Effect of Frit Material on External Transport Numbers in Molten Salts

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Molten salt external transport numbers have been examined with respect to the possible influence of the frit material. Improved measuring techniques revealed a slight temperature dependence for the transference of $PbCl_2$ in Pyrex frits over the range 529 to 610 °C, but generally confirmed the values obtained by most of the earlier workers who used porous glass or related materials. Within experimental error the figures were found to be identical in Pyrex frits of two different pore sizes. On the other hand, significant deviations were detected when a boron nitride frit was used. These experiments confirm that the transport properties of the interfacial layer between the melt and the solid depend on the nature of the solid.

Introduction

The phenomenon studied in a measurement of the external transport numbers in a molten salt is no different from what is called "electro-osmosis" in an electrolytic solution [2]. Electro-osmotic transport depends on the transport properties of the interfacial layer, which in turn is determined not only by the composition of the electrolyte, but also by the nature of the solid surface past which the ions are moving. The relevant properties would normally be expected to depend to some extent on the kind frit employed. For a particular frit material, however, they should be independent of the pore diameters as long as the pores are much larger than the thickness of the interfacial layer.

We selected $PbCl_2$ for our studies since this salt is easy to work with and has been subject to more external transport number studies than any other. An earlier study [3] has purported to demonstrate the independence of $PbCl_2$ transport numbers on the nature of the frit material. The materials employed in that work, Pyrex glass, porcelain, and asbestos are, however, structurally similar since they all have oxide ions at the surface. Thus a choice of an entirely different frit material (in our case boron nitride) should be able to demonstrate the effect.

A method developed by Fischer and Klemm [4] eliminates the possibility of errors due to salt leakage and enables the comparison of transport numbers obtained with either of two procedures, one involving electrolysis to a steady state in which no net volume transport occurs, the other requiring the observation of volume transport. We have used this method, the initial transport being obtained by extrapolation from a sequence of measurements.

Experimental

Fisher Certified Reagent grade lead metal and lead choride were used.

The transport cell was a modification of the design by Fischer and Klemm [4], the entire assembly being constructed of Pyrex glass. It is shown in Figure 1. The electrode compartments were vertical 10 mm tubes through which tungsten wire contacts were sealed. The connecting tube containing the frit was also vertical throughout most of its length, connections to the two compartments being made by elbows at either end. Above the upper elbow connecting tube both compartments tapered into 2.0 mm capillary tubing selected for uniformity of its bore. After extending upward for 27 cm the capillaries were flared and joined to tubing having about 20 mm O.D. The latter tubes were at least 20 cm in length, so that the points at which they projected above the top of the furnace would be far above the electrode compartment and capillary zones. Near the top of each of these two tubes, 6 mm tubing projected horizontally and was bent to make contact with opposite ends of a three-way stop-cock.

The heating unit consisted of two vertical tube furnaces positioned one above the other and separated by an 1 cm layer of Marinite insulating sheet. A vertical hole of the same bore as the furnaces was cut through this sheet, as well as a horizontal opening 2 cm wide across one entire diameter, dividing

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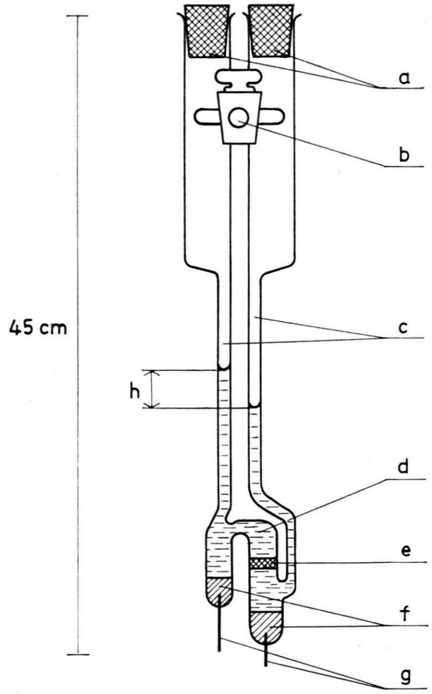

Fig. 1. Cell for external transport number measurements. The three lower tubes form the corners of a triangle in order to fit into the cylindrical furnace, but for clarity they are drawn in one plane. a) Slicone rubber stoppers, b) Three-way stopcock, connected to vacuum and argon systems, c) Glass capillaries (I.D. 2.00 mm), d) Molten salt (lead chloride), e) Fritted disc (Pyrex or boron nitride), f) Molten metal electrodes (lead), g) Tungsten wires sealed through the glass.

the disk into two sections. The ends of this slit were sealed with mica windows, making it possible to observe the interior in this region from one side, while illuminating from the other.

