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GOTHENBURG DISSERTATIONS IN SCIENCE

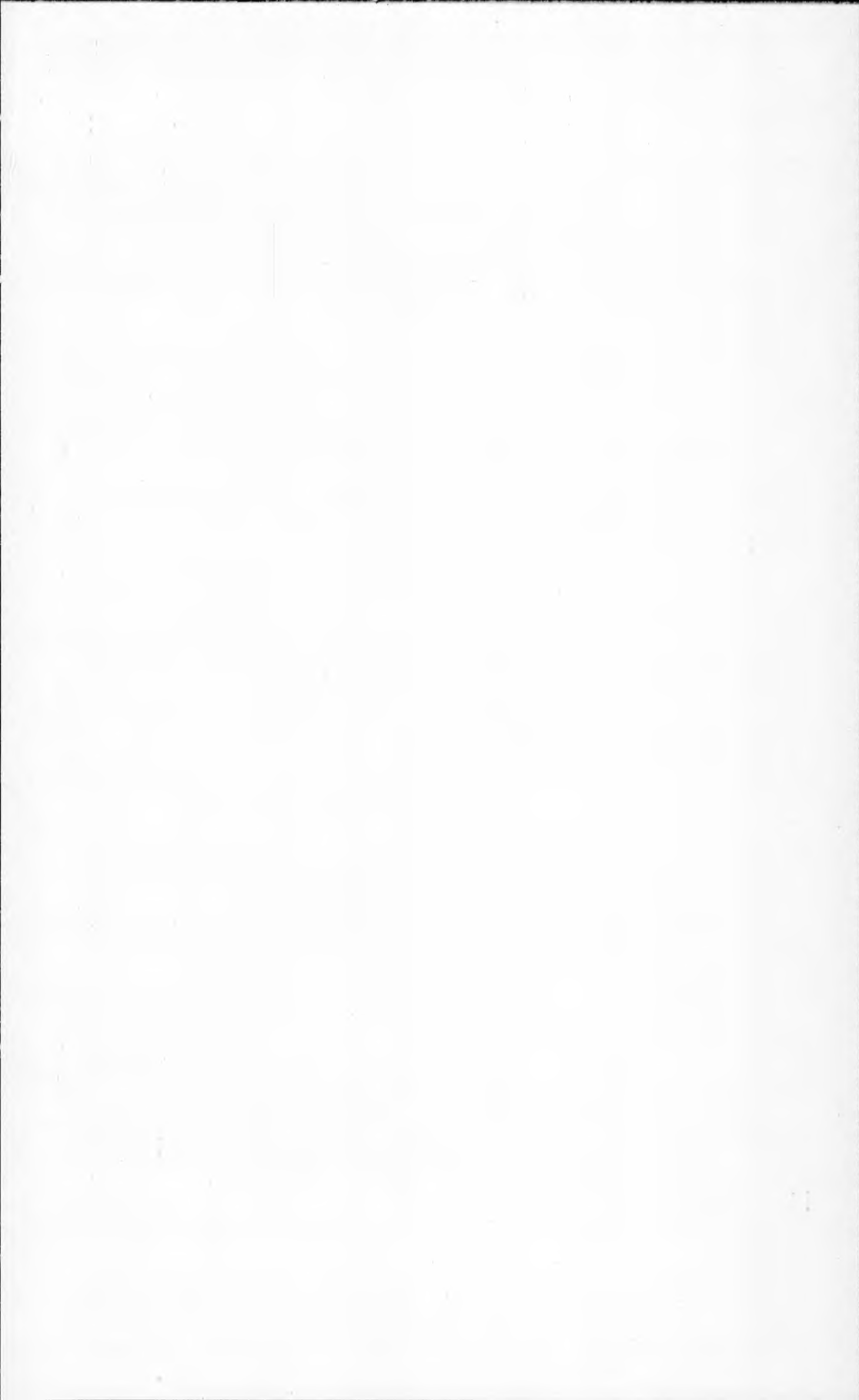
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TRANSPORT STUDIES
IN MOLTEN SALTS

