The Electrical Conductivity and Density of Pure Molten Thallium Sulphate and Equimolar Mixtures between Thallium Sulphate and Alkali Sulphates

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The electrical conductivity and density of pure molten thallium sulphate and the conductivity of TlMeSO_4 , where $\text{Me} = \text{Li, Na, K, Rb, or Cs}$, have been measured between 700 and 1150 °C. We have also measured the densities of four equimolar sulphate mixtures and their pure components. The excess volumes were less than 0.5%. The deviations from ideality for the conductivities and their Arrhenius activation energies have been compared with other sulphate systems. The electrical conductivity of a pure univalent sulphate depends both on the radius of the cation and on its mass. In mixtures, there are large negative excess conductivities and positive excess activation energies, when we have cations of different sizes.

In some recent papers^{1–5} we have reported on conductivity and also on some density measurements in different molten sulphate systems. Since we wanted to compare conductivities for mixtures, where the univalent cations have as different masses and radii as possible, we have now measured the electrical conductivity of Tl_2SO_4 , TlLiSO_4 , TlNaSO_4 , TlKSO_4 , TlRbSO_4 and TlCsSO_4 , and the densities of Tl_2SO_4 , Li_2SO_4 and TlLiSO_4 . For comparison, we have also measured the densities of some other sulphate mixtures and calculated the excess volumes.

Experimental

Conductivity measurements: The experimental technique is described elsewhere in detail⁴.

Density measurements: The method described previously⁴ was used with small modifications. The density bob was made of platinum and had a weight of about 20 g.

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

No decomposition of thallium sulphate was observed up to 1000 °C, but at temperatures above about 750 °C the evaporation of salt was considerable at normal pressure. This is in agreement with observations made by HEGEDÜS and FUKKER⁶.

Results and Discussion

The specific electrical conductivities and densities were generally determined from some degrees to

100–200 °C above the melting points (Table 1 and 2). No conductivity data have previously been reported for these salts.

t °C	κ $\Omega^{-1} \text{ cm}^{-1}$	t °C	κ $\Omega^{-1} \text{ cm}^{-1}$
Tl_2SO_4		KTlSO_4	
651.8	0.933	828.0	1.254
665.0	0.957	851.8	1.306
667.0	0.961	868.5	1.334
680.6	0.989	892.2	1.377
704.2	1.031	912.2	1.418
720.8	1.066	931.8	1.456
731.0	1.084	RbTlSO_4	
LiTlSO_4		848.0	1.148
764.8	1.192	880.2	1.215
781.8	1.239	901.8	1.250
802.0	1.296	917.2	1.275
816.0	1.335	CsTlSO_4	
848.0	1.426	798.2	0.991
866.2	1.474	824.5	1.036
880.0	1.506	848.8	1.068
897.5	1.550	864.2	1.095
920.8	1.607	875.0	1.113
922.0	1.615	902.0	1.163
NaTlSO_4		915.8	1.184
787.6	1.236	933.2	1.209
807.5	1.282	945.0	1.233
827.5	1.319		
843.5	1.361		
862.5	1.399		
886.0	1.448		
902.2	1.479		
917.5	1.510		
937.2	1.551		

Table 1. The specific electrical conductivities of the investigated salts.

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⁴ A. KVIST, Z. Naturforsch. **22 a**, 208 [1967].

⁵ A. KVIST, Z. Naturforsch. **22 a**, 467 [1967].

⁶ A. J. HEGEDÜS and K. FUKKER, Z. Anorg. Chem. **284**, 20 [1965].

t °C	ρ g/cm ³	t °C	ρ g/cm ³
Li_2SO_4		LiNaSO_4	
915	1.982	737	2.096
936	1.969	793	2.074
959	1.963	853	2.046
998	1.948	912	2.019
Na_2SO_4		962	1.995
903	2.062	LiKSO_4	
942	2.043	789	2.009
996	2.022	830	1.990
1047	2.000	887	1.965
K_2SO_4		939	1.944
1083	1.869	1009	1.913
1131	1.845	1064	1.889
1151	1.832	LiTiSO_4	
Ti_2SO_4		775	4.168
680	5.565	801	4.145
710	5.525	832	4.116
726	5.500	878	4.073
741	5.474	902	4.054
757	5.455	925	4.029
784	5.417	967	3.989
825	5.369	1006	3.952
842	5.347	NaKSO_4	
867	5.318	931	1.985
888	5.289	959	1.971
914	5.259	1018	1.945
943	5.219	1087	1.916

Table 2. The densities of the investigated salts.

