

5-1961

## Ion mobilities in fused salts

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## Ion mobilities in fused salts

### **Abstract**

The transport numbers of the chloride ion in the pure molten alkaline earth chlorides have been determined. A modified Stokes' law was applied to the motion of the individual ions. Application of the assumptions made in invoking this law gave a qualitative estimate as to the degree of association in  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{PbCl}_2$ . Several trends were observed which were consistent with the chemical properties of the salts studied.

### **Disciplines**

Chemistry



Physical Sciences Reading Room

IS-344

## ION MOBILITIES IN FUSED SALTS

By  
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F. R. Duke

May 1961

Ames Laboratory  
Iowa State University  
Ames, Iowa

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Work performed under Contract No. W-7405-eng-82.

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IS-344

CHEMISTRY

ION MOBILITIES IN FUSED SALTS

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May, 1961

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## ION MOBILITIES IN FUSED SALTS\*

by

Edward Dean Wolf and F.R.Duke

## ABSTRACT

The transport numbers of the chloride ion in the pure molten alkaline earth chlorides have been determined. A modified Stokes' law was applied to the motion of the individual ions. Application of the assumptions made in invoking this law gave a qualitative estimate as to the degree of association in  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$ ,  $BaCl_2$ ,  $ZnCl_2$ , and  $PbCl_2$ . Several trends were observed which were consistent with the chemical properties of the salts studied.

Because no suitable radioactive metal isotopes were available, tracer studies on metal transport were not included. Stable isotopes could be used in conjunction with a mass spectrometer to determine isotopic transport.

The temperature increase due to the passage of current within the membrane was found to be extreme in some cases. Previous transport number determinations in Pyrex cells at high temperatures and high amperage were placed in question.

An additional "tracer" experiment using a foreign univalent cation was proposed, in principle, for following the  $MCl^+$  ion.

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\*This report is based on a Ph.D. thesis by Edward Dean Wolf, submitted May, 1961, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

## INTRODUCTION

Chemical investigations of fused salts attracted much attention in the early 1920's. Early studies were especially concerned with electrical conductance, melting point, density, viscosity, and surface tension of pure salts. Many phase diagram determinations and electrode potential studies were included, particularly as they applied to the winning of metals from their ores. Interest then seemed to wane in the late 1920's and 1930's.

In recent years the demands of modern high temperature technology have caused a resurgence of interest in these and numerous other studies in cryometry, spectroscopy, X-ray diffraction, solubility, and electromotive force of fused salts. Some excellent reviews and bibliographies of these studies have been compiled (1, 2, 3). The structural, kinetic, and thermodynamic properties of interest in these studies must be explained and elucidated further in order to establish a sound theoretical basis for molten salts.

The study of highly dissociated liquids, such as fused salts afford, should lend understanding to the properties of highly concentrated electrolytes in aqueous solutions. The broader aspects of liquids have been treated by Frenkel (4), Born and Green (5), and by Debye and Hückel (6) for certain limiting cases.

The present study has been limited to molten inorganic

salts; i.e., four of the alkaline earth chlorides, in which the structural units are wholly or predominately ionic, as distinct from slags and silicates which may be considered as macromolecules and highly polymerized forms of molten salts. The scope has been further limited to the experimental determination and discussion of the transport of ionic species under the influence of an electric field. The purpose of the study was to experimentally determine properly defined transport numbers and then infer certain structural properties of the respective melts.

Laity (7) reviewed the relevant transport studies prior to his bubble-cell experiments. Methods using electrode displacement (8), capillary rise (9), moving boundary (10), and radioactive tracer techniques (11, 12, 13, 14, 15) have since been reported.

To summarize the salient facts concerning the above experiments, it has been found that no simple relationships of masses, radii, or Coulombic interactions describe the results. No temperature dependence for the transport numbers of ions has been observed for divalent salt melts in which dissociation might be expected to change the relative concentrations of the ionic species. In the particular case of  $ZnCl_2$  for which several sources of information (16, 17, 18) indicate association in the melt, Lundén (15) found no temperature dependence for the amount of activity transported

through the membrane. An explanation may be that only the first dissociation step (i.e.,  $\text{ZnCl}_2 \rightleftharpoons \text{ZnCl}^+ + \text{Cl}^-$ ) was predominant in the temperature range studied.

To parallel the experiments, several theories of ionic conduction have been proposed. However divergent the views, with the camouflage of semantics removed and with more data relevant to the proposed theories forthcoming, a unified approach must surely result.

There is a certain conceptual difficulty in applying the conventional definition for transport numbers used in aqueous solutions to a pure molten salt; the convenient solvent to which movement is generally referred is absent. Misconceived ideas can lead to experiments in which only the electrochemical equivalent of an element is redetermined. For example, an apparent transport number of unity may be found for an ion if the electrodes are reversible to that ion and if the transport measurements are made using the electrodes as the reference frame.

Kortüm and Bockris, (19, p. 210) using the same reasoning as Schwarz, (20) concluded that the definition of separate cationic and anionic mobilities is meaningless for simple pure salts since the ions cannot move independently. More recently, Bockris et al. (21) determined the self-diffusion coefficients for the individual ion in pure NaCl using isotopic tracers. Esin et al. (22) pointed out in a brief review

of the meaning of transport numbers for one component systems of fused electrolytes, that at present there is no sufficient basis to consider it impossible in principle to measure the transport numbers for pure one-component molten salts.

Duke and Laity (23) defined the transport number of an ionic species in a pure fused salt as the fraction of current carried by the ions of that species which are moving, measured with respect to the large group of ions of all species present which are at rest relative to each other. This definition is based on absolute rate theory in which only a small fraction of the ions move and in which a certain free energy of activation is required in order to move from one equilibrium position to another.

This definition becomes operationally meaningful in an experiment in which the molten salt is separated by a porous nonconducting membrane (used to minimize viscous flow due to gravity), and the movement of ions is measured through the membrane. The critical factor in this type of experiment is to ascertain that the ionic species do indeed move through the membrane in the same mechanistic way as they move in the bulk under the applied electric field. Since the pore diameters are many thousands times larger than atomic dimensions this assumption appears justified. Furthermore, the independence of transport numbers on membrane composition has been verified experimentally (7, 24).

An electrokinetic phenomenon that is relevant to this discussion is electro-osmosis. This phenomenon results when one of the ions is preferentially adsorbed, either by chemisorption or by physical adsorption, by the wall of the capillary leaving the bulk of the salt in the capillary to assume a net charge of opposite sign. Since the salt is in an electric field a streaming of material in the direction of one of the electrodes occurs.

Preliminary studies by Klemm (25) indicated that the membrane composition had very little effect on the electro-osmosis observed for molten mercury. However, as pointed out by Lundén (15), it is interesting to note that no experiments in molten salts have yielded results in which transport by electro-osmosis contradicted the limits set by the expression,

$$-t_+ \leq t_{os} \leq t_-, \quad (1)$$

otherwise transport numbers of greater than unity would have resulted. It thus seems evident that electro-osmosis is small and perhaps absent for transport experiments on fused salts using nonconducting membranes.

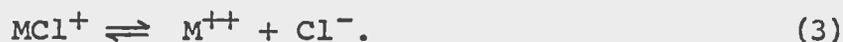
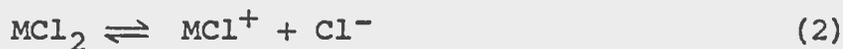
It is well established that momentum balance proposed by Sundheim (26) to explain ionic transport in fused salts is indeed a unique treatment, suitable only for lead chloride and perhaps the alkali nitrates. As interpreted by its proponents, this theory infers nothing about the electric properties of the melt. It should be noted that ion mass usually parallels

ion size so that no clear unambiguous relation is possible. However, this theory has been recently extended to include momentum transfer from the salt to the membrane, which when treated with the principles of hydrodynamics introduces important quantities called ionic viscosity or shear coefficients.

Laity (27) has recently presented a general formulation in which a single rate constant, called a friction coefficient, characterizes the results of conductivity, diffusion, and transference measurements. This formulation has its origin in the irreversible thermodynamics of mass transport by diffusion as put forward by Onsager (28). Quantitative verification of this useful description of mass transport awaits forthcoming experimental data (e.g., inter-diffusion coefficients in mixtures of molten salts).

Klemm (29) has proposed a method for determining a ratio,  $t_+/t_-$ , in which the quantities represented may or may not be the true transport numbers of the salt depending on the non-interaction or interaction respectively of the salt with the membrane.

For most uni-univalent molten salts, complete dissociation is generally assumed. However, for divalent salts, incomplete dissociation (or association) may result. Consider the possible reactions of the alkaline earth chlorides, represented by  $MCl_2$ , in the molten state:



There are three species,  $\text{M}^{++}$ ,  $\text{Cl}^-$ , and  $\text{MCl}^+$  to which transport numbers  $t_{++}$ ,  $t_-$ , and  $t_+$  can be assigned. In principle there are three experiments that can be carried out using radioactive tracers to determine all three ascribed transport numbers.

- I.) Radioactive M initially in anolyte migrates through membrane as  $\text{M}^{++}$  or  $\text{MCl}^+$  to give  $t_{++} + t_+$ .
- II.) Radioactive Cl initially in catholyte migrates through membrane as  $\text{Cl}^-$  to give  $t_-$ .
- III.) Radioactive Cl initially in anolyte migrates through membrane as  $\text{MCl}^+$  to give  $t_+$ .

