a compensation bridge (Norma Model 317) and the electrical conductivity with an impedance bridge (Radiometer, Copenhagen, type GB 11 a). Frequences from 1 to 10 kc/s were used, and the frequency dependence of the resistance was found to be small.

In some preliminary measurements 1 mm thick glass partitions were used, but to obtain more accurate data the glass partition was increased to 4.2 mm in our final experiment. No significant difference between the specific conductance of Vycor and quartz could be found. The Vycor glass, but not quartz, was however slightly corroded by the melt. This difference between Vycor and quartz is much more marked when lithium tungstate is used; Vycor, but not pure quartz, is attacked furiously and a 2 mm thick glass tube is completely destroyed within one day. After the cell had been filled, the resistance was decreasing, but became constant after one day. This is in agreement with observations made by STERN [3].

We have plotted the specific conductance of silica glass as a function of temperature (Fig. 1). The results can be written as an ARRHENIUS' equation

$$\varkappa = \varkappa_0 \, e^{-Q/RT} ,$$

$\varkappa_0 = 0.604 \, \Omega^{-1} \, \mathrm{cm}^{-1}$, $Q = (23\,900 \pm 300)$ cal/mole.

There is a small change of Q at the melting point of lithium sulphate, 860 °C, but we have not taken this change into account. The magnitude of Q is in agreement with reported activation energies of diffusion [4] and electrical conduction [3] of other cations in glass.

The resistivity of quartz immersed in lithium sulphate is approximately $3.6 \cdot 10^4 \, \Omega$ cm at 930 °C, but

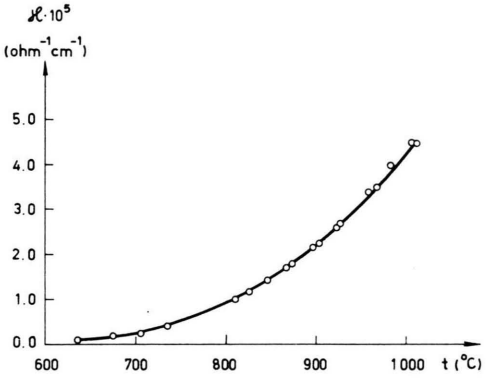

Fig. 1. The electrical conductivity of Vycor immersed in lithium sulphate as a function of temperature.

the resistivity of lithium sulphate is only 0.22 Ω cm. Simple experiments with quartz capillaries with one end closed, showed however that it is not possible to neglect the permeation of lithium ions through the glass, since the area of the glass capillary is extremely big compared with its cross section.

From the measurements above we concluded that it is difficult to use dip cells [5] at high temperatures in lithium salts and we therefore constructed a capillary cell of pure quartz (Fig. 2), which we have found usable up to at least 1200 °C.

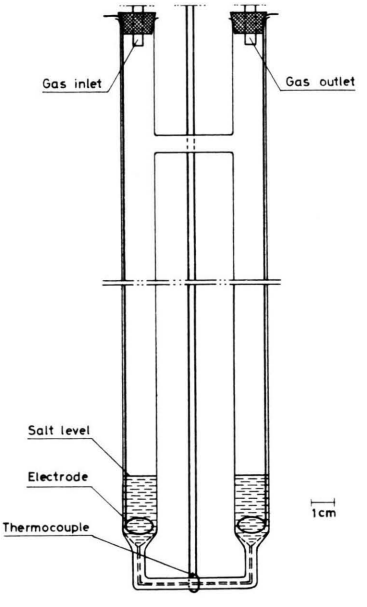

Fig. 2. Quartz capillary cell for conductivity measurements.

[2] J. E. STANWORTH, Physical Properties of Glass, Chap. VI, Clarendon Press, Oxford 1950.

[3] K. H. STERN, J. Electrochem. Soc. **112**, 208 [1965].

[4] C.-A. SJÖBLOM and J. ANDERSSON, Z. Naturforschg. **21 a**, 274 [1966].

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

Each cell was calibrated at least three times with normal potassium chloride solution at about 25 °C. The frequency dependence of the conductivity was only 0.1% from 2.5 to 25 kc/s, the cell constant about 450 cm^{-1} and the phase angle of the impedance generally less than 0.3°. The cells were placed in an air thermostate in a big furnace, where it was possible to keep the temperature constant within 0.3 °C.