BY
CARL-AXEL SJÖBLOM



ACTA UNIVERSITATIS GOTHOBURGENSIS



TRANSPORT STUDIES IN MOLTEN SALTS

AKADEMISK AVHANDLING

SOM MED VEDERBÖRLIGT TILLSTÅND AV MATEMATISK-NATUR-
VETENSKAPLIGA FAKULTETEN VID GÖTEBORGS UNIVERSITET FÖR
VINNANDE AV FILOSOFISK DOKTORSGRAD FRAMLÄGGES TILL
OFFENTLIG GRANSKNING Å FYSIKSAL A, CHALMERS TEKNISKA
HÖGSKOLA, MÅNDAGEN DEN 22 APRIL 1968 KL. 10.15
AVHANDLINGEN FÖRSVARAS PÅ ENGELSKA OCH SVENSKA.

AV

CARL-AXEL SJÖBLOM
FIL. LIC.

GÖTEBORG
ELANDERS BOKTRYCKERI AKTIEBOLAG
1968



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Distr.:
ALMQVIST & WIKSELL
STOCKHOLM
GÖTEBORG UPPSALA

GÖTEBORG 1968
ELANDERS BOKTRYCKERI AKTIEBOLAG

To Inger

This thesis is mainly a summary of the following papers:

- I. C.-A. SJÖBLOM and A. LUNDÉN, Selbstdiffusion in geschmolzenen Halogeniden, *Z. Naturforsch.* **18 a**, 942–949 (1963).
- II. C.-A. SJÖBLOM, Self-Diffusion in Molten Zinc Bromide, *Z. Naturforsch.* **18 a**, 1247–1248 (1963).
- III. C.-A. SJÖBLOM, Interdiffusion and Self-Diffusion in Binary Mixtures of Molten Salts, *Z. Naturforsch.* **20 a**, 1572–1577 (1965).
- IV. C.-A. SJÖBLOM and J. ANDERSSON, Diffusion of Silver into Glass from a Melt of Silver Nitrate, *Z. Naturforsch.* **21 a**, 274–276 (1966).
- V. C.-A. SJÖBLOM and J. ANDERSSON, Self-Diffusion in Molten Silver Nitrate, *Z. Naturforsch.* **21 a**, 276–278 (1966).
- VI. R. W. LAITY and C.-A. SJÖBLOM, Double-Layer Effect on “External Transport Numbers” in Molten Lead Chloride, *J. Phys. Chem.* **71**, 4157–4158 (1967).
- VII. C.-A. SJÖBLOM and J. ANDERSSON, Self-Diffusion in Molten Thallous Chloride. A Re-Determination, *Z. Naturforsch.* **23 a**, 197–198 (1968).
- VIII. C.-A. SJÖBLOM and J. ANDERSSON, External Transport Numbers in Molten Zinc Bromide, *Z. Naturforsch.* **23 a**, 235–238 (1968).
- IX. C.-A. SJÖBLOM and J. ANDERSSON, Self-Diffusion in Molten Lead Bromide, *Z. Naturforsch.* **23 a**, 239–241 (1968).
- X. C.-A. SJÖBLOM and A. BEHN, Self-Diffusion in Molten Zinc Chloride, *Z. Naturforsch.* **23 a**, (1968), in press.
- XI. C.-A. SJÖBLOM, Self-Diffusion in Molten Salts. A Comparison between Diffusion Theories and Experimental Data, *Z. Naturforsch.* **23 a**, (1968), in press.

Introduction

Molten salt studies are affected by considerable experimental difficulties due to the high temperatures involved and the corrosive nature of salt melts and vapours. Thus despite the fact that molten salts have been investigated since the beginning of the nineteenth century there is still a need to develop new techniques which can be used under particularly unfavourable experimental conditions.

The theoretical models of ionic liquids are not very well developed either. This state of affairs is primarily due to the complex nature of the interactions in the melts but it is also due to the lack of reliable and accurate experimental data. Several models attempting to describe transport properties in molten salts have been advanced but it has been difficult to make a general decision as to which model that is "correct". Most theories are not able to describe all studied salts equally well which means that a theory might be successful for one group of salts but not for another.

