The Electrical Conductivity of Molten Lithium Sulphate with Small Quantities of Foreign Cations

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The electrical conductivity of molten lithium sulphate with small quantities of foreign cations (Na⁺, K⁺, Rb⁺, Cs⁺, Mn²⁺, Cd²⁺ and Ba²⁺) has been measured from 700 to 950 °C. The temperature dependence of the specific conductivity can in all cases with good accuracy be described by straight lines. The decrease in the specific conductivity is approximately proportional to the volume of the foreign cation. If it is assumed that the cations are moving in groups, the number of ions in each group is found to be 2.7. The change in free volume of molten lithium sulphate, when a small quantity of foreign ions is added, seems to have little importance for the change in electrical conductivity. An estimation of the mobility of Cd²⁺ ions indicates the existence of Wagner effect in molten lithium sulphate.

Little is known about the changes in transport properties of a pure molten salt, when small quantities of foreign ions are added, though intense studies of such systems have been made in the solid state.

Several conditions must be fulfilled to make measurements of the electrical conductivity of pure salts with small quantities of impurities; the change in conductivity must be comparably big when the foreign ions are added and the reproducibility of the results must be good.

Cleaver, Rhodes and Ubbelohde have found that the conductivity of molten KNO₃ decreases on adding Ba(NO₃)₂, in contrast to solid KNO₃. As a probable explanation to this was proposed that there is an electrostrictive shrinkage of the free volume when the divalent cations are added to the melt. Papianno and Harrington have measured the electrical conductivity of nitrates with small quantities of Co²⁺ and Ni²⁺ ions, but their results are complicated.

It has been found by the author that the decrease in electrical conductivity of pure molten lithium sulphate is almost 8%, when 3 mole % of potassium sulphate is added and it was therefore assumed that this change should be big also when other univalent or divalent sulphates were added. We have thus made a systematical investigation, using Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Cd²⁺ and Ba²⁺ ions as impurities. Fe²⁺ ions were also tried, but it was found that the decomposition of this salt was considerable.

All salts were analytical grade and were used without further purification. The chemicals were dried at least for 1 day at 180 °C, MgSO₄ at 220 °C.

The experimental technique is described elsewhere in detail. The salts were mixed and melted in vacuum in quartz capillary cells, but several of the measurements were performed in argon atmosphere. Only very slight corrosion of the cells was observed, except when Li₂SO₄ — Na₂SO₄ and Li₂SO₄ — MgSO₄ mixtures were used. This attack could however be somewhat reduced by keeping the salts completely free from water.

**Results**

The results are summarized in Table 1. The specific electrical conductivities can with good accuracy be described by straight lines

\[ \kappa = a + b \]

where \( \kappa \) is the specific conductivity, \( a \) und \( b \) constants, and \( t \) the temperature in °C. The standard deviation

\[ s = \sqrt{\frac{\sum (\kappa - \kappa_m)^2}{(n - 1)}} \]

is in all cases less than 0.3%. \( \kappa - \kappa_m \) is the difference between the measured value and the value obtained from the regression line and \( n \) is the number of measured values.


