Self-diffusion of Silver Ions in the Cubic High Temperature Modification of Silver Iodide

ARNOLD KVIST and ROY TÄRNEBERG

Department of Physics, Chalmers University of Technology, Göteborg


The self-diffusion coefficient \( D \) of silver ions in silver iodide has been measured between 200 °C and 500 °C. The results can be described by the Arrhenius equation

\[
D = 16.62 \times 10^{-5} \exp(-2190/R T),
\]

where \( R \) is the gas constant in cal/mole, °K and \( T \) the temperature in °K. The standard deviation was 0.12 cm²/s.

The results coincide with TUBANDT et al. 1, who investigated a small temperature interval around 200 °C.

In 1928 TUBANDT et al. 1 published the results of a few measurements on self-diffusion of silver ions in the cubic high temperature phase of silver iodide. Only the temperature interval 157 to 222 °C was investigated, but since the high temperature modification is stable from 147 to 555 °C, we have extended the measurements to the whole temperature interval.

Experimental

The experimental set-up is shown in Fig. 1. The salt was molten in a quartz tube. When it had solidified and the experimental temperature was reached, a small quantity (about 1 g) of silver iodide containing radioactive silver ions was molten in the upper tube by means of the small winding. In this way a thin layer of radioactive silver iodide was obtained on top of the four centimeter long salt column. After about 2.5 hours the salt was taken out of the furnace and the column was divided into about 1 mm thick slabs. Activity was found only in the upper 2 cm of the column.

Since the salt column can be considered semi-infinite, we can calculate \( D \) from the relation

\[
c = c_0 \exp\left(-\frac{x^2}{4 D t}\right),
\]

where \( c_0 \) is the concentration of the diffusing ion in the surface layer at the time \( t \) and \( c \) the concentration at the distance \( x \) from the surface. If \( \log c \) is plotted as a function of \( x^2 \), \( D \) can easily be obtained from the slope of a straight line. Figure 2 shows one of the obtained diffusion curves.

It has several times been reported that the log \( c \) values for \( x^2 = 0 \) have deviated considerably from the straight line. No such effect, which probably is caused by oxidation or decomposition of the salt, has been found for silver iodide.

Commercial silver iodide of the same quality as we have used previously for conductivity measurements 2 was used.

Results

The obtained diffusion coefficients are given in Table 1. In Fig. 3 we have plotted \( \log D \) as a function of the inverse absolute temperature. Two of the


It should be observed that Tubandt used salt cylinders which had been pressed at high pressure for his investigations.

**Discussions**

According to the Strock model for silver iodide\(^3\), the silver iodide lattice is built up by the iodide ions which form a b.c.c. lattice. The silver ions are then distributed over a great number of different positions\(^4\), between which they can move rather freely.

The diffusion coefficient of the iodide ions is thus very low compared with the diffusion coefficient of the silver ions (they differ by a factor 10\(^7\) \(^5\) \(^6\)) and the current through the crystal is transported entirely by the silver ion. The electronic conductivity is negligible.

The diffusion coefficient of ions moving by a series of random jumps in an isotropic lattice can be written

\[
D = \frac{1}{6} \Gamma r^2 f,
\]

where \(r\) is the jump distance, \(\Gamma\) the number of jumps per second and \(f\) a correlation factor. \(f\) has different values for different transport mechanisms, but unfortunately \(\Gamma\) can not be calculated with sufficient accuracy and \(f\) can not be determined.

It is, however, possible to compare the results of the diffusion measurements with the diffusion coefficient calculated from the Nernst-Einstein relation.

### Table 1. The self-diffusion coefficient of silver in cubic silver iodide.

<table>
<thead>
<tr>
<th>(t) (°C)</th>
<th>(D \cdot 10^5) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>4.14</td>
</tr>
<tr>
<td>500</td>
<td>4.11</td>
</tr>
<tr>
<td>475</td>
<td>3.71</td>
</tr>
<tr>
<td>450</td>
<td>3.68</td>
</tr>
<tr>
<td>400</td>
<td>3.07</td>
</tr>
<tr>
<td>350</td>
<td>2.64</td>
</tr>
<tr>
<td>300</td>
<td>2.41</td>
</tr>
<tr>
<td>250</td>
<td>2.14</td>
</tr>
<tr>
<td>225</td>
<td>1.85</td>
</tr>
<tr>
<td>200</td>
<td>1.59</td>
</tr>
<tr>
<td>200</td>
<td>1.59</td>
</tr>
</tbody>
</table>

This relation can be tested by calculating

$$\alpha = \frac{t^+ A D_m^+ z^+}{F^2 R T \cdot a^+} = \frac{D_c}{D_m},$$

where $D_c$ is the calculated diffusion coefficient and $D_m$ the measured one. The cation valency $z^+$ and the transport number $t^+$ are both unity. $F$ is the Faraday constant. We have previously measured the electrical conductivity of silver iodide and the molar volume was estimated from values given by LIESER.

In Fig. 4 we have plotted $\alpha$ as a function of the temperature for four salts which all form high temperature modifications. The temperature dependence is small for the three b.c.c. salts, while there is a definite increase in $\alpha$ with the temperature for lithium sulphate which forms a f.c.c. phase.

For a simple vacancy mechanism we should obtain $D_c/D_m = 1.28$, i.e. equal to the Bardeen-Herring correlation factor, but the obtained values indicate transport mechanisms, where several cations cooperate. A formation of Li$^+ - $Li$^+$ and Ag$^+ - $Ag$^+$ ion pairs in LiAgSO$_4$ has been discussed and this might also explain that $D_{Na}$ is considerably lower than $D_{Li}$ and $D_{Ag}$ in LiAgSO$_4$ and $D_{Ag}$ lower than $D_{Li}$ and $D_{Na}$ in LiNaSO$_4$.

In e.g. AgBr the $\alpha$ also is greater than two, while the ratio is smaller than one for molten salts.

The b.c.c. phases of LiNaSO$_4$, LiAgSO$_4$ and AgI seem to have the same type of transport mechanism and the activation energy for diffusion is lower than that for electrical conduction. In a f.c.c. phase the situation is reversed (Table 2).

<table>
<thead>
<tr>
<th>Salt</th>
<th>Structure</th>
<th>$Q_D$ (kcal/mole, °C)</th>
<th>$Q_A$ (kcal/mole, °C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNaSO$_4$</td>
<td>b.c.c.</td>
<td>14.6</td>
<td>8.4</td>
<td>8, 17</td>
</tr>
<tr>
<td>LiAgSO$_4$</td>
<td>b.c.c.</td>
<td>12.0</td>
<td>7.1</td>
<td>9, 18</td>
</tr>
<tr>
<td>AgI</td>
<td>b.c.c.</td>
<td>2.2</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>f.c.c.</td>
<td>7.9</td>
<td>10.2</td>
<td>11, 19</td>
</tr>
</tbody>
</table>

Table 2. The activation energies for diffusion compared with the activation energies for electrical conduction for some salts forming high temperature modifications.

The electrical conductivity of the melt is about 12% lower than of the solid at the melting point 555 °C (l.c. 2) Sjöblom has in some preliminary measurements found that $D_{Ag}$ for the melt is about 6 cm$^2$/s, e.g. much higher than in the solid. This fact might be of great interest for the understanding of the transport mechanisms of molten salts.

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7 K. H. LIESER, Z. Phys. Chem. 5, 125 [1955].
8 A. KVIST, A. BENGTZELIUS, and A. SCHIRALDI, to be published.