In den Daten der Autoren[18] wurden die Korrekturen näher abgeschätzt zu maximal 20%. Da bei den hier vorliegenden Aktivierungsenergien 0,8% Temperaturfehler bereits zu 14% Abweichungen im DK führen, liegt die Vernachlässigung sicherlich in der Fehlerbreite der Messung. Sie können auch die verbliebenen Abweichungen auf der Nickelseite nicht erklären.

Es kann daher der Schluß gezogen werden, daß auch nach den Darkenschen Formeln ein Wiederanstieg des gemeinsamen DK auf der Nickelseite nicht zu erwarten ist. Er bleibt dort sogar, trotz des fast exponentiellen Anstiegs der Selbstdiffusion beider Komponenten mit steigendem Kupfergehalt über einen weiten Konzentrationsbereich annähernd konstant, da dieser Anstieg durch den stark fallenden thermodynamischen Faktor fast kompensiert wird. Die beobachteten Abweichungen im Diffusionsverhalten sind daher wohl auf andere Diffusionsmechanismen als die Volumendiffusion zurückzuführen, die sich auf der Nickelseite bei gegebener Temperatur zuerst bemerkbar machen sollten. Daß bei 1000 °C im Bereich der Korngrenzendiffusion gemessene DK wesentlich höher liegen, lassen die in Abb. 7 mit eingetragenen Werte von [10] gut erkennen.

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External Transport Numbers in Molten Zinc Bromide

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The external transport number[1] in pure molten zinc bromide has been measured as a function of temperature using a porous plug as velocity reference. The results can be described by the equation (obtained by least squares fitting)

$$t_{Zn^{++}} = 0.791 - 3.68 \times 10^{-4}\ (T - 394) \qquad (469 - 562\ ^\circ C)$$

where T is expressed in degrees Centigrade. The result is in excellent agreement with values calculated according to the so-called "new formalism" developed by Laity[1, 2].

Measurements of external transport numbers in pure molten salts require a choice of a reference frame. The fact that this choice is not only an experimental problem but actually defines the quantity to be measured has been clearly established by Laity[1] and Klemm[3] in two review articles. Thus the measurement of an external transport number (in a pure molten salt) is in effect a study of the interaction between the salt and the chosen porous separator between the electrode compartments. Different separator materials tended to give similar experimental results[4] and this fact was taken as an evidence that a property of the salt only (and not of the separator material) was measured. A closer analysis of the plug materials used (glass, porcelain, asbestos, aluminum oxide) shows however that which the obtained experimental accuracies there is little reason to expect any noticeable effect when these materials are interchanged since they are chemically similar to each other. (Work prior to 1964 is summarized in Ref. [3]). Moreover, careful experiments[5] showed a small but significant difference between the observed transport number of the nitrate ion in molten sodium nitrate when a pyrex glass[6] and a selas porcelain[7] separator was used. This result does not invalidate measurements of external transport numbers as such, it merely restates (the already obvious) fact that the composite system molten salt — porous plug is studied[8].

The justification of an operationally defined quantity such as the external transport number lies in its potential usefulness. It has been shown[9] that

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[1] R. W. Laity, article on "Molten Salt Transport Numbers" in Encyclopedia of Electrochemistry, ed. by C. A. Hampel, Reinhold Publishing Co., New York 1964, p. 653.

[2] R. W. Laity, Disc. Faraday Soc. **32**, 172 [1962].

[3] A. Klemm, "Transport Properties of Molten Salts", a chapter in "Molten Salt Chemistry", ed. by M. Blander, Interscience Publishers, New York 1964, p. 538 and 593.

[4] F. R. Duke and R. W. Laity, J. Phys. Chem. **59**, 549 [1955].

[5] R. J. Labrie and V. A. Lamb, J. Electrochem. Soc. **110**, 810 [1963].

[6] Obtained from Corning Glass Works, USA.

[7] Obtained from Selas Corporation of America, USA.

[8] C. Sinistri, J. Phys. Chem. **66**, 1600 [1962].

