

Transport Numbers in the Molten System NaF-KF-AlF₃-Al₂O₃

Pavel Fellner¹, Ján Híveš¹, Jomar Thonstad²

¹Slovak University of Technology in Bratislava, Radlinského 9, Bratislava, 812 37, Slovakia

²Norwegian University of Science and Technology, Trondheim, 7491, Norway

Keywords: Transport Number, Cryolite, Aluminium

Abstract

Transport numbers in the molten system NaF – KF – AlF₃ (Al₂O₃, CaF₂) were investigated by the Hittorf method. It was confirmed that in molten cryolite, Na₃AlF₆, at 1010°C, the current is transported almost exclusively by the Na⁺ cations ($t(\text{Na}^+) = 0.99$). When AlF₃ is added to a Na₃AlF₆ melt, the transport number of sodium cations decreases to 0.74 at the composition corresponding to NaAlF₄. In molten K₃AlF₆ the transport number of K⁺ cations equals 0.836 at 1005°C. In melts containing both Na⁺ and K⁺, the cations contribute to the charge transport approximately in the ratio of the squares of their ionic radii.

Introduction

The transport number t_j of the ion j , is defined as the fraction of the electric current carried by that ion in a solution of uniform composition, i.e. without a concentration gradient. Other names for t_j are “transference number” or “electrical transport number”. This parameter is always positive, and it does not reflect the direction of transport. Transport numbers are called “internal” when another ion of the system or a neutral solvent is the frame of reference. “External” transport numbers have a porous plug or a wall as reference. The sum of the transport numbers of all ions equals one. A detailed discussion of this topic together with examples can be found in the paper by Ratkje et al. [1].

Principal data on the transport phenomena in cryolite melts was discussed in the monograph “Aluminium Electrolysis” [2]. Transference (transport) numbers are discussed also in the 3rd edition of “Aluminium Electrolysis” [3]. The treatment is based on results published by Frank and Foster [4], Tual and Rolin [5, 6] and Dewing [7]. Frank and Foster investigated transport phenomena in cryolite-alumina melts by means of a radioactive tracer method. It was found that $t_{\text{Na}}^+ = 0.99$. Tual and Rolin applied the classical Hittorf method. These authors also came to the conclusion that in neutral or basic electrolytes the transference number of the sodium cation is close to unity. With increasing acidity of the bath, the transport number of Na⁺ decreases. This is often explained by participation of the F⁻ ions in the conduction [2, 3]. Even in electrolytes with an excess of 7 mass % AlF₃, the transference number of the sodium cation did not drop below $t_{\text{Na}}^+ = 0.9$ [5, 6]. For Li₃AlF₆ melt at 1030 K, Dewing [7] found that the transport number $t_{\text{Li}}^+ = 0.957 \pm 0.08$. This strongly supports the notion that electrical charge in cryolite-based melts is transported mainly by cations.

Sterten et al. [8] reported transference numbers for Na⁺ based on emf measurements for CR = 2 – 3 (molar ratio $n(\text{NaF})/n(\text{AlF}_3)$) to be 0.96 – 0.99. It was assumed that fluoride anions carry the remainder of the current.

In the present work we used the Hittorf method in a similar way as was done by Tual and Rolin [5, 6].

Experimental

Chemicals

Aluminium fluoride was purified by sublimation in a platinum crucible (inner diameter 75 mm, height 270 mm). The temperature at the bottom of the crucible was 1250 °C; the Pt lid covering the crucible was cooled in an argon atmosphere. In each run, 100 g of sublimated AlF₃ was prepared.

Potassium fluoride of grade “pro analysis” was dried in a vacuum furnace for 10 days. The drying procedure starts at ambient temperature. At the bottom of the vacuum furnace a dish with P₂O₅ is placed. After 4 days the temperature is gradually increased up to 200 °C. This procedure ensures a very low moisture content in the system. Sodium fluoride and alumina were of analytical grade, and prior to use they were heated to remove any moisture.

Apparatus and Experimental Procedure

The scheme of the apparatus used to measure the transport numbers of Na⁺ and K⁺ in the molten system NaF – KF – AlF₃ – Al₂O₃(sat.) is shown in Figs. 1-2. The cell was made of hot-pressed boron nitride (BN). Open channels between the anode and the neutral compartments and between the cathode and the neutral compartments were made, the diameter of the hole being 2.1 mm. The anode was made of platinum, and a graphite cathode was used. The temperature was measured by means of a Pt10Rh-Pt thermocouple.