The density results can be described by simple linear relations (Table 3) with a standard deviation of less than 0.1%. A comparison between our results

Salt	a g/cm ³	$-b \cdot 10^{-3}$ g/cm ³ , °C	s g/cm ³	Interval °C	$\rho(1000^\circ\text{C})$ g/cm ³	Ref.
Li_2SO_4	2.340	0.3929	0.002	915—998	1.947	
	2.285	0.329	0.002	880—960	1.956	⁴
	2.354	0.407	—	910—1110	1.947	⁷
Na_2SO_4	2.445	0.4249	0.001	903—1047	2.020	
	2.496	0.483	—	926—1046	2.013	⁷
K_2SO_4	2.450	0.5360	0.001	1083—1151	1.914	
	2.417	0.545	—	1102—1291	1.972	⁷
Ti_2SO_4	6.440	1.2963	0.004	680—943	5.144	
LiNaSO_4	2.430	0.4515	0.002	737—962	1.976	
LiKSO_4	2.351	0.4337	0.001	789—1064	1.817	
LiTiSO_4	4.894	0.9355	0.002	775—1006	3.958	
NaKSO_4	2.394	0.4399	0.001	931—1087	1.954	

Table 3. The densities described by the relation $\rho = a + bt$, where t is the temperature in °C, compared with previous results. s is the standard deviation.

and previous ones shows good agreement for Li_2SO_4 (l. c.^{4,7}) and Na_2SO_4 (l. c.⁷), but not for K_2SO_4 , where our results are more than 3% higher than those obtained by JAEGER and KAHN⁷.

According to UBBELOHDE⁸ most molten salt systems show a change from a negative excess volume at low melting temperatures to relative large positive deviations at higher temperatures. In the investigated sulphate mixtures (Table 4) and also in LiAgSO_4 (l. c.⁴) the excess volumes at 1000 °C, which are positive, are less than 0.5%. These systems can thus be considered ideal.

Salt	V (measured) cm ³ /mole	V (ideal) cm ³ /mole	Difference (%)
LiNaSO_4	63.68	63.40	0.4
LiKSO_4	74.13	73.76	0.5
LiTiSO_4	77.65	77.30	0.4
NaKSO_4	80.95	80.69	0.3

Table 4. The measured molar volumes compared with the ideal molar volumes at 1000 °C.

For the calculation of the molar electrical conductivities (Λ) of TiRbSO_4 and TiCsSO_4 , we have used density data for Rb_2SO_4 and Cs_2SO_4 obtained by JAEGER and KAHN⁷ and assumed that the excess volume is negligible.

The temperature dependence of Λ can be expressed in several different ways⁹. In all molten sulphates we have studied so far, we have found that the results with satisfactory precision can be written as $\Lambda = a + bt$. The standard deviation of Λ is then about 0.2% and no definite curvatures have been observed. Λ has often been described by the relation $\Lambda = a + bt + ct^2$, which leads to a conductivity maximum. For LiI (l. c.¹⁰) and Li_2WO_4 (l. c.¹¹) this should occur at comparably low temperatures, but in more careful measurements no low temperature maxima could be detected^{12,13}. Also discontinuous conductivity changes have been reported¹⁴.

Deviations from linearity might probably with few exceptions¹⁵ be explained by decomposition of the salt.

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Linear equations for Λ are given in Table 5.

Salt	$-a$ $\Omega^{-1}\text{cm}^2$	b $\Omega^{-1}\text{cm}^2\text{ }^\circ\text{C}^{-1}$	s $\Omega^{-1}\text{cm}^2$	Interval $^\circ\text{C}$
Ti_2SO_4	43.8	0.19620	0.1	651–731
LiTiSO_4	84.5	0.22534	0.2	764–922
NaTiSO_4	55.9	0.19699	0.2	787–937
KTiSO_4	59.4	0.20883	0.2	828–931
RbTiSO_4	65.8	0.20881	0.2	848–917
CsTiSO_4	55.0	0.19720	0.4	798–945

Table 5. The temperature dependence of the molar electrical conductivities described by the equation $\Lambda = a + bt$, where t is the temperature in $^\circ\text{C}$. s is the standard deviation.

We have calculated two parameters for our further discussions; the molar electrical conductivity at 900°C (Table 6) and the Arrhenius activation energy Q (Table 7) obtained from the relation

$$\Lambda = \Lambda_0 \exp(-Q/RT).$$

Salt	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	Ti_2SO_4	Ag_2SO_4
Li_2SO_4	242.5	174.0	122.6	95.6	84.0	118.3	172.0
Na_2SO_4	174.0	159.3	128.4	105.4	96.3	121.4	—
K_2SO_4	122.6	128.4	134.6	121.6	113.4	128.6	—
Rb_2SO_4	95.6	105.4	121.6	112.8	105.6	122.1	—
Cs_2SO_4	84.0	96.3	113.4	105.6	111.3	122.4	—
Ti_2SO_4	118.3	121.4	128.6	122.1	122.4	132.8	—
Ag_2SO_4	172.0	—	—	—	—	—	156.5

Table 6. The molar electrical conductivities in $\Omega^{-1}\text{cm}^2$ of pure molten sulphates and equimolar sulphate mixtures at 900°C .