In order to establish a relationship between the transport numbers defined in molten alkaline earth chlorides and the amount of activity transported during an experiment, consider the following: Assume for the present time that only the species  $\text{M}^{++}$  and  $\text{Cl}^-$  are in the melt. Let Z faradays of charge pass through the cell. Let m equal the equivalents of  $\text{Cl}^-$  ions which pass through the membrane. By definition  $t_-Z$  equivalents of chloride ions move through the membrane into the anode compartment. This assumes that only current carrying ions move through the membrane. This is realized experimentally by reducing diffusion and eliminating hydrostatically

induced viscous flow. Let the catholyte originally contain  $(Cl^*)_c^0$  equivalents of radioactive  $Cl^-$  ions and a total number of equivalents of  $Cl^-$  ions  $(Cl)_c^0$ , and after electrolysis suppose  $(Cl^*)_a$  equivalents of radioactive  $Cl^-$  ions are found in the anolyte. Then

$$m = t_- Z = [(Cl^*)_a / (Cl^*)_c^0] (Cl)_c^0 = [(Cl^*)_a / (Cl^*)_c] (Cl)_c. \quad (4)$$

Now, since isotopic effects are small for this mass range, it can be assumed that the  $Cl^{36}$  ion moves the same as the normal mixture of  $Cl^{35}$  and  $Cl^{37}$  ions through the membrane. In this case the ratio,  $Cl^*/Cl$ , in the catholyte will remain the same, and the third equality in Equation 4 follows.

If the specific activities,  $C_a$  and  $C_c$  (counts  $\text{min}^{-1}$  milligram $^{-1}$ ), of the anolyte and catholyte are determined at the end of the experiment, then

$$(Cl^*)_a = K_a C_a W_a \quad (5)$$

$$(Cl^*)_c = K_c C_c W_c \quad (6)$$

where  $W_a$  and  $W_c$  are the total sample weights of the anolyte and catholyte salts. The proportionally constants  $K_a$  and  $K_c$  become equal when all samples are counted using the same geometry and corrections. And finally  $(Cl)_c = W_c/M$  where  $M$  is the equivalent weight of the salt. The resulting expression becomes

$$t_- = m/Z = (1/Z) (C_a/C_c) (W_a/M). \quad (7)$$

An independent calculation can establish the relationship

$$t_- = 1/2 + (1/2Z) (C_a/C_c) (W_a/M) \quad (8)$$

if the assumed species are  $MCl^+$  and  $Cl^-$  ions only. However, to show this conversion without recourse to a discussion of the previous type, consider the following:

$$m/Z = (t_-)^a - (t_+)^a \quad (9)$$

where  $a$  denotes complete association. This follows because now chloride is transported by two ions. The net transport is the only measurable quantity because of the assumed rapid exchange between the two species (i.e.,  $MCl^+ \rightleftharpoons M^{++} + Cl^-$ ).

But

$$(t_+)^a + (t_-)^a = 1. \quad (10)$$

Therefore,

$$m/Z = 2(t_-)^a - 1 \quad (11)$$

or

$$(t_-)^a = (1 + m/Z)/2 = 1/2 + (1/2Z) (C_a/C_c) (W_a/M). \quad (12)$$

A closely related electrochemical quantity is the equivalent ionic conductivity,  $\lambda_i$ , defined by

$$\lambda_i = t_i \Lambda \quad (13)$$

where  $\Lambda$  is the total equivalent conductivity of the salt.

Obviously  $\sum_i \lambda_i = \Lambda$  since  $\sum_i t_i = 1$ . Another important rela-

tionship is that of the equivalent ionic conductivity to the velocity of the ion,

$$\mu_i = \lambda_i/F = t_i \Lambda /F \quad (14)$$

where  $\mu_i$  is the ionic mobility of the ion,  $i$ , measured in

units of  $\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}$ , and  $F$  is Faraday's constant. Equations 13 and 14 invoke the assumption of complete ionization. The equations, as they appear, can only apply to the two assumed cases (i.e., either only  $M^{++}$  and  $\text{Cl}^-$  or only  $\text{MCl}^+$  and  $\text{Cl}^-$  ions) for the alkaline earth chlorides.

## EXPERIMENTAL

## Materials

The hydrated alkaline earth chlorides were all recrystallized using "Baker Analyzed" reagent grade chemicals. The ammonium hydroxide and silver nitrate used in the precipitation of silver chloride were also "Baker Analyzed" reagent grade. Ethyl silicate received from the Anderson Chemical Company, Weston, Michigan, was greater than 99% pure with metal impurities less than 1 ppm.

The radioactive isotope, chlorine 36 (P), with a half-life of  $4.4 \times 10^5$  y and  $\beta^-$  decay energy of 0.714 Mev was obtained from the Oak Ridge National Laboratory as a hydrochloric acid solution.

Spectroscopic graphite rods 0.120 inch in diameter and 12 inches in length made by National Carbon Company were used as electrodes in all experiments.

Preparation of anhydrous magnesium chloride

Several methods were considered for the preparation of anhydrous magnesium chloride (30, 31, 32). The vacuum filtration method (30) was viewed critically from the point of view of oxide solubility in the molten magnesium chloride. Even with negligible solubility the filtration step seemed cumbersome when compared with vacuum distillation. The

reaction of excess metal with silver chloride, used by Lundén (15) in preparing pure zinc chloride, was feasible when translated over to the preparation at hand. The end-products could have been separated by repeated fractional distillations, but the situation was complicated by the very similar volatilities of magnesium and magnesium chloride.

Any suitable method must be equally applicable to the preparation of magnesium chloride containing tracer amounts of  $\text{Cl}^{36}$ . Procedures in which appreciable exchange reactions were expected or preparations using large volumes of gases which were likely to become contaminated were eliminated. In order to use the aqueous  $\text{HCl}^{36}$  tracer directly a method was sought wherein the hydrated chloride would be the starting material. However, preliminary studies indicated some hydrolysis during vacuum or inert atmospheric dehydration of the hydrated chloride.

It was observed during the experiments with the heavier alkaline earth chlorides that hydrolysis never occurred in the anode compartment while some "hydrolysis" apparently took place in the cathode compartment.\* Since chlorine gas was an electrolysis product at the anode, this suggested that perhaps

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\* The apparent "hydrolysis" product was shown to be the hydroxide which resulted from the decomposition of the metal carbide when the catholyte salt was dissolved in water.

the reaction,  $2MO_{(s)} + Cl_{2(g)} \rightleftharpoons O_{2(g)} + 2MCl_{2(l)}$  where M represents the alkaline earth metal, lay far to the right at temperatures above the melting point of the chloride. This was further evidenced in an industrial preparation of magnesium chloride (31) and also in the preparation of anhydrous lithium chloride in LiCl-KCl eutectic melts (33). In the latter case small amounts of lithium hydroxide, rather than the oxide, were removed by sweeping dry chlorine gas through the melt. The reaction proposed was  $2OH^{-}(l) + 2Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + 2Cl^{-}(l) + O_{2(g)}$ .

Several attempts were made to prepare anhydrous magnesium chloride by dehydrating the hydrate under vacuum, and then dry chlorine gas was purged through the resultant slurry of magnesium chloride and oxide above the melting point of pure magnesium chloride. No visible improvement was observed even when the chlorine gas was bubbled through the melt for approximately one hour. One reason for the apparent failure of this procedure may be that the reaction was extremely slow as was observed by Maricle and Hume (33) for the reaction of chlorine with the hydroxide ion in fused LiCl-KCl eutectic. They found that the effectiveness of the chlorine diminished greatly as the temperature was increased from 450° to 740°C. They proposed the formation of a poor oxidizing chlorine species due to the red-brown coloration of the solution. At any rate, this method was not deemed satisfactory

for the preparation of pure anhydrous magnesium chloride and was abandoned in favor of a very convenient method.

During the attempted preparation just discussed, some distillate, presumably magnesium chloride, was observed to condense on the cooler portion of the Vycor tube several centimeters above the magnesium chloride and oxide mixture. At 778°C (melting point is 714°C (34)) magnesium chloride has a vapor pressure of one millimeter (35) and consequently should distill very rapidly under vacuum at this temperature. These observations led to a preparation in which the hexahydrate was dehydrated under vacuum by slowly increasing the temperature. Near 800°C the distillation of magnesium chloride away from the oxide was rapid. The distillate was transferred in the dry box and stored in vacuum. This procedure gave very pure anhydrous magnesium chloride (oxide impurity was approximately 0.3 mole per cent) with yields of about 75 per cent.

The radioactive anhydrous magnesium chloride was prepared similarly, except prior to the recrystallization of the hydrate a predetermined amount of  $\text{HCl}^{36}$  was added to the solution of magnesium chloride.\* Because of the hydrolysis

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\*In the later stages of this work, it was learned that both chlorine 36 gas and hydrogen chloride 36 gas were available with purities greater than 99%. Direct chlorination or hydrochlorination of magnesium metal would have been possible. However, a distillation step is often necessary in these procedures to eliminate oxide contamination.

during the procedure it was necessary to trap the radioactive hydrogen chloride gas by-product, along with the water from the dehydration, in a large cold trap cooled with liquid nitrogen. The hydrogen chloride was then transferred under vacuum to a more suitable container for disposal. Final disposal was attained by bubbling the gas through a concentrated solution of sodium hydroxide.