Two different bridges have been used, one commercial (see above) and one constructed in this laboratory [6]. The results obtained with the two bridges agree within 0.05%.

Density measurements: The densities were measured by the Archimedian principle, where we used the method of JANZ and LORENZ [7] with small modification. A Mettler H15GD analytical balance was used and the density bob (1.824 cm^3) was made of Au – 20% Pd, an alloy which has been found useful in molten nitrates. No corrosion of the bob by lithium sulphate was found and the weight of the bob was exactly the same (within 0.0001 g) after 50 hours in molten lithium sulphate at 920 °C. The bob was however slightly discoloured by silver sulphate and also a small weight change was found. The density equipment was calibrated with benzene, toluene and CCl_4 at room temperature and with molten potassium nitrate between 350 °C and 550 °C. The temperature was measured with a calibrated Pt – PtRh (10% Rh) thermocouple, giving an estimated accuracy of ±1 °C of the temperature measurements.

Results and Discussion

The conductivity data are tabulated in Table 1 and the densities in Table 2. The conductivity of pure lithium sulphate has recently been published by the author [8].

A. Molten $Li_2SO_4 - Ag_2SO_4$

The density results of molten lithium sulphate are in excellent agreement with results obtained by JAEGER and KAHN [9]. The scattering in the results of melts containing silver sulphate is somewhat bigger than for pure lithium sulphate due to the attack on the bob.

The deviation from volumetric additivity is less then 1% and we can thus consider the system as ideal (Table 3). This is the case also for $Li_2SO_4 - K_2SO_4$ (l. c. [10]).

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[7] G. JANZ and M. LORENZ, J. Electrochem. Soc. **108**, 1052 [1961].
[8] A. KVIST, Z. Naturforschg. **21 a**, 487 [1966].
[9] F. JAEGER and J. KAHN, Koninkl. Akad. Wetenschap. Proc. **19**, 381 [1916].
[10] D. JAMES and C. LIU, J. Chem. Eng. Data **8**, 469 [1963].

t °C	$\varkappa$ $\Omega^{-1}cm^{-1}$	t °C	$\varkappa$ $\Omega^{-1}cm^{-1}$	t °C	$\varkappa$ $\Omega^{-1}cm^{-1}$
pure Ag_2SO_4		80.0 mole% Ag_2SO_4		50.0 mole% Ag_2SO_4	
744.2	1.908	565.5	0.9989	469.5	0.7140
726.2	1.862	545.4	0.5564	454.6	0.6300
708.5	1.820	512.0	0.2296	446.2	0.5950
705.2	1.810	496.2	0.1592	441.2	0.5690
691.0	1.770	478.5	0.1174		
668.8	1.711	459.0	0.08684	40.0 mole% Ag_2SO_4	
644.0	0.2005	440.5	0.06451	780.8	2.448
624.0	0.1390	418.0	0.04504	760.2	2.338
601.8	0.08827	395.2	0.01753	733.8	2.222
579.6	0.05800			716.2	2.145
556.2	0.03710	60.0 mole% Ag_2SO_4		696.0	2.048
534.0	0.02415			689.2	2.004
515.0	0.01641	747.6	2.093	661.2	1.872
477.2	0.00794	727.2	2.009	642.8	1.781
465.8	0.00602	702.5	1.920	622.5	1.685
		680.2	1.833	600.8	1.576
90.0 mole% Ag_2SO_4		652.8	1.718		
		620.8	1.580	40.0 mole% Ag_2SO_4	
748.2	1.998	600.2	1.489		
718.8	1.902	580.2	1.387	566.0	1.405
701.2	1.843	558.5	1.197	556.2	1.224
680.8	1.772	532.8	1.060	540.2	1.124
657.8	1.700	506.0	0.9171	520.5	1.005
639.2	1.638	477.0	0.7687	500.8	0.7200
611.5	0.9003	462.0	0.5670	485.0	0.4947
597.4	0.4143			467.5	0.3867
575.0	0.5061	50.0 mole% Ag_2SO_4		446.0	0.2770
548.0	0.1250			427.8	0.2157
520.0	0.07856	742.0	2.138		
486.2	0.04205	718.2	2.041		
		699.5	1.963	17.5 mole% Ag_2SO_4	
80.0 mole% Ag_2SO_4		676.5	1.865		
		652.8	1.763	751.0	2.766
724.2	1.949	617.8	1.614	736.8	2.690
705.0	1.880	603.2	1.536	715.2	2.572
690.5	1.830	582.2	1.438	699.0	2.498
669.8	1.755	562.2	1.228	676.0	2.195
651.8	1.692	542.8	1.122	654.2	1.924
632.2	1.609	528.8	1.041	625.8	1.626
618.5	1.555	501.8	0.8920	608.2	1.468
602.0	1.493	487.2	0.8020	588.0	1.309
582.6	1.418	485.2	0.7990	567.2	1.167
				540.0	0.9747
				524.0	0.8818

