APR 30 [illegible]

IS-443

MASTER

Facsimile Price $ 1.60
Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Transference Numbers and Ion Association in Pure Fused Alkaline Earth Chlorides[1]

Edward D. Wolf[2] and Frederick R. Duke

Institute for Atomic Research and Department of Chemistry
Iowa State University, Ames, Iowa

ABSTRACT

The transference number of the chloride ion was determined in pure fused $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ utilizing radioactive chloride ions in a porous quartz membrane cell. On the basis of a two-step dissociation for these salts, $MCl_2 \rightleftarrows MCl^+ + Cl^- \rightleftarrows M^{++} + 2Cl^-$, the extent of the second dissociation was qualitatively predicted from a consideration of the relative mobilities of the ions.

Introduction

There is some controversy about the physical significance of Hittorf type transference experiments in pure single component fused salts. It is obvious that ambiguity about the reference frame for the velocities of the ions could result, since in the pure fused salt the solvent, to which ion motion is generally referred, is absent. Indeed one might consider

---

[1] Contribution No. 1142. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Present Address: Department of Chemistry, Princeton University, Princeton, New Jersey.

DISCLAIMER

the phenomenon as electroosmosis since experimentally there is no distinction. On this basis Sundheim (1) has extended conventional hydrodynamic equations of motion to describe the movement of the ions and has found that the transference numbers defined in the reference frame of the cell (i.e., porous plug experiments) can be expressed in terms of partial viscosities of the ions.

Laity (2) has discussed the conceptual difficulties of defining transference numbers in pure single component fused salts. The idea conveyed is that the conventional porous plug transference experiments do indeed measure a property of the salt, but the significance of this property has not yet been clarified. However, Esin et al. (3) in a short review expressed the view that there is no basis for considering it impossible in principle to measure transference numbers in pure single component fused salts using the porous plug method.

In the present paper the transference number measured with respect to the porous plug will be interpreted as a measure of the mobility of the ion relative to the bulk fused salt. Further comments on transference numbers in pure fused salts will be reserved for a future publication.

The purpose of this paper is to report the experimental values of the transference number of the chloride ion in pure fused alkaline earth chlorides and then to infer certain structural properties (i.e., association) of the melts.

Experimental

Materials: "Baker Analyzed" reagent grade alkaline earth chloride hydrates were recrystallized and dried under vacuum to remove surface water and some hydration water. Complete dehydration was realized for barium, strontium, and calcium chloride during the course of the transference experiments during which a dry argon atmosphere covered the salt at all times. Vacuum fusion analyses (4) after sample runs indicated a total oxygen content (calculated as MO) of less than 1 mole % for each of these salts.

Pure anhydrous magnesium chloride was prepared by vacuum sublimation of the chloride (near 800°C) away from the dehydration impurities. Similar vacuum gas analyses gave an oxygen contamination of less than 0.5 mole % MgO.

Radioactive salts were prepared in the same manner except that prior to recrystallization a predetermined amount of HCl^{36} was added to the aqueous solution.

Apparatus: A Vycor cell holder which extended about 10 in. into an upright tube furnace was used to support the quartz transference cell (Fig. 1). This arrangement allowed for a dry inert atmosphere over the salt at all times. The construction of cells and the porosity reduction treatment of the quartz disks have been described previously (5). Spectroscopic graphite rods 12 in. in length and 1/8 in. in diameter were used for the electrodes.

The 230-v furnace was controlled by a Bristol Electronic Controller sensitized by a Chromel-Alumel thermocouple.

Initially a Heathkit Model PS-5 variable voltage regulated power supply served as the d-c source. In some of the later work a full-wave

