Self-diffusion in Molten Silver Iodide

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The self-diffusion coefficients of the cation (D^+) and of the anion (D^-) have been measured in molten silver iodide between 580 °C and 620 °C with the porous-frit technique. At 610 °C it is found that $D^+ = D^- = 5.4 \times 10^{-5}$ cm² s^{-1}. At the melting point (556 °C) D^+_{melt} (4.4×10^{-5} cm² s^{-1}) is very close to D^+_{solid} (4.3×10^{-5} cm² s^{-1}). The Klemm friction coefficients do not indicate the existence of complex entities. D^+ and D^- calculated according to the Nernst-Einstein equation agree with observed data within 20%.

The properties of the high-temperature form of silver iodide differ from those of most solid salts due to the pre-melting phenomenon of the cations. As a result the thermal expansion below 146.5 °C is negative[1] and moreover the electrical conductivity of the high-temperature modification is very high, indeed higher than that of the melt[2, 3]. A similar but not so pronounced case of pre-melting occurs in lithium sulphate. The cubic high-temperature lithium sulphate does have a high electrical conductivity but there is no temperature region with a negative thermal expansion and $\varkappa_{\text{melt}}$ is higher than $\varkappa_{\text{solid}}$ at the melting point. It would be of a considerable interest to find out if the cation diffusion in silver iodide is strongly pre-melting influenced also. Consequently the present investigation of D^+_{melt} and D^-_{melt} was initiated (D^+_{solid} has recently been measured by KVIST and TÄRNEBERG[4]).

Experimental

Commercially available silver iodide with a purity better than 98% was used after a careful drying in a drying oven at 120 °C. The experiments were performed in a dry argon atmosphere with the porous-frit technique previously described[5]:

A porous disc is filled with radioactive molten salt and counted (at room temperature). It is then re-heated to the desired experimental temperature, immersed into an inactive melt for a suitable diffusion time, and withdrawn for re-counting. The self-diffusion coefficient in the melt may be calculated from the observed data and the cell constant of the disc.

A modification of the porous-frit method was also used in order to check the internal consistency of the observed data: The total volume of the pores inside each frit was determined by weighing the frits dry and filled with distilled water. Since the frits are filled with an AgI melt with a constant specific activity the total activity of a frit before a diffusion run is proportional to the pore volume of the frit. The specific melt activity may be measured separately while the initial activity data for the cells can be calculated from their pore volumes. Thus the changes in cell constant that may occur when the AgI inside the cell is cooled past 146.5 °C take place *after* the diffusion is completed.

The frits were made from quartz glass in order to avoid silver ion exchange between the melt and the glass. Each frit was used only once. Radioactive tracers (Ag^{110m} and I^{125}, both γ-emitters) were obtained from N.E.N., Boston, Mass., USA.

Results and Discussion

The observed diffusion coefficients are given in Table 1. Considerable experimental problems were encountered due to the limited structural strength of the quartz frits. Silver iodide expands upon cooling past 146.5 °C and tests showed that this effect might affect the cell constant of the frits in an irreproducible fashion. The table data are means of several experiments performed at the stated temperatures and the errors of these means are estimated to about 10%. Thus it was not considered meaningful to calculate an Arrhenius coefficient for the temperature dependence since the error in this coefficient would be great.

Table 1. Self-diffusion coefficients in molten silver iodide. a = extrapolated value according to the present work (liquid phase). b = extrapolated value according to Ref. 4 (solid phase). c = obtained with the modified technique (mean deviation).

T (°C)	$D^+ \times 10^5$ (cm² s^{-1})	T (°C)	$D^- \times 10^5$ (cm² s^{-1})
580	4.77	590	3.85
598	5.28	607	5.11
620	5.52	621	6.37
556	4.4 [a]		
556	4.3 [b]		
600	5.7 ± 0.8 [c]		

The expansion of the solidified AgI inside the frits may also systematically change the cell constants in such a way that the observed diffusion coefficients are too high. In order to exclude this possibility additional experiments were performed with a modified technique described above. These data scatter due to difficulties involved in the pore volume measurement (see Table 1). It is nevertheless found that the data obtained with the "ordinary" technique are confirmed within experimental error.

An extrapolation of the D^+_{solid} data by KVIST and TÄRNEBERG[4] and the present D^+_{melt} data to the melting

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point 556 °C shows that there is no marked change in D^+ upon melting (see Table 1) and that D^+_{melt} is slightly higher than D^+_{solid}. Thus diffusion is influenced less than electrical conductivity by the pre-melting phenomenon.

Kvist and Tärneberg[4] have compared D^+_c (the diffusion coefficient calculated according to the Nernst-Einstein relation) to D^+_{observed} for some pre-melting solid salts and salt mixtures. They showed that the quotient $\alpha_+ = D^+_c/D^+_{\text{obs}}$ in these cases is always greater than unity, α_+ being 1.9 for solid AgI. In order to make the corresponding comparison for molten AgI the external transport number t_+ has to be known. This quantity has not been measured, but for one-one salts it can be calculated with good accuracy from conductance- and diffusion measurements[6–8]. It is found (see Table 2) that at 600 °C $t_+ = 0.54$ which means that at the same temperature $\alpha_+ = 0.8$. The equivalent conductivity decreases[3] by about 12% upon melting, and D^+ (see Table 1) is almost unchanged. Thus the decrease in α_+ is mainly determined by the decrease in t_+. There must be a decrease in the single ion mobility of the cation on melting. It must not be overlooked, however, that this conclusion relies upon the transport number t being a quantity which should have the same meaning in the melt as in the solid salt. In pure molten salts the external transport number has been only semi-empirically correlated to self-diffusion and equivalent conductivity[8]. The Klemm model[6] is a possible rationalization of this correlation but this model is, on the other hand, unsatisfactory in the case of solid AgI.

Table 2. t_+ = external transport number calculated according to Ref. [7]. α_+ and α_- = Nernst-Einstein factors. r_{++}, r_{+-}, and r_{--} = cation-cation, cation-anion, and anion-anion friction coefficients calculated according to Ref. [9]. D-values from the present work, Λ-values from Ref. [3].

T (°C)	t_+	α_+	α_-	$r_{++} \times 10^{-8}$	$r_{+-} \times 10^{-8}$ (joule s cm^{-2} mole^{-1})	$r_{--} \times 10^{-8}$
600	0.54	0.84	0.82	1.00	1.82	1.36
620	0.46	0.69	0.72	0.85	1.79	0.59

The Klemm friction coefficient formalism[9] can be used in order to investigate the existence of complex entities in a liquid. Such coefficients are given in Table 2 and neither does their magnitude nor their temperature dependence give any indication of complex formation. The fact that the Nernst-Einstein factor α is close to unity for both ions in the melt also indicates a "simple" melt since complex formation would tend to make this factor smaller.

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