A new method has been proposed for determination of transference numbers from emf measurements in systems having one degree of freedom. The method is applied to molten fluorides, using literature data. Data for the system NaF–AlF₃–Al₂O₃(sat) gives the relative movement of the Na⁺ ion with respect to a fixed frame of reference. A consistent data set is given for \( t_{Na⁺} \) from different concentration cells. The transference number is also discussed for different frames of reference. Emf measurements for a cell containing NaF and AlF₃ give transference numbers which are physically unlikely.

INTRODUCTION

This work presents an extended discussion of a new method for evaluation of transference numbers of concentration cells. The method has been developed for concentration cells with ion exchange membranes (1). It was already applied and briefly discussed for cells with molten fluorides (2). Some additional applications are shown in this work. Transference numbers in fluoride melts are needed for calculations of cell potentials and local heat productions at the electrodes during aluminium electrolysis (3).

PRINCIPLES

Our approach to electrochemistry is operational; i.e. the quantities used are all measurable (4). We shall consider a cell consisting of three compartments. The left-hand side half cell (I), the right-hand side half cell (II), and the junction compartment. In compartments (I) and (II) there is no gradient in concentration. The emf is derived from the flux equations of irreversible thermodynamics. No other assumptions than those inherent in the Onsager reciprocal relations are involved. This leads to the expression for
the emf of isothermal cells:

$$\Delta \varphi = -| \sum_i t_i \mu_i + \int \sum_i \mu_i \, \mathrm{d}t_i | = -\int \sum_i t_i \, \mathrm{d}\mu_i$$  \[1\]

where $\Delta \varphi$ is given in units $J \text{ mol}^{-1}$ of electric charge ($J \text{ F}^{-1}$), $\Delta \varphi = EF$, $E$ is the emf in Volts, and $F$ is the Faraday constant ($F=96485 \text{ C mol}^{-1}$). What is essential in equation [1] is that $i$ is an electrically neutral component, not an ion. Thus the chemical potential $\mu_i$ (units $J \text{ mol}^{-1}$) is a well defined quantity. Correspondingly, $t_i$ is a transference coefficient of a neutral component referring to a chosen frame of reference. (see equations [4]). The transference coefficients describe the change in composition in the electrolyte by charge transfer, irrespective of the mechanism, i.e. they are operational. Thus changes by electrode reactions are included in the transference coefficient.

The integral of equation [1] will hereafter, be given without the integration limits.

The transference number of the ion $j$, $t_j$, is defined as the fraction of the electric current density, $j$, carried by the ion in a solution of uniform composition i.e. $\Delta c = 0$, (see e.g. refs. 5–8)):

$$t_j = \left. |z_j \, J_j / j| \right|_{\Delta c = 0}$$  \[2\]

where $z_j$ and $J_j$ are charge and flux respectively of the ion. $J_j$ is given in mol m$^{-2}$ s$^{-1}$ and $j$ in mol of electric charge m$^{-2}$ s$^{-1}$ or F m$^{-2}$ s$^{-1}$.

Other names for $t_j$ are "transport number" or "electrical transport number". The fraction is positive by definition; it does not show the direction of transport. Transference numbers are called "internal" when another ion of the system or a neutral solvent is the frame of reference. "External" transference numbers have a porous plug or a wall reference. From the definition [2] it follows that:

$$\sum_i t_i = 1$$  \[3\]

The transference coefficient for a neutral component $i$ is defined as the number of moles of $i$, $\Delta n_i$, transferred, divided by the number of moles of electric charge, $\Delta Q$, passing a cell of uniform composition, in the limit $\Delta Q \to 0$:
\[ t^H_i = \lim_{\Delta Q \to 0} \left( \frac{\Delta n_i}{\Delta Q} \right) \] \[ 4a \]

In a Hittorf type experiment \( \Delta n_i \), and hence \( t^H_i \), is referred to a fixed amount of a compound or ion. Superscript \( H \) means Hittorf type experiment. In aqueous solutions, water is often chosen as the frame of reference. Another common choice for the frame of reference used together with equation \( 4a \) is the wall or a porous plug. If one of the ions, e.g. \( X^- \) is used as the reference, it is indicated in the superscript as \( t^{LX^-}_i \).