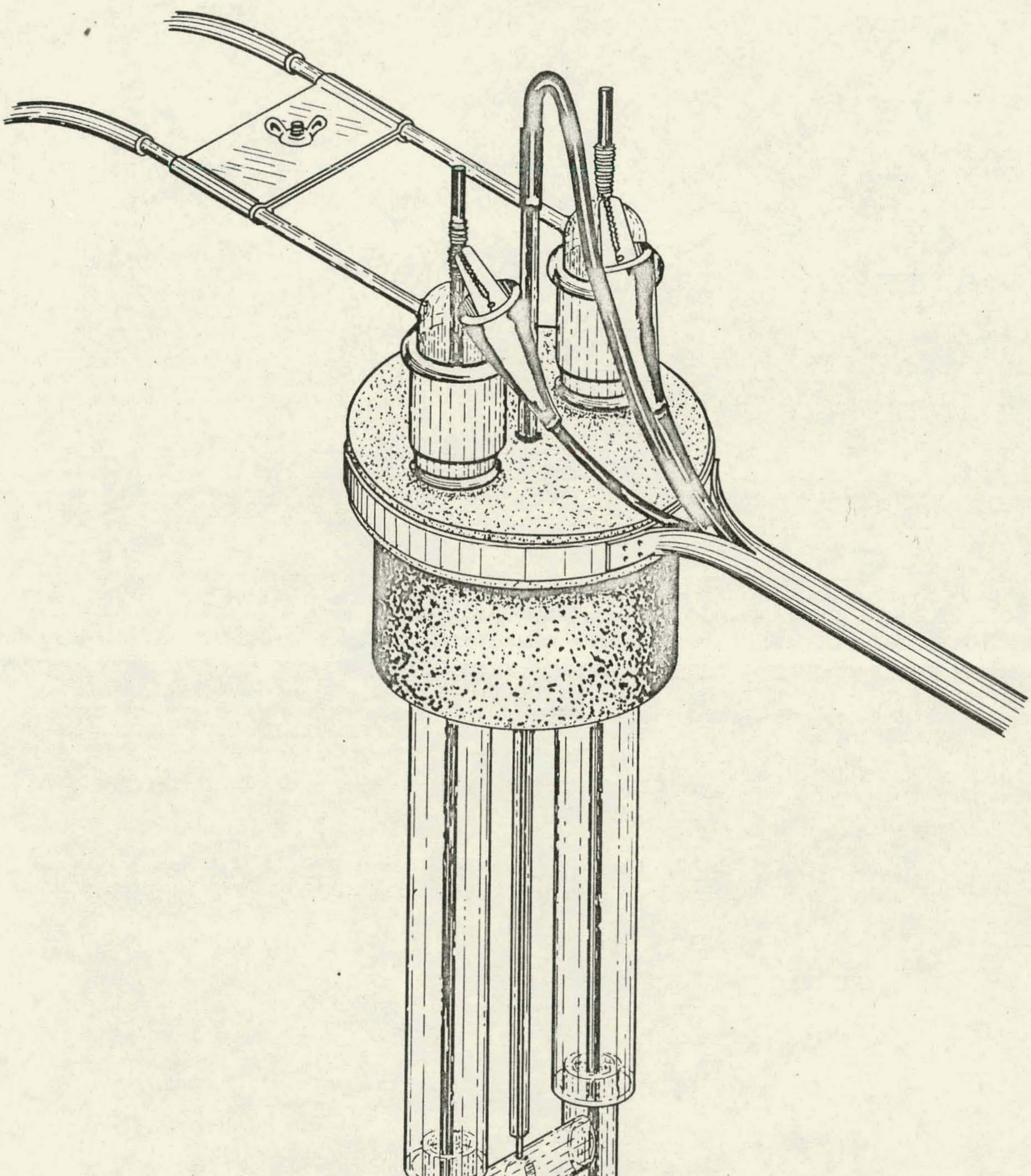

Fig. 1. Cell holder and cell

selenium rectifier in conjunction with a pi-section filter circuit was employed. A silver coulometer was used to determine the charge passed through the cell.

A Model 181A Nuclear-Chicago Decade Scaler and a Tl Dual Timer were used with a Tracerlab TGC-1 Geiger-Mueller tube for determining the beta activity.