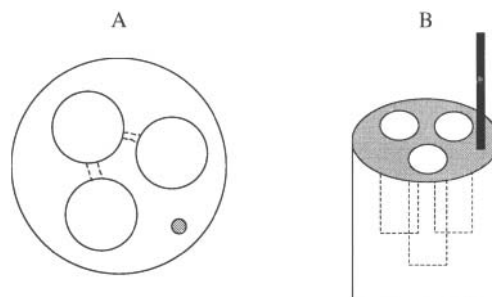


Figure 1. BN electrolysis cell. A - top view, B – side view. Outer diameter 51 mm, inner diameter of compartments 17 mm, crucible height 59 mm. Diameter of channels between compartments (dotted lines) 2.1 mm.

The principle of the measurement is as follows:

Electrolyte of desired composition was pre-melted in a platinum apparatus. (ca 55 g of electrolyte was prepared.) The sample was pulverized. The electrolyte (8 – 11 g) was placed into each compartment of the cell. The cell was placed in a vertical resistor-heated furnace with a controlled argon atmosphere. When the desired temperature was reached, it was kept constant ± 1 K. Electrolysis was carried out with 100 – 200 mA current for 30 – 60 minutes. (Duration and current should be as low as possible. However, the total charge passed through the cell must be large enough to provide measurable changes in the composition in the cathodic and anodic compartments.) Initially 60 min electrolysis

time was used. However, we found that 30 min electrolysis is optimal for obtaining reliable data on transport numbers. It was found that a charge of about 550 C was optimal. After the experiment, the cell was withdrawn from the furnace and cooled in a stream of argon. Samples of the electrolyte were drilled out of each compartment for analysis.

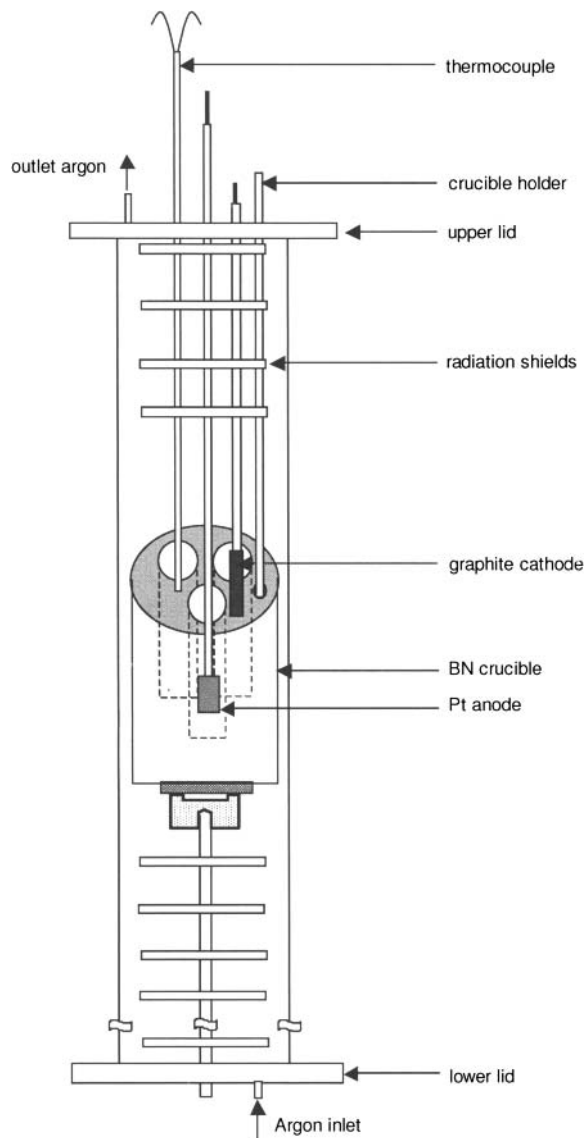


Figure 2. Scheme of the apparatus.

Analysis

The main difference in comparison with previous studies consists in the analysis of the samples. While in the past radioactive tracers were used for the determination of the composition of the samples, in this work samples of the solidified electrolyte were dissolved in aqueous solutions and analysed by atomic absorption spectroscopy. Dissolution (decomposition) of cryolite-based electrolytes was carried out as follows (procedure ISO 2366:1974).

Prior to the analysis the sample was ground in an agate mortar and homogenized. 0.2 g of the sample was transferred to a PTFE dish (Teflon) and 5 ml of concentrated H_2SO_4 was added. The sample was heated with stirring for 30 min in a sand bath until white fumes appeared. After cooling, 5.0 ml of concentrated HCl was carefully added. The sample was again heated in the sand bath for 30 min. After cooling, the sample was transferred to a 100 ml flask and diluted to 100 ml of solution (exactly) with distilled water. This procedure was repeated 4 times for each sample.

