The Electrical Conductivity of the Molten System (Li,K)$_2$(SO$_4$,WO$_4$)

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The electrical conductivities of molten Li$_2$SO$_4$, K$_2$WO$_4$, K$_2$SO$_4$, K$_2$W$_2$O$_7$ and their equimolar mixtures have been measured up to 1100 °C. The equivalent conductivities and the Arrhenius activation energies indicate that the transport mechanism is mainly determined by the cations.

One of the authors has recently found that the molar electrical conductivity ($\Lambda$) of Li$_2$SO$_4$ is considerably lower than $\Lambda$ of pure Li$_2$SO$_4$ and K$_2$SO$_4$, while the conductivity of equimolar Li$_2$SO$_4$–Li$_2$WO$_4$, where $\Lambda$ (Li$_2$WO$_4$) $\approx \Lambda$ (K$_2$SO$_4$), is almost ideal. The anions thus seem to have little importance for the conduction mechanism in such melts. We therefore found it interesting to compare the conductivities of Li$_2$SO$_4$, Li$_2$WO$_4$, K$_2$SO$_4$, and K$_2$W$_2$O$_7$ with their equimolar mixtures.

The experimental technique is described elsewhere in detail. The salts, Li$_2$SO$_4$ (Hopkinson & Williams Anal. R.), K$_2$SO$_4$ (Merrick p. a.), Li$_2$WO$_4$ (Hopkinson & Williams) and K$_2$WO$_4$ (Hopkinson & Williams), were used without further purification.

The specific conductivities (\kappa) of K$_2$WO$_4$, K$_2$SO$_4$–K$_2$WO$_4$, Li$_2$WO$_4$–K$_2$WO$_4$ and Li$_2$SO$_4$–K$_2$WO$_4$ are given in Table 1. The conductivity of K$_2$WO$_4$ agrees within 1% with results obtained by Morris and Robinson.

\[
\kappa \text{ and } \Lambda \text{ of } \text{Li}_2\text{SO}_4, \text{Li}_2\text{SO}_4–\text{K}_2\text{SO}_4, \text{Li}_2\text{SO}_4–\text{Li}_2\text{WO}_4 \text{ and Li}_2\text{WO}_4–\text{K}_2\text{WO}_4 \text{ have recently been published.}
\]

The molar conductivities were calculated by assuming volumetric additivity of the salts. The densities were obtained from Morris and Robinson, Jäger and Kärrn and Kvist. The volumetric additivity was checked by comparing the mean value of the molar volumes of Li$_2$SO$_4$ and K$_2$WO$_4$ ($V_t$) with that of Li$_2$WO$_4$ and K$_2$SO$_4$ ($V_2$). A difference of about 4% was found, but this difference is neglectable in this case. The molar volume of LiK(SO$_4$WO$_3$)$_{1/2}$ was taken as the mean value of $V_t$ and $V_2$.

Linear equations for $\Lambda$ are given in Table 2.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$a$</th>
<th>$-b$</th>
<th>$s$</th>
<th>Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$WO$_4$</td>
<td>0.22379</td>
<td>89.0</td>
<td>0.4</td>
<td>933–1036</td>
</tr>
<tr>
<td>LiKWO$_4$</td>
<td>0.21816</td>
<td>88.6</td>
<td>0.2</td>
<td>691–918</td>
</tr>
<tr>
<td>K$_2$W$_2$O$_7$</td>
<td>0.24420</td>
<td>98.3</td>
<td>0.3</td>
<td>928–992</td>
</tr>
<tr>
<td>LiK(SO$_4$WO$<em>3$)$</em>{1/2}$</td>
<td>0.23015</td>
<td>105.8</td>
<td>0.2</td>
<td>810–974</td>
</tr>
</tbody>
</table>

Table 2. The molar electrical conductivity described by the relation $\Lambda = a t + b$, where $t$ is the temperature in °C. $s$ is the standard deviation.
In Table 3 we have tabulated $A$ at 900 °C and in Table 4 the Arrhenius activation energies ($Q$) obtained from

$$A = A_0 \exp \left(-\frac{Q}{RT}\right).$$

The standard deviation of $Q$ is generally a few hundred cal/mole.

<table>
<thead>
<tr>
<th>Anion Cation</th>
<th>SO$_4^{2-}$</th>
<th>(SO$_4$WO$<em>4$)$</em>{1/2}^{-}$</th>
<th>WO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>121.1</td>
<td>89.7</td>
<td>69.6</td>
</tr>
<tr>
<td>(LiK)$_{1/2}^+$</td>
<td>61.3</td>
<td>50.7</td>
<td>44.3</td>
</tr>
<tr>
<td>K$^+$</td>
<td>67.3</td>
<td>60.7</td>
<td>55.0</td>
</tr>
</tbody>
</table>

Table 3. The equivalent conductivities of the investigated salts at 900 °C.

