Self-Diffusion in Molten Lead Bromide

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The self-diffusion coefficients of both ions in molten PbBr₂ have been measured with a modification of the porous-frit technique.¹⁻³ The results can be described with Arrhenius relations:

\[ D_{Pb} = 7.4 \times 10^{-4} \exp( -6500 \pm 900) / RT \] (380—540 °C),

\[ D_{Br} = 8.3 \times 10^{-4} \exp( -6100 \pm 700) / RT \] (380—555 °C).

D is expressed in cm² s⁻¹, R in cal·mole⁻¹ degree⁻¹ and T in degrees Kelvin. The relative merits of different experimental techniques are discussed and a comparison between the (experimental) external transport number and the corresponding calculated quantity using Laitty’s “new formalism” is made.

Relatively few diffusion studies have been made on high temperature liquids such as pure molten salts due to experimental difficulties. This is very unfortunate since there is a great need for more accurate data as an aid in developing a theory for transport in ionic melts. Finding a way to correlate the diffusion mobilities and electrical mobilities of the ions in a pure molten salt would be a step in this direction. The proper definition of electrical mobility in a pure molten salt is of course a problem of this direction. The so-called “new formalism” developed by LAITY⁷ can be used with remarkable accuracy to correlate diffusion and electrical mobility in all monovalent salts studied up till now⁴⁻⁷, and also one divalent salt ZnBr₂. PbCl₂ deviates from this pattern having a transference number of only 0.23 for the lead ion at 560 °C. Since the transference number for PbBr₂ is 0.35 it was considered valuable to measure the self-diffusion coefficients of both ions in lead bromide in order to see if the two lead salts behave similarly in this respect. The porous-frit technique¹⁻³ is particularly suitable for this work since one of the ions (Br⁻) has radioactive isotopes with short half-lives only.

Experimental

BDH laboratory reagent lead bromide was further purified by recrystallization from hot 0.01 M HBr solution and dried at 150 °C for more than 48 hours. PbBr₂ was obtained from Aktiebolaget Atomenergi, Studsvik, and Pb²¹⁰(NO₃)₂ from NEN, Boston, Massachusetts.

\[ D_{Pb} \] and \[ D_{Br} \] were determined in separate runs, using different techniques for the radio-analysis. The analysis of Pb²¹⁰ was similar to the procedure used by ANGELL and TOLMINSKIS⁸ who utilized the strong β-radiation of the daughter Bi²¹⁰ and counted the samples in a liquid Geiger counter. The samples were counted about three weeks after the runs when the initially pure Pb²¹⁰ sample had come to equilibrium with the Bi daughter. The amount of lead in each sample was determined electrolytically as peroxide⁹ and the specific activity of each sample was calculated.

The analysis of PbBr₂ was performed in an entirely different way. It was possible to measure the total γ-activity of the cell with a scintillation counter before and after each run, since Pyrex glass frits with a thickness of only 2 mm were used. The frit was allowed to cool down and was mounted behind a circular lead diaphragm with the flat surfaces of the frit parallel to the nearest face of the scintillation crystal. The distance between the frit and the center of the crystal was about 15 cm and the frit could be replaced with an accuracy of better than ± 0.3 mm. The error introduced by this procedure was thus negligible. The cells were used up to three times in the \[ D_{Pb} \]-experiments since careful tests showed that the frit was unaffected by lead bromide melting and solidifying inside it.

The experimental set-up has been described elsewhere⁶. The furnace was blanketed with argon gas in order to minimize the effect of water vapor in the atmosphere. Commercial Pyrex glass frits, JOBLING 3610/62, 20 mm POR 4 were used. The effective length of each frit was determined by the gravimetric diffusion

\[ \Delta m / \Delta t = \frac{4 \pi D}{R^2} \cdot \frac{d}{R} \int_{0}^{L} \frac{1}{r} \, dr \] \[ \Delta T \]

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technique developed by Wall and coworkers. The present procedure is described by Sjöblom, the only difference being that 0.5-m KCl solution is diffusing out into 0.075-m KCl solution. The average frit thickness was 2.2 mm and the corresponding effective thickness about 2.7 mm. The labyrinth factor (the correction factor with which the experimental diffusion coefficient is to be multiplied) ranged from 1.3 to 1.9.