\[ t^{LX^-}_i = \lim_{\Delta Q \to 0} \left( \frac{\Delta n_i}{\Delta Q} \right) \] \[ 4b \]

A modification of the Hittorf transference coefficient is obtained by using one of the ions e.g. \( X^- \), as a fixed frame of reference. This is then a quasi lattice of immobile \( X^- \) ions, that is, we consider the transport of all other ions with respect to the \( X^- \) ions. The transference coefficient of a component \( i \) is then defined as:

\[ t^{LX^-}_i = \left( J_i / J \right)_{\Delta c=0} \] \[ 5 \]

where \( J_i \) expresses the transfer of the neutral component \( i \) from left to right. Superscript \( L \) means a quasi lattice reference. We shall use this definition in the present derivation (see equations \[10a,b,c\]).

Both transference coefficients, equations \( 4,5 \) depend on the electrodes used, and for the specific choice of electrodes, they are related. When \( X^- \) is not involved in the electrode reaction, they are identical. The definition \( 5 \) is often convenient to describe cells with solid electrolytes. The \emf\ of an electrochemical cell is of course invariant to our choice of the frame of reference. A more extensive discussion of the types of frame of reference is given in refs. (2,9).

THE SYSTEM NaF–AlF₃–Al₂O₃

The solvent for \( \text{Al}_2\text{O}_3 \) in the industrial electrolysis of aluminium is a molten mixture of NaF and AlF₃, with a composition in the neighborhood of cryolite \( \text{Na}_3\text{AlF}_6 \). A large number of studies of the thermodynamics of the mixture NaF–AlF₃–Al₂O₃ has been
carried out. In all studies relevant in this context, the system has been saturated with $\text{Al}_2\text{O}_3$.

The dissociation of the cryolite according to:

$$\text{AlF}_6^{2-} = \text{AlF}_4^- + 2 \text{F}^- \quad [I]$$

was first estimated by Grjotheim (10) from phase diagram analysis. Spectroscopic evidence for cryolite dissociation was first obtained by Ratkje and Rytter (11). The following reaction is likely at high concentrations of oxide (12,13):

$$3 \text{NaF(l)} + \text{AlF}_3(l) + \text{Al}_2\text{O}_3(s) = 1\frac{1}{2} \text{Na}_2\text{Al}_2\text{O}_2\text{F}_4(l) \quad [II]$$

At low oxide concentrations another complex is formed:

$$\text{Al}_2\text{O}_2\text{F}_4^{2-} + 2 \text{AlF}_4^- = 2 \text{Al}_2\text{OF}_6^{2-} \quad [III]$$

The first experimental evidence for the complex ions, $\text{Al}_2\text{OF}_6^{2-}$ and $\text{Al}_2\text{OF}_2\text{F}_4^{2-}$ was given by Førland and Ratkje (12,13) for dilute solutions of cryolite and oxide in NaF. Their experiments showed that complexes of the type $\text{AlOF}_6^{2-}$ were negligible and that $\text{Al}_2\text{OF}_6^{2-}$ will be present only at low oxide concentrations, or high AlF$_3$ concentrations. Their results were further confirmed by enthalpy data at higher concentrations by Julsrud (14), and by Raman spectroscopy by Gilbert et al. (15). For the composition in the industrial cell, the ions Na$^+$, F$^-$, AlF$_4^-$, AlF$_6^{3-}$ and Al$_2$OF$_4^{2-}$ are probably most important. Sterten (16) has calculated melt compositions assuming an ideal Temkin model over extended concentration ranges.

**Derivation of transference numbers from emf measurements of concentration cells**

The emf has been measured at 1000°C in cells [a] and [c] by Sterten et al. (20) and in cell [b] by Yoshida and Dewing (19) and by Thonstad and Rolseth (25).

$$\text{Na(Pb)(l) | (NaF, AlF}_3, \text{Al}_2\text{O}_3\text{(sat)})_1 || (\text{NaF, AlF}_3, \text{Al}_2\text{O}_3\text{(sat)})_II | \text{Na(Pb)(l)} \quad [a]$$
The basic components of the electrolyte are NaF, AlF₃, and Al₂O₃. For the derivations, we may choose any combinations of these to make a new set of neutral components. The most practical choice of components in this system turns out to be NaF, AlF₃, and Al₂O₂F₂. This choice is made because the fluoride lattice frame of reference is convenient. Furthermore, Al₂O₂F₂ is chosen due to the presence of the group Al₂O₂Fx as expressed in equations [II,III]. We shall derive the transference numbers for the Na⁺ ion using these components.

