we have, according to (24),
\[ c(n) = a \left( \frac{1}{1 + 2(k - 1)} \right) \left( 1 - \frac{v}{2} \right) s + b. \quad (32) \]

After freezing, eqn. (6) holds. Elementary calculations yield
\[ c_s = \left[ k + \frac{(k - 1)^2}{3k} \right] a + b, \quad (33) \]
i.e., the linear relationship should remain linear (except for the top section, as mentioned above). The slope of the line should increase by a factor very nearly equal to \( a \). However, hitherto no attempt has been made to utilize this relationship.

**Acknowledgements**

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**Zinc Ion Self-diffusion in Molten Zinc Bromide**

**A re-determination**

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The diffusion coefficient of zinc in molten zinc bromide has been re-measured with a new technique over the temperature interval 400 — 565 °C. The result is a downward shift of the values as compared to previous data. Assuming a relation of the form
\[ D = D_0 e^{-\frac{Q}{RT}} \]
the values of the constants are:
\[ D_0 = 0.405 \text{ cm}^2/\text{sec}, \quad Q = 19,000 \text{ cal/mole.} \]

In a previous paper, a modified diffusion couple method was described for the measurement of self-diffusion coefficients in molten salts. The technique is here used for a re-determination of the zinc ion self-diffusion in zinc bromide. This salt was chosen in order to have a direct comparison with previous data, obtained with the open-ended capillary method in the same laboratory.

**Experimental**

The oven, in which the diffusion runs were carried out, was built of a vertical glass tube with a Kanthal winding (see Fig. 1). This winding was supplied with some extra terminals; shunting parts of it allowed the temperature to be kept constant (or slightly increasing upwards) over a sufficient length in the oven.

The insulation consisted of rockwool, a section of which could be removed temporarily, thus providing a window for observation of the interior. A lamp, placed in the opposite wall, served for illumination. (At the higher temperatures the life-time of this lamp was of course rather short.)

During the runs the diffusion capillaries were placed in holes, drilled in a cylindrical block of aluminium bronze (30% Al). (This is a suitable material, since it combines three important features: it is a good heat conductor, is easily machined and does not scale at high temperatures.) Eight such holes were drilled, so that several values of the diffusion constant could be obtained in each run.

A chromel-alumel thermocouple, the hot junction of which was placed close to the oven winding, was fed into an AEG temperature regulator. Five other thermocouples of the same kind were placed at different heights in the wall of the metal block, thus allowing observation of the temperature distribution. The e.m.f. of the central thermocouple was almost compensated through a Leeds and Northrup potentiometer; the small unbalance was fed directly to the galvanometer of a commercial point recorder. The sensitivity thus obtained was 2 °C per scale division, so the temperature fluctuations could be recorded through a complete run. The absolute values of temperature were measured directly with the potentiometer and a mirror galvanometer.

The controlling and recording instruments were kept in a constant temperature box, since the long durations of the runs made it necessary to have uniform conditions.

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over long periods of time. The thermocouple cold junctions were kept in an accurately controlled water thermostat.

In most of the runs the temperature was kept within ±2 °C or better (cf. Table 1), neglecting a few disturbances of short duration. The time of an experiment ranged from a few days to several weeks.