#### Preparation of calcium chloride hexahydrate

Calcium chloride hexahydrate was recrystallized from distilled water and dried in a vacuum dessicator charged with anhydrous magnesium perchlorate.

Calcium chloride hexahydrate containing tracer amounts of Cl 36 (P) was prepared in the same manner, except prior to the recrystallization a predetermined aliquot of HCl<sup>36</sup> (usually one microcurie/gram of salt) was added to the solution of calcium chloride.

#### Preparation of strontium chloride hexahydrate

The method of preparation was identical with that used for calcium chloride hexahydrate.

#### Preparation of barium chloride dihydrate

The method of preparation was identical with that used for calcium chloride hexahydrate.

### Purity of materials

Analyses by a vacuum fusion technique (36) gave an oxygen content of less than one mole per cent when computed as metal oxide for all four chlorides. Samples were taken directly from the prepared stock material of magnesium chloride for analysis. The three other chlorides were sampled for analysis after simulated experiments. Silica contamination and handling of the samples in air from cell holder to dry box and from argon purged container to vacuum fusion apparatus make this a maximum oxygen content for the latter three salts. Alkalinity tests on dissolved salt solutions after the experiments also indicated that the oxide and/or oxychloride content was very low. Furthermore, it was reasoned that oxide contamination would enter only as a weight error since it was doubtful if the oxide ion was sufficiently mobile to contribute appreciably to the total conductivity of the melt.

### Description of Apparatus

#### Cell

A typical cell used in all experiments is shown in Figure 1. These cells were constructed from 10 mm I.D. quartz tubes with sintered quartz membranes, porosity #4 (average pore size was 5 to 15 microns), 1.5 mm thick, sealed in the centers of the tubes. The sealing tubes were received from Engelhard

Industries, Inc., Amersil Quartz Division. However, in the latter part of this work the membranes were salvaged from previous experiments and new cells were constructed from 10 mm I.D. quartz tubing.

The porosity was reduced further by successively passing ethyl silicate and conc. hydrochloric acid through the membranes under suction from a water aspirator. The cells were then baked at 800°C in a sixteen-inch Marshall Tube Furnace. As many as a dozen or more treatments were often necessary to reduce the porosity to the point where viscous flow due to a hydrostatic head of one to two centimeters of salt was negligible. This was found experimentally to be the porosity required to restrain one milliliter of water from moving through the membrane under vacuum (approximately 20 mm) during a period of one to two hours. Cells made from previously used membranes often required no additional treatment.

#### Cell holder

The cell holder and auxiliary apparatus are also shown in Figure 1. The cell holder was made from 19/38 ground Vycor tapers. In order to form gas tight seals, the extended inner guide tubes were specifically selected 4 mm O.D. quartz tubing, which gave very close tolerance for the graphite electrodes. The support material was cut from fire brick and held together by a clamp. A squirrel cage electrical fan was used to cool

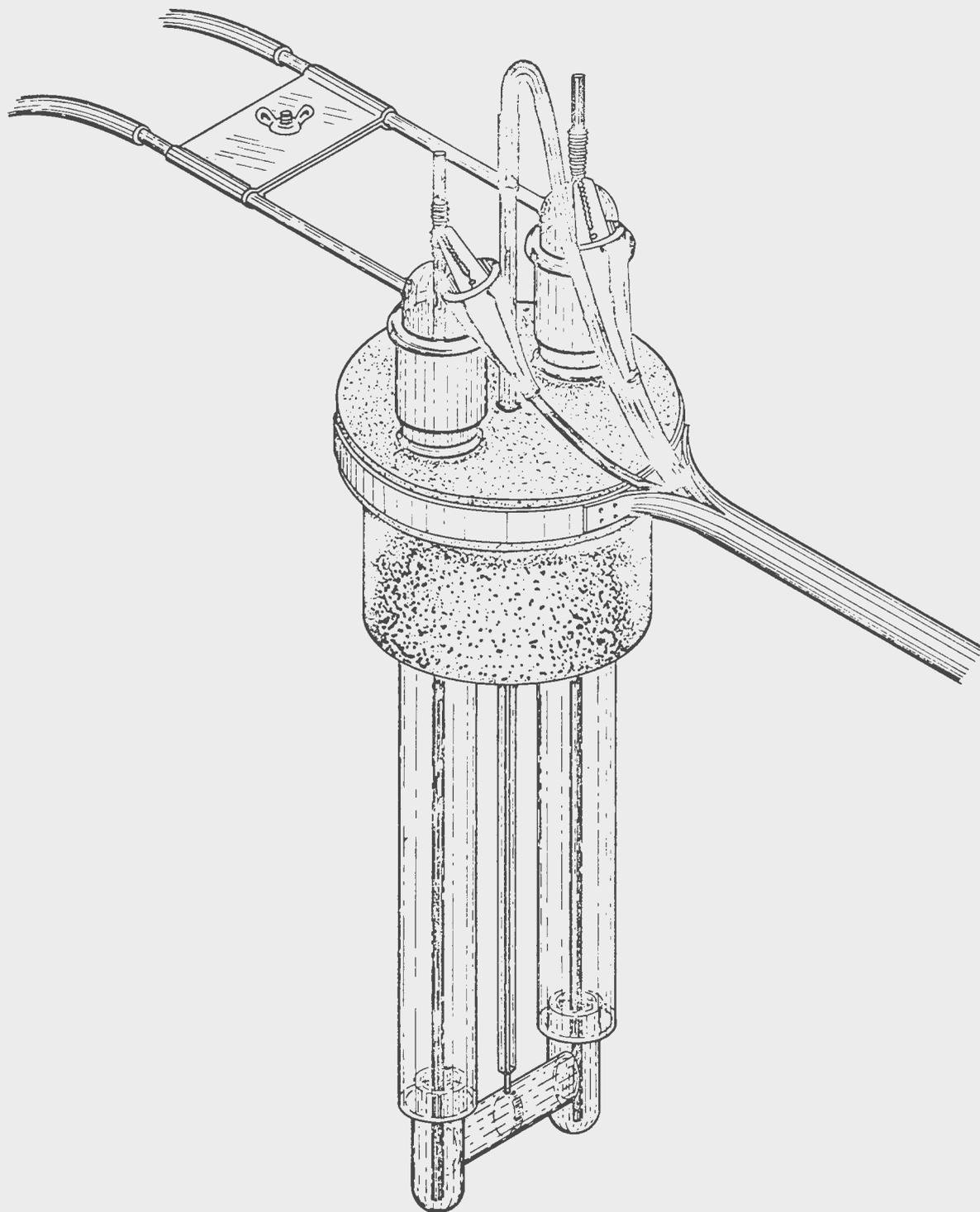


Figure 1. The cell holder and a typical cell used in the determination of transport numbers

the portion of the cell holder which extended from the furnace. The platinum, platinum and rhodium (13%) thermocouple was standardized at the melting point of pure silver (960.8°C). Only a few tenths of a degree discrepancy was observed. During an actual run, the thermocouple rested on top of the cell directly above the membrane. All potential readings were taken with a Rubicon Precision Potentiometer, Model 2745 (temperature compensated) made by Minneapolis-Honeywell Regulator Company. The cell was held in place by springs made from nichrome resistance wire (not shown in Figure 1).

#### Pyrometer

It was found that the thermocouple did not sense the rather drastic temperature changes that occurred within the membrane in some of the experiments. This temperature rise resulted from the dissipation of electrical energy in the form of heat due to the extremely high resistance of the membrane. The insensitive response of the thermocouple was most likely due to the poor radial thermal conductivity of the membrane. Thermal conduction to the salt was a more probable route for heat dissipation than to the outer surface of the cell where the thermocouple rested. In order to follow the temperature rise in the membrane, a Pyro Micro-Optical Pyrometer made by the Pyrometer Instrument Co., Bergenfield, New Jersey, was employed. The pyrometer was mounted directly above the fur-

nance. Readings were taken by focusing on the membrane through the thermocouple well. Corrections were made for those experiments determined prior to the use of the pyrometer. Figure 2 shows a typical temperature versus power correction curve. Such relationships were evaluated for all previous base temperatures used. In case of slight mechanistic changes in energy dissipation, the same salt was used in each of the temperature versus power curves as was used in each of the experiments corrected.