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Table 1. The specific electrical conductivity $\chi = a T - b$ of molten lithium sulphate with small quantities of other sulphates. $s$ is the standard deviation and $\Delta \chi$ the difference between the conductivity of pure Li$_2$SO$_4$ and the mixtures at 890 °C. $n$ is the number of mole per cent impurities and $(\Delta \chi/n)_{MV}$ the mean value of the change of $\chi$ per mole per cent impurities.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Mole-% impurities</th>
<th>Temperature interval °C</th>
<th>$a \cdot 10^3$</th>
<th>$b$</th>
<th>$s$</th>
<th>$\chi_{890}$</th>
<th>$-\Delta \chi$</th>
<th>$-\Delta \chi/n$</th>
<th>$(\Delta \chi/n)_{MV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>—</td>
<td>866 930</td>
<td>5.4488</td>
<td>0.516</td>
<td>0.008</td>
<td>4.333</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>2.00</td>
<td>866 917</td>
<td>5.4453</td>
<td>0.577</td>
<td>0.008</td>
<td>4.269</td>
<td>0.064</td>
<td>0.032</td>
<td>0.045</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>4.89</td>
<td>843 909</td>
<td>5.0930</td>
<td>0.505</td>
<td>0.001</td>
<td>4.048</td>
<td>0.285</td>
<td>0.058</td>
<td>0.106</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>3.00</td>
<td>825 904</td>
<td>5.3295</td>
<td>0.737</td>
<td>0.004</td>
<td>4.006</td>
<td>0.327</td>
<td>0.109</td>
<td>0.150</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>4.89</td>
<td>770 911</td>
<td>5.3530</td>
<td>0.933</td>
<td>0.007</td>
<td>3.829</td>
<td>0.504</td>
<td>0.103</td>
<td>0.199</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
<td>2.00</td>
<td>820 887</td>
<td>5.3085</td>
<td>0.677</td>
<td>0.006</td>
<td>4.048</td>
<td>0.285</td>
<td>0.143</td>
<td>0.015</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
<td>6.51</td>
<td>809 853</td>
<td>5.2063</td>
<td>1.369</td>
<td>0.006</td>
<td>3.318</td>
<td>1.015</td>
<td>0.156</td>
<td>0.303</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$</td>
<td>2.00</td>
<td>818 895</td>
<td>5.5353</td>
<td>1.026</td>
<td>0.007</td>
<td>3.900</td>
<td>0.433</td>
<td>0.217</td>
<td>0.199</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$</td>
<td>4.89</td>
<td>764 859</td>
<td>5.0831</td>
<td>1.083</td>
<td>0.003</td>
<td>3.441</td>
<td>0.892</td>
<td>0.181</td>
<td>0.036</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>4.00</td>
<td>838 950</td>
<td>5.7575</td>
<td>0.934</td>
<td>0.011</td>
<td>4.190</td>
<td>0.143</td>
<td>0.036</td>
<td>0.022</td>
</tr>
<tr>
<td>CdSO$_4$</td>
<td>3.92</td>
<td>841 895</td>
<td>5.3065</td>
<td>0.478</td>
<td>0.009</td>
<td>4.245</td>
<td>0.088</td>
<td>0.022</td>
<td>0.071</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>3.92</td>
<td>826 918</td>
<td>5.1399</td>
<td>0.519</td>
<td>0.003</td>
<td>4.056</td>
<td>0.277</td>
<td>0.071</td>
<td></td>
</tr>
</tbody>
</table>

Both with univalent and divalent impurity ions, the change in the temperature dependence of the specific conductivity is small (less than 7%), but the constant $b$ changes considerably.

We have also calculated the change in specific conductivity

$$\Delta \chi = \chi(\text{mixture}) - \chi(\text{Li}_2\text{SO}_4)$$

when the foreign ions are added; $\Delta \chi$ is always negative. In Fig. 1 we have plotted $\Delta \chi$ as a function of the quantity of univalent impurity ions. It is possible to draw four straight lines through these points. The slope of the lines is increasing with increasing size of the foreign ions, and we therefore also plotted the change in conductivity per mole per cent impurities $(\Delta \chi/n)$ as a function of the volume of the foreign cations (Fig. 2), where we have used Pauling radii. It is seen that a straight line is obtained and $\Delta \chi/n$ with Cd$^{++}$ and Ba$^{++}$ ions is also on the same straight line as the univalent ions. There is however no reason to believe that the connection between the ionic volume and the specific electrical conductivity has a physical meaning (see below).

The results obtained with 4.00 mole per cent MgSO$_4$ are less reliable, since the corrosion of the cell was considerable.

Discussion

In the foregoing we have only considered the specific electrical conductivity. As for the density when two salts are mixed, James and Liu have found that...
the system Li₂SO₄ — K₂SO₄ shows volumetric additivity, and it is thus possible to calculate the densities at different concentrations from data given by Jæger and Kahn⁸.

There is an increase of the volume of the cations per mole of salt, but also a change in total molal volume, when a small quantity M₂SO₄ (M = Na, K, Rb, Cs) is added to molten lithium sulphate. If volumetric additivity is assumed for the mixtures with univalent cations the change in free volume ΔVₐ can be calculated from the relation

$$ΔV = ΔV - ΔV'$$

where ΔV is the change in the molal volume and ΔV' the change in the volume of the cations. Table 2 shows that the free volume is increasing with increasing size of the impurity cation and this increase thus seems to have little importance for the conductivity change in (Li, M)₂SO₄.

In Table 2 we have also tabulated the relative change of the equivalent electrical conductivity obtained from

$$ΔA/Δ = ΔV/ΔV + Δx/Δ.$$

The external mobility of the nitrate ion is approximately constant in different nitrate mixtures⁹ and we have assumed that this is valid also for the sulphate ion in the studied sulphate mixtures.

When a small quantity of M₂SO₄ is added to molten Li₂SO₄, then mean mobility of the Li⁺ ions decreases. If the number of M⁺ ions is so small that there is no interaction between them and if it is assumed that the ions are moving in groups, a few groups will contain one M⁺ ion and some Li⁺ ions. We now assume that these Li⁺ ions have the same mobility as the M⁺ ions and the rest of the Li⁺ ions have the same mobility as the Li⁺ ions in pure lithium sulphate. The number of Li⁺ ions whose mobility has decreased is thus comparably small and it is possible to calculate the mean value of the number of cations in a group from the following relations.

