Self-Diffusion in Molten Zinc Chloride

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The self-diffusion coefficients of both ions in molten zinc chloride have been measured with the porous-frit technique [1–3]. The result can be described with Arrhenius equations:

$$D_{\mathrm{Zn}} = 5.85 \times 10^{-2} \exp\left\{-\frac{15400 \pm 1000}{R\,T}\right\} \qquad (329-530\ ^\circ\mathrm{C})$$

$$D_{\mathrm{Cl}} = 13.7 \times 10^{-2} \exp\left\{-\frac{16300 \pm 800}{R\,T}\right\} \qquad (330-526\ ^\circ\mathrm{C})$$

where D is expressed in $\mathrm{cm}^2\,\mathrm{s}^{-1}$, R in cal mole^{-1} degree^{-1}, and T in degrees Kelvin. A comparison is made with earlier data by Bockris et al. [4] and an attempt is made to correlate the experimentally observed external transport number [5] and the corresponding calculated quantity [6, 7].

Systematic studies of self-diffusion coefficients, equivalent conductivities, and external transport numbers of pure molten salts are still very scarce despite the fact that they might give valuable checks on the development of transport theories for ionic melts. The experimental difficulties involved are of course the main reason for this state of affairs. Particularly few divalent salts have so far been studied in all three respects (only $CdCl_2$, $PbCl_2$, $ZnCl_2$, $ZnBr_2$, and $PbBr_2$). The available zinc chloride self-diffusion data by Bockris, Richards, and Nanis [4] are very scattered and their temperature-dependence is stated to be quite different from all other (pure) salts. Moreover, if these data are used the agreement between the observed external transport number and the value calculated from the correlation equation proposed by Laity [6, 7] is extremely poor. This equation has been remarkably accurate for monovalent salts but only partly successful for divalent salts. Thus it was decided to re-determine the self-diffusion coefficients of both ions in molten zinc chloride in order to be able to check the correlation equation more decisively. The porous-frit technique is particularly well suited for an investigation of this salt since the expected diffusion coefficients are of the order of $10^{-7}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$. The diffusion times of the conventional capillary technique would thus be prohibitively long.

Experimental

Water-free reagent grade zinc chloride was obtained from E. Merck AG., Darmstadt, in sealed containers. The salt was dried under vacuum for 50 hours prior to use. The melting-point of the salt was measured as a check of the purity. The obtained value agreed exactly with the most recent literature value [8]. (The remarkable scatter in the available melting-point data, the lowest value being 262 °C and the highest 363 °C, indicates the experimental difficulties involved.)

$Zn^{65}Cl_2$ was obtained from Aktiebolaget Atomenergi, Studsvik. $ZnCl_2^{36}$ was made by mixing inactive $ZnCl_2$ and about 0,3% (by weight) $AgCl^{36}$ with high specific activity obtained from NEN, Boston, Mass. The mixture was kept molten long enough to become homogenous.

D_{Zn} and D_{Cl} were determined in separate runs. A whole experimental series (covering the whole temperature range) was performed without cooling and reheating the furnace (which was carefully blanketed with argon gas in order to avoid atmospheric contamination of the melt which is extremely hygroscopic). The salt was very rapidly transferred from the vacuum storage to the furnace which was already at the temperature of the first experiment.

The experimental set-up and technique have been described earlier [1–3]. Commercial Pyrex glass frits (JOBLING 3610/62, 20 mm Por 4) with 20 mm diameter and 2 mm thickness were used. The "effective" thickness of the frits (determined with the gravimetric

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diffusion technique[3, 9, 10]) ranged in the present investigation between 2.3 and 3.3 mm. Each frit was used only once since the manipulation of it after the run had to be done in air outside the furnace. (Water-free zinc chloride will pick up moisture from the air even above 100 °C.) Special care was taken to remove all inactive salt clinging to the surface of the frit after the run. The comparatively high surface tension of the melt made an unusually large amount of salt stick to the frit faces. The diffusion times ranged from 1000 seconds to 30 000 seconds. The temperature was kept constant to about ±1 °C during a run with a temperature controller (type West Gardsman JP).

The radio-analysis of Zn^{65} and Cl^{36} were performed with conventional liquid γ- and β-counting techniques respectively. The amount of zinc chloride in each sample was determined by titration[11] and the specific activity was calculated. Only a negligible fraction of the initial activity inside the frit remained in the glass as was expected from the diffusion results by Sjöblom and Andersson[12]. They found that the diffusion coefficient of silver into Pyrex glass from a melt of silver nitrate was about $3 \times 10^{-11}\ \mathrm{cm^2\,s^{-1}}$ at 350 °C. The mobility in glass of doubly charged ions is expected to be much smaller than the mobility of singly charged ions.

Result and Discussion

The results are given in Fig. 1 and they can be summarized in two Arrhenius equations obtained by least squares fitting[13]. The stated errors are standard deviations.

$$D_{\mathrm{Zn}} = 5.85 \times 10^{-2} \exp\left\{-\frac{15400 \pm 1000}{R\,T}\right\} \qquad (329-530\ ^\circ\mathrm{C})$$

$$D_{\mathrm{Cl}} = 13.7 \times 10^{-2} \exp\left\{-\frac{16300 \pm 800}{R\,T}\right\} \qquad (330-526\ ^\circ\mathrm{C}).$$

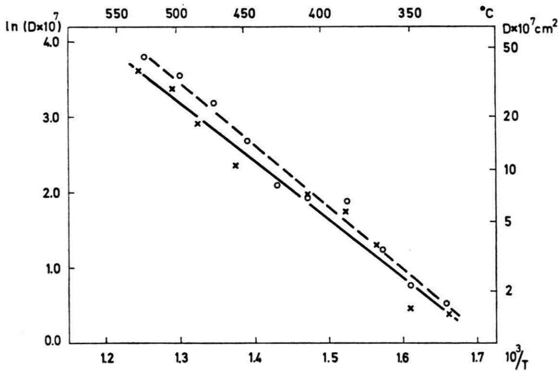

Fig. 1. The self-diffusion coefficients of the cation, D_{Zn}, (×), and the anion, D_{Cl}, (○), in molten $ZnCl_2$. The lines correspond to the Arrhenius equations quoted in the text.