#### Furnace and controller

The furnace was constructed from a 3-inch alundum core, 18 inches in length, which was wound with nichrome wire. The alundum core was held in place by two transite end-pieces secured to a cylindrical galvanized sheet metal jacket. The intervening space (about  $3\frac{1}{2}$  inches) was filled with Dicolite, a powdered insulation for high temperature furnaces. To reduce radiation losses, the exterior of the furnace was wrapped with successive layers of asbestos paper, glass wool, and aluminum foil. A chromel-alumel thermocouple located near the center of the furnace sensitized a Bristol Series 536 Free-Vane electronic controller which controlled the power from a 230 volt Powerstat. The control thermocouple readings agreed very well with the measuring thermocouple situated in the cell holder which indicated a very small temperature gradient in

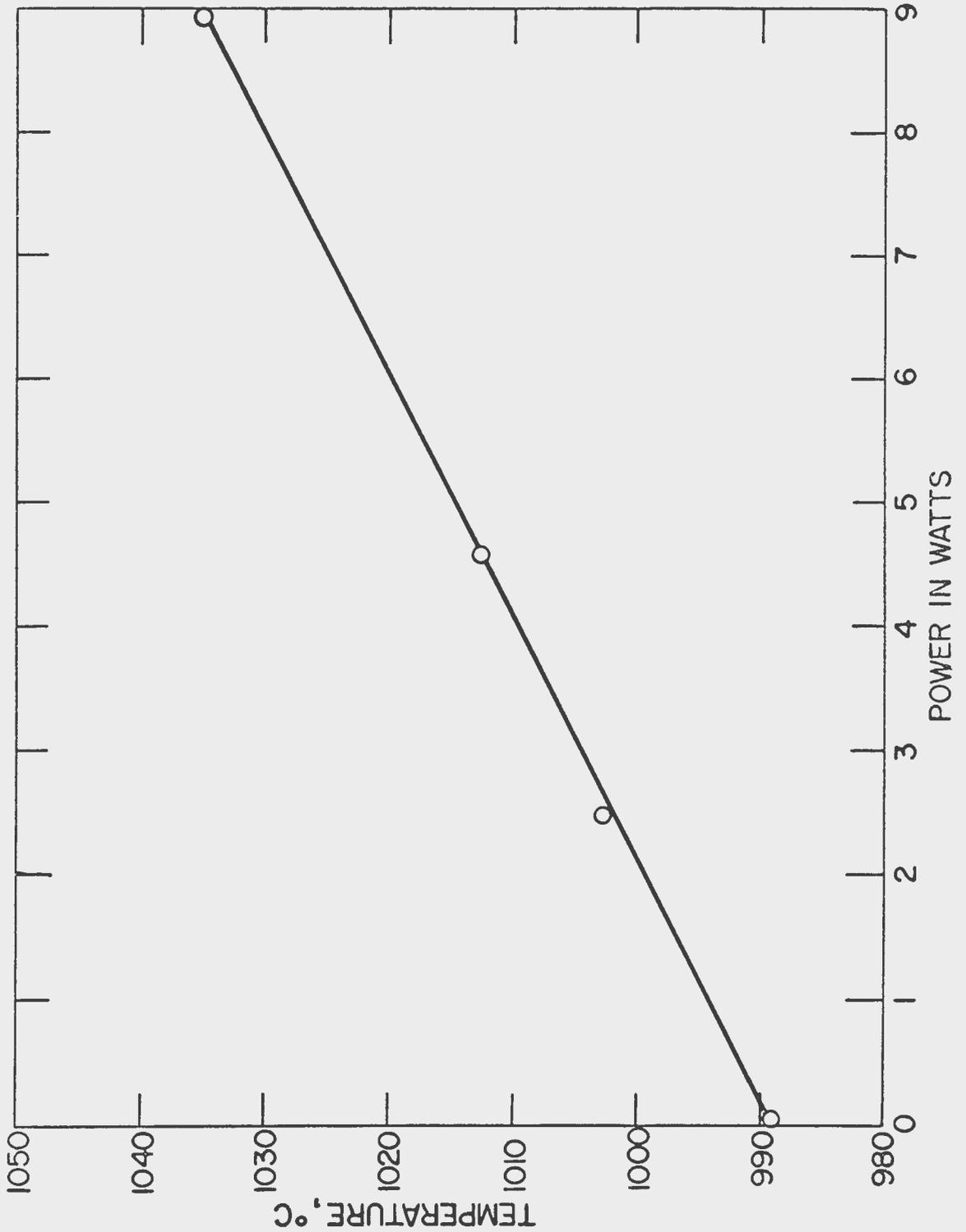


Figure 2. Temperature versus power correction curve for temperature rise in the quartz membrane of a cell containing calcium chloride

the vicinity of the cell. Operating temperatures of 1100°C were obtainable, but in most of the experiments the operating temperatures were appreciably lower. An 8 mm Vycor tube with small holes located along a one foot portion of it was situated in the furnace, so that gaseous electrolysis products could be removed from the furnace and bubbled through a sodium hydroxide solution before passing through a water aspirator. In operation, the furnace was set upright on fire bricks with the thermocouple leads, exit gas tube, and furnace power leads extending from the bottom of the furnace. A circular fire brick plug and Fiberfrax, a ceramic fibrous packing, placed in the bottom of the furnace helped to eliminate the "chimney" effect.

#### Direct current power supply

Preliminary studies were carried out using a Heathkit Model PS-3 variable voltage regulated power supply. In later experiments, a power supply with a full-wave selenium rectifier circuit combined with a pi-section filter circuit was used. This power supply was monitored on an oscilloscope to verify that the a.c. ripple was negligible. A d.c. ammeter was wired in series with a silver coulometer and the charge passed during electrolysis was determined by the amount of silver deposited. Generally, time-integrated readings of the ammeter agreed with the charge measured by the coulometer.

Dry box

A stainless steel dry box with electrical and gas inlets and an evacuable entry chamber was secured from P. M. Lennard Company, Inc. The box was mounted on a movable angle iron rack which supported the large Welsh vacuum pump, cold traps, and two gas cylinders. In order to regain atmospheric pressure inside the entry chamber with a dry inert gas, nitrogen gas was passed through two large copper cold traps filled with copper turnings prior to entering the chamber. The copper cold traps were immersed in Dry Ice and acetone mixtures. Argon was passed through a Dry Ice and acetone cold trap and a series of three anhydrous magnesium perchlorate drying towers before being admitted to the box. A small squirrel cage fan in the dry box circulated the argon through a column of Linde molecular sieves Type 4A. This absorbent was reactivated periodically by purging with air at 320°C. A Voland two pan analytical balance was stripped of its non-essential case and was used for weighing the anhydrous magnesium chloride samples inside the dry box.

Radioactivity analysis equipment

The  $\beta^-$  decay radiation was detected with a Tracerlab, Inc., TGC-1 end-window Geiger-Muller tube. The tube was mounted in a Model AL14A housing, Technical Associates. A

Model 181A Nuclear-Chicago Decade Scaler and a Model T1 Dual Timer were used in conjunction with the Geiger tube. Aluminum sample holders were constructed so that a uniform center portion of the sample was exposed to the Geiger tube when they were placed in a Lucite holder within the lead housing.

Standard methods were used for determining the plateau region and the operating voltage. Coincidence corrections were calculated from recovery times obtained by two different methods. The paired-source method (37, p. 290) was periodically checked by a simplified procedure.\* Figure 3 shows the experimentally determined self-absorption correction curve used to correct all samples to a common weight (150 mg).

#### Procedure

The cell was partially filled with inactive salt in the anode compartment and radioactive traced salt in the cathode compartment. Initial sample weights were obtained by difference. In all experiments with magnesium chloride, the weighing was done in the dry box followed by a rapid transfer to the cell holder. For the three heavier alkaline earth chlorides the hydrates were weighed in initially with the degree of hydration previously determined by EDTA titrations using magnesium-Eriochromschwartz T indicator.

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\* R. Reade. Ames Laboratory of the Atomic Energy Commission, Ames, Iowa. Information on determination of Geiger tube recovery times. Private communication. 1959.

The cell was attached to the cell holder and the entire assembly was placed in the furnace. Dry argon was passed through the system several minutes prior to and during each run. The temperature was increased slowly, particularly in the regions where the dehydrates decomposed. After the desired temperature was reached, the graphite electrodes were lowered into the melt and a measured d.c. current was passed through the cell. The electrolysis time varied from five hundred seconds to two thousand seconds depending on the amperage setting. Generally, a total charge of approximately one hundred coulombs was used. After the electrolysis the electrodes were lifted out of the melt and the cell removed from the furnace to cool. The dry argon flush was continued during the cooling process. The cell was then split carefully at the membrane so as not to contaminate the anolyte with the more radioactive catholyte salt. Both halves of the cell were dissolved in water. The anolyte weight was found by weighing the half-cell before and after the salt was dissolved. Corrections were made for absorption of salt by the graphite electrode.