Since the fused mixture is saturated with alumina, we have the following formal equilibrium:

\[ \text{AlF}_3 + \text{Al}_2\text{O}_3(\text{sat}) = \frac{1}{2} \text{Al}_2\text{O}_2\text{F}_2 \]  

[IV]

This gives the stoichiometric relationship:

\[ \Delta n_{\text{AlF}_3} = -\frac{1}{2} n_{\text{Al}_2\text{O}_2\text{F}_2} \]

[6]

where \( \Delta n_{\text{AlF}_3} \) is the change in the content of AlF₃ by the reaction [IV], and the relationship between the chemical potentials:

\[ d\mu_{\text{Al}_2\text{O}_2\text{F}_2} = \frac{1}{2} d\mu_{\text{AlF}_3} \]

[7]

The system consists of 3 components and 2 phases. At constant temperature and pressure there is only one degree of freedom, i.e. there is only one independent transference coefficient or one independent ionic transference number. The Gibbs–Duhem equation for this system gives:

\[ n_{\text{NaF}} d\mu_{\text{NaF}} + n_{\text{AlF}_3} d\mu_{\text{AlF}_3} + n_{\text{Al}_2\text{O}_2\text{F}_2} d\mu_{\text{Al}_2\text{O}_2\text{F}_2} = 0 \]

[8a]
By introducing equations [6] and [7] into the Gibbs–Duhem equation we obtain:

$$d\mu_{\text{AlF}_3} = - n_{\text{NaF}} d\mu_{\text{NaF}}/n_{\text{AlF}_3}^o$$  \[8b\]

where the original content of AlF$_3$, $n_{\text{AlF}_3}^o$, is $n_{\text{AlF}_3} + 2\tfrac{1}{2} n_{\text{AlOF}}$.

The electrode reactions on the right hand side electrode for the cells are:

For Na electrodes: $\text{Na}^+ + e^- = \text{Na(Fb)}(l)$ \[V\]

For Al electrodes: $\tfrac{1}{2} \text{Al}^{3+} + e^- = \tfrac{1}{2} \text{Al}(l)$ \[VI\]

For O$_2$ electrodes: $\tfrac{1}{2} \text{Al}^{3+} + \tfrac{1}{4} \text{O}_2(g) + e^- = \tfrac{1}{4} \text{Al}_2\text{O}_2^{2+}(l)$ \[VII\]

Equation [3] for the three cells gives:

$$t^{\text{F}^-}_{\text{Na}^+} + t^{\text{F}^-}_{\text{Al}^{3+}} + t^{\text{F}^-}_{\text{AlOF}^{2+}} = 1$$  \[9\]

The relations between the transference coefficients and the transference numbers differ for the three cells. For known ionic equilibria, we obtain for:

**Na electrodes:** $t^{\text{F}^-}_{\text{NaF}} = t^{\text{F}^-}_{\text{Na}^+} - 1$, $t^{\text{F}^-}_{\text{AlF}_3} = \tfrac{1}{2} t^{\text{F}^-}_{\text{Al}^{3+}}$  \[10a\]

and $t^{\text{F}^-}_{\text{AlOF}} = \tfrac{1}{2} t^{\text{F}^-}_{\text{AlOF}^{2+}}$

**Al electrodes:** $t^{\text{F}^-}_{\text{NaF}} = t^{\text{F}^-}_{\text{Na}^+}$, $t^{\text{F}^-}_{\text{AlF}_3} = \tfrac{1}{2} t^{\text{F}^-}_{\text{Al}^{3+}} - \tfrac{1}{2}$,  \[10b\]

and $t^{\text{F}^-}_{\text{AlOF}} = \tfrac{1}{2} t^{\text{F}^-}_{\text{AlOF}^{2+}}$

