On the Validity of Inter- and Self-Diffusion Measurements in Molten Salts by Methods Applying Multiporous Fritted Discs

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A gravimetric method has been used to study inter-diffusion in binary mixtures of AgNO₃ and KNO₃ over the range 50–75 mole % AgNO₃ at temperatures below 200 °C. The obtained cation diffusion coefficients are of the order of $2 \times 10^{-8}$ cm² sec⁻¹, i.e. considerably lower than what might have been expected from other diffusion measurements. It has previously been found that there is a tendency for self-diffusion coefficients obtained with fritted discs to be lower than those obtained with the conventional open-end capillary technique. Some possible sources of error are discussed.

At present very little information is available on inter-diffusion coefficients in molten salt mixtures. A gravimetric method, previously used at room temperature

![Graph showing interdiffusion coefficient at 190 °C plotted versus concentration of AgNO₃. The indicated errors (6%) are estimated from the observed maximum spread of 3 % for the calibration and 5 % for the salt experiments.]

$D_{c} = 10^{-6}$ (cm² s⁻¹)

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Fig. 1. Inter diffusion coefficient at 190 °C plotted versus concentration of AgNO₃. The indicated errors (6%) are estimated from the observed maximum spread of 3 % for the calibration and 5 % for the salt experiments.

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3. C.-A. Sjöblom, to be published.
4. C.-A. Sjöblom and A. Lundén, Z. Naturforsch. 18 a, 942 [1963]. In Table 2 $10^{3} D_{c}$ should read 1220 instead of 122 for the range 452–498 °C.
14. B. R. SUNDHEIM and A. BERLIN, J. Phys. Chem. 68, 1266 [1964], have recently studied the apparent conductivity of fused AgNO₃ and TINO₃ in fritted Pyrex glass discs over the temperature range 213–318 °C. Our inter-diffusion measurements were made far below the temperature, 280 °C, up to which they found a normal conductivity for AgNO₃ (although not for TINO₃). Above this temperature both salts showed an evident increase in apparent conductivity which was interpreted as “being due to ion exchange of the salt with the glass under the influence of an electric field”. This observation might be of importance for interpreting our self-diffusion results, even if a mechanism that gives an increase in apparent conductivity hardly can be responsible also for a decrease in transport by diffusion.

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a comparison with results from other capillary methods is possible. For ZnBr$_2$ three methods gave about the same temperature dependence for the cation self-diffusion coefficient ($D^+$), but a plot shows a considerable displacement of the curves, the fritted disc giving $D^+$ values nearly a factor of two lower than those obtained with the conventional capillary with an open end, here called the A-S (Anderson-Saddington) method. The results obtained with a long capillary fall inbetween, see Table 1. For TlCl there are two independent investigations with the A-S method$^{16, 17}$, both in good agreement with each other, but in conflict with the disc method. Thus the latter gave a much more pronounced temperature dependence. For both cation and anion the two methods give the same diffusion coefficients at about 535 °C, but a hundred degrees lower the disc method gives values that are about 70% of those obtained by the A-S method, cf. Table 1. It has recently been claimed that the self-diffusion coefficients previously obtained with the A-S method should be reduced considerably$^9$. This would reduce the discrepancies between the A-S method and the disc method. However, at the present stage all methods used so far for diffusion measurements in melts should be viewed with some suspicion. In comparison with other capillary methods disc methods are characterized by numerous irregular capillaries of small dimensions and a very large glass surface exposed to the melt. If the small dimensions of the capillaries and pores have a reducing effect on the diffusion within the disc, this should mean that "wall effects" have a much larger range in melts than in aqueous solutions. For some A-S experiments with molten metals the self-diffusion coefficient seems to decrease with decreasing capillary diameter$^{18}$, but it has been suggested that such observations are due to disturbance by convection in the capillaries$^{19, 20}$. The "capillaries" in fritted discs are narrow compared with those used in the A-S method, 10 $\mu$m might be taken as a typical diameter of a pore, but this is still a large distance compared with the dimensions of the diffusing units, even if these are assumed to be globules consisting of perhaps a hundred atoms$^{21}$. The other typical property of the discs is the large glass area exposed to the melt. If an exchange of ions takes place between the two phases, this could explain why the disc methods give low diffusion coefficients$^{14}$. However, it seems unlikely that both anions (Br$^-$, Cl$^-$) and cations (Zn$^{2+}$, Tl$^+$) are involved to the same extent in exchange reactions. The self-diffusion measurements with the disc have shown for both ZnBr$_2$ and TlCl that the ratio $D^+/D^-$ remains constant over the whole investigated temperature range, and that this ratio is about the same whether the disc or the A-S method is used. We consider this as a strong indication that reactions between the melt and the glass are negligible at least for the two halides in question. There has so far not appeared any experimental support for assuming a priori that methods using fritted discs are inferior to other diffusion methods tested, or that "low" inter- and self-diffusion coefficients are erroneous. We hope that our results obtained with the gravimetric method will stimulate the development of new methods for diffusion measurements in melts. Comparisons with new methods are urgently needed for settling the question of the reliability of the methods used so far.

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<thead>
<tr>
<th>Salt</th>
<th>ZnBr$_2$</th>
<th>TlCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusing ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temp. °C</td>
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<td>550</td>
</tr>
<tr>
<td>$D_{\text{AS}}/D_{\text{DH}}$</td>
<td>1.90</td>
<td>1.81</td>
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<tr>
<td>$D_{\text{w}}/D_{\text{DH}}$</td>
<td>1.24</td>
<td>1.40</td>
</tr>
</tbody>
</table>


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16 E. Berne and A. Klemm, Z. Naturforschg. 8a, 400 [1953].
— A. Klemm and W. Herr, unpublished.
18 J. Rohlin and A. Lodding, Z. Naturforschg. 17a, 1081 [1962].
20 In spite of the suggestion in ref. 19 A. Lodding (priv. com.) still considers the diameter effect reported in ref. 18 to be a reality.