This thesis covers the following general fields:

1. Self-diffusion measurements: Development of a reliable method suitable for difficult experimental conditions. (Papers I, II, IV, V, VII, IX, X.)
2. Interdiffusion measurements: Development of a generally applicable technique for molten salt studies. (Paper III.)
3. External transport numbers in pure molten salts: Development of a method for measurements of and studies of double-layer effects on transport numbers. Test of a correlation equation between self-diffusion coefficients, equivalent conductivity, and external transport number. (Papers VI, VIII, IX, X.)
4. A comparison between diffusion theories and available self-diffusion data for pure molten salts. (Paper XI.)

1. Self-diffusion measurements

The "conventional" capillary method^{1,2} is the most common technique for self-diffusion measurements in molten salts. A capillary (length about 4 cm and inner diameter about 1 mm) is filled with a radioactive melt which is allowed to diffuse out into a large volume of inactive melt. This method is capable of a good accuracy when the experimental conditions are favourable (non-corrosive salts and self-diffusion coefficients of the order of 10^{-5} cm² s⁻¹ or higher). The time needed for an experiment is, however, of the order of 50 hours which precludes the study of salts having only short-lived radioactive isotopes.

The porous-frit technique was developed in order to obtain a method where the diffusion time could be reduced drastically without any serious loss of experimental accuracy (papers I, II, VII, IX, and X). The capillary mentioned above is in this method replaced with a fritted disc which can be regarded as composed of many small, irregularly shaped capillaries. The effective length of these capillaries must be determined by suitable calibration. A first version of the porous-frit technique was tried by DJORDJEVIC and HILLS³ but their attempt was unsuccessful⁴. In the case of TiCl some problems have been encountered in the present investigations also, but they have been shown (paper VII) to be of a chemical nature and they are not due to a property of the porous frit technique.

The present version of the porous frit technique is described in detail in paper IX together with paper I. The experimental set-up is shown in Figure 1.

Self-diffusion results for molten TiCl, ZnBr₂, PbBr₂, and ZnCl₂ obtained with the porous-frit method are given in papers I, II, VII, IX, and X and also some data for the KNO₃-AgNO₃ mixture in paper III. The data are well described by ARRHENIUS equations

$$D = D_0 \exp(-Q/RT) \quad (1)$$

where D_0 and Q (the activation energy) are constants. R is the gas constant expressed in cal mole⁻¹ degree⁻¹ and T is the absolute temperature. D_0 and Q obtained by least squares fitting for the salts mentioned above are given in Table 1.

The porous frit technique is shown to be a reliable and straightforward experimental method. Self-diffusion studies of salts with

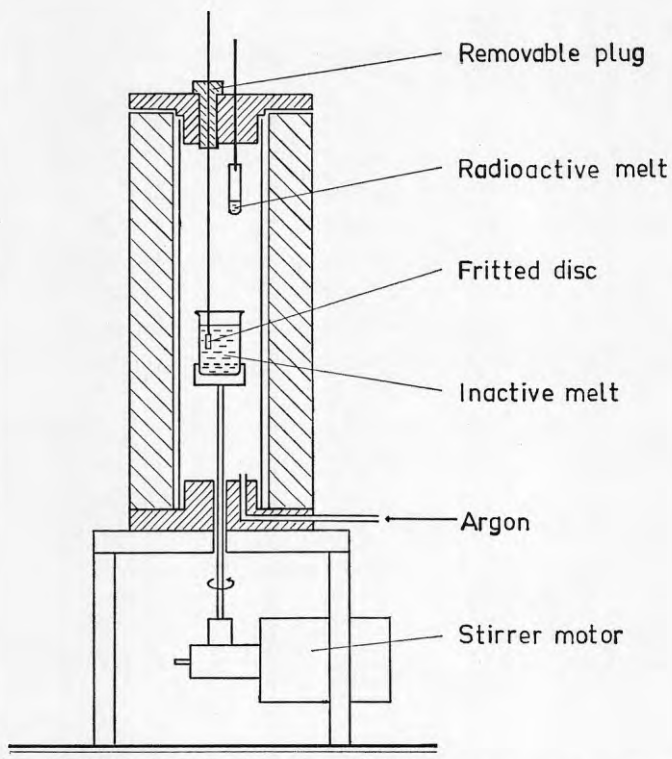


Fig. 1. Experimental set-up of the porous-frit technique for self-diffusion measurements in molten salts. (Furnace windings not shown.)