**O$_2$ electrodes:** $t^{\text{F}^-}_{\text{NaF}} = t^{\text{F}^-}_{\text{Na}^+}$, $t^{\text{F}^-}_{\text{AlF}_3} = \tfrac{1}{2} t^{\text{F}^-}_{\text{Al}^{3+}} - \tfrac{1}{2}$,  \[10c\]

and $t^{\text{F}^-}_{\text{AlOF}} = \tfrac{1}{2} t^{\text{F}^-}_{\text{AlOF}^{2+}} + \tfrac{1}{4}$

From equations [9] and [10], we obtain the same relationship between transference...
coefficients for all the three cells:

\[ t^{L^F}_{Na^F} + 3 t^{L^F}_{Al^F} + 2 t^{L^F}_{AlO^F} = 0 \]  \[11\]

For any of the cells (a, b, c), the emf can be expressed according to equation [1] as:

\[ \Delta \varphi = -f(t^{L^F}_{Na^F} d\mu_{Na^F} + t^{L^F}_{Al^F} d\mu_{Al^F} + t^{L^F}_{AlO^F} d\mu_{AlO^F}) \]  \[12\]

By introducing equation [7] into [12] we obtain:

\[ \Delta \varphi = -f(t^{L^F}_{Na^F} d\mu_{Na^F} + [t^{L^F}_{Al^F} + \frac{1}{2} t^{L^F}_{AlO^F}] d\mu_{Al^F}) \]  \[13\]

The independent transference coefficient is here \( t^{L^F}_{Na^F} \). Only the sum of the two others, \([t^{L^F}_{Al^F} + \frac{1}{2} t^{L^F}_{AlO^F}]\), can be obtained.

By introducing equations [8b] and [11] into [13] we obtain:

\[ \Delta \varphi = -f(t^{L^F}_{Na^F}/(1 - x_{Na^F})) d\mu_{Na^F} \]  \[14\]

where \( x_{Na^F} \) is the equivalent fraction of NaF in the system, defined as:

\[ x_{Na^F} = n_{Na^F}/(n_{Na^F} + 3 n_{Al^F} + 2 n_{AlO^F}) = n_{Na^F}/(3 n_{Al^F} + n_{Na^F}) \]  \[15\]

Cells [b] and [c] have identical emfs because for both these cells, \( t^{L^F}_{Na^F} = t^{L^F}_{Na^+} \). (see equations [10b,c,14]). For cell [a], \( t^{L^F}_{Na^F} \) is different and therefore \( \Delta \varphi_{Na} = \Delta \varphi_{Al} = \Delta \varphi_{O^2} \), where the subscript represents the electrode used.

The transference numbers of Na+ ions for the three cells can thus be expressed as:

\[ t^{L^F}_{Na^+} = 1 - x_{Na^F}(d\varphi_{Na}/d\mu_{Na^F}) \]  \[16a\]
An alternative choice of components, NaF, AlF₃ and Al₂OF₆, leads to the same equations [16]. The expression for $t^{L,F}_{\text{Na}^+}$ is thus independent of the specific choice of aluminium–oxygen–complex.

The experiments are performed in the following way. The composition of compartment I is kept constant while the composition of compartment II varies. The emf of the cell is measured for each composition difference. The incremental change in emf, $d\varphi$, is due to the change $d\mu_{\text{NaF}}$ in compartment II. The slope of the plot of $\Delta\varphi$ against $\mu_{\text{NaF}}$ in this compartment, gives $t^{L,F}_{\text{Na}^+}$ as a continuous function of concentration in compartment II.

Literature data (19,20,25,27) were used to plot emf as a function of $\Delta\mu_{\text{NaF}}$ in cells [a,b,c]. Plots using data for cells [b] and [c] are shown in Fig.1. A similar plot for cell [a] gives approximately constant $d\varphi_{\text{NaF}}/d\mu_{\text{NaF}} = +0.02 \pm 0.004$. The transference number of $\text{Na}^+$, $t^{L,F}_{\text{Na}^+}$, is obtained from equations [16a,b,c] and shown in Table I.

\[
t^{L,F}_{\text{Na}^+} = -(1-x_{\text{NaF}})(d\varphi_{\text{AlF}}/d\mu_{\text{NaF}}) \quad [16b]
\]

\[
t^{L,F}_{\text{Na}^+} = -(1-x_{\text{NaF}})(d\varphi_{\text{O}}/d\mu_{\text{NaF}}) \quad [16c]
\]
Table I. Transference number of Na⁺ ₇⁻ Na⁺ in the system NaF-AlF₃-Al₂O₃(sat) for cells [a,b,c].