In order to obtain a suitable precipitate for counting (i.e., one that deposited evenly and did not crack or curl on drying), the radiotraced chloride was precipitated from an ammoniacal solution with excess silver nitrate. Three samples from each anolyte and catholyte were precipitated and prepared

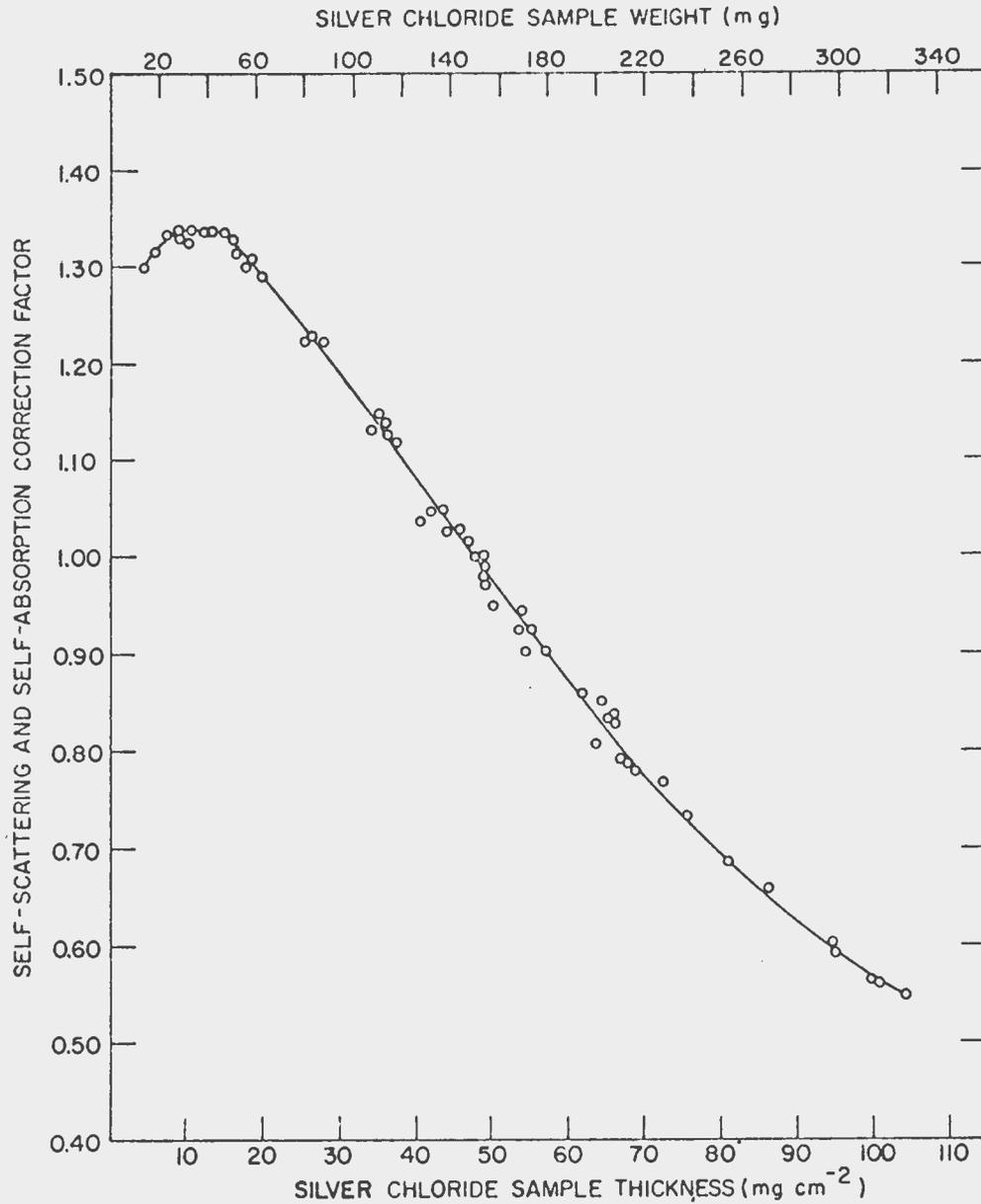


Figure 3. Self-absorption correction curve for silver chloride samples containing radioactive chlorine 36

for counting. The precipitates were washed thoroughly with water and acetone, dried, weighed, mounted on cards, and covered with cellophane. The procedure was modified slightly in the case of samples precipitated from magnesium chloride solutions. To prevent the formation of magnesium hydroxide the solutions were buffered with ammonium hydroxide and ammonium acetate at a pH of less than 10. The silver chloride precipitate was washed with dilute nitric acid prior to the water and acetone washings.

Standard coincidence, self-absorption, and background corrections were made and the specific activities of the samples (counts/milligram minute) were recorded.

## RESULTS

The quantity  $m/Z$ , where  $m = (C_a/C_c)(W_a/M)$  (see Equation 7 in the Introduction), was determined for the four alkaline earth chlorides,  $MgCl_2$ ,  $CaCl_2$ ,  $SrCl_2$ , and  $BaCl_2$ . The results are listed in Table 1 along with values obtained from the data of Lundén (15) for  $ZnCl_2$  and Laity (7) for  $PbCl_2$  ( $m/Z = t_-$  on a  $M^{++}$ ,  $Cl^-$  basis).

Since the experimental temperature range was from  $730^\circ C$  (dull red color) to  $1165^\circ C$  (bright white-orange color), fairly accurate temperature measurements ( $\pm 5^\circ C$ ) were possible with

Table 1. Net fraction of the charge transported by the chloride ion

Salt	Experiments	(m/Z)	$\delta(m/Z)^a$	Temperature range, $^\circ C$
$ZnCl_2^b$		0.27	$\pm 0.08$	435 to 673
$MgCl_2$	6	0.52	$\pm 0.04$	730 to 920
$CaCl_2$	29	0.58	$\pm 0.09$	780 to 1100
$SrCl_2$	19	0.74	$\pm 0.09$	880 to 1165
$BaCl_2$	15	0.77	$\pm 0.07$	960 to 1100
$PbCl_2^c$		0.76	$\pm 0.01$	565 to 635

<sup>a</sup>Standard deviation.

<sup>b</sup>Tracer method.

<sup>c</sup>Bubble-cell method.

the Micro-Optical pyrometer. To be consistent with the experimental definition of transport numbers in pure fused salts all conditions of the experiment must be referred to the membrane.

In a few rare instances, temperature rises of nearly 200°C in the membrane were observed with the pyrometer whereas only 20-40°C rises were registered by the platinum, platinum-rhodium (13%) thermocouple. For these cases, arcing was generally observed at a few "hot spots" in the membrane. The arcing was interpreted as dielectric breakdown of the air and salt vapor prior to the complete wetting of the membrane. Generally,  $m/Z$  results were low which was consistent with some transport of charge by electronic conduction. However, as indicated by Figure 2 in the Experimental section, the heating was for the most part moderate and uniform throughout the membrane with no arcing observed. Most of the runs were made using 50 to 200 milliamperes currents and the cell resistances usually varied from 100 to 1500 ohms. No dependence of  $m/Z$  with current density was observed.

It is not unreasonable to assume similar temperature rises in Pyrex membranes. Experiments in Pyrex cells using high amperages at temperatures near the softening point of Pyrex should be viewed with concern. Under extreme heating conditions, the fused Pyrex could act as an ion exchange medium exhibiting only cationic conduction.

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Previous investigators have been concerned with the temperature rise in the membrane, and in some cases attempts have been made to measure it. Lundén (15) wrapped a small platinum, platinum-rhodium (13%) thermocouple around the cell with the metal bead in contact with the outer wall near the membrane. However, for the most part, experimenters have measured the temperature using sheathed thermocouples in the proximity of the cell. For those cases where decomposition or a change in transport number with temperature did not occur, no serious problem resulted.

In the present work, no temperature dependence was found for  $m/Z$  for either  $BaCl_2$  or  $SrCl_2$ . For  $CaCl_2$  a slight increase in  $m/Z$  was found for increasing temperatures as shown in Figure 4. However, if the standard deviation ( $\pm 0.08$ ) of the least squares fit to the straight line is compared with the standard deviation ( $\pm 0.09$ ) of the averages irrespective of temperature, some doubt may exist for interpreting this as a trend. For  $MgCl_2$  no trend was found; however, if more runs were made at even higher temperatures, it is conceivable that an increase in  $m/Z$  with temperature might be found.

Diffusion and viscous flow due to gravity can play a major role in the experimental error of experiments of this type. If the membrane is prepared too fine, considerable heating takes place which will decrease the viscosity of the salt in the capillaries. If the membrane is too porous,