Salt	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	Ti_2SO_4	Ag_2SO_4
Li_2SO_4	2590	5170	6420	6340	6370	5310	4590
Na_2SO_4	5170	4460	5680	4910	6190	4720	—
K_2SO_4	6420	5860	4910	4850	4970	4430	—
Rb_2SO_4	6340	4910	4850	4970	4630	4690	—
Cs_2SO_4	6370	6190	4970	4630	4530	4380	—
Ti_2SO_4	5310	4720	4430	4690	4380	3940	—
Ag_2SO_4	4590	—	—	—	—	—	3180

Table 7. The Arrhenius activation energies in cal/mole for pure molten sulphates and equimolar sulphate mixtures.

The physical meaning of Q is perhaps doubtful, but Q has been discussed in the literature for various systems.

As we have found previously⁵, the conductivities of the pure alkali sulphates increase when the radii of the cations decrease. The Pauling radii of the thallium and rubidium ions are almost equal, but the conductivity of Ti_2SO_4 is considerably higher than of Rb_2SO_4 . Also for Ag_2SO_4 the conductivity is comparably higher than for the alkali sulphates. This mass dependence of the conductivity has the

opposite direction compared with the isotopic enriched salts $^6\text{Li}_2\text{SO}_4$ and $^7\text{Li}_2\text{SO}_4$, where the conductivity is 4.2% higher in $^6\text{Li}_2\text{SO}_4$ than in $^7\text{Li}_2\text{SO}_4$, and which has been explained by the mass difference^{1,16}. However, the molar volume of Ti_2SO_4 is greater than of Rb_2SO_4 and this means that also the free volume is greater, which might explain the difference.

Fig. 1. The equivalent electrical conductivity of Ti_2SO_4 , Me_2SO_4 and TiMeSO_4 .

Fig. 2. The equivalent electrical conductivity of Li_2SO_4 , Me_2SO_4 and LiMeSO_4 .

¹⁶ A. Kivist, Thesis, Göteborg 1967.

In the equimolar mixtures, the conductivity mainly depends on the heavier cation. This can be explained by assuming some sort of cooperative motions in the salt⁵, where a light cation, for instance a lithium ion in thallium sulphate, moves with the same velocity as the thallium ions. A result of this is that the conductivity of TlMeSO_4 almost is the same for all Me (Fig. 1). For LiMeSO_4 the situation is reversed (Fig. 2). It can also be observed that in the mixture $\text{Li}_2\text{SO}_4 - \text{Rb}_2\text{SO}_4$ and in other mixtures, where the cation radii are nearly equal, both Δ and

Q are ideal. This has been observed also for nitrates¹⁷. A comparison between Table 6 and 7 shows that when we mix two salts with very different cation radii, we obtain a very large positive excess activation energy and a negative excess conductivity. This is in agreement with the model mentioned above, since the free volume of a sulphate increases with the radius of the cation⁵.

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Diffusion in Cubic Sulphates

I. Univalent Cations in Pure Lithium Sulphate

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The interdiffusion coefficients (D) of Na^+ , Ag^+ , K^+ , Rb^+ and Tl^+ in pure f.c.c. Li_2SO_4 have been measured between 590 and 820 °C. D and the Arrhenius' activation energies decrease in the same order as the ionic radii increase. D is a function both of the masses and the radii of the impurity cations. The results show that the Na^+ and Ag^+ ions mainly diffuse in the sulphate lattice with the same mechanism as the lithium ions, while the larger ions are mobile in defects in the lattice. The Li^+ , Na^+ and Ag^+ ions are probably diffusing between octahedral positions.

Some salts form cubic high temperature modifications with extremely high mobility of the cations. Such modifications can be found in e. g. AgI (l.c. ¹⁻²), Li_2SO_4 (l.c. ³⁻⁵), LiAgSO_4 (l.c. ⁶⁻⁷) and LiNaSO_4 (l.c. ⁷⁻⁸). During the last years we have made a great number of investigations of especially lithium sulphate and we have now started a series of measurements of different diffusion coefficients in cubic sulphates. We report here on measurements of the interdiffusion coefficients of the univalent cations Na^+ , Ag^+ , K^+ , Tl^+ and Rb^+ in f.c.c. Li_2SO_4 . The self-diffusion coefficient of lithium in this modification has recently been published⁴ and measurements of thermal diffusion coefficients have also been reported⁸⁻⁹.

Experimental

All salts were of reagent quality and were used without further purification. The diffusion cells were made of pure quartz (Fig. 1) and all measurements were performed in air. Pure lithium sulphate was molten in the bottom of the tube, which was placed in a big furnace. When the salt had solidified to an about 70 mm long column and the experimental temperature was reached, we inserted a funnel, which contained a few small lumps of lithium sulphate with 2–3 mole% of the impurity cation. The salt in the funnel was molten by means of a small winding around the tube and in this way an about 0.5 mm thick layer of salt containing impurities was obtained on the surface of the salt column. The cell was then held at constant temperature for 3–8 hours, when it was rapidly cooled to room temperature. Samples were taken at every fourth mm of the salt column, and were analysed by means of flame spectrophotometry.

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