The emf results are taken from Sterten et al. (O₂ and Na electrodes) (20), and Yoshida and Dewing (Al electrodes) (19). Activity data are from ref. (20). The derivatives dqₒ/dµ NaF and dqₐ/dµ NaF are taken from Fig.1, and dqₒ/dµ NaF = 0.020 ± 0.004. The error in the derivatives are estimated from the uncertainty of the emf and µ NaF.

\( r = \frac{n_{NaF}}{n_{AlF}} \)

| Electrode: | (O₂) | (Al) | (Na) |
|-----------|------|------|------|
| \( d_{L}^{F-Na⁺} \) | \( d_{L}^{F-Na⁺} \) | \( d_{L}^{F-Na⁺} \) | \( d_{L}^{F-Na⁺}(av) \) |
| ± 0.06    | ± 0.06 | ± 0.04 |

| \( r \) | 1.4 | 1.09 | 1.01 |
|---------|-----|------|------|
| 1.6     | 1.05 | 1.04 |
| 1.8     | 1.05 | 1.03 | 1.04±0.02 |
| 2.0     | 1.00 | 1.00 | 1.00±0.01 |
| 2.2     | 0.97 | 0.96 | 0.99±0.02 |
| 2.4     | 0.93 | 0.92 | 0.94±0.05 |
| 2.6     | 0.90 | 0.88 | 0.98±0.06 |
| 2.8     | 0.89 | 0.85 | 0.96±0.06 |
| 3.0     | 0.84 | 0.82 | 0.98±0.07 |
| 3.2     | 0.79 |       |      |
| 3.4     | 0.76 |       |      |
| 3.6     | 0.73 |       |      |
| 3.8     | 0.71 |       |      |
| 4.0     | 0.69 |       |      |
In Table II the results from cell [b] are further analyzed. The transference number of Na\(^+\) is shown with two reference choices, L\(_F\) and L\(_{Al}^{13+}\). For the latter frame of reference, the derived expression is:

\[
\n{^L_{Al}^{13+}Na^+} = -\{x_{NaF}/(1-x_{NaF})\} - (d\varphi_{Na}/d\mu_{NaF})
\]

Table II. Transference number of Na\(^+\) in the system NaF–AlF\(_3\)-Al\(_2\)O\(_3\) (sat) for cell [b].

Two different reference frames are shown. The emf values are from Yoshida and Dewing (19) for 2\(<r<4\) and from Thonstad and Rolseth (25) for \(r>4\). Activity data are from ref. (20) and \(r = n_{NaF}/n_{AlF}\). The error in the derivative \(d\varphi_{Na}/d\mu_{NaF}\) is estimated from the uncertainty of the emf and \(\mu_{NaF}\).

| \(r\) | \(\Delta\varphi/kJ\) | \(d\varphi/d\mu_{NaF}\) | \(t_{L,F}^{Na^+}\) | \(t_{L,Al}^{13+}Na^+\) |
|---|---|---|---|---|
| ± 1 | ± 0.06 | ± 0.06 | ± 0.06 |
| 2 | 15.9 | -1.47 | 1.00 | 0.80 |
| 2.4 | 6.9 | -1.47 | 0.92 | 0.67 |
| 3 | 0.3 | -1.63 | 0.82 | 0.63 |
| 3.5 | -4.8 | -1.78 | 0.82 | 0.61 |
| 4 | -7.5 | -1.37 | 0.58 | 0.03 |
| 4.5 | -9.1 | -1.47 | 0.63 | 1.03 |
| 5 | -10.6 | -1.68 | 0.63 | 0.01 |
| 5.5 | -11.6 | -1.92 | 0.68 | 0.09 |
| 6 | -12.6 | -2.19 | 0.73 | 0.19 |
| 7 | -14.5 | -2.69 | 0.81 | 0.36 |
| 8 | -15.9 | -3.13 | 0.85 | 0.46 |
| 9 | -17.4 | -3.49 | 0.87 | 0.49 |
| 10 | -18.8 | -3.79 | 0.87 | 0.45 |
| 12 | -20.3 | -4.23 | 0.85 | 0.23 |
| 14 | -21.7 | -4.84 | 0.85 | 0.17 |
THE SYSTEM NaF–AlF₃