Table 1. The specific electrical conductivity of the system $Li_2SO_4 - Ag_2SO_4$. The conductivity of pure lithium sulphate has recently been published by the author [8].

t °C	ϱ g/cm^3	t °C	ϱ g/cm^3	t °C	ϱ g/cm^3
pure Li_2SO_4		equimolar $(Li, Ag)_2SO_4$		pure Ag_2SO_4	
958	1.971	738	3.489	773	4.707
937	1.977	735	3.490	756	4.719
923	1.980	730	3.504	747	4.729
915	1.985	727	3.498	724	4.756
910	1.983	694	3.566	712	4,774
904	1.988	663	3.577	702	4.783
880	1.997	645	3.588	691	4.797
		619	3.610	679	4.801

Table 2. The density of Li_2SO_4, Ag_2SO_4 and equimolar $Li_2SO_4 - Ag_2SO_4$.

Salt	a	$-b$	t_0 °C	s	Range °C
Li_2SO_4 (this investigation)	2.005	0.329	850	0.002	880–960
Li_2SO_4 (JAEGER and KAHN)	2.008	0.407	850	—	910–1110
equimolar Li_2SO_4-Ag_2SO_4	3.580	1.049	650	0.013	620–740
Ag_2SO_4	4.838	1.089	650	0.004	680–770

Table 3. The density of Li_2SO_4, Ag_2SO_4 and equimolar $Li_2SO_4-Ag_2SO_4$ described by the equation $\varrho = a + b(t - t_0) \cdot 10^{-3}$. The density results of pure lithium sulphate are in excellent agreement with results obtained by JAEGER and KAHN [9]. s is the standard deviation.

We have calculated the molar conductivity (Table 4) and in Fig. 3 we have plotted the equivalent conductivity at 750 °C as a function of the concentration. The conductivity calculated from Eq. (4) with $k = 4.3$ is in complete agreement with the experimental curve. Also shown are b_{Ag} and b_{Li} as calculated from Eq. (5) with $k = 4.3$.

Mole % Ag_2SO_4	$-a$	b	s	Range °C
100	21.0	0.19718	0.1	670–750
90	48.3	0.23720	0.2	640–750
80	62.6	0.25682	0.2	585–725
60	71.7	0.26726	0.4	560–750
50	77.8	0.27760	0.4	580–740
40	91.6	0.30221	0.3	600–780
17.5	91.3	0.32799	0.1	570–750
0	65.0	0.34166	0.4	860–930

Table 4. The molal electrical conductivity of molten $Li_2SO_4-Ag_2SO_4$ described by the equation $\Lambda_M = a + b\,t \cdot 10^{-3}$, where t is the temperature in °C. The deviation from linearity is very small. s is the standard deviation.

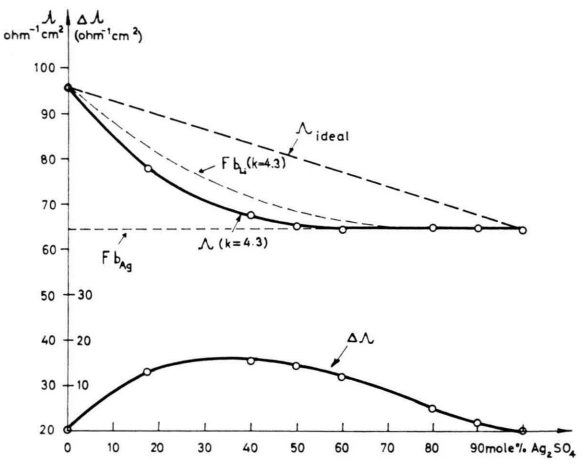

Fig. 3. The equivalent electrical conductivity of molten $Li_2SO_4-Ag_2SO_4$ at 750 °C and theoretical curves according to Eqs. (4) and (5) with $k = 4.3$.