The temperature of both furnaces was controlled by feeding the output of a thermoregulating unit through suitably proportioned variable transformers. The sensing element was a platinum resistance thermometer located in the lower furnace. By suitable use of firebrick and Marinite baffles at the extremities the temperature could be kept constant within 0.5 °C.

Electrolysis current was furnished by a 12 volt storage battery, using external resistors in series with the cells in order to help maintain constant current. Accurate current measurements were made by using a sensitive potentiometer to determine the IR drop across a calibrated 1 ohm precision resistor.

"Ultrafine" (UF) porosity Pyrex frits were obtained in the form of small Buchner funnels, and "fine" (F) porosity frits in the form of sealing tubes. The pore diameters in UF frits range from 0.9 to 1.4 μ and in F frits from 4.0 to 5.5 μ. Each frit was washed with hot concentrated nitric acid followed by concentrated hydrochloric acid. It was then flushed with distilled water, during which the time was noted for a measured quantity of water to pass through under the pressure of 1 atm. Significant variations in porosity and/or pore size distribution from one frit to another were observed.

Boron nitride has a graphite structure and it is thus considerably different from the glassy structures used earlier as reference materials. Two different purities were available from the manufacturer (the Carborundum Company), grade A and HP (high purity). It was found that grade A showed considerably better wetting by the melt than grade HP, and thus grade A was chosen. Another reason for this choice was that the pore distribution was accurately known for grade A only: The average pore size was 3.3 μ, but the pore distribution (as measured with a mercury porosimeter) was much wider than in the Pyrex frits: Pores above 3 μ account for 53%, between 3 and 1 μ for 13%, between 1 and 0.1 μ for 24% and smaller pores for 10%. The porosity is very small, 1.3 – 1.8%. A 1 mm thick BN frit was sealed into a 10 mm I.D. Pyrex glass tube. Due to its low porosity and the difficulty of wetting the pores, it was incorporated into the cell without further treatment.

The cell was positioned in such a way that the electrode compartments were in the lower furnace with the capillaries running between the two furnaces. Molten lead covered the tungsten wires at the bottom, above which the molten salt filled the remaining space up to the observable region of the capillaries. Any air bubbles entrapped during the cell filling could be removed by application of vacuum at the open end of the stopcock.

To carry out a run, suitable temperature equilibration was first established by maintaining an alternating current between the electrodes equal in magnitude to the D.C. electrolysis current to be used in the run over a period of at least 30 minutes. A precision cathetometer was used to note the initial levels of liquid in each of the capillaries to within 0.005 cm. An electric timer was started at the moment the A.C. was replaced by D.C. Frequent readings of the two levels were made and the corresponding time noted. In most cases a significant number of such readings could be taken before the difference in liquid levels arrived at a steady state value. Once the latter was attained, measurements were made to determine the rate at which the levels returned to their original height in the absence of electrolysis. A.C. was used during these measurements to ensure that the frit temperature remained unchanged. By reversing the current after each run, many consecutive determinations could be made without depleting the lead content of either compartment.

There was a temperature differential of several degrees between a thermocouple located near the frit in the lower furnace and another at the observation point in the capillary tubes. This difference was found to be fairly constant with changes in the overall furnace temperature. To correct for possible lateral gradients near the capillaries, the upper thermocouple was calibrated against the freezing point of lead chloride (501 °C). Possible differences between the temperature of the salt inside the frit and that of the lower thermocouple are not so readily detectible. It is possible, however, to construct a calibration curve by carrying out a series of flow measurements while passing alternating current through the cell and relating them to the well known temperature dependence of the viscosity of lead chloride. The readings of the lower thermocouple can thus be corrected for the heating effects of the applied current to obtain the value to be associated with the transference number measured in the same run. The upper temperature must be used to relate the observed volume change to a specific number of equivalents of salt.

An accurate determination of the capillary cross-section was carried out when a series of runs had been completed. A piece of each capillary was cut from the exact region where the salt levels had been located during the runs. After dissolving the remaining salt in hot water the ends were ground flat and the bore diameters observed with a measuring microscope.

Results and Discussion

Such electrolysis current leveels were chosen that the electrical heating during the runs would cause a negligible temperature rise (less than 2 °C).

