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

ARNOLD KVIST and KJELL SCHROEDER

Department of Physics, Chalmers University of Technology, Göteborg, Sweden

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The electrical conductivity and density of pure molten thallium sulphate and the conductivity of $TlMeSO_4$, where Me = 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 detail[4].

Density measurements: The method described previously[4] 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 FUKKER[6].

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

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

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t °C	ϱ g/cm³
Li_2SO_4	
915	1.982
936	1.969
959	1.963
998	1.948
Na_2SO_4	
903	2.062
942	2.043
996	2.022
1047	2.000
K_2SO_4	
1083	1.869
1131	1.845
1151	1.832
Tl_2SO_4	
680	5.565
710	5.525
726	5.500
741	5.474
757	5.455
784	5.417
825	5.369
842	5.347
867	5.318
888	5.289
914	5.259
943	5.219

t °C	ϱ g/cm³
$LiNaSO_4$	
737	2.096
793	2.074
853	2.046
912	2.019
962	1.995
$LiKSO_4$	
789	2.009
830	1.990
887	1.965
939	1.944
1009	1.913
1064	1.889
$LiTlSO_4$	
775	4.168
801	4.145
832	4.116
878	4.073
902	4.054
925	4.029
967	3.989
1006	3.952
$NaKSO_4$	
931	1.985
959	1.971
1018	1.945
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 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 KAHN [7].

Salt	a g/cm³	$-b \cdot 10^{-3}$ g/cm³, °C	s g/cm³	Interval °C	ϱ(1000 °C) g/cm³	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
Tl_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	
$LiTlSO_4$	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 $\varrho = a + b\,t$, where t is the temperature in °C, compared with previous results. s is the standard deviation.

According to UBBELOHDE [8] 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) cm³/mole	V (ideal) cm³/mole	Difference (%)
$LiNaSO_4$	63.68	63.40	0.4
$LiKSO_4$	74.13	73.76	0.5
$LiTlSO_4$	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 $TlRbSO_4$ and $TlCsSO_4$, we have used density data for Rb_2SO_4 and Cs_2SO_4 obtained by JAEGER and KAHN [7] and assumed that the excess volume is negligible.

The temperature dependence of Λ can be expressed in several different ways [9]. In all molten sulphates we have studied so far, we have found that the results with satisfactory precision can be written as $\Lambda = a + b\,t$. 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 $\Lambda = a + b\,t + c\,t^2$, 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 discontinous conductivity changes have been reported [14].

Deviations from linearity might probably with few exceptions [15] be explained by decomposition of the salt.

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Linear equations for Λ are given in Table 5.

Salt	$-a$ Ω^{-1} cm^2	b Ω^{-1} cm^2 °C^{-1}	s Ω^{-1} cm^2	Interval °C
Tl_2SO_4	43.8	0.19620	0.1	651−731
$LiTlSO_4$	84.5	0.22534	0.2	764−922
$NaTlSO_4$	55.9	0.19699	0.2	787−937
$KTlSO_4$	59.4	0.20883	0.2	828−931
$RbTlSO_4$	65.8	0.20881	0.2	848−917
$CsTlSO_4$	55.0	0.19720	0.4	798−945

Table 5. The temperature dependence of the molar electrical conductivities described by the equation $\Lambda = a + b\,t$, where t is the temperature in °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

$$\Lambda = \Lambda_0 \exp(-Q/R\,T).$$

Salt	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4	Tl_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	—
Tl_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 Ω^{-1} 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	Tl_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	—
Tl_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 previously [5], 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 Tl_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 $^6Li_2SO_4$ and $^7Li_2SO_4$, were the conductivity is 4.2% higher in $^6Li_2SO_4$ than in $^7Li_2SO_4$, and which has been explained by the mass difference [1, 16]. However, the molar volume of Tl_2SO_4 is greater than of Rb_2SO_4 and this means that also the free volume is greater, which might explain the difference.

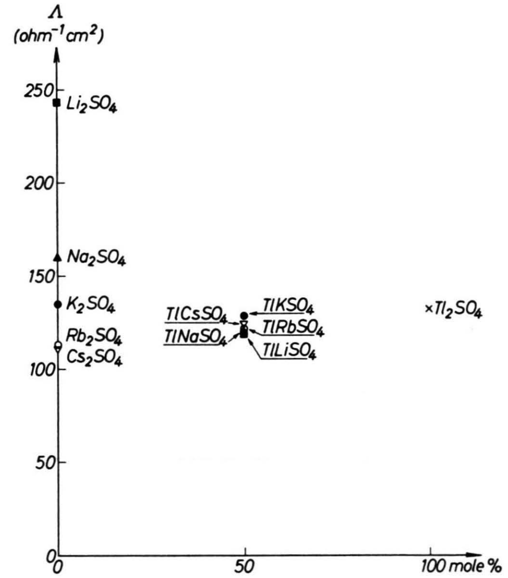

Fig. 1. The equivalent electrical conductivity of Tl_2SO_4, Me_2SO_4 and $TlMeSO_4$.

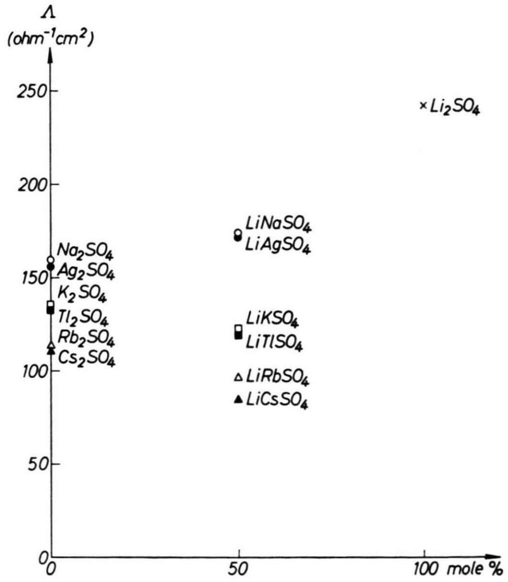

Fig. 2. The equivalent electrical conductivity of Li_2SO_4, Me_2SO_4 and $LiMeSO_4$.

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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 salt[5], 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 $Tl_2SO_4 - Rb_2SO_4$ and in other mixtures, where the cation radii are narly equal, both Λ and Q are ideal. This has been observed also for nitrates[17]. 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 cation[5].

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Diffusion in Cubic Sulphates

I. Univalent Cations in Pure Lithium Sulphate

Arnold Kvist and Ante Bengtzelius

Department of Physics, Chalmers University of Technology, Göteborg

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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 serie 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 published[4] and measurements of thermal diffusion coefficients have also been reported[8–9].

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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