Table 1. Results of self-diffusion measurements. D_0 and Q are constants in the Arrhenius equation (1) obtained by least squares fitting. ^a=Diffusion of silver into Pyrex glass from an AgNO_3 melt.

Salt		$D_0 \times 10^3$ (cm^2s^{-1})	Q (cal mole^{-1})	Temp. range ($^{\circ}\text{C}$)	Paper
AgNO_3	D^+	0.32	3,400	220-336	V
TiCl	D^+	2.2	6,000	450-556	VII
ZnCl_2	D^+	58.5	15,500	329-530	X
	D^-	137	16,300	330-526	
ZnBr_2	D^+	80	16,900	449-555	I
	D^-	114	17,050	415-547	II
PbBr_2	D^+	0.74	6,500	380-540	IX
	D^-	0.83	6,100	380-555	
AgNO_3^a	D^+	0.60	20,500	216-354	IV

isotopes having half-lives as short as 30 minutes are possible. The short diffusion times make it easier to keep reactive salts free from contamination. The reproducibility of the results is about as good as that which is generally obtained with the conventional capillary technique (except when the experimental conditions favour that technique^{2,5}).

An alternative method for self-diffusion studies, the paper strip technique, is investigated in paper V. This method is found to be reliable in general but it has certain drawbacks which make it less suitable in many cases. The self-diffusion coefficient of the cation in molten AgNO_3 (measured with this technique) is given in the paper (D_0 and Q also in Table 1).

Problems involving exchange of ions between the glass apparatus and the melt are studied in paper IV. It is found that in techniques where a large glass surface is exposed to a molten salt for a long time (i.e. the paper strip technique) certain precautions must be taken in order to avoid errors due to this exchange of ions. This source of error is negligible for the porous-frit technique due to the short diffusion times.

The diffusion coefficient of silver into Pyrex glass from an AgNO_3 melt is given in paper IV. D_0 and Q are also given in Table 1.

2. Interdiffusion measurements in molten salts

Apart from chronopotentiometric measurements in very dilute salt solutions (which are not considered here) very few interdiffusion studies in molten salts have been performed. This is due to the lack of a generally applicable (and reliable) experimental technique. Thus the gravimetric technique for diffusion measurements in aqueous solutions was developed into a method for interdiffusion measurements in molten salts (paper III). The principal experimental set-up is shown in Figure 2. A porous frit is filled with a salt mixture which is allowed to diffuse out into a large volume of salt with another composition. The change in buoyancy of the frit as a function of time is a measure of the interdiffusion coefficient.

The only previously available interdiffusion technique for molten salts is the constant mass diffusion cell devised by STOKES for aqueous solutions and employed by LAITY and MILLER⁶ for salt melts. The two methods give reasonable agreement for interdiffusion in $\text{NaNO}_3\text{-AgNO}_3$ mixtures rich in NaNO_3 and the relative merits of these two techniques

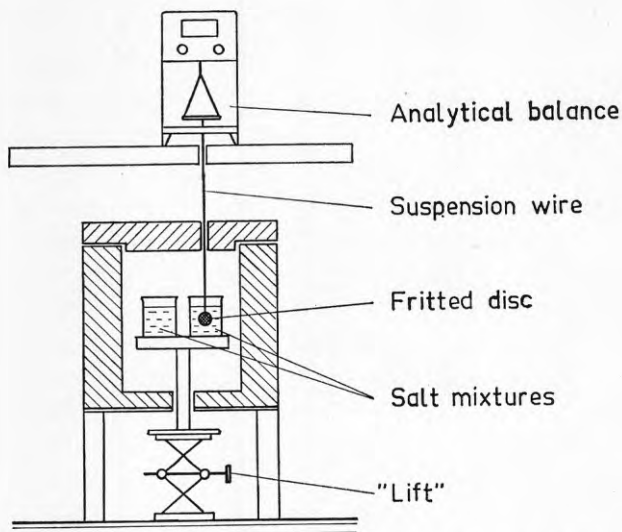


Fig. 2. Experimental set-up of the gravimetric technique for interdiffusion measurements in molten salts. (Not to scale, furnace windings not shown.)

are discussed in paper III. The applicability of the constant mass cell is restricted by the method of determining concentration differences which is done by measurements of electromotive force. No such limitations exist for the gravimetric technique.

