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 TlMeSO₄, 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 papers¹—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 Tl₂SO₄, Tl₂LiSO₄, Tl₂NaSO₄, Tl₂KSO₄, Tl₂RbSO₄ and Tl₂CsSO₄, and the densities of Tl₂SO₄, Li₂SO₄ and Tl₂LiSO₄. For comparison, we have also measured the densities of some other sulphate mixtures and calculated the excess volumes.

### 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.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (Ω⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tl₂SO₄</td>
</tr>
<tr>
<td></td>
<td>KTlSO₄</td>
</tr>
<tr>
<td>651.8</td>
<td>0.933</td>
</tr>
<tr>
<td>665.0</td>
<td>0.957</td>
</tr>
<tr>
<td>667.0</td>
<td>0.961</td>
</tr>
<tr>
<td>680.6</td>
<td>0.989</td>
</tr>
<tr>
<td>704.2</td>
<td>1.031</td>
</tr>
<tr>
<td>720.8</td>
<td>1.066</td>
</tr>
<tr>
<td>731.0</td>
<td>1.084</td>
</tr>
<tr>
<td></td>
<td>Li₂TlSO₄</td>
</tr>
<tr>
<td>764.8</td>
<td>1.192</td>
</tr>
<tr>
<td>781.8</td>
<td>1.239</td>
</tr>
<tr>
<td>802.0</td>
<td>1.296</td>
</tr>
<tr>
<td>816.0</td>
<td>1.335</td>
</tr>
<tr>
<td>848.0</td>
<td>1.426</td>
</tr>
<tr>
<td>866.2</td>
<td>1.474</td>
</tr>
<tr>
<td>880.0</td>
<td>1.506</td>
</tr>
<tr>
<td>897.5</td>
<td>1.550</td>
</tr>
<tr>
<td>920.8</td>
<td>1.607</td>
</tr>
<tr>
<td>922.0</td>
<td>1.615</td>
</tr>
<tr>
<td></td>
<td>Na₂TlSO₄</td>
</tr>
<tr>
<td>787.6</td>
<td>1.236</td>
</tr>
<tr>
<td>807.5</td>
<td>1.282</td>
</tr>
<tr>
<td>827.5</td>
<td>1.319</td>
</tr>
<tr>
<td>843.5</td>
<td>1.361</td>
</tr>
<tr>
<td>862.5</td>
<td>1.399</td>
</tr>
<tr>
<td>886.0</td>
<td>1.448</td>
</tr>
<tr>
<td>902.2</td>
<td>1.479</td>
</tr>
<tr>
<td>917.5</td>
<td>1.510</td>
</tr>
<tr>
<td>937.2</td>
<td>1.551</td>
</tr>
</tbody>
</table>

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

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

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### References

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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 is the temperature in °C, compared with previous results.

According to Ubbelohde 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 LiAgSO₄ (I.c.⁴) the excess volumes at 1000 °C, which are positive, are less than 0.5%. These systems can thus be considered ideal.

The temperature dependence of \( \Lambda \) can be expressed in several different ways. In all molten sulphates we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum. For LiI, LiKl, and Li₂WO₄ we have studied so far, we have found that the results with satisfactory precision can be written as \( \Lambda = a + b t + c t^2 \) which leads to a conductivity maximum.

Deviations from linearity might probably with few exceptions be explained by decomposition of the salt.
Linear equations for $A$ are given in Table 5.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$-a$</th>
<th>$b$</th>
<th>$s$</th>
<th>Interval °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Tl_2SO_4$</td>
<td>43.8</td>
<td>0.19620</td>
<td>0.1</td>
<td>651–731</td>
</tr>
<tr>
<td>LiTISO$_4$</td>
<td>84.5</td>
<td>0.22534</td>
<td>0.2</td>
<td>764–922</td>
</tr>
<tr>
<td>NaTISO$_4$</td>
<td>55.9</td>
<td>0.19999</td>
<td>0.2</td>
<td>787–937</td>
</tr>
<tr>
<td>KtISO$_4$</td>
<td>59.4</td>
<td>0.20883</td>
<td>0.2</td>
<td>828–931</td>
</tr>
<tr>
<td>RbTISO$_4$</td>
<td>65.8</td>
<td>0.20881</td>
<td>0.2</td>
<td>846–917</td>
</tr>
<tr>
<td>CsTISO$_4$</td>
<td>55.0</td>
<td>0.19720</td>
<td>0.4</td>
<td>798–945</td>
</tr>
</tbody>
</table>