The container for the radio-active salt was filled with salt for several experiments and the frits were inserted and removed through a port in the furnace top without changing the furnace temperature. The experiments could thus be performed in a rapid succession when the temperature had reached equilibrium at the chosen value. The temperature was measured with a Croydon potentiometer type P 3 using a calibrated thermocouple and it was constant to better than ±0.5 °C. When a cell was re-used it was already partly filled with active salt. Before next experiment it was replaced into the cell was re-used it was already partly filled with active salt. Before next experiment it was replaced into the radioactive melt for a time long enough to allow the activity to be evenly distributed through the frit again (about 10 times the actual diffusion time was considered adequate). The diffusion times were very short (200–350 seconds) due to the thin frits.

Results and Discussion

The results are given in Fig. 1. They can be summarized by least-squares fitting in two Arrhenius equations (all stated errors are standard deviations):

$$D_{\text{Pb}} = 7.4 \times 10^{-4} \exp(-6500 \pm 900)/RT$$

$$(380 - 540 °C),$$

$$D_{\text{Br}} = 8.3 \times 10^{-4} \exp(-6100 \pm 700)/RT$$

$$(380 - 555 °C).$$

The standard errors of estimate in the $\ln(D \times 10^6)$ vs. $10^3/T$ plots are about 4.5%.

The "activation energies" for diffusion of cations and anions in lead bromide are thus equal within the experimental accuracy. This fact is in agreement with the results for all investigated molten salts. Both self-diffusion coefficients and activation energies are very close to the values for lead chloride obtained by Perkins, Escue, Lamb, and Wimberley and independently by Angell and Tomlinson (and the values of $D^+$ are smaller than those of $D^-$ at corresponding temperatures for both lead salts and also for zinc bromide).


12 J. T. Edward, J. Chromatogr. 1, 446 [1958].


Table 1. The external transport number of the lead ion in molten lead bromide as a function of temperature. The experimental values are measured by Läti and Sjöblom and the theoretical values are calculated according to the Eqs. (4.5) and (2.2) in Ref. using density data by Lorenz, Frei, and Jabs and conductivity data by Harrap and Heymann.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.38</td>
<td>0.61</td>
</tr>
<tr>
<td>450</td>
<td>0.37</td>
<td>0.62</td>
</tr>
<tr>
<td>500</td>
<td>0.36</td>
<td>0.62</td>
</tr>
<tr>
<td>550</td>
<td>0.34</td>
<td>0.64</td>
</tr>
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</table>

one hour for β-active isotopes (provided the chemical analysis is reasonably easy) and shorter than 30 minutes for γ-active isotopes. This fact represents an important improvement over conventional capillary techniques using diffusion times of the order of 20–70 hours. This advantage is of course obtained at the expense of a certain decrease in accuracy. The gravimetric calibration of the frits has a spread of ±3% (see for instance Ref.) due to the minute weight changes involved in the process. The diffusion times are very short but they can be determined to better than 2% since the manipulation of the cell in the furnace is very simple. The immersion errors can be minimized for the same reason. The flow rate of salt past the frit was 5 mm/sec (corresponding to a stirring speed of 20 rev/min). Thus there is no reason to believe that the errors are more serious in this technique (although they might be in part responsible for the somewhat higher spread in the data compared to the conventional capillary technique).

As far as the technique is concerned it can be concluded that it has been developed into a method capable of measuring diffusion coefficients with reasonably good precision and well suited for difficult experimental conditions. It is also very easy and straightforward to work with and requires no complicated auxiliary apparatus. No accuracy is sacrificed if the total radio-activity of the frit before and after the run is measured with a scintillation counter instead of determining the specific activity of liquid samples of the active melts. Careful tests show that the effective length of the frits is unaffected by lead bromide melting and solidifying inside the frits (this is of course a property of this particular salt since an attempt to do the same thing in zinc bromide or silver nitrate would certainly fail).

The experimental external transport number of the Pb²⁺ ion in molten lead bromide is 0.36 at 500 °C while the “theoretical” value is 0.62. It is probable that the doubly charged Pb²⁺-ion is preferentially bound to the glass-salt interface in the porous-plug transport number experiment. This view is supported by the fact that the result of such an experiment can be changed by applying an external potential to the frit. The flow-corrected formalism works well for monovalent salts and also for a divalent salt such as zinc bromide which is considered as having a complex structure in the melt. Cadmium chloride has a position in between in this respect being a divalent salt but partially “associated” to CdCl⁺-ions. Thus the experimental and theoretical values of the external transference numbers can be expected to agree reasonably well and this is also the case.

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