### Table 1.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Duration of exp. * (days)</th>
<th>α (cm)</th>
<th>$D \cdot 10^6$ (cm²/sec)</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 ± 3</td>
<td>43.54</td>
<td>5.0</td>
<td>0.26</td>
<td>8.4</td>
</tr>
<tr>
<td>421 ± 5</td>
<td>13.70</td>
<td>3.5</td>
<td>0.42</td>
<td>11.2</td>
</tr>
<tr>
<td>452 ± 1</td>
<td>19.00</td>
<td>5.0</td>
<td>0.76</td>
<td>5.2</td>
</tr>
<tr>
<td>460 ± 1</td>
<td>21.04</td>
<td>5.0</td>
<td>0.85</td>
<td>19.4</td>
</tr>
<tr>
<td>477 ± 2</td>
<td>9.33</td>
<td>5.0</td>
<td>1.34</td>
<td>1.3</td>
</tr>
<tr>
<td>498 ± 2</td>
<td>3.95</td>
<td>3.0</td>
<td>1.98</td>
<td>14.2</td>
</tr>
<tr>
<td>517 ± 2</td>
<td>10.84</td>
<td>5.0</td>
<td>2.42</td>
<td>7.9</td>
</tr>
<tr>
<td>540 ± 2</td>
<td>10.86</td>
<td>5.0</td>
<td>2.83</td>
<td>10.9</td>
</tr>
<tr>
<td>540 ± 2</td>
<td>4.18</td>
<td>3.5</td>
<td>2.97</td>
<td>7.3</td>
</tr>
<tr>
<td>564 ± 1</td>
<td>4.73</td>
<td>5.0</td>
<td>4.29</td>
<td>5.8</td>
</tr>
</tbody>
</table>

* referring to capillary with longest time of diffusion.

The diffusion capillaries were filled by means of very thin, S-shaped capillaries, drawn from a tube containing the melt. A medical syringe, connected by means of a rubber tube to the top of the container tube, was used to press the liquid over into the diffusion capillaries. These were supplied with a funnel-shaped top, which allowed them to be lifted out of the metal block by means of a glass fork, fixed on a vertically movable screw mechanism. By means of two perpendicular screw mechanisms, attached to the oven stand, the oven could be moved at will in the horizontal plane. The diffusion capillaries could thus be accurately positioned, so that, when lifted, they would accommodate the filler capillary. They were first filled with radioactive salt up to a mark a few centimeters from the bottom. This procedure in general left some small droplets on the capillary wall; these were easily evaporated and removed in an argon gas stream through a dry filler capillary. Finally, the inactive salt was loaded in the same way as the radioactive salt.

The sharpness of the boundary surface was attained simply by cautious work. Preliminary experiments with coloured water solutions showed that mixing was not serious in the narrow capillaries used (0.8 mm). In support of the above is the obtained agreement between theory and experiment when capillaries have been examined, in which no diffusion has taken place.

The diffusion was interrupted in the following way. The capillary, in which the diffusion was to be interrupted, was gently lifted out into an auxiliary oven (see Fig. 1). The latter was transparent, so it was possible to observe the capillary. It was then slowly (three to four minutes) allowed to slide out into the open air, so that the melt was freezing from the bottom. Capillaries, accidentally falling rapidly out, were of course freezing irregularly, which resulted in non-reproducible concentration distributions.

Zinc bromide has a rather high vapour pressure and consequently all the capillaries were sealed, using the following technique:

A 0.7 mm Kanthal wire was wound on a parallel-epipedical piece of pyrophyllite, supplied with tracks to hold the turns of the wire. Two steel rods, attached to the pyrophyllite, connected the terminals of the wire to a transformer, able to deliver a sufficiently high current (10—15 amps). The upper ends of the steel rods were fixed in a wooden shaft. By means of this device, small pieces of Pyrex glass could easily be sealed to the Supremax glass of the capillaries.

The inactive zinc bromide used was distilled from commercial salt. The radioactive salt was made as previously described, the zinc metal being activated at the R 1 Reactor in Stockholm.

After the diffusion was interrupted, the capillaries were divided into small samples, about 2 mm each, by means of a diamond cutter. The activity of each sample was measured by standard techniques. The amount of salt was determined by EDTA-titration. A great deal of trouble was experienced in the analytical work, leading to unnecessarily large errors in part of it. However, since the number of samples from each capillary was usually large, the accuracy of the calculated diffusion coefficients was in most cases acceptable.

Usually, the different capillaries of a single run were taken out of the oven at different times. The distance $a$ from the bottom of the capillary to the original boundary surface was generally 5 cm; in a few cases it was smaller (see Table 1).