[9] R. W. Laity and C.-A. Sjöblom, J. Electrochem. Soc., to be published.

transport numbers can be used with excellent accuracy to correlate diffusional and electrical mobility in all studied monovalent molten salts (a somewhat more extensive comparison is made in Table 1) but not in the divalent salts lead chloride and lead bromide [1, 2, 10]. Thus the difference between these two salt types can be studied in this way. It will be shown below that there is at least one divalent salt ($ZnBr_2$) for which the correlation works and that conclusions can be drawn about different degrees of "association" of the ions in the melts.

Experimental

Commercially available zinc bromide (Riedel-de Haen AG., Seelze-Hannover) was vacuum distilled and stored under vacuum until the time for the experiment. Reagent grade zinc metal (E. Merck AG., Darmstadt) was used for the electrodes without further purification.

A method similar to that of FISCHER and KLEMM [11] was used. The metal and the salt were molten under vacuum in the upper part of the experimental cell (see Fig. 1) and the experiments were performed in an argon atmosphere. A Pyrex glass frit (James A. Jobling & Co., Ltd.) with diameter 10 mm and thickness 1.5 mm was used as a separator between the electrode compartments. The mean pore diameter of each frit was individually measured by the factory and it ranged from 0.9 to 1.4 microns (corresponding to porosity grade 5). Veridia precision-bore vertical capillaries with a diameter of 2.00 mm were used and the salt level changes during the electrolysis were recorded with a Griffin & George (London) cathetometer. Three separate furnace windings were used in order to eliminate vertical temperature gradients. The heating current was supplied by a voltage stabilizer (Philips PE 1002 Elektron). The temperature during a run could be kept constant to better than ±0.2 °C (which is the accuracy of the temperature recording equipment). The practical upper temperature limit was about 600 °C since the cell was made of pyrex glass.

Electrolysis currents of the order of 50 mA were used in order to keep local heating inside the frit low. The temperature was measured with a thermocouple pressed against the cell wall at the edge of the frit. Thus most of the heating effects inside the frit were not recorded by the thermocouple. This local heating can however be estimated with good accuracy as follows: The hydrostatic flow of salt through the cell is almost entirely determined by the viscosity of the salt inside the frit. Comparing the flows when known alternating currents pass through the cell to the flow without current (when the frit temperature is equal to the furnace temperature) gives a measure of the change in viscosity due to local heating inside the frit. This change is converted into a temperature increase and thus the true frit temperature can be calculated [12]. The maximum power dissipated inside the frit was less than 1 watt which corresponds to a temperature correction of +5 °C.

The external transport number is calculated with one of the two equations [11]

$$\text{a)}\quad t_{Br^-} = \frac{1}{V_{ZnBr_2}}\left(V_{Zn} - \left(\frac{dh}{dt}\right)_{t=0}\frac{F\,A}{I}\right)$$

(low hydrostatic resistance),

$$\text{b)}\quad t_{Br^-} = \frac{1}{V_{ZnBr_2}}\left(V_{Zn} + \frac{h_\infty F\,A\,(d\ln h/dt)_{I=0}}{I}\right)$$

(high hydrostatic resistance)

where

t_{Br^-} = external transport number of the Br^--ion,
V_{ZnBr_2} = molar volume of zinc bromide [13],
V_{Zn} = molar volume of zinc [14],
F = Faraday constant,
A = cross-sectional area of the vertical capillaries,
I = electrolysis current (about 50 mA),
h = height difference between the salt levels in the capillaries. h is counted positive when the salt level is highest in the cathodic compartment,
h_∞ = h at infinite time (equilibrium),
t = time.

In order to obtain $(d\ln h/dt)_{I=0}$ the hydrostatic backflow under a hydrostatic head is measured when an alternating current equivalent to the electrolysis current is passed through the cell. In the present case $(d\ln h/dt)_{I=0}$ was of the order of (60 minutes)$^{-1}$ and thus both equations could be used although eq. a) was preferred due to its simplicity. (The agreement between results from the two equations was excellent.)

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[10] C.-A. SJÖBLOM and J. ANDERSSON, Z. Naturforsch. **23 a**, 239 [1968].