The gravimetric interdiffusion technique was also used to measure the concentration dependence of the interdiffusion coefficient in molten $\text{KNO}_3\text{-AgNO}_3$ in the range 50–75 mole% AgNO_3 .

The gravimetric technique is the only generally applicable experimental method available at present. It is, however, restricted to temperatures below 600°C due to the use of Pyrex glass in the experimental cells but this restriction could be easily circumvented by substituting a more heat-resistant material such as quartz. In the paper III version the frits are calibrated by allowing 1 M KCl solution to diffuse out into distilled water. The weight recording technique is now improved, allowing 0.5 M KCl solution to be used inside the frit and 0.075 M KCl solution outside. (D varies much less with concentration in the latter range, giving a more accurate calibration.)

3. External transport numbers in pure molten salts

The transport number of an ion in a salt is defined as the fraction of the total electrical current that is carried by this ion during electrolysis. Since in a pure molten salt there exists no natural reference frame in which the velocities of the individual ions can be measured it is necessary to choose an external reference such as the porous partition between the two compartments in a transport number cell. Thus the observed transport numbers are called "external transport numbers".

Measurements of transport numbers in pure molten salts are described in papers VI and VIII. An attempt to change the electrical double-layer between the porous glass plug (the velocity reference) and the melt is made in paper VI. A more comprehensive study of this problem will be published later⁷ but a short review of the obtained results will be given here.

The general features of the experimental cell are shown in Figure 3 and a detailed description is given in paper VIII. Molten lead electrodes

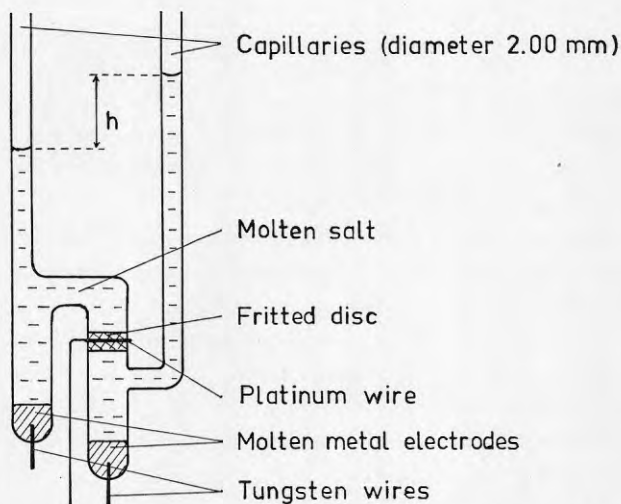


Fig. 3. Cell for external transport number measurements in (pure) molten salts. The level difference h is measured with a cathetometer. In the "double layer effect" studies an electrical potential is applied to the platinum wire with respect to one of the electrodes (the anode). A more detailed drawing of a cell is given in paper VIII.

were used in the lead salt (PbCl_2 and PbBr_2) experiments. Fritted Pyrex glass discs with a diameter of about 10 mm (CORNING GLASS WORKS, Corning, N.Y.) served as the partition between the electrode compartments. The temperature dependence of the transport numbers could be determined due to the improved precision of these experiments (as compared to previous work on these salts):

For PbCl_2 (69 runs)

$$t_+ = 0.239 + (3.37 \pm 1.05)(T_c - 565) \times 10^{-4} \quad (529-610^\circ\text{C}) \quad (2)$$

For PbBr_2 (46 runs)

$$t_+ = 0.390 - (2.64 \pm 0.77)(T_c - 370) \times 10^{-4} \quad (446-551^\circ\text{C}) \quad (3)$$

where T_c is expressed in degrees Centigrade. The stated errors are standard deviations and the standard error of estimate in Eq. (2) is 0.024 and in Eq. (3) it is 0.020. Pyrex frits grade UF (pore diameters 0.9–1.4 microns) were used and the results are in very good agreement with previous values^{8, 9}.