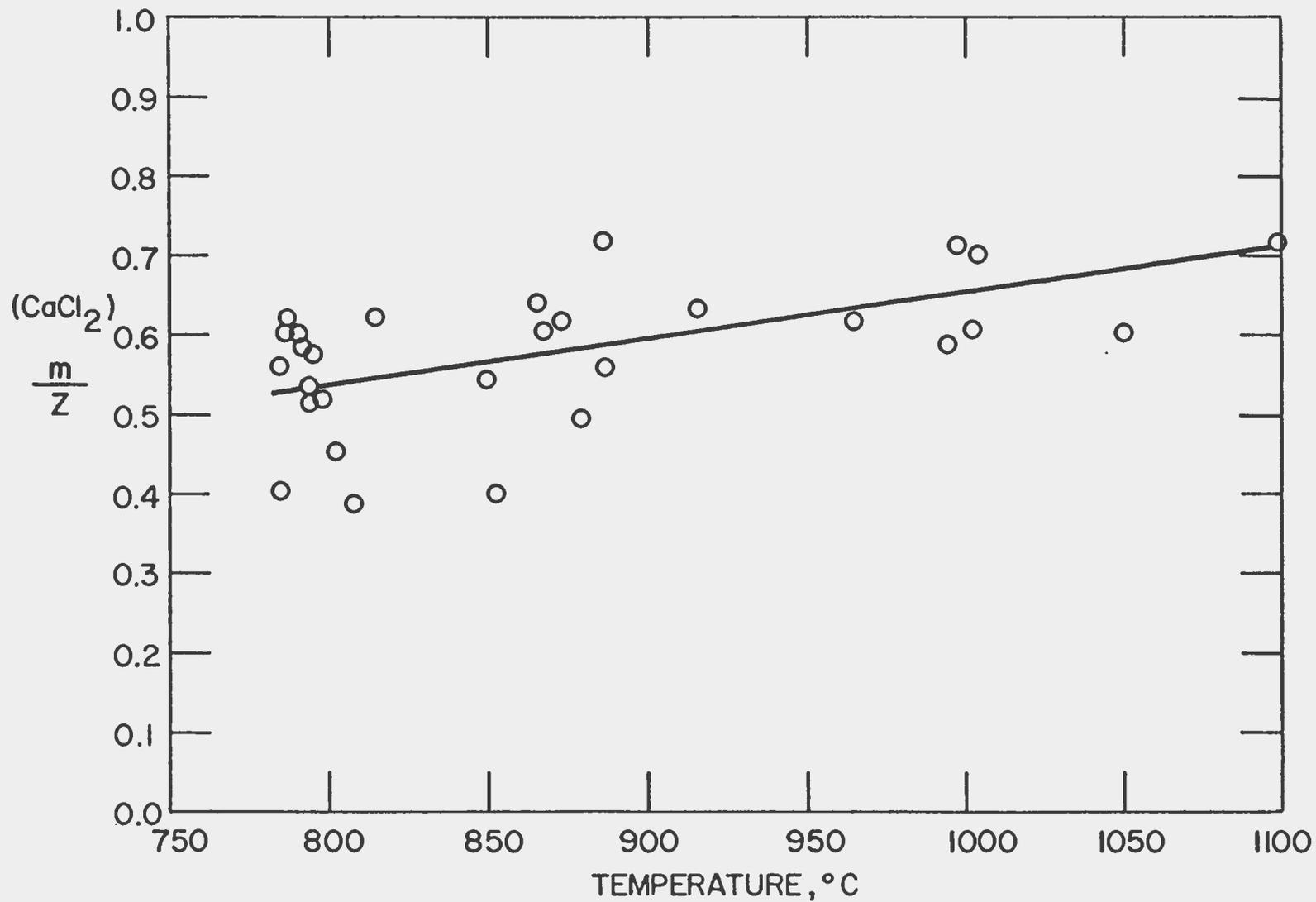


Figure 4.  $m/Z$  versus temperature for  $\text{CaCl}_2$

diffusion is appreciable. To reduce heating in the very fine membranes, very low current densities are necessary. This requires a longer period of time to transport a measurable quantity of  $\text{Cl}^-$  ions through the membrane. By extending the period of time, appreciable diffusion is likely to occur. Therefore, experimental conditions are adjusted to minimize the total error for all factors involved.

## DISCUSSION

If the definition of transport numbers in pure fused salts proposed by Duke and Laity, stated in the Introduction, is expressed mathematically for a multicomponent melt, then

$$t_i = \frac{I_i}{\sum_k I_k} \quad (15)$$

where  $t_i$  = transport number of component  $i$   
 $I_i$  = current carried by component  $i$   
 $\sum_k I_k$  = total current carried by all components.

Consider a one-square centimeter cross section normal to the direction of the current flow in a molten electrolyte. The total current  $I$  passing through this area is the sum of that carried by the positive and that carried by the negative ions. In general terms, the current carried by any one of these components may be expressed by

$$I_k = n_k Z_k e V_k \quad (16)$$

where  $I_k$  = current carried by component  $k$  in a  $1 \text{ cm}^2$  cross section  
 $n_k$  = concentration of component  $k$  in ions  $\text{cm}^{-3}$   
 $Z_k$  = charge on component  $k$   
 $e$  = charge on the electron  
 $V_k$  = velocity of component  $k$  in  $\text{cm sec}^{-1}$ .

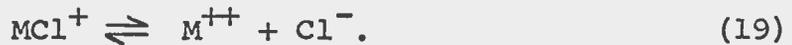
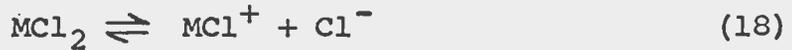
Let  $I_k$  be multiplied by the total cross-sectional area to give

the current carried by component k. Then, by substitution, Equation 15 becomes

$$t_i = \frac{n_i z_i e V_i}{\sum_k n_k z_k e V_k}, \quad (17)$$

where the area is cancelled in the ratio.

Now consider the reactions that may reasonably occur for the alkaline earth chlorides, represented by  $MCl_2$ , in the molten state:



There are three ionic components to which transport numbers may be assigned. In terms of the general Equation 17, these transport numbers are represented by

$$t_- = \frac{n_- z_- e V_-}{n_{++} z_{++} e V_{++} + n_+ z_+ e V_+ + n_- z_- e V_-} \quad (20)$$

$$t_+ = \frac{n_+ z_+ e V_+}{n_{++} z_{++} e V_{++} + n_+ z_+ e V_+ + n_- z_- e V_-} \quad (21)$$

$$t_{++} = \frac{n_{++} z_{++} e V_{++}}{n_{++} z_{++} e V_{++} + n_+ z_+ e V_+ + n_- z_- e V_-} \quad (22)$$

or,

$$t_- = \frac{n_- V_-}{2n_{++} V_{++} + n_+ V_+ + n_- V_-} \quad (23)$$

$$t_+ = \frac{n_+ V_+}{2n_{++} V_{++} + n_+ V_+ + n_- V_-} \quad (24)$$

$$t_{++} = \frac{2n_{++} V_{++}}{2n_{++} V_{++} + n_{+} V_{+} + n_{-} V_{-}} \quad (25)$$

There is some evidence that various forms of Stokes' law give fair agreement with experimental data in fused salts. Owens (38) found reasonable agreement with experimentally determined transport numbers for the alkali nitrates and those calculated from assumptions essentially contained in Stokes' formula. Although Stokes' equation applies to uncharged bodies moving through a continuous medium, if proper cognizance is made of the "viscosity coefficient" it does not seem unreasonable, at least for a first approximation, to assume Stokes' relationship which may be written as

$$\vec{F}_i = k_i r_i \vec{V}_i \quad (26)$$

where  $\vec{F}_i$  = frictional force (viscous drag) on component i

$k_i$  = proportionality constant which in hydrodynamic theory is  $6\pi\eta$  where  $\eta$  is the viscosity coefficient of the medium through which motion is referred

$r_i$  = radius of component i

$\vec{V}_i$  = velocity of component i.

Now under steady state conditions, the force experienced by the ion due to the electric field will be exactly balanced by the "viscous drag", given by Stokes' formula. That is,

$$Z_i e \vec{E} = - k_i r_i \vec{V}_i. \quad (27)$$

It is probably not valid to assume a priori that the  $k_i$ 's are the same for all species in the melt.

Because of the double charge on the unassociated metal ion,  $M^{++}$ , the "effective viscosity" of the medium which it sees may be quite different from the "effective viscosity" seen by the singly charged entities,  $MCl^+$  and  $Cl^-$ . It is reasonable to assume that the high charge density of the  $M^{++}$  ion will polarize the surrounding medium to a much greater extent than will the relatively large singly charged  $MCl^+$  and  $Cl^-$  ions. The polarization of the immediate environment has a double effect on the mobility of the  $M^{++}$  ion since the effective charge is reduced and at the same time the polarization interaction should decrease the mobility. These effects will be reflected in the relative magnitudes of the  $k_i$ 's. Analogously, it can be argued from absolute rate theory that the free energy of activation for the movement of a doubly charged ion will be larger than that expected for a singly charged ion. Carrying over the concepts of hole theory from the solid state where the alkaline earth chlorides are anionic conductors (39) to the melt, one can consider the relative distribution of "doubly charged holes" and "singly charged holes". Since it takes more energy to form a "doubly charged hole" than it does a "singly charged hole", the number of equilibrium positions available to the doubly charged ion will be much less than those available to the singly charged

ions. Similarly, since  $MCl^+$  and  $Cl^-$  are roughly the same size and more important, since they both have a charge of unity, the "effective viscosity" seen by these ions may be assumed approximately equal.