[11] W. FISCHER and A. KLEMM, Z. Naturforsch. **16 a**, 563 [1961].

[12] The temperature dependence of the viscosity of $ZnBr_2$ is unknown. The temperature dependence of the (conductivity)$^{-1}$ can be used with sufficient accuracy since the correction term is very small (less than 5 °C): J. O'M. BOCKRIS, E. H. CROOK, H. BLOOM, and N. E. RICHARDS, Proc. Roy. Soc. London **A 255**, 558 [1960].

[13] J. O'M. BOCKRIS, A. PILLA, and J. L. BARTON, J. Phys. Chem. **64**, 507 [1960].

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The experimental cell is shown in Fig. 1. A more detailed description of a similar apparatus is given in Ref. [9].

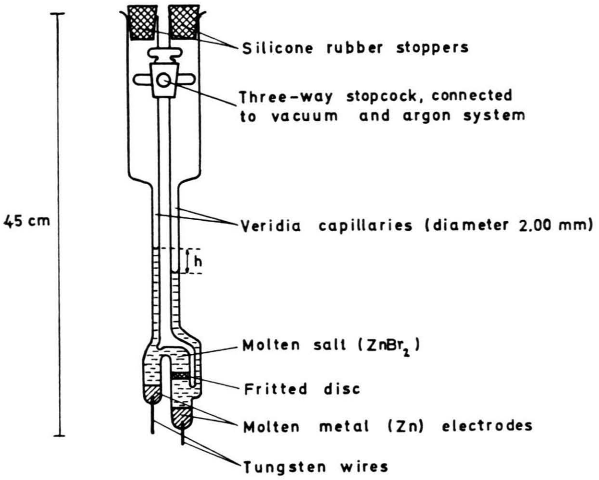

Fig. 1. Experimental cell for measurements of external transport numbers in molten salts. The three lower tubes are actually not in one plane (in order to save room inside the cylindrical furnace).

Results and Discussion

The experimental results (46 independent measurements) can be summarized by "least squares" fitting [15] in the equation

$$t_{\mathrm{Br}^-} = 0.791 - (3.68 \pm 0.59)\,(T - 394) \times 10^{-4} \quad (469 - 562\ {}^\circ\mathrm{C})$$

where T is the temperature in degrees Centigrade. The stated error is a standard deviation [15] and the eqution has a standard error of estimate [16] of 0.004. The agreement between the results from experiments with different cells is seen to be excellent in spite of the experimental difficulties always encountered with zinc bromide.

A comparison with the zinc chloride results obtained by Fischer and Klemm [11] shows that the transport numbers of the two zinc salts are very close to each other and that the temperature dependences are almost the same. The calculation according to the "new formalism" [1, 2]

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

gives a $t_{\mathrm{Zn}^{++}}$ of 0.76 at 450 °C as compared to the experimental value 0.77 (see Table 1). A similar comparison is not yet possible for zinc chloride since no reliable self-diffusion data are available [17].

It has been noted elsewhere [11] that the pore size should be larger than a certain (yet unknown) critical size in order to avoid influences of the pore size on the transport. The critical pore size is very small since the external ion transport is determined within a few ionic diameters of the interface between salt and pore wall [1, 9, 18]. This view is supported by the results of the experiments by Laity and Sjöblom [9, 18] where a change in the properties of the double-layer at the frit-melt interface produced a pronounced change in the observed transport number. Moreover, different frit materials do give different experimental results [5, 9, 18].

A comparison between experimentally obtained cationic transport numbers and the corresponding values calculated according to Laity [1, 2] is made in Table 1. The accuracy of the calculated values cannot be expected to be better than about 10 – 20% in view of the errors involved in the self-diffusion measurements. There is nevertheless a remarkable agreement between the two sets of values for all salts except $PbCl_2$ and $PbBr_2$ (and perhaps $CdCl_2$). An attempt has also been made to predict the temperature dependence. There is reason to expect some success since the temperature dependences of the diffusion and conductivity data are often more accurately known than the absolute values. Unfortunately only few transport number experiments have been accurate enough to detect any temperature dependence at all. Nevertheless the direction and magnitude of the temperature dependence is reasonably well described for $AgNO_3$ and $ZnBr_2$ while TlCl is somewhat undecided. There is of course no reason to expect agreement for $PbCl_2$ and $PbBr_2$.