Table 5. The temperature dependence of the molar electrical conductivities described by the equation $A = a + b \cdot t$, 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

$$A = A_0 \exp (-Q/RT).$$

<table>
<thead>
<tr>
<th>Salt</th>
<th>Li$_2$SO$_4$</th>
<th>Na$_2$SO$_4$</th>
<th>K$_2$SO$_4$</th>
<th>Rb$_2$SO$_4$</th>
<th>Cs$_2$SO$_4$</th>
<th>Tl$_2$SO$_4$</th>
<th>Ag$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$SO$_4$</td>
<td>242.5</td>
<td>174.0</td>
<td>122.6</td>
<td>95.6</td>
<td>84.0</td>
<td>118.3</td>
<td>172.0</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>174.0</td>
<td>159.3</td>
<td>128.4</td>
<td>105.4</td>
<td>96.3</td>
<td>121.4</td>
<td>—</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>122.6</td>
<td>128.4</td>
<td>134.6</td>
<td>121.6</td>
<td>113.4</td>
<td>128.6</td>
<td>—</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
<td>95.6</td>
<td>105.4</td>
<td>121.6</td>
<td>112.8</td>
<td>105.6</td>
<td>122.1</td>
<td>—</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$</td>
<td>84.0</td>
<td>96.3</td>
<td>113.4</td>
<td>105.6</td>
<td>111.3</td>
<td>122.4</td>
<td>—</td>
</tr>
<tr>
<td>Tl$_2$SO$_4$</td>
<td>118.3</td>
<td>121.4</td>
<td>128.6</td>
<td>122.1</td>
<td>122.4</td>
<td>132.8</td>
<td>—</td>
</tr>
<tr>
<td>Ag$_2$SO$_4$</td>
<td>172.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>156.5</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Salt</th>
<th>Li$_2$SO$_4$</th>
<th>Na$_2$SO$_4$</th>
<th>K$_2$SO$_4$</th>
<th>Rb$_2$SO$_4$</th>
<th>Cs$_2$SO$_4$</th>
<th>Tl$_2$SO$_4$</th>
<th>Ag$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$SO$_4$</td>
<td>2590</td>
<td>5170</td>
<td>6420</td>
<td>6340</td>
<td>6370</td>
<td>5310</td>
<td>4590</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>5170</td>
<td>4460</td>
<td>5680</td>
<td>4910</td>
<td>6190</td>
<td>4720</td>
<td>—</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>6420</td>
<td>5860</td>
<td>4910</td>
<td>4850</td>
<td>4970</td>
<td>4430</td>
<td>—</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
<td>6340</td>
<td>4910</td>
<td>4850</td>
<td>4970</td>
<td>4630</td>
<td>4690</td>
<td>—</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$</td>
<td>6370</td>
<td>6190</td>
<td>4970</td>
<td>4630</td>
<td>4530</td>
<td>4380</td>
<td>—</td>
</tr>
<tr>
<td>Tl$_2$SO$_4$</td>
<td>5310</td>
<td>4720</td>
<td>4430</td>
<td>4690</td>
<td>4380</td>
<td>3940</td>
<td>—</td>
</tr>
<tr>
<td>Ag$_2$SO$_4$</td>
<td>4590</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3180</td>
</tr>
</tbody>
</table>

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, 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. 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.

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\(^4\), 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 \(\text{TlMeSO}_4\) almost is the same for all \(\text{Me}\) (Fig. 1). For \(\text{LiMeSO}_4\) the situation is reversed (Fig. 2). It can also be observed that in the mixture \(\text{TlSO}_4 - \text{RbSO}_4\) and in other mixtures, where the cation radii are nearly equal, both \(\lambda\) and \(Q\) are ideal. This has been observed also for nitrates\(^5\). 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\(^6\).

This work was supported financially by Magnus Bergvalls Stiftelse.

\(^{17}\) V. Wagner and S. Forcheri, Z. Naturforsch. 22 a, 891 [1967].

**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. \(\text{Li}_2\text{SO}_4\) 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. \(^{1-2}\)), \(\text{Li}_2\text{SO}_4\) (l. c. \(^{3-5}\)), \(\text{LiAgSO}_4\) (l. c. \(^6\)) and \(\text{LiNaSO}_4\) (l. c. \(^7\)). 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. \(\text{Li}_2\text{SO}_4\). 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.

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2. G. Burley, American Mineralogist 48, 1266 [1963].