Determination of Na and K

Na and K were determined by flame AAS (Perkin Elmer 1100, USA) in a C_2H_2 -air flame. In order to depress ionisation of the analyte, addition of Cs (1 g/l) was used. Calibration was made using one-element standard solutions (Merck) with Na concentrations (0.5; 1.0; 1.5) $mg\ l^{-1}$ and K concentrations (0.2; 0.5; 1.0; 2.0) $mg\ l^{-1}$.

Determination of Al

Aluminium was determined by flame AAS (Perkin Elmer 5000, USA) in a $C_2H_2-N_2O$ flame. For calibration, solutions having the concentrations 10.0; 20.0; 50.0 $mg\ l^{-1}$ were used. The conditions of the measurement are given in Table I. The accuracy of the determination and the uncertainty characterizing the analytical procedure are given in the Table II.

Table I. Conditions of AAS analysis.

	Na	K	Ca	Al
lamp current of the lamp	HCl Na+K 12 mA	HCl Na+K 12 mA	HCl Ca 10 mA	HCl Al 25 mA
wave-length	589.0 nm	766.5 nm	422.7 nm	309.3 nm
opening	0.7 nm	0.7 nm	0.7 nm	0.7 nm
flow of fuel/oxidizer	2.5 / 8 $l.min^{-1}$	2.5 / 8 $l.min^{-1}$	4 / 8 $l.min^{-1}$	5.5 / 10 $l.min^{-1}$

Results and Discussion

All results are summarized in Table II.

Table II. Transport numbers in the system NaF-KF- AlF_3 - Al_2O_3 .

CR	Al_2O_3 /wt. %	CaF_2 /wt. %	$\frac{n(NaF)}{n(KF)}$	$t / ^\circ C$	$t(Na^+)$	$t(K^+)$	$t(F^-)$
3.0	0	0	only NaF	1018	0.990 ± 0.003	-	0.010 ± 0.003
2.0	sat.	0	only KF	920	-	0.676 ± 0.006	0.323 ± 0.006
1.3	sat.	0	1	767	0.504 ± 0.002	0.264 ± 0.005	0.232 ± 0.007
1.3	sat.	5	1	800	0.520 ± 0.009	0.394 ± 0.031	0.086 ± 0.040
1.22	-	-	only NaF	795	0.742 ± 0.003	-	0.258 ± 0.003
1.5	-	-	only NaF	825	0.816 ± 0.007	-	0.184 ± 0.007
2.2	-	-	only NaF	1004	0.883 ± 0.005	-	0.117 ± 0.005
3.0	-	-	only KF	1005	-	0.863 ± 0.009	0.137 ± 0.009

It can be seen that the reproducibility of the measurements is good. We always found aluminium deposited on the bottom of the graphite cathode (see Fig. 3).

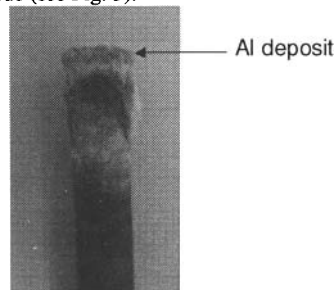


Figure 3. A view of a used graphite cathode with Al deposit.

Analysis showed high current efficiency for Al (94-97 %); while in the case of potassium cryolite it was lower, i.e. 91.8 %. In the case of a melt prepared by melting pure cryolite, the transport number of sodium was found to be 0.99, in agreement with previous studies [1,5, 6]. When AlF_3 was added to the melt, the transport number of sodium cations decreased, as shown in Fig. 4.

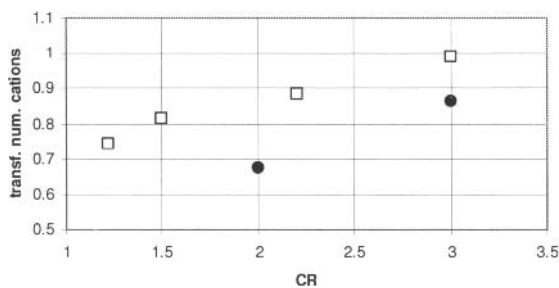


Figure 4. The transport number of sodium (squares) and potassium (circles) cations as a function of the cryolite ratio (CR). Temperature range 795 - 1018 °C.