Table 1 shows that the salts can be divided into two groups: One group (containing all monovalent salts plus zinc bromide) where the theoretical transport numbers agree with the experimental values and one group (containing the divalent salts lead chloride, lead bromide, and cadmium chloride) where the theoretical and experimental values disagree. The reason for this general behaviour is probably

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[15] A. Hald, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522.

[16] Handbook of Chemistry and Physics, 46th ed. p. A-198, The Chemical Rubber Co., Cleveland 1965.

[17] Work is in progress in this laboratory in order to measure the self-diffusion coefficients in molten $ZnCl_2$.

[18] R. W. Laity and C.-A. Sjöblom, J. Phys. Chem., in press.

Salt	Temperature °C	External transport number t_+ Calculated	Data from Ref. No.	Observed	Data from Ref. No.
NaCl	860	0.60	21, 22	0.62 ± 0.04	25
RbCl	785	0.54	21, 22	0.58 ± 0.04	25
CsCl	685	0.46	21, 22	0.57 ± 0.01	25
TlCl	450	0.47	21, 23	0.42 ± 0.01	11
	500	0.47		0.43	
	550	0.47		0.44	
$LiNO_3$	350	0.81	21, 22	0.84 ± 0.06	25
$NaNO_3$	350	0.65	21, 22	0.70 ± 0.01	5
KNO_3	350	0.54	21, 22	0.60 ± 0.03	25
$CsNO_3$	450	0.50	21, 22	0.4 (uncertain)	25
$AgNO_3$	200	0.68	21, 22	0.80 ± 0.02	26
	250	0.67		0.78	
	300	0.66		0.76	
$CdCl_2$	605	0.85	21, 22	0.66 ± 0.01	25
$PbCl_2$	550	0.53	21, 23	0.23 ± 0.02	9
	600	0.52		0.24	
$ZnBr_2$	400	0.83	21, 24	0.79 (extrapolated)	27
	450	0.76		0.77	
	500	0.75		0.75	
	550	0.76		0.73	
$PbBr_2$	450	0.62	21, 10	0.37 ± 0.02	9
	500	0.62		0.36	
	550	0.64		0.34	

Table 1. Cationic transport numbers in pure molten salts. A comparison between the experimentally observed values and the theoretical values according to Laity [1, 2]. The calculated values cannot be expected to be accurate to better than ±10—20% due to the errors involved in the determinations of the self-diffusion coefficients. The errors stated in the "observed" column are the reproducibilities reported by each worker.

to be found in the interaction at the salt – frit wall interface where the value of the observed transport number is determined. A larger fraction of doubly charged positive ions (in this case lead ions) than of singly charged positive ions will be immobilized in this layer due to electrostatic interaction with the (negative) oxygen ions in the glass surface. Thus a greater fraction of the current will be carried (relative to the glass surface) by the anions in the divalent salt than might be expected from the theoretical equation (which holds for the monovalent salts according to Table 1). The reason for the agreement in the case of zinc bromide is that this salt has a complex structure in the melt [19]. Cadmium chloride has been discussed in terms of partial "association" to $CdCl^+$-ions [20]. The comparison in Table 1 supports this view since the agreement between observed and theoretical values is much better than of the lead salts but not as good as that of zinc bromide.

The authors are indebted to Dr. Arnold Lundén for his interest in this work and also to Mr. Roland Eliasson for his help with the glass-blowing. The work was financially supported by Åke Wibergs Stiftelse.

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[20] C. A. Angell and J. W. Tomlinson, Disc. Faraday Soc. **32**, 237 [1962].

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[22] Self-diffusion data obtained from Ref. [3], p. 590.

[23] C. A. Angell and J. W. Tomlinson, Trans. Faraday Soc. **61**, 2312 [1965].

[24] C.-A. Sjöblom, Z. Naturforsch. **18 a**, 1247 [1963].

[25] External transport number data from Ref. [3], p. 593.

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