The equivalent conductivity of a pure salt can be written

$$A₀ = F b₀$$

where F is the Faraday constant and b₀ the mobility of the cation relative to the anion.

If we make use of the assumptions above, we can write for a mixture of Li₂SO₄ and 1 mole% M₂SO₄

$$A₁ = (F/100) ((100 - k) b_{Li} + k b_M)$$

where k is the number of ions taking part in a cooperative motion, bₚLi = b₀ and bₚM is the mobility of a group containing a M⁺ ion.

This gives

$$Δ₁ = Δ₀ - Δ₁ = (F/100) k (b_{Li} - b_M) = (F/100) k (Δb)$$

and

$$k = 100 (Δ₁/Δ) (b/Δb).$$

The only sulphate system in which Δb/b has been measured is (Li, K)₂SO₄ (loc. cit.¹⁰). We have calculated k of this system by extrapolating the mobility of the potassium ion to concentration zero. This gives k = 2.7, a value which should be compared with k = 2.0 for solid Li₂SO₄ calculated from the difference in mobility of the two lithium isotopes."""¹¹.

An interesting consequence of the higher k-value in the melt is that the isotope effect should be lower in the melt than in the solid. This is in agreement with observations made by Ljubimov and Lundén¹⁰ in Li₂SO₄ — K₂SO₄.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$V$</th>
<th>$V₁$</th>
<th>$ΔV$</th>
<th>$ΔV₁$</th>
<th>$ΔV₂$</th>
<th>$ΔV / V$ (Li₂SO₄)</th>
<th>$ΔV / V$ (M₂SO₄)</th>
<th>$Δx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂SO₄</td>
<td>55.20</td>
<td>—</td>
<td>0.14</td>
<td>0.03</td>
<td>0.11</td>
<td>0.25</td>
<td>1.04</td>
<td>0.79</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>68.76</td>
<td>55.34</td>
<td>0.33</td>
<td>0.10</td>
<td>0.23</td>
<td>0.60</td>
<td>2.45</td>
<td>1.85</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>87.74</td>
<td>55.53</td>
<td>0.45</td>
<td>0.15</td>
<td>0.30</td>
<td>0.82</td>
<td>3.46</td>
<td>2.64</td>
</tr>
<tr>
<td>Rb₂SO₄</td>
<td>100.09</td>
<td>55.65</td>
<td>0.60</td>
<td>0.24</td>
<td>0.36</td>
<td>1.09</td>
<td>4.59</td>
<td>3.50</td>
</tr>
<tr>
<td>Cs₂SO₄</td>
<td>115.62</td>
<td>55.80</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2. The change of the free volume ($ΔV$) and the relative change of the equivalent conductivity ($ΔA/Δ$) when 1 mole% M₂SO₄ is added to pure Li₂SO₄. $V$ is the molal volume of the pure salts and $V₁$ the molal volume of the mixtures. $ΔV₁$ is the change of the volume of the cations and $ΔV₂$ the change of the free volume when the two salts are mixed.

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¹⁰ V. Ljubimov and A. Lundén, Z. Naturforsch. 21 a, 1592 [1966].
For divalent impurity ions Eq. (1) can be written when we add 1 mole% MSO$_4$

\[ k = 100 \left( \frac{AA}{A} \right) \left( \frac{b}{Ab} \right) - \frac{1}{2} \left( \frac{b}{Ab} \right). \]

If we assume that the number of ions taking part in a cooperative motion in molten lithium sulphate in not influenced by the foreign cation, it is possible to calculate the mobility of the impurity ion (Table 3). $Ab/b$ increases with increasing size of the foreign ion and with Cs$^+$ $Ab/b$ even exceeds one. It seems therefore probable that $k$ increases somewhat with increasing size of the impurity ions. In molten metals it has been proposed that 3.3 atoms are moving in phase, a value which seems to be in reasonable agreement with our results $^{12}$.

Since the densities of BaSO$_4$ and CdSO$_4$ are unknown, it is only possible to make a very rough estimation of $Ab/b$ of lithium sulphate with these salts. With BaSO$_4$ $Ab/b$ is less than 0.1 and with CdSO$_4$ about 0.4. The difference in mobility between the Ba$^{++}$ and the Li$^+$ ions should thus be very small, but there is also a possibility that the mobility of the Li$^+$ ion is higher in (Li$_2$,Ba)SO$_4$ than in pure lithium sulphate due to the formation of vacancies in the pseudo-lattice (Wagner effect).

This work was financially supported by the Swedish Technical Research Council.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ab/b$</td>
<td>0.27</td>
<td>0.64</td>
<td>0.91</td>
<td>1.21</td>
</tr>
</tbody>
</table>

Table 3. The relative mobility of the M$^+$ ion in molten Li$_2$SO$_4$ calculated from Eq. (1). It is assumed that $Ab/b$ is independent of temperature.