<table>
<thead>
<tr>
<th>Anion Cation</th>
<th>SO$_4^{2-}$</th>
<th>(SO$_4$WO$<em>4$)$</em>{1/2}^{-}$</th>
<th>WO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>2590</td>
<td>5180</td>
<td>5460</td>
</tr>
<tr>
<td>(LiK)$_{1/2}^+$</td>
<td>6420</td>
<td>6280</td>
<td>7530</td>
</tr>
<tr>
<td>K$^+$</td>
<td>4910</td>
<td>5440</td>
<td>5600</td>
</tr>
</tbody>
</table>

Table 4. The Arrhenius activation energies of the investigated salts.

Some regularities in $A$ and $Q$ can be observed.
a) If we have the same cation $[\text{Me} = \text{Li}, \text{K}, (\text{LiK})_{1/2}]$

$$A(\text{Me}_2\text{SO}_4) > A(\text{Me}_2(\text{SO}_4\text{WO}_4))_{1/2} > A(\text{Me}_2\text{WO}_4)$$

and $A(\text{Me}_2(\text{SO}_4\text{WO}_4))_{1/2}$ is not far from the mean value of the conductivities of the pure salts.

b) $A(\text{LiKX})$ [X = SO$_4$, WO$_4$, (SO$_4$WO$_4$)$_{1/2}$] is much smaller than both $A(\text{LiX})$ and $A(\text{LiKX})$.

c) $Q(\text{Me}_2\text{SO}_4) < Q(\text{Me}_2(\text{SO}_4\text{WO}_4))_{1/2} < Q(\text{Me}_2\text{WO}_4)$ except for LiKX, where

$$Q(\text{LiK}(\text{SO}_4\text{WO}_4))_{1/2} \approx Q(\text{LiKSO}_4).$$

d) $Q(\text{LiKX})$ is much greater than $Q(\text{LiX})$ and $Q(\text{K}_2\text{X})$. For instance for the mixture of Li$_2$SO$_4$ and K$_2$WO$_4$, where $Q(\text{Li}_2\text{WO}_4) \approx Q(\text{K}_2\text{WO}_4)$, the activation energy is almost 40% higher than for the pure salts.

In the mixtures there is thus an increase in $Q$ and a decrease in $A$ compared with the pure salts if we have the same anion but different cations. This agrees with observations made for nitrate mixtures by others $^8, 9$. On the other hand the conductivities and activation energies are almost ideal if we mix two salts with a common cation.

The difference in radius between the potassium ion and the lithium ion is the same as the difference between the tungstate ion and the sulphate ion (0.7 Å). The Tobolsky parameter $^10$ is thus approximately the same for LiKX and Me$_2$(SO$_4$WO$_4$)$_{1/2}$, but the deviations from ideality of the conductivities are very different. A possible explanation to this is that the transport mechanism mainly is determined by the cations in this system.

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$^8$ V. Wagner and S. Forcheri, Z. Naturforsch. 22 a, 891 [1967].


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**Differential Thermal Analysis of Lithium Sulphate with Small Quantities of Sodium, Rubidium and Cesium Sulphate**

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Previously obtained results for the system (Li,K)$_2$SO$_4$ with small quantities of K$_2$SO$_4$ show a second order transition below the solidus curve, probably due to the rotation properties of the sulphate ions. To obtain more information about the high temperature behaviour, the systems (Li,Na)$_2$SO$_4$, (Li,Rb)$_2$SO$_4$ and (Li,Cs)$_2$SO$_4$ have been studied. From differential thermal analysis we have constructed the phase diagrams for Li$_2$SO$_4$ with small quantities of Na$_2$SO$_4$, Rb$_2$SO$_4$, and Cs$_2$SO$_4$.

Mechanical properties and electrical conductivity of the system (Li,K)$_2$SO$_4$ with small quantities of K$_2$SO$_4$ have recently been studied in this laboratory $^1$. At a certain temperature below the solidus curve, a notable change in the temperature dependence of the apparent viscosity takes place, and a similar behaviour of the electrical conductivity is also observed. Our interpretation was that the sulphate lattice is affected by the presence of small amounts of foreign cations, and that this effect should depend on the size of the added ion. Considering data from X-ray measurements $^2, 3$ this effect would vanish if the foreign cation is small enough, but would appear for larger cations. A differential thermal analysis of the system (Li,K)$_2$SO$_4$ shows a change in the slope of the thermal curve at the considered temperature $^4$. Similar systems could then be studied with this method.