Instead using a Pyrex glass frit grade F (pore diameters 4.0–5.5 microns) one obtains for PbCl_2 at 565°C (22 runs)

$$t_+ = 0.248 \pm 0.018 \quad (\text{standard error of estimate})$$

The results using UF and F grade frits are thus in excellent agreement despite the fact that the glass-salt interface is about 25 times larger for the UF frit. It is seen that the area of this interface does not affect the observed external transport number. Neither is the postulated critical (minimum) size of the pores reached even for the UF frit (there is, however, no reason to expect any effect of this kind at least until the pores are so small that a large fraction of the salt inside the frit is in the double-layer).

It is well known that the observed external transport number is a property of the composite system molten salt—frit wall. Thus different plug materials should give different external transport numbers. A weak effect of this kind has been observed¹⁰. The effect should be more pronounced if the difference between the used frit materials were greater and thus a frit of boron nitride (mean pore diameter 3.3 microns) was used. The result for PbCl_2 (32 runs):

$$t_+ = 0.150 + (9.30 \pm 7.37)(T_c - 565) \times 10^{-4} \quad (560-596^\circ\text{C}) \quad (4)$$

with a standard error of estimate of 0.062. The spread in the data in this case is greater since the electrolysis current had to be kept low (5–10 mA) in order to avoid excessive heating of the frit (the true frit temperature was of course calculated as described in paper VIII). Nevertheless a pronounced difference in the observed transport number is noted which corresponds to the change in frit material from Pyrex glass to boron nitride.

Another support for the view that the value of the external transport number is determined in the electrical double-layer between the melt and the frit wall is given by the results in paper VI. Similar studies have been carried out in PbBr_2 too, and the temperature dependence of the observed effect was studied between 461 and 551°C. The result is given in Table 2 and Figure 4. As a comparison the PbCl_2 results from

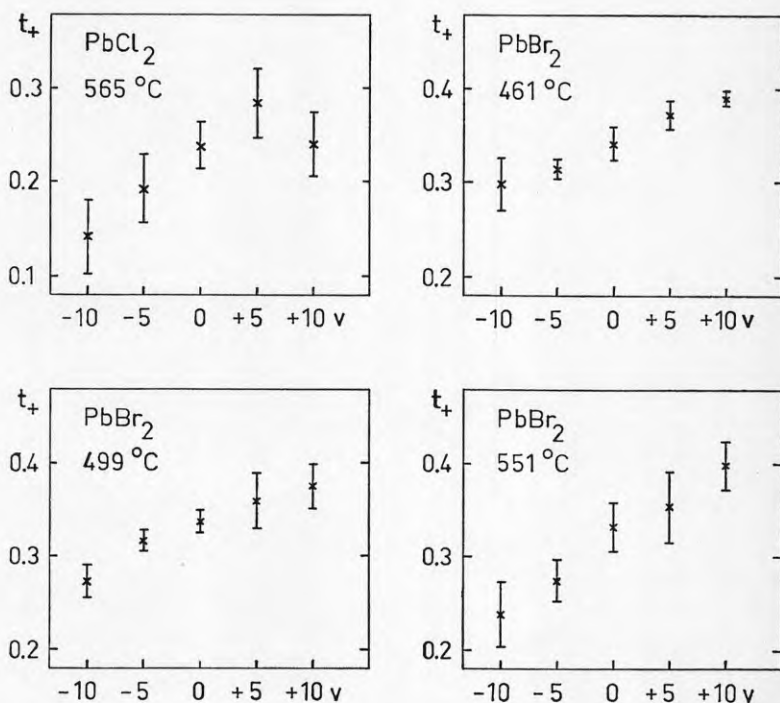


Fig. 4. Double-layer effect on the external transport number t_+ of the cation in molten lead chloride and lead bromide. The stated errors are standard deviations.

Table 2. Double-layer effect on the external transport number t_+ of the cation in molten lead chloride and lead bromide (126 runs). An electrical potential (-10 to +10 volts relative to the anode) is applied to a platinum wire wrapped around the edge of the fritted disc. The stated errors are standard deviations.