The position of the maximal difference between the "ideal" conductivity and the measured one can easily be obtained from Eq. (4)

$$a_{max} = k^{-1/(k-1)}.$$

When $k = 4.3$, $a_{max} = 0.64$. The maximum is thus situated on the Li_2SO_4 rich side, which is the case in all investigated melts containing lithium ions and a common anion.

Our model can not explain the minimum of the Λ curve in $Li_2SO_4-K_2SO_4$ (l. c. [11]) or the crossing-over of the mobilities which has been found in several systems [12].

The minimum can perhaps be explained by the decrease in free volume when lithium sulphate is added to K_2SO_4 since this should give a decrease in the K^+ mobility when the lithium sulphate concentration increases. The calculated value of k is then perhaps a little too big. On the other hand the electrostatic forces between the sulphate ions and the lithium ions are greater than between sulphate ions and potassium ions and polarisation of the SO^{2-} ions by Li^+ ions in the K^+ rich region might then decrease the mobility of the lithium ions appreciably.

B. *Solid $Li_2SO_4-Ag_2SO_4$*

Only a few comments on the conductivity results for the solid salt will be given here.

Several sulphates form high temperature modifications with cubic or hexagonal structures, which are characterized by higher mobility of the cations than in ordinary solids [8, 11–14]. In the system $Li_2SO_4-Ag_2SO_4$ there are three high temperature phases with different structures. ØYE [15] has recently

[11] A. KVIST, Z. Naturforschg. **21 a**, 1221 [1966].

[12] L. LJUBIMOV and A. LUNDÉN, Z. Naturforschg. **21 a**, 1592 [1966].

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

[14] A. KVIST and A. LUNDÉN, Z. Naturforschg. **21 a**, 1509 [1966].

[15] H. ØYE, Theses, Trondheim 1963 and Acta Chem. Scand., in press.

Mole% Ag_2SO_4	a	$-b$	$s_\varkappa$	Λ $\Omega^{-1}cm^2$	t °C	$10^4 \cdot b_{Li^+}$ cm^2/Vs	Q cal/mole
0	2.0888	1.7791	0.033	30.3	610	3.14	9609
17.5	2.2713	1.8546	0.005	40.4	610	—	10017
40	1.9938	1.5800	0.003	32.3	545	3.35	7229
50	1.9902	1.5844	0.003	32.6	545	3.38	7242
60	1.8540	1.4753	0.005	33.7	545	3.39	6982

Table 5. The specific electrical conductivity of solid $Li_2SO_4-Ag_2SO_4$ described by the relation $\ln \varkappa = a + b\,t$, where t is the temperature in °C. $s_\varkappa$ is the standard deviation of $\varkappa$, Λ the equivalent conductivity, b_{Li^+} the mobility of the lithium ion and Q the ARRHENIUS' activation energy. Q of Li_2SO_4 with 60 mole% Ag_2SO_4 is a mean value of two measurements. The densities were obtained from ØYE [15].

performed a thermodynamic investigation of the system.

In the cubic (f.c.c.) modification of lithium sulphate the electrical conductivity inreases when silver sulphate is added (Table 5) and this is the case also when K_2SO_4, Rb_2SO_4 or Cs_2SO_4 is added [1]. The mobility of the silver ion is bigger than that of the lithium ion [15], but when silver sulphate is added, it is probable that also the mobility of the lithium ions increases, due to coupling between the ions. A notable result is also that the "activation energy" Q is about the same in the pure salt and in the mixture. The deviation from the ARRHENIUS' equation is however considerable.

In the b.c.c. modification the mobilities (b) of the cations are equal [15] and we can thus calculate b from the conductivity results (Table 5). The mobility of the lithium ion is higher than in pure lithium sulphate and the very small change of the specific conductivity at the melting point (Table 6) shows

Mole% Li_2SO_4	$\varkappa_m/\varkappa_s$	t °C
100	1.30	860
60	1.09	566
50	1.08	570
40	1.06	570
0	7.1	657

Table 6. The ratio $\varkappa_m/\varkappa_s$ of the specific conductivity of molten and solid $Li_2SO_4-Ag_2SO_4$ at the melting point.

that the structure of the solid is comparably disordered. Q and the equivalent conductivity are constant in this modification and Q is lower than in pure Li_2SO_4.

The change in conductivity upon melting in pure silver sulphate is big compared with the cubic transitions.

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