Making the above assumptions, it follows that if

$$k_{++} \gg k_+ \doteq k_- \quad (28)$$

then

$$\frac{v_{++}}{v_+} \ll 1 \text{ and } \frac{v_{++}}{v_-} \ll 1 \quad (29)$$

also

$$\frac{v_+}{v_-} \doteq \frac{r_-}{r_+} \quad (30)$$

where the magnitudes of the velocities have been used disregarding sign. If Equations 23, 24, and 25, are subjected to these conditions, then

$$t_- \doteq \frac{n_- r_+}{n_+ r_- + n_- r_+} \quad (31)$$

$$t_+ \doteq \frac{n_+ r_-}{n_+ r_- + n_- r_+} \quad (32)$$

$$t_{++} \doteq 0. \quad (33)$$

Consider one mole of  $MCl_2$  and let  $\alpha$  equal the fraction of  $MCl^+$  associated in the melt. Then

$$n_+ = \alpha N \quad (34)$$

$$n_- = 2N - n_+ = (2 - \alpha)N \quad (35)$$

where  $N$  is the total number of  $MCl^+$  ions if all associated

(i.e.,  $N = \text{Avagadro's number}$ ). If Equations 34 and 35 are substituted into Equations 31, 32, and 33, then

$$t_- \doteq \frac{(2 - \alpha) r_+}{(2 - \alpha) r_+ + \alpha r_-} \quad (36)$$

$$t_+ \doteq \frac{\alpha r_-}{(2 - \alpha) r_+ + \alpha r_-} \quad (37)$$

$$t_{++} \doteq 0. \quad (38)$$

Very rapid equilibration among the proposed ions is assumed because of the high temperatures required for the experiments and because of the highly ionic nature of the alkaline earth chloride melts. Since the time required for the ions to move through the membrane is long compared to expected exchange times, the tracer technique is assumed to give only the net motion of the component traced. Thus, if  $m$  is the net equivalents of  $\text{Cl}^-$  ions transferred to the anolyte during electrolysis,

$$m = t_- Z - t_+ Z, \quad (39)$$

where  $t_{++} + t_+ + t_- = 1$ . This condition is true regardless of the relative concentrations of the  $\text{MCl}^+$ ,  $\text{M}^{++}$ , and  $\text{Cl}^-$  ions. Now, making use of the argument proposed earlier that  $t_+ + t_- \doteq 1$ , Equation 39 becomes

$$2t_- \doteq m/Z + 1. \quad (40)$$

Since  $m/Z$  is determinable from experimental data and  $t_-$  may be expressed by Equation 36, the quantity  $\alpha$  may be evaluated.

That is

$$2t_- = \frac{2(2 - \alpha) r_+}{(2 - \alpha) r_+ + \alpha r_-} = m/Z + 1 \quad (41)$$

or,

$$\alpha = \frac{2(b - 1)}{r(b + 1) - 2} \quad (42)$$

where

$$r = 1 - r_-/r_+ \text{ and } b = m/Z. \quad (43)$$

Utilizing Pauling's crystalline ionic radii as reported by Moeller (40, p. 140) for the evaluation of  $r_-/r_+$  and making the assumptions that Case I:  $r_+ = 2r_-$ , Case II:  $r_+ = r_{++} + r_-$ , and Case III:  $r_+ = r_-$ , Equation 42 was solved for the respective values of  $\alpha$ . The results of these calculations are shown in Table 2.

Table 2. Per cent association of the species  $MCl^+$

Salt	m/Z	$r_{++}$ Å	$r_-$ Å	$\alpha \times 100$		
				Case I $r_+ = 2r_-$	Case II $r_+ = r_{++} + r_-$	Case III $r_+ = r_-$
ZnCl <sub>2</sub>	0.27 <sup>a</sup>	0.74	1.81	107	90	73
MgCl <sub>2</sub>	0.52	0.65	1.81	77	60	48
CaCl <sub>2</sub>	0.58	0.99	1.81	69	58	42
SrCl <sub>2</sub>	0.74	1.13	1.81	46	39	26
BaCl <sub>2</sub>	0.77	1.35	1.81	41	37	23
PbCl <sub>2</sub>	0.76 <sup>b</sup>	1.32 <sup>c</sup>	1.81	43	38	24

<sup>a</sup>Transport data reported by Lundén (15).

<sup>b</sup>Transport data reported by Laity (7).

<sup>c</sup> $Pb^{++}$  ionic radius, Goldschmidt's value reported by Moeller (40, p. 142).

The change of  $t_-$  with  $\alpha$  may be calculated for Cases I, II, and III for the salts using Equation 36. The results are shown graphically in Figure 5.

The fraction of the current carried by each specie and the number of ions of each specie available for ionic conduction must be considered in order to calculate ionic mobilities from conductivity data.

Let one mole of molten  $MCl_2$  (i.e., one equivalent of  $MCl^+$  and one equivalent of  $Cl^-$  if  $\alpha$  equals unity) be contained in a tube of cross-sectional area  $A$  and length  $l$ , closed at both ends by two metal plates as electrodes. Suppose a potential of  $E$  is applied to the electrodes, then the homogeneous field strength is  $E/l$  volt  $cm^{-1}$ . Now Equation 15 can be rewritten as

$$A e Z_i n_i V_i = t_i I. \quad (44)$$

Defining  $\mu_i = V_i / (E/l)$  ( $cm \text{ sec}^{-1} / (volt \text{ cm}^{-1})$ ) as the absolute ionic mobility of component  $i$ ; Equation 44 becomes

$$\mu_i = (t_i I l) / (e Z_i n_i E A). \quad (45)$$

Since  $I/E = l/R$  (Ohms Law) and  $R = l/(\Lambda A)$ , where  $\Lambda$  is the equivalent conductivity, Equation 45 can be written as

$$\mu_i = (t_i \Lambda) / (e Z_i n_i). \quad (46)$$

Imposing the assumptions (i.e.,  $v_{++} \ll v_+$  and  $v_{+-} \ll v_-$ ) used in the formulation of Equations 31 and 32, gives

$$\mu_+ = (t_+ \Lambda) / (e n_+) \quad (47)$$

and

$$\mu_- = (t_- \Lambda) / (e n_-). \quad (48)$$

Substitution of  $n_+ = \alpha N$  and  $n_- = (2 - \alpha)N$  yields

$$\mu_+ = (t_+ \Lambda) / (\alpha F) \quad (49)$$

and

$$\mu_- = (t_- \Lambda) / (2 - \alpha)F \quad (50)$$

because  $eN = F$ , where  $F$  is Faraday's constant.

And finally one correction needs to be made. Literature values for  $\Lambda$  are calculated on the basis of complete dissociation (i.e., one mole of  $MCl_2$  equals two equivalents) so that a factor of two needs to be included in Equations 49 and 50.

That is

$$\mu_+ = \frac{2 t_+ \Lambda}{\alpha F} \quad (51)$$

and

$$\mu_- = \frac{2 t_- \Lambda}{(2 - \alpha)F}. \quad (52)$$

It is of interest to note that if  $\alpha = 1$  and  $r_+ = r_-$  (see Equations 31 and 32), then  $\mu_+ = \mu_-$  as expected.

Using the conductivity data of Bockris et al. (30) and the data in Table 2, the ionic mobilities of the ions were calculated for Case II:  $r_+ = r_{++} + r_-$ . The results of these calculations for  $\theta = T^\circ K / T_{m.p.}^\circ K = 1.10$  are shown in Table 3.

To digress for a moment, consider the case where the  $k_i$ 's are assumed equal in Stokes' equation. It follows that

$$\frac{V_{++}}{V_+} = \frac{2r_+}{r_{++}}, \quad \frac{V_{+-}}{V_-} = \frac{2r_-}{r_{+-}}, \quad \text{and} \quad \frac{V_+}{V_-} = \frac{r_-}{r_+}. \quad (53)$$

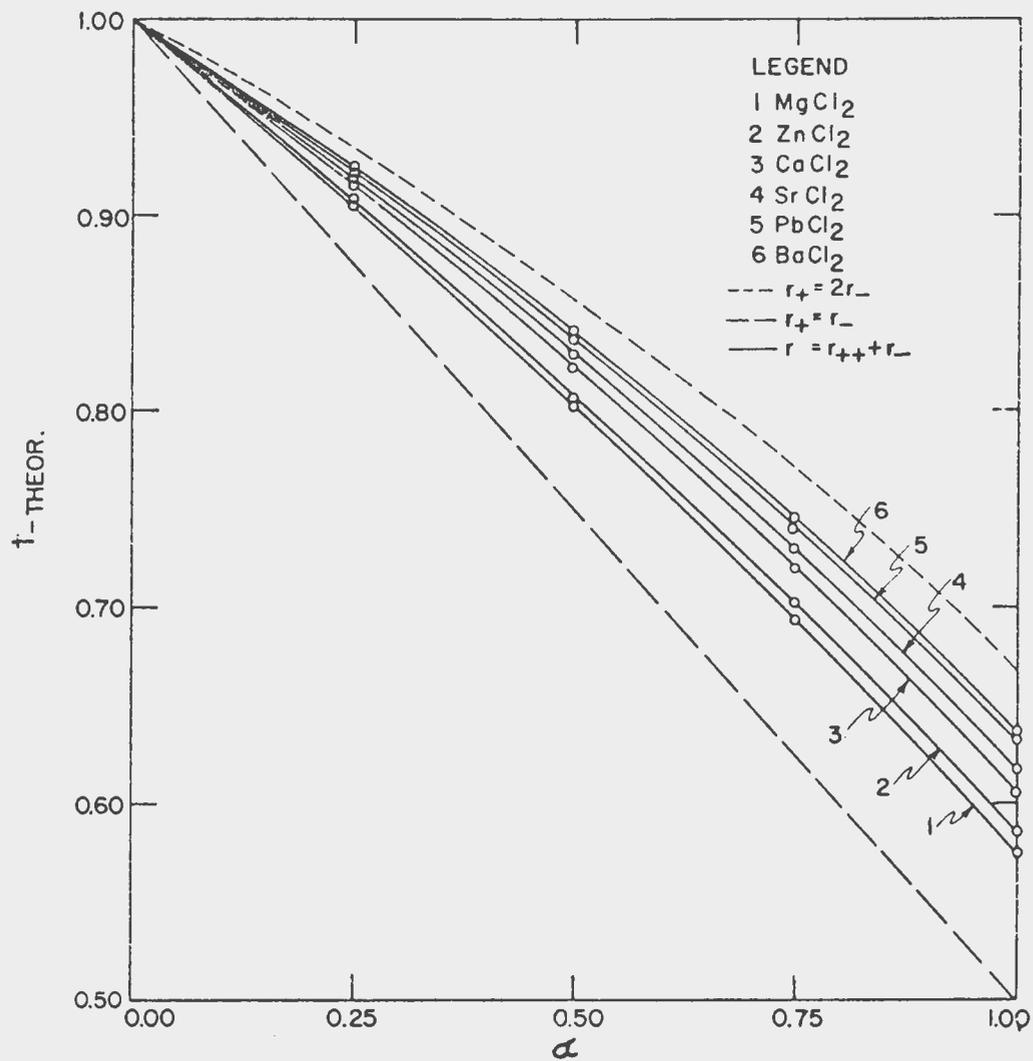


Figure 5. Plot of  $t_{-theor}$  versus  $\alpha$  to show the relative changes for the individual salts

