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

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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

$$c = c_0 \exp(-x^2/4\,D\,t),$$

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.

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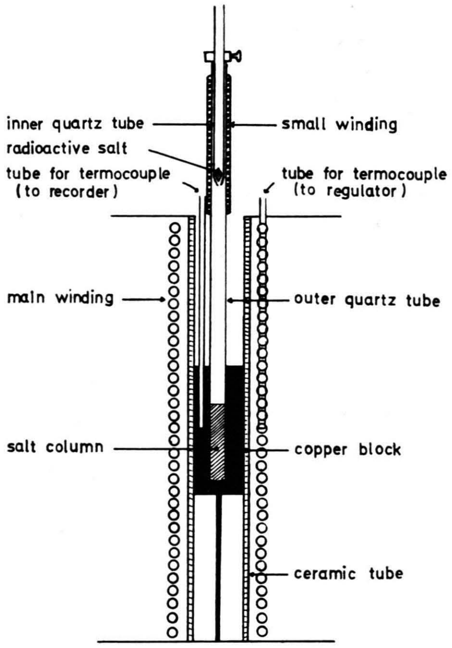

Fig. 1. The furnace and the cell used for the experiments.

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

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[1] C. TUBANDT and E. LORENZ, Z. Phys. Chem. **87**, 513 [1914]. — C. TUBANDT, H. REINHOLD, and W. JOST, Z. anorg. Chem. **177**, 253 [1928].

[2] A. KVIST and A.-M. JOSEFSON, Z. Naturforsch. **23 a**, 625 [1968].

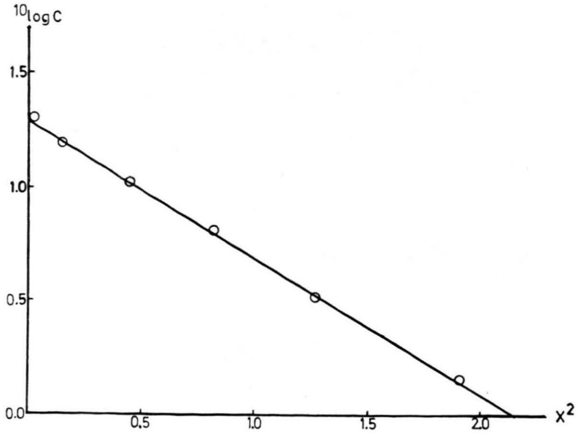

Fig. 2. A typical diffusion experiment in b.c.c. silver iodide. x is the distance from the surface of the salt column and c the concentration of radioactive silver.

three measuring points obtained by TUBANDT et al. are also shown in the figure. The agreement between his results and our measurements is excellent, especially since his experimental technique was rather complicated.

Our results can be described by the relation

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

where R is the gas constant in cal/mole·degr. and T the temperature in °K.

With Tubandt's values we obtain

$$D = 16.3 \times 10^{-5} \exp(-2230/R\,T).$$

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 negligable.

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

$$D = \tfrac{1}{6}\,\Gamma\,r^2\,f\,,$$

where r is the jump distance, Γ the number of jumps per second and f a correlation factor. f has different values for different transport mechanisms, but unfortunately Γ 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.

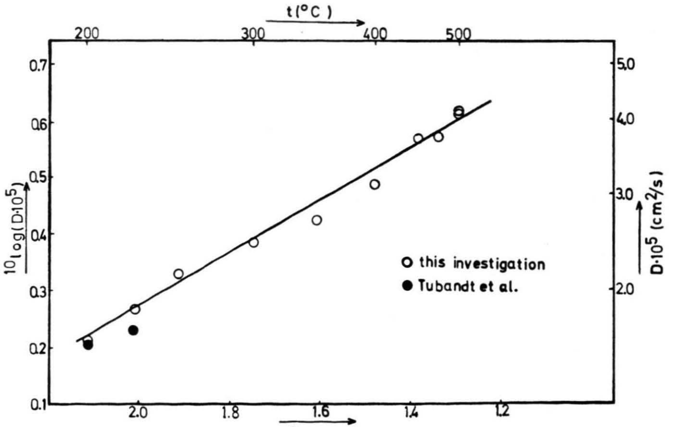

Fig. 3. The diffusion results for silver ions in b.c.c. silver iodide.

t (°C)	$D \cdot 10^5$ (cm²/s)
500	4.14
500	4.11
475	3.71
450	3.68
400	3.07
350	2.64
300	2.41
250	2.14
225	1.85
200	1.59
200	1.59

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

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[3] L. W. STROCK, Z. Phys. Chem. **B 25**, 441 [1934].

[4] G. BURLEY, Acta Cryst. **23**, 1 [1967].

[5] P. JORDAN and M. POCHON, Helv. Phys. Acta **30**, 33 [1957].

[6] J. NÖLTING, Z. Phys. Chem. **19**, 118 [1959].

This relation can be tested by calculating

$$\alpha_+ = \frac{t^+ \Lambda}{F^2} \frac{D_m{}^+ z^+}{R T} .$$

$\alpha_+ = D_c/D_m$, 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[2] and the molar volume was estimated from values given by LIESER[7].

In Fig. 4 we have plotted α_+ 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 α_+ with the temperature for lithium sulphate which forms a f.c.c. phase[8–11].

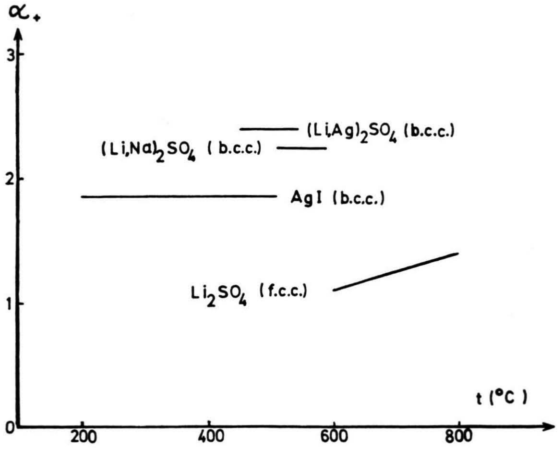

Fig. 4. The Nernst-Einstein correlation factor as a function of the temperature for some salts forming high temperature modifications.

For a simple vacancy mechanism we should obtain $D_c/D_m = 1.28$, i. e. equal to te 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[12, 13] 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[14, 15] α_+ 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).

Salt	Structure	Q_D (kcal/mole, °C)	Q_Λ (kcal/mole, °C)	Ref.
$LiNaSO_4$	b.c.c.	14.6	8.4	8, 17
$LiAgSO_4$	b.c.c.	12.0	7.1	9, 18
AgI	b.c.c.	2.2	1.2	2
Li_2SO_4	f.c.c.	7.9	10.2	11, 19

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[16] has in some preliminary measurements found that D_{Ag} for the melt is about 6 cm^2/s, e. g. murch 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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