Salt	Temp. (°C)	External transport number t_+				
		-10 V	-5 V	Applied potential 0 V	+5 V	+10 V
PbCl ₂	565	0.142 ± 0.040	0.192 ± 0.037	0.238 ± 0.025	0.284 ± 0.037	0.240 ± 0.034
	461	0.298 ± 0.028	0.314 ± 0.010	0.341 ± 0.018	0.372 ± 0.015	0.391 ± 0.007
PbBr ₂	499	0.273 ± 0.018	0.317 ± 0.011	0.337 ± 0.012	0.359 ± 0.030	0.375 ± 0.024
	551	0.238 ± 0.035	0.275 ± 0.022	0.332 ± 0.026	0.354 ± 0.038	0.399 ± 0.026

paper VI are also included. For both PbCl₂ and PbBr₂ t_+ is found to increase when a positive potential relative to one of the lead electrodes (the anode) is applied to a platinum wire wrapped around the outer edge of the frit (and to decrease when a negative potential is applied). The voltage drop across the cell due to the electrolysis current is about 1 volt. The anomaly for PbCl₂ at +10 volts is not found for PbBr₂. The effect of the applied potential is more pronounced at higher temperatures but it is still significant at 461°C. More studies of this kind are needed to see if the double-layer effect can be found in other salts. It is, however, likely that the double-layer effect will become insignificant at lower temperatures since the properties of the frit material (Pyrex glass) are involved.

In paper VIII the external transport numbers of pure ZnBr₂ are measured using a Pyrex glass plug (J. A. JOBLING & Co. Ltd., Por 5, pore diameters between 0.9 and 1.4 microns) as velocity reference. As above, the results are least squares fitted into the equation¹¹ (46 runs)

$$t_+ = 0.791 - (3.68 \pm 0.59)(T_c - 394) \times 10^{-4} \quad (469-562^\circ\text{C}) \quad (5)$$

having a standard error of estimate of 0.004.

A correlation equation suggested by LAITY¹² between external transport number, self-diffusion coefficients, and equivalent conductivity (Λ) is also studied in paper VIII:

$$t_+ = \frac{1}{2}(\Lambda/F^2 + z_+ D_+/RT - z_- D_-/RT)/(\Lambda/F^2) \quad (6)$$

where z_+ and z_- are the valencies of the ions in the salt. This equation is found to be able to predict the external transport numbers of all studied monovalent salts and also some divalent salts with remarkable accuracy. On the other hand, the calculated transport number disagrees with the observed value for PbCl_2 , PbBr_2 , and (paper X) ZnCl_2 .

4. A comparison between diffusion theories and observed self-diffusion data

The study covers (paper XI):

- a) The hole model developed by FÜRTH¹³.
- b) The free volume model by COHEN and TURNBULL (and its more recent ADAM-GIBBS version)¹⁴.
- c) The local density fluctuation models (three versions by SWALIN, REYNIK, and NACHTRIEB)¹⁵.
- d) The cubic cell model by HOUGHTON (and a theory by WALLS and UPTHEGROVE leading to essentially the same theoretical equation)¹⁶.

The abilities of the theoretically derived equations to describe the observed data are compared to that of the ordinary ARRHENIUS equation (1) which can be derived from the rate-theory approach by EYRING *et al.*¹⁷. The result of the comparison can be summarized as follows: The ARRHENIUS equation describes the experimental data as well as, or better than, the other equations. The hole model leads to an equation of the ARRHENIUS type but the prediction $Q=3.74 RT_m$ (T_m =the melting point in °K) is in general inaccurate. The equations derived from the free volume model and the local density fluctuation models describe the data less well than the other equations. The cubic cell model gives a correct correlation between self-diffusion and kinematic viscosity for several (but not all) salts.

Acknowledgements

The work presented in this thesis has been performed at the Physics Department, Chalmers University of Technology, Gothenburg, and at Wright Laboratory, Rutgers the State University, New Brunswick, New Jersey.