The molten mixture of NaF and AlF₃ has been investigated at 1020°C using the concentration cell (25)

\[
\text{Al(l)} | (\text{NaF, AlF}_3)_I \parallel (\text{NaF, AlF}_3)_II | \text{Al(l)} \quad [d]
\]

The electrolyte has two components and one phase. At constant \(P\) and \(T\) this means that also in this case we have only one degree of freedom; i.e. only one independent transference number. Using a similar procedure as above, the transference number of Na⁺ ions for this cell is expressed as:

\[
t^{\text{Na}^+} = -(1-x_{\text{NaF}})(d\varphi_{\text{Al}}/d\mu_{\text{NaF}})
\]

where \(x_{\text{NaF}}\) is the equivalent fraction of NaF in the system defined as:

\[
x_{\text{NaF}} = n_{\text{NaF}}/(3n_{\text{AlF}} + n_{\text{NaF}})
\]

The same form of the equation for the transference number of Na⁺ is obtained as for the ternary electrolyte, compare equations [17] and [16b]. This means that a difference in \(emf\) between cells [d] and [b] is due to the participation of oxygen-containing complexes in the charge transfer.

Equation [17] is used to calculate \(t^{\text{Na}^+}_{\text{NaF}}\) in cell [d] from \(emf\) data of Saget et al. (26) and activity data from Sterten and Mæland (29). The results are given in Table III.
Table III. Transference number of Na⁺, $t^{\text{LF}_{\text{Na}^+}}$, in the system NaF–AlF₃ for cell [d].

The $emf$ values are from Saget et al. (26) and activity data are from ref. (29).

$r = n_{\text{NaF}}/n_{\text{AlF}_3}$.

| $r$  | $\Delta \varphi / kJ \cdot F^{-1}$ | $d\varphi / d\mu_{\text{NaF}}$ | $t^{\text{LF}_{\text{Na}^+}}$ |
|------|-----------------------------------|---------------------------------|-----------------------------|
| ±4   | ±0.5                              | ±0.5                            | ±0.5                        |
| 2.0  | 15                                | -1.3                            | 0.8                         |
| 2.2  | 12                                | -1.2                            | 0.7                         |
| 2.4  | 9                                 | -1.5                            | 0.7                         |
| 2.8  | 3                                 | -2.3                            | 1.2                         |
| 3.0  | 0                                 | -2.6                            | 1.3                         |
| 3.4  | -6                                | -3.1                            | 1.5                         |
| 3.7  | -9                                | -3.2                            | 1.5                         |
| 4.0  | -12                               | -3.2                            | 1.4                         |

DISCUSSION

The method

One advantage of the operationally defined method described above is that it allows consistency checks of different experiments. This is demonstrated by the results of Table I. Results from the different cells [a,b,c] should yield the same values for $t^{\text{LF}_{\text{Na}^+}}$. When this is the case, we may have more confidence in the results. We have thus calculated average value for $t^{\text{LF}_{\text{Na}^+}}$ from the different cells in the concentration range where approximately the same values are obtained. According to the derivations $\Delta \varphi_{\text{Al}} = \Delta \varphi_{\text{O}_2}$. Fig. 1 shows a significant difference in the value of the $emf$ for cell [b] and cell [c] in a concentration range of low $r$–values. The error may be due to an irreversible reaction between aluminium metal and the electrolyte (2). Also, the results in Table III, indicate large errors in the reported $emfs$. There is a need for further investigations.
One further advantage of the method is that the definition of the transference coefficients includes the frame of reference. Knowledge of the relative velocities makes further analysis of the data possible. For example, a value of $t_{Na^+}^{F^-}$ close to unity does not imply that the $F^-$ ions does not carry current in the melt. Recalculation of $t_{Na^+}^{F^-}$ to another frame of reference in Table II demonstrates this. The same physical phenomena must explain the data in the two columns in this table. It is more easily seen from the $Al^{3+}$-reference choice that fluoride ion moves, and has a velocity different from that of $Na^+$. The point that one measures relative movements has been neglected in the literature. A frequent statement is that the $Na^+$ ions carries approximately all current, without a definition of the frame of reference.