When extrapolating the data for the $\text{NaF} - \text{AlF}_3$ system to the NaAlF_4 composition ($\text{CR} = 1$), we obtain $t(\text{Na}^+) = 0.73$. From models of cryolite-based melts [2, 3] it follows that this melt contains almost exclusively AlF_4^- anions. These anions apparently contribute to the transport of charge. On the other hand, in Na_3AlF_6 melts the fluoride ions, as predicted according to the cited model, do not contribute to charge transfer. The ionic radius of the sodium cation is 100 pm and that of the AlF_4^- anion is 165 pm [9, 10], so that $r(\text{AlF}_4^-) / (r(\text{Na}^+) + r(\text{AlF}_4^-)) = 0.626$. This estimate gives the order of the transference number of Na^+ cation observed experimentally. This fact should be taken into account in ionic models of molten aluminates with complex anions. When the electrolyte was composed of an equimolar mixture of NaF and KF (+ AlF_3), the sodium cation transferred about twice as much electrical charge as the potassium cation. The ionic radius of the sodium cation, $r(\text{Na}^+) = 100$ pm and that of the potassium cation $r(\text{K}^+) = 133$ pm. The ratio $r(\text{K}^+) / r(\text{Na}^+) = 1.33$. The ratio of the squares of the ionic radii $r^2(\text{K}^+) / r^2(\text{Na}^+) = 1.77$. It appears that the ratio of the transport numbers of $t(\text{Na}^+) / t(\text{K}^+)$ is approximately proportional to the square of their ionic radii.

Conclusions

An apparatus for measurement of transference numbers in cryolite-based electrolytes was constructed and tested. The heart of the apparatus is a BN cell having three compartments connected with narrow capillaries.

The cathode is made of graphite; the anode is made of platinum. Electrolysis is carried out in argon atmosphere in a vertical furnace. After electrolysis the cell is cooled in a stream of argon. The current passing through the cell was (100 – 200) mA. (60 – 30) min of electrolysis was sufficient for obtaining reproducible data on the transference numbers.

After cooling, the electrolyte from each compartment is drilled out, homogenized, dissolved (treated with sulphuric and hydrochloric acid) and analysed by AAS for the contents of Na, K, and Al (and Ca if present).

From the difference in the composition of the electrolyte in the cathodic and middle (neutral) compartments, the transference numbers of Na^+ and K^+ can be determined. The transference number of anions is obtained by difference: $1 - t(\text{Na}^+) - t(\text{K}^+)$.

The obtained transference numbers at different composition of the cryolite-based electrolyte are summarized in Table II.

We assume that the temperature does not have a pronounced influence on the transference number. It follows that the transference number of Na^+ is about twice as high as that of K^+ . The more acidic the electrolyte, the higher is the role of the fluoride anions in charge transfer.

It was found out that addition of CaF_2 to the electrolyte diminishes the contribution of the fluoride ions to the charge transfer.

Acknowledgement

The authors are grateful for financial assistance from the Grant Agency of the Slovak Republic under the project VEGA 1/0535/08. Financial support from ALCOA INC. is gratefully acknowledged.

References

- S.K. Ratkje, H. Rajabu, and T. Førland, "Transference coefficients and transference numbers in salt mixtures relevant for the aluminium electrolysis," *Electrochim. Acta*, 38 (1993), 415-423.
- K. Grjotheim et al., *Aluminium Electrolysis - Fundamentals of the Hall-Héroult Process* (Düsseldorf, Germany: Aluminium-Verlag, 1982), 175-178.
- J. Thonstad et al., *Aluminium Electrolysis - Fundamentals of the Hall-Héroult Process* (Düsseldorf, Germany: Aluminium-Verlag, 2001), 127-128.
- W.B. Frank, and L.M. Foster, "Investigation of Transport Phenomena in the Cryolite-Alumina System by Means of Radioactive Tracers," *J. Phys. Chem.*, 61 (1957), 1531-1536.
- A.Tual, and M. Rolin, "Etude des nombres de transport ioniques dans les mélanges cryolithe-alumine selon le principe de la methode de Hittorf—I. mise en oeuvre de la methode," *Electrochim. Acta*, 17 (1972), 1945-1954.
- A.Tual, and M. Rolin, "Etude des nombres de transport ioniques dans les melanges cryolithe—alumine fondus selon le principe de la methode de hittorf—II. Resultats," *Electrochim. Acta*, 17 (1972), 2277-2291.

7. E.W. Dewing, "Thermodynamics of the System LiF-AlF₃," *J. Electrochem. Soc.*, 123 (1976), 1289-1294.
8. Å. Sterten, K. Hamberg, and I. Mæland, "Activities and Phase Diagram Data of NaF-AlF₃-Al₂O₃ Mixtures Derived from Electromotive Force and Cryoscopic Measurements. Standard Thermodynamic Data of β -Al₂O₃(s), Na₃AlF₆(s), and NaAlF₄(l)," *Acta Chem. Scand.*, A36 (1982), 329-344.
9. R.D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.* A32 (1976), 751-767.
10. Z. Akdeniz et al., "Ionic Interactions in Alkali - Aluminium Tetrafluoride Clusters," *Z. Naturforsch.*, 54a (1999), 570-574.