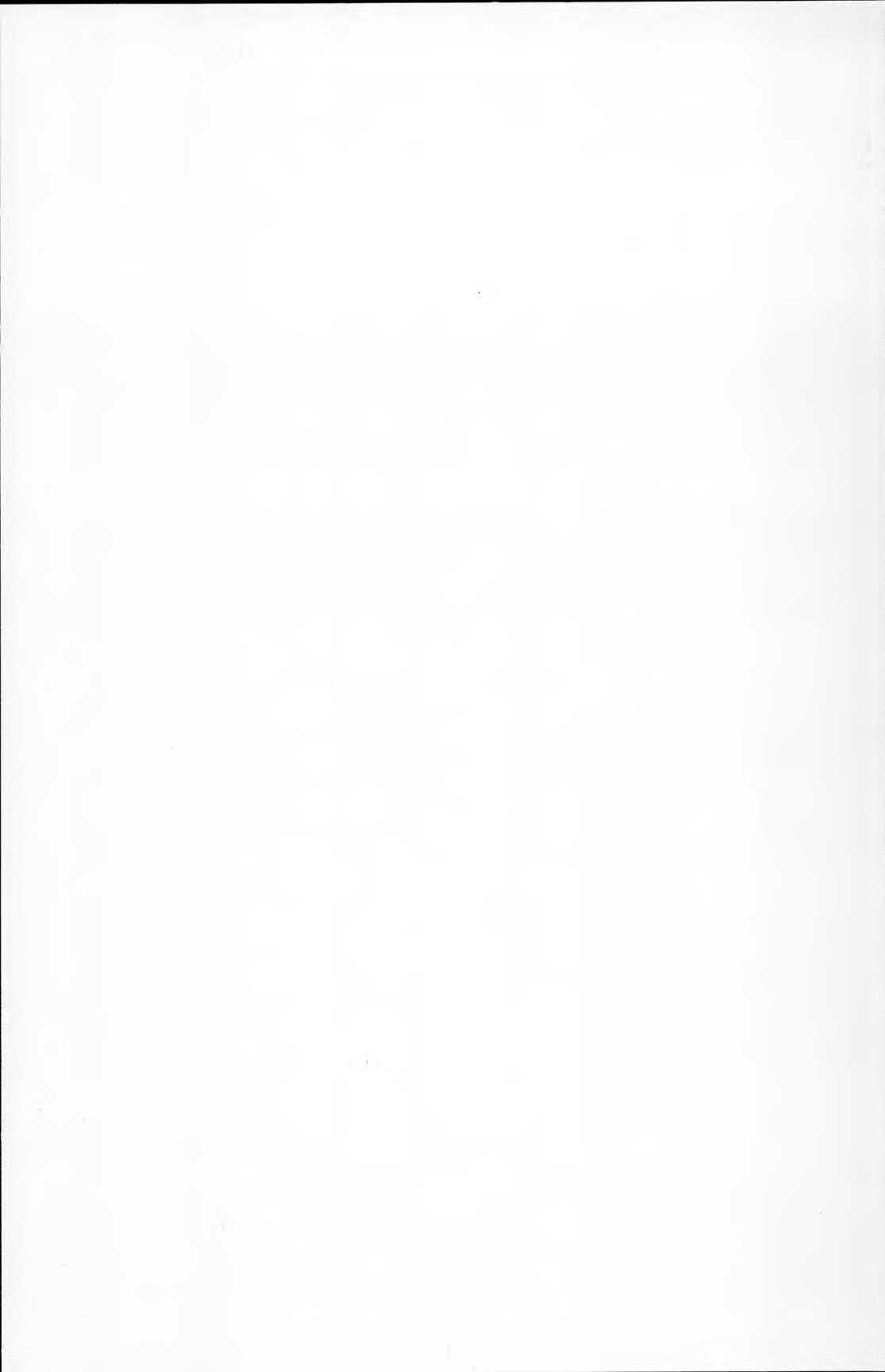
I wish to express my sincere gratitude to Dr. ARNOLD LUNDÉN for his continuing interest and valuable discussions during the course of this work. I am also grateful to Professor RICHARD W. LAITY for his hospitality and his valuable advice during my work at Rutgers University. Thanks are also due to my co-authors Fil. mag. JERRY ANDERSSON and Mr. ANDERS BEHN.

The work has been financially supported by Wilhelm och Martina Lundgrens Vetenskapsfond, Hierta-Retzius fond för vetenskaplig forskning, Göteborgs Universitets fond för främjande av ograduerade forskares vetenskapliga verksamhet, Magnus Bergwalls Stiftelse, Adlerbertska Forskningsfonden, Chalmerska Forskningsfonden, The Sweden-America Foundation, The U.S. Atomic Energy Commission, Statens Naturvetenskapliga Forskningsråd, and Åke Wibergs Stiftelse.

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