Another advantage of the method is that the transference number is obtained as a continuous function of melt composition. Frequently, only average values have been reported for ranges of composition. The lack of continuity shown in the data of Table II for data from cell [b], imply that these experiments contain errors. We have previously discussed (2) the uncertainties in the experiments by Thonstad and Rolseth (25).

Furthermore, it is a necessity that the limiting value of the transference number of $Na^+$, $t_{Na^+}^{F^-}$ is unity when $x_{AlF_5} \rightarrow 0$.

The difference between transference numbers obtained from the two systems described above should give information on the participation of oxygen-containing complexes in the charge transfer. Unfortunately such a comparison cannot be carried out due to uncertainty in emf measurements for cell [d].

**Transference numbers of $Na^+$ in molten fluoride melts**

Table I give reliable values for the transference number of $Na^+$ only in the narrow concentration range $1.8<r<2.2$. This is, however, the range of interest for industrial electrolysis of aluminium. For $2.2<r<3$ the error is $< \pm 0.07$. For $3<r<4$ we use values obtained with Al(1)-electrodes.

Given the limiting value $t_{Na^+}^{F^-} = 1$ when $x_{AlF_5} \rightarrow 0$ and the values of Table II, we see that the transference number as a function of concentration passes a minimum. This can be understood by considering a frame of reference $L,Na^+$. In this frame of reference, we may assume that the velocity of the $F^-$ ions to the left is larger than that of the $Al^{3+}$ containing negative species e.g $AlF_4^-$, $Al_2O_2F_4^{3-}$. This gives a movement of the $Al^{3+}$ species to the right, relative to the sum of the separate $F^-$ ions and the $F^-$ ions in the negative complexes. This effect vanishes as $x_{AlF_5} \rightarrow 0$. Thus the transference numbers $[t_{Al^{3+}}^{F^-} + \frac{1}{2} t_{AlO_2F_4^{3-}}^{F^-}]$ may have a maximum, giving a minimum for $t_{Na^+}^{F^-}$. 

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Table III give values of $t^{F-}_{Na^+} > 1$ which means that $t^{F-}_{Al^3+}$ is negative. This is physically unlikely in a L,F$^-_F$ frame of reference. However, the uncertainty in the emf values is so large that the values of the transference numbers are not reliable.

CONCLUSION

We have applied a method of data analysis for finding transference numbers in systems having one degree of freedom according to the phase rule. The method has been applied to molten fluoride mixtures and several advantages of the method are pointed out. The transference coefficient of NaF has been derived as a function of the derivative $d\phi/d\mu_{NaF}$ and the equivalent fraction of NaF, in mixtures of NaF–AlF$_3$ and NaF–AlF$_3$–Al$_2$O$_3$(sat). We have used the electrochemical cell theory of Forland et al.(4). The applicability of this theory has thus been further demonstrated.

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Fig. 1. The emf, $\Delta \psi$, of the cell:

$$E \mid (\text{NaF, AlF}_3, \text{Al}_2\text{O}_3(\text{sat}))_1 \parallel (\text{NaF, AlF}_3, \text{Al}_2\text{O}_3(\text{sat}))_\text{II} \mid E$$

for different electrodes, $E$, as a function of the activity of sodium fluoride, $\Delta \mu_{\text{NaF}}$, as given by Sterten et al. (20).

Results for oxygen electrodes, from Sterten et al. (20), are given by filled circles, while results for aluminium electrodes, from Yoshida and Dewing (19), are given by empty circles. The temperature is 1273 K and the cryolite ratio is in the range $0.8<r<3.0$. 