Procedure: The anode and cathode compartments were filled with inactive and radioactive salts respectively. In the case of the magnesium chloride experiments the filling of the cells was done in a dry box followed by a rapid transfer to the cell holder through which dry argon was flowing. The cell was attached to the cell holder with small Nichrome springs and the entire assembly lowered into the furnace. After the desired temperature was reached and sufficient time allowed for the salt to come to equilibrium temperature, the graphite electrodes were lowered into the melt and a measured d-c current was passed through the cell. The electrolysis time varied from 500-2000 sec depending on the current used. Generally a total charge of approximately 100 coulombs was employed. After electrolysis the electrodes were lifted out of the melt and the cell was removed from the furnace to quickly freeze and cool. The dry argon flush was continued during the cooling process. The cell was then split carefully at the disk so as not to contaminate the anolyte with the more radioactive catholyte salt. Both halves were dissolved in water. The anolyte weight was found by weighing the half cell before and after the salt was dissolved with corrections made for adsorption of the salt by the electrode. The solutions were buffered below pH 10 with ammonium acetate and ammonium hydroxide and the chloride ion was precipitated with excess silver nitrate. Three samples from each anolyte and catholyte were prepared for counting. Standard coincidence, self-absorption, and background corrections were made and the specific activities of the samples, recorded.[1]

To be consistent with the operational definition of transference numbers all conditions of the experiment must be referred to the disk. It was discovered during the experiments that the standardized Pt, Pt-Rh thermocouple did not sense the rather large temperature rises within the disk even though it was in contact with the cell directly above the disk. In order to follow the temperature of the disk a fading element Pyro Micro-Optical Pyrometer was mounted directly above the furnace. Readings were taken by focusing on the disk through the small thermocouple well in the top of the cell holder. In a few cases in which the membrane porosity had been reduced to extremes, arcing was observed in a few "hot" spots in the disk. However, for most experiments the heating was moderate (0-50°C, with no arcing) and uniform throughout the disk. Cell resistances varied from 100-1000 ohms and the current was generally 100 ma, however, even a sixfold variation of 50 ma to 300 ma caused no appreciable change in the equivalents of Ce^- ion transported. The temperature of the disk varied linearly with the power dissipation within the disk which was usually less than 5 w.

---

[1] Note to Editor: This paragraph may be replaced with: The experimental procedure was essentially that of Duke and Bowman (5) with a few modifications.

Previous transference experiments have been done with little or no consideration for this dissipation of energy within the disk. Lunden (6) did attempt to measure it by wrapping the leads of a small thermocouple around the disk with the thermocouple in contact with the outer surface of the cell. It is reasonable to assume similar heating in Pyrex disks. Experiments with Pyrex cells in which a high current density was maintained near the softening point of Pyrex should be viewed with this in mind. Under extreme heating the fused Pyrex glass would act as an ion exchange medium exhibiting only cationic conduction.

Diffusional and viscous flow due to gravity can play a major role in the experimental error of the data. However, for sufficiently fine disks, blank runs for diffusion and experiments in which hydrostatic heads of several millimeters were used, indicated negligible corrections for these effects during the short duration of each transference experiment.

Results and Discussion

For most uni-univalent molten salts complete dissociation is generally assumed. However, for molten salts containing multivalent ions incomplete dissociation (or association) may occur. Consider possible reactions for the alkaline earth chlorides in the molten state,

$$\begin{array}{rll} MCl_2 \rightleftarrows & MCl^+ + Cl^- & \alpha_1 \\ & \quad\uparrow\downarrow & \\ & M^{++} + Cl^- \ . & \alpha_2 \end{array} \tag{1}$$

There are three species, M^{++}, MCl^+, and Cl^-, to which transference numbers, t_{++}, t_+, and t_-, may be assigned.

The equivalents of chloride ion transferred from cathode to anode compartment during a radioactive chloride traced electrolysis of a pure fused alkaline earth chloride can be shown to be

$$m = (C_a/C_c)(W_a/M), \tag{2}$$

where C_a and C_c are the specific activities of the anolyte and catholyte salts respectively at the end of the experiment. W_a is the weight of the salt in the anode compartment at the end of the experiment and M is the equivalent weight of the salt.

Cathodic migration of radioactive chloride was not observed in experiments in which the radioactive salt was initially in the anode compartment. This does not exclude the existence of the MCl^+ ion. On the contrary this is consistent with rapid equilibration of the MCl^+ ions with its chloride ion environment. The only conditions required are that the rate of exchange of Cl^- ions is rapid with respect to the time required (a few seconds) for the ion to pass through the disk and that $t_- > t_+$. The first condition is satisfied by the very nature of these fused salts. Had the last condition been reversed (i.e., $t_- < t_+$) then anodic migration of radioactive chloride would not be observed. And finally, if $t_- = t_+$ the radioactive tracer would not migrate, other than by diffusion, from either compartment. Thus the net motion of the chloride ion may be described by defining the net equivalents of chloride ion transferred as

$$m = t_-Z - t_+Z \tag{3}$$

where Z is the number of Faradays of electricity passed through the cell.