Table 3. Ionic mobilities ( $\epsilon = 1.10$ )

Salt	$t_+$	$t_-$	Case	$(\text{ohm}^{-1}\text{cm}^2\text{eq}^{-1})$	$(\text{cm}^2\text{sec}^{-1}\text{volt}^{-1})$	
			II	$\Lambda$	$\mu_+ \times 10^4$	$\mu_- \times 10^4$
			$\alpha$			
ZnCl <sub>2</sub>	0.36	0.64 <sup>a</sup>	0.90	00.35 <sup>b</sup>	0.29	0.42
MgCl <sub>2</sub>	0.24	0.76	0.60	34.8 <sup>b</sup>	2.8	3.9
CaCl <sub>2</sub>	0.21	0.79	0.58	67.1 <sup>b</sup>	5.0	7.7
SrCl <sub>2</sub>	0.13	0.87	0.39	72.4 <sup>b</sup>	5.0	8.1
BaCl <sub>2</sub>	0.11	0.89	0.37	83.2 <sup>b</sup>	5.1	9.4
PbCl <sub>2</sub>	0.12	0.88 <sup>c</sup>	0.38	45.28 <sup>d</sup>	3.0	5.1

<sup>a</sup>Transport data from Lundén (15).

<sup>b</sup>Conductivity data of Bockris et al. (30).

<sup>c</sup>Transport data from Laity (7).

<sup>d</sup>Conductivity data of Bloom and Heymann (41).

If these conditions are substituted into Equations 23, 24, and 25, the results are

$$t_- = \frac{n_- r_{++} r_+}{4n_{++} r_+ r_- + n_+ r_{++} r_- + n_- r_{++} r_+} \quad (54)$$

$$t_+ = \frac{n_+ r_{++} r_-}{4n_{++} r_+ r_- + n_+ r_{++} r_- + n_- r_{++} r_+} \quad (55)$$

$$t_{++} = \frac{4n_{++} r_+ r_-}{4n_{++} r_+ r_- + n_+ r_{++} r_- + n_- r_{++} r_+} \quad (56)$$

Since electrical neutrality requires that  $n_- = 2n_{++} + n_+$ , these equations become

$$t_- = \frac{(2n_{++} + n_+) r_{++} r_+}{4n_{++} r_+ r_- + n_+ r_{++} r_- + (2n_{++} + n_+) r_{++} r_+} \quad (57)$$

$$t_+ = \frac{n_+ r_{++} r_-}{4n_{++} r_+ r_- + n_+ r_{++} r_- + (2n_{++} + n_+) r_{++} r_+} \quad (58)$$

$$t_{++} = \frac{4n_{++} r_+ r_-}{4n_{++} r_+ r_- + n_+ r_{++} r_- + (2n_{++} + n_+) r_{++} r_+} \quad (59)$$

Equation 57 does not agree with an equation cited by Bockris et al. (30, Eq. 23)

$$t_- = \frac{(n_{++} + n_+) r_{++} r_+}{4n_{++} r_+ r_- + n_+ r_{++} r_- + (n_{++} + n_+) r_{++} r_+} \quad (60)$$

which was presumably derived by Markov and Delimarskii (42). Since the original paper was not available, the method of its derivation could not be checked. If Stokes' equation applies, as the form of the equation suggests, then the equation was possibly miscopied or an error was made in its derivation. For one limiting case,  $n_+ = 0$ , the equation does not reduce to  $t_- = r_{++}/(r_{++} + 2r_-)$  as Bockris et al. said it should. As a result of this apparent error, the second equation cited (30, Eq. 24) should have been

$$\frac{3r_{++} r_+}{4r_+ r_- + r_{++} r_- + 3r_{++} r_+} \quad (61)$$

for the case  $n_+ = n_{++}$ , instead of

$$\frac{2r_{++} r_+}{4r_+ r_- + r_{++} r_- + 2r_{++} r_+} . \quad (62)$$

If Equations 57 and 58 with the appropriate substitution of  $\alpha$  for the concentrations  $n_{++}$ ,  $n_+$ , and  $n_-$  are used in conjunction with Equation 39, an expression analogous to Equation 42 results:

$$\alpha = \frac{2 - 2b(1 + 2r_2)}{(b + 1)r_1 - b(1 + 4r_2) + 1} \quad (63)$$

where

$$r_1 = r_-/r_+ \text{ and } r_2 = r_-/r_{++}. \quad (64)$$

Sample calculations for Case I using  $\text{ZnCl}_2$  and  $\text{BaCl}_2$  gave values for  $\alpha$  of 1.83 and 1.72; for Case III, 0.93 and 1.22, respectively.

Thus, the microscopic interpretation of the  $k_i$ 's in Equation 26 gives values for  $\alpha$  consistent with the chemical properties of the salts. If the  $k_i$ 's are assumed equal, unmeaningful results are obtained.

There are several items of interest that result from this treatment of the data. The general trend of increasing association from the heavier to lighter alkaline earth chlorides is reasonable since the smaller cation exhibits a greater polarizing effect. Because of the low conductivity of  $\text{ZnCl}_2$  and since  $\alpha$  is near unity, it may be that there is an appreciable concentration of associated  $\text{ZnCl}_2$  molecules in the

melt. This argument would also apply to  $\text{BeCl}_2$  which has a very low equivalent conductivity. The molecular association would not be reflected in a transport experiment since there is no change in relative concentration for this first dissociation step.

The association for  $\text{PbCl}_2$  agrees well with that for  $\text{BaCl}_2$  and  $\text{SrCl}_2$  as might be expected from similar chemical properties.

The trends exhibited in Figure 5 indicate that there should be a slightly greater change in  $t_-$  with increasing temperature (decreasing  $\alpha$ , since  $\alpha$  is related to temperature through the association constant,  $K_a \sim e^{-\frac{\Delta H}{RT}}$ ) for  $\text{MgCl}_2$  and  $\text{ZnCl}_2$  than for  $\text{BaCl}_2$  and  $\text{PbCl}_2$ . This result is meaningful since as the concentration of  $\text{MCl}^+$  increases more of the current should be carried by these ions in  $\text{MgCl}_2$  than in  $\text{BaCl}_2$ . This follows from the consideration of the relative sizes of the  $\text{MCl}^+$  ions in the two melts.

However, in view of the stability of the ion pairs, it might be expected that the  $\text{MgCl}^+$  ion would be more stable than  $\text{BaCl}^+$  and thus dissociate less with increasing temperature. So this trend is perhaps not unambiguous, yet it is not unreasonable.

As discussed earlier, no temperature dependence was observed except possibly for  $\text{CaCl}_2$ . Because of the rather large experimental error (undoubtedly, diffusion played a minor

role)  $\alpha$  could change as much as 20 or 30 per cent and still the change in  $t_-$  would lie within the experimental error (see Figure 5). However, the very precise value for  $\text{PbCl}_2$  (7) did not show any change with temperature. Since there is no way at present of knowing how much  $\alpha$  changes with temperature for these salts, this question remains unanswered. It is reasonable to assume that  $\Delta H$  is small for association at these temperatures which would reflect only a small change in  $\alpha$  with temperature.

Alternatively, the association postulated for the alkaline earth chlorides need be no more than a charge transfer mechanism. That is, as a doubly charged metal ion moves a corresponding chloride ion moves with it. In this way, association in the thermodynamic sense does not have to be implied to interpret the data.

Further transport studies using radioactive or stable tracer isotopes would be valuable for determining the relative mobilities of the  $\text{MCl}^+$  and  $\text{M}^{++}$  ions. From studies of this nature, the validity of the assumptions that  $v_{++} \ll v_+$  and  $v_{++} \ll v_-$  could be determined.

An additional tracer experiment could, in principle, infer the relative concentrations of  $\text{MCl}^+$  and  $\text{M}^{++}$ . There is some experimental evidence that a minor ionic constituent assumes the mobility of the major constituent having the same

charge.\* A small concentration of KCl could be added to the alkaline earth chlorides and the motion of the  $K^+$  ion followed. The transport by  $MCl^+$  ion could in principle then be inferred, and hence its relative concentration.

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