For frits of low porosity and small pore diameter the approach to the steady state was impracticably slow. Therefore in in such cases the transport numbers were determined by the "initial slope" (IS) method. When using frits with high porosity and large pore diameters the levels attain a steady-state height difference in a short period of time. The slope changes rapidly making it difficult to apply the IS method. Instead, transport numbers are calculated from the steady-state (SS) level difference, along with the measured current, the known densities of lead choride and lead metal and the "time constant" of the frit under the experimental conditions. For a number of frits used in the present work, particularly those of UF Pyrex, the pore characteristics were such that both methods could be applied to the data collected in a single run. Agreement was generally found to be excellent, the calculated transport numbers being identical within the reproducibility of the measurements.

The accuracy of the calculations was limited by the uncertainity in the difference of the two liquid levels. Both levels fluctuated in the same direction at the same time, indicating that small temperature variations occurring over intervals of several minutes could cause erratic behaviour in the height of each salt column even though the level *difference* during each run was a smooth function of time. (An increase of only 0.5 °C in a cell corresponds to more than 0.1 mm rise in the height of each liquid column, and this figure is about 1% of the maximum height difference that could be observed with our apparatus.) Results from the IS measurements generally showed somewhat greater precision, but no systematic correlation could be found between the small differences between the two values obtained in the individual runs. Both methods were thus regarded as equally valid, the results reported here representing an average of all the values calculated from experimental data with no distinction as to the method employed. The results of all our transference measurements will now be discussed, grouped according to the nature of the frit used.

Pyrex glass. The present results for the transference number of the chloride ion in lead chloride relative to UF frits are in excellent agreement with those reported by most previous workers, as well as those where porous porcelain and packed asbestos fibers acted as external references[3]. In the study that included the porcelain and asbestos separators, most of the runs on lead chloride were carried out with UF Pyrex at a nominal temperature of 565 °C, while on the basis of the present calibration studies we now find that the frit temperature at the current levels employed in that work was probably about 16 °C higher than that measured by the thermocouple. This is not enough difference to spoil the comparison of results since the temperature dependence of the transference numbers in lead chloride is very small. Indeed, no significant variation with temperature has been detected in previous studies, but we have been able to observe a slight decrease with increasing temperature (see the equation below). The fact that back-flow through the frit has been a significant source of error in the previous bubble-cell experiments using frits with larger pore diameters is substantiated in the present work by the results obtained with F Pyrex. The figure listed below is well within the range of values found for UF frits. Although the nominal pore diameter of the F frits is only four times larger than that of the UF frits, the fact that the hydrostatic flow through a given pore increases as the fourth power of the diameter seems to justify the claim that a substantial variation in pore size has been tested. We thus conclude that the external transport numbers of lead chloride in Pyrex glass are independent of pore size, and they can be described by the following equation, which is based on 69 runs on UF frits:

$$t_{\mathrm{Cl}^-} = 0.769 - (3.4 \pm 1.1) \times 10^{-4} \times (T - 565),$$

where T = the temperature in °C, ($529\,°\mathrm{C} < T < 610\,°\mathrm{C}$) (the stated error is a standard deviation). Totally 23 runs on F Pyrex give:

$$t_{\mathrm{Cl}^-} = 0.752 \pm 0.018 \quad (T = 565\,°\mathrm{C}).$$

Boron nitride. This material has a crystal structure that is very similar to the graphite structure, a hexagonal plane lattice. As mentioned above the pore characteristics are similar to the UF Pyrex frits, although the porosity is much lower. Our success in sealing into 1 mm thick, 10 mm O.D. boron nitride frits Pyrex tubes may partly be due to the flexibility of these thin frits which pressed them tightly to the glass. The cell resistances were much higher with the BN frits due to the low porosity. The resistance was used to follow the wetting of the frit by the melt, and we found that stable wetting was obtained after about one week (the cell resistance decreased from 20 000 to 1600 ohms during this interval). An electrolysis current between 5 and 10 mA was found to be a suitable compromise beetween keeping the frit heating down and the salt flow high as compared to the temperature-induced fluctuations. Totally 32 independent values for BN grade A frits give:

$$t_{\mathrm{Cl}^-} = 0.850 - (9.3 \pm 7.4) \times (T - 565)$$
$$(561\,°\mathrm{C} < T < 596\,°\mathrm{C}).$$

Conclusion

In experiments on molten lead chloride we have shown the influence of the frit material (Pyrex glass and boron nitride) upon the external transport numbers of a molten salt. This fact strongly supports our assertion that external transport numbers are properties of the interfacial layer between the melt and the solid and depend not only on the nature of the salt but also on the nature of the solid. A small temperature dependence of the transport numbers is also demonstrated.

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