The experimentally determined quantity, m/Z, is listed in Table I for each of the four alkaline earth chlorides over the indicated temperature range. Included also are values obtained from the data of Lunden (6) for $ZnCl_2$ and Duke and Laity (7) for $PbCl_2$. Although the m/Z values are reported as temperature independent, it should be mentioned that a slight linear increase of m/Z with temperature was observed for $CaCl_2$.

The probability of existence of doubly negative vacancies in the liquid seems small with univalent anions present. On this basis, if the mobility of the M^{++} ion is assumed to be negligible in comparison with the mobilities of the MCl^+ and Cl^- ions, then the relative concentrations of the ions may be estimated. For the mobility of the MCl^+ ion satisfying the condition $u_-/2 < u_+ < 2u_-$, values of the degree of dissociation for the reaction, $MCl^+ \rightleftarrows M^{++} + Cl^-$, were found to range between zero and unity as shown in Table I. Dissociation increased for each salt progressively down the Group II_A chlorides. One may conclude from the small value found for $ZnCl_2$ that an appreciable concentration of associated $ZnCl_2$ molecules exists in the melt. Equivalent conductivity and viscosity data argue in favor of this conclusion also. The dissociation for $MgCl_2$ was somewhat greater than for $ZnCl_2$, and the dissociation for $PbCl_2$ was approximately that found for $BaCl_2$.

Degrees of dissociation for the alkaline earth chlorides have been predicted by Markov and Delimarskii (8). From a consideration of a semi-empirical expression for the electrical conductivity and the rather drastic assumption that the chloride ion will have the same mobility in the corresponding states (i.e., in the neighborhood of the melting points) for the different salts, they conclude that $BeCl_2$ is mostly molecular while $BaCl_2$ exists mainly as Ba^{++} and Cl^- ions with about 30% of the Ba^{++} ions associated as $BaCl^+$. While their results are compatible with those proposed in this paper, the means by which they were obtained are questionable.

In conclusion, analogous dissociation could be predicted by assuming Stokes' law and effective ion radii for the singly charged species after setting $u_{++} \doteq 0$. However, the use of Stokes' equation for describing the motion of ions in fused salts is fundamentally unsound even though order of magnitude agreement is generally found between observed and calculated values.

Table I. Chloride transference numbers and per cent dissociation in fused alkaline earth chlorides

				a_2 x 100			
Salt	Number of exp'ts	m/Z	$t_-^{\dagger\dagger}$	Case I $u_+=u_-/2$	Case II $u_+=u_-$	Case III $u_+=2u_-$	Temp. range, °C
$ZnCl_2$*		0.27±.08**	0.64	0	27	55	435 to 673
$MgCl_2$	6	0.52±.04	0.76	23	52	73	730 to 920
$CaCl_2$	29	0.58±.09	0.79	31	58	76	780 to 1100
$SrCl_2$	19	0.74±.07	0.87	54	74	86	880 to 1165
$BaCl_2$	15	0.77±.09	0.89	59	77	88	960 to 1100
$PbCl_2$†		0.76±.01	0.88	57	76	87	565 to 635

* Tracer method.

** Standard deviation errors.

† Bubble-cell method.

†† Calculated as MCl^+ and Cl^- from the experimental data.

REFERENCES

1. B. R. Sundheim, Private communication.
2. R. W. Laity, J. Chem. Ed., 39, 67 (1962).
3. O. A. Esin, G. A. Teterin, and I. N. Zakharov, Zhurn. Fiz. Khim., 33, 1887 (1959).
4. V. M. Horrigan, V. A. Fassel, and J. M. Goetzinger, Anal. Chem., 32, 787 (1960).
5. F. R. Duke and A. L. Bowman, J. Electrochem. Soc., 106, 626 (1959).
6. A. Lundén, U. S. Atomic Energy Commission Rept. IS-114, April, 1960.
7. F. R. Duke and R. W. Laity, J. Phys. Chem., 59, 549 (1955).
8. B. F. Markov and Yu K. Delimarskii, Ukrain. Zhurn. Khim., 19, 255 (1953).