D is expressed in $\mathrm{cm^2\,s^{-1}}$, R in cal $\mathrm{mole^{-1}}$ $\mathrm{degree^{-1}}$, and T in degrees Kelvin. The standard errors of estimate[14] in the ${}^{e}\log(D \times 10^7)$ vs. $10^3/T$ plots are approximately 7%. A regression analysis shows that the data are not significantly better fitted by an equation quadratic in $10^3/T$ despite the fact that another adjustable parameter is introduced.

The observed self-diffusion coefficients agree reasonably well with the values by Bockris et al.[4] in the middle of the investigated temperature interval. Moreover, the present results are very close to the values obtained for zinc bromide at the same temperatures[2]. The "activation energies"[15] for diffusion of cations and anions are equal within experimental error (this is the case for all investigated molten salts) and also very close to the corresponding values for zinc bromide. D_{Cl} is slightly greater than D_{Zn} in the whole temperature interval ($D_{\mathrm{Cl}}/D_{\mathrm{Zn}} = 1.2$ at 450 °C, while in $ZnBr_2$ $D_{\mathrm{Br}}/D_{\mathrm{Zn}} = 1.3$ at 450 °C).

Bockris et al.[4] claim to have found a strongly non-linear dependence of ${}^{e}\log(D \times 10^7)$ on $10^3/T$ for both ions in zinc chloride. A statistical analysis[13] of their data shows, however, that the statistical support for this assumption is nonexistent in the case of D_{Zn} and very weak in the case of D_{Cl} (no estimation of their obtained experimental accuracy is given.) Moreover, all the (apparent) curvature occurs at the *highest* temperatures. According to a theory by Cohen and Turnbull[16] (which has been extensively investigated by Angell and coworkers[17]) the correct temperature dependence of the diffusion coefficient is of the form

$$D = A\,T^{1/2} \exp\left\{-\frac{k}{T-T_0}\right\}$$

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where A, k, and T_0 are constants. Most diffusion measurements have been performed too high above the temperature T_0 to make the expected curvature in the ${}^{e}\log D$ vs. T^{-1} plot detectable with the obtained experimental accuracies. The curvature should, however, be pronounced at low temperatures only and not at high temperatures. It can thus be concluded that the nonlinearity (if any) observed by Bockris et al. is caused by unknown factors (decomposition of the salt is known to have caused similar downward trends [18] in plots of specific conductivity vs. T). The overall difference between the two sets of values (the results by Bockris et al. are 17% higher on the average) might be attributed to their use of a particular correction method [19] for end errors in the capillaries. This method has been criticized [20] and so far it has not been adopted anywhere else.

The correlation equation [6, 7]

$$t_+ = \tfrac{1}{2}\left(\Lambda/F^2 + z_+ D_+/R T - z_- D_-/R T\right)/(\Lambda/F^2)$$

between equivalent conductivity, self-diffusion coefficients, and external transport numbers which gave excellent results for zinc bromide (and for most salts investigated so far) gives rather poor agreement for zinc chloride (see Table 1) regardless of which set of self-diffusion data that is used. The reliability of the available conductivity data is by no means as good as usual (i. e. three different investigations of the electrical conductivity of zinc chloride differ by up to 40%). It is nevertheless unlikely that the discrepancy shown in Table 1 is entirely due to experimental inaccuracies. The present investigation covers a fairly wide temperature interval which makes it possible to make a comparison between the calculated and observed external transport numbers with respect to both magnitude and temperature dependence. It is thus possible to conclude that the correlation equation is not supported by the zinc chloride results.

Temperature (°C)	External transport number t_+ Observed	Calculated (S)	Calculated (B)
350	0.71	2.0	3.9
400	0.69	1.7	3.6
450	0.68	1.2	2.1
500	0.66	1.0	1.7
550	0.64	1.1	1.6

Table 1. External transport number t_+ of the cation in molten zinc chloride. Observed values by Fischer and Klemm [5], calculated values from equivalent conductivity data by Janz et al. [22] and self-diffusion data by Sjöblom and Behn [23] (S) and by Bockris et al. [4] (B). The agreement is better using the present self-diffusion data but it is still unsatisfactory, particularly at low temperatures.

The derivation of the correlation equation mentioned above has been criticized as being physically inconsistent [21]. It is necessary to introduce an extra (arbitrary) mathematical restriction when the correlation equation is obtained from the thermodynamic flow equations (since three parameters related with only one equation are used to describe only one experiment [6]). The chosen additional restriction is equivalent to setting the term $L_{ik} = 0$ when components i and k are chemically identical. This is at least mathematically permissible (in a two-component system) while the physical interpretation of the coefficients in the thermodynamic flow equations becomes somewhat unnatural. The derivation is nevertheless a convenient mathematical way to obtain the correlation equation the value of which must be demonstrated by its potential usefulness. The equation has turned out to be remarkably successful for monovalent salts while its applicability to divalent salts still remains in doubt. More systematic diffusion and transport number studies of divalent salts are needed to settle this question.

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