Since it was first intended to extend the measurements to higher temperatures than those actually realized, the diffusion capillaries were made of Supremax glass. At the time when the present series of experiments were started, we were unable to obtain glass capillaries, having a high softening point, reasonably constant cross section and of sufficient length. They were therefore made in this institute in the following way: An 0.8 mm stainless steel wire, having a high softening point, reasonably constant cross section and of sufficient length, was used to press the liquid over into the diffusion capillary. The wire was stretched to a transformer, able to deliver a sufficiently high current (10—15 amps). The upper ends of the steel rods were fixed in a wooden shaft. By means of this device, small pieces of Pyrex glass could easily be sealed to the Supremax glass of the capillaries.

This technique was developed in cooperation with Mr. M. Lövessvay, who also contributed to the solution of some of the problems in connection with experimental design and manipulation.
ZINC ION SELF-DIFFUSION IN MOLTEN ZINC BROMIDE

Fig. 1. Oven, schematic.
1) Pyrex glass tube with Kanthal winding
2) Rockwool insulation
3) Aluminium envelope
4) Brass top plate with aluminium cover
5) Auxiliary oven
6) Aluminium bronze block
7) Sand bedding
8) Capillaries, extending from metal block (only two shown)
9) Filler tube with S-shaped capillary
10) Movable stand (Thermocouples not shown).

Fig. 2. Arrhenius plot.
a) previous data (ref. 2)
b) present investigation; the curved line has the equation
\[
\log(D \cdot 10^7) = -0.697 + 6.79 \frac{10^3}{T} - 4.08 \left( \frac{10^3}{T} \right)^2.
\]

Results

From the experimental data, the self-diffusion coefficients were calculated by means of an electronic computer, see Table 1. Figure 2 shows a graph of \( \log D \) versus \( 1/T \), both for the previously published and for the present data. The points of the latter series seem to form a curved line. They have therefore been adapted to a parabolic equation by means of a least squares fitting. The “apparent activation energy” of the so obtained curve is 20 600 cal/mole at 450 °C and 14 300 cal/mole at 550 °C. This is qualitatively in agreement with conductivity data, where a similarly curved line was obtained.

However, a critical examination of the data by means of a statistical test shows that, with respect to the precision of the measurements, nothing contradicts a linear dependence of \( \log D \) on reciprocal temperature. The least squares straight line has got a slope, corresponding to an “activation energy” of 19 000 cal/mole, to be compared to 16 100 cal/mole for the old series.

The concentration distribution data have also been treated in the “conventional” way, i.e., the correction applied is a multiplication of measured distances by a constant factor. The values of \( D/D_{\text{avg}} \), where \( D_{\text{avg}} \) is the average value for an experiment, were plotted against \( \sqrt{D_{\text{avg}} \cdot t} \), which is a measure of the form of the penetration curve. The resulting graph showed a very marked time-dependence of \( D \), especially for short diffusion times, as was expected.

When the data, obtained from the new equation, are treated in the same way, there is still obvious a certain time-dependence. This is very small, however, and is likely to be the effect of the non-ideal boundary formation. The error introduced there should not exceed 1 or 2%.

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5 See ref. 1.
6 The computations were made by Mr. Gunnar Häggström.
Suggestions for improvement

It is strongly believed that the actual measurements do not do justice to the presented technique. A few modifications in mode of procedure should be carried out in order to improve the accuracy. One of the most important changes is a better determination of the contraction factor $k$ (empirical calculations indicate that the quotient $\frac{\Delta D}{D} / \frac{\Delta k}{k}$ is approximately equal to 1.5 for typical values of $D$, $t$ and $k$). Also, the diffusion process ought to be interrupted without moving the capillaries. Though it is not likely that any appreciable disturbance is produced in this way, since the capillaries are so narrow, the possibility must not be overlooked. Thus, it is believed that the method should be able to give a better reproducibility than what is shown in Table 1.

Acknowledgements

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