On the Connection between Electrical Potential and Free Energy for Concentration Cells with Transference

T. FÖRLAND

N.T.N.F.'s Institutt for Silikatforskning, N.T.H., Trondheim, Norway, and

J. KROGH-MOE

Svenska Silikatforskningsinstitutet, Göteborg, Sweden

From knowledge about the transport numbers the chemical changes have been calculated in a concentration cell when an electrical charge is transported through the cell. For the case that the electrolyte is a good conductor, so changes in dipol layers can be neglected, a rigorous correlation between electromotive force and free energy of the components has been derived.

In the classical treatment of concentration cells with transference, the transport number of the cations or anions appears in the equation for the potential. *E.g.*, for a concentration cell

$$Ag; \ AgNO_3 \ in \ H_2O(I): \ AgNO_3 \ in \ H_2O(II); \ Ag$$
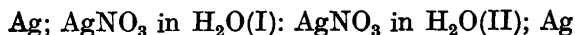
where the two electrolytes are silver nitrate-water solutions of different concentrations, the E.M.F. of the cell is given by:

$$E = (t_{NO_3^-}) \ \frac{RT}{F} \ \ln \frac{a_{II}}{a_I}$$

Here $t_{NO_3^-}$ is the transport number of the nitrate ion, R is the gass constant, T the absolute temperature, F Faraday's number, and a_I and a_{II} are the activities of silver nitrate in the two solutions.

It has been shown by Sundheim [1] that for a system of fused salts absolute transport numbers have no meaning. Whether the electrical charge is transported by the cations or by the anions is not a property of the fused salt, but of the experimental arrangement. As was pointed out by Förland and Krogh-Moe [2], this also applies to water solutions where hydroxyl ions take
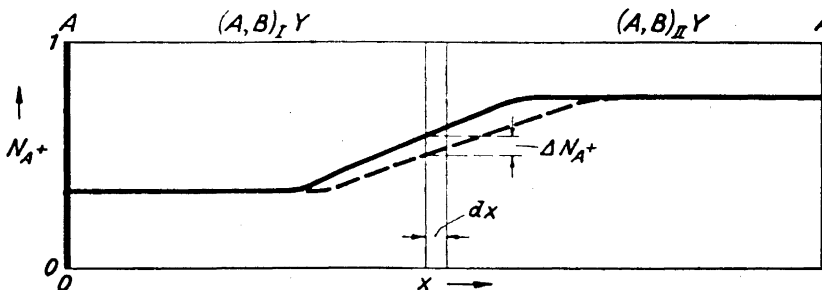
Fig. 1. The content of the component AY as a function of the distance from one side for the concentration cell A; (A, B)$_I$Y : (A,B)$_{II}$Y; A.

part in the electrical transport, and thus the water cannot be considered as a neutral reference frame.

The question now arises how to formulate the equation of the potential of a concentration cell when the electrolyte is a fused salt. As the fused salt lacks a reference frame, an equation like eqn. (1) obviously cannot be used.

It is also of interest to know under what conditions the liquid junction potential will be of importance, and if it is significant, how it may be calculated. Concentration cells are often experimentally simple, and it would therefore be of importance to eliminate the uncertainty connected with the liquid junction potential.

We will consider the following concentration cell

$$A; (A,B)_I Y : (A,B)_{II} Y; A$$

where the electrolytes consist of a fused mixture of two salts AY and BY (A^+ and B^+ forming cations and Y^- forming the anion) the A^+/B^+ ratio being different on the two sides of the cell. Further the electrodes are reversible only to the metal A.

In Fig. 1 is plotted the ionic fraction N_{A+} and N_{B+} of the two cations as a function of the distance x from one side of the cell. The ionic fractions are defined as

$$N_{A+} = \frac{n_{A+}}{n_{A+} + n_{B+}} \text{ and } N_{B+} = \frac{n_{B+}}{n_{A+} + n_{B+}}$$

where n with subscript indicate the number of moles of an ion. With a cell arrangement as indicated, we have $t_{Y^-} = 0$. (In a thermodynamic treatment we are not interested in whether the transport of the cations is a highly coupled process or not.)

We will assume that the transport number of A^+ is a function of the ionic fraction of A^+:

$$t_{A+} = t_{(N_A+)} \tag{2}$$

We may first calculate the changes taking place in the region of the concentration gradient of the cell, when an electrical charge (Q) is transported through the cell.

The transport number of A^+ at a distance x from one side of the cell we denote by $t_{A+\ (x)}$. At a distance $x + dx$ the transport number is

$$t_{A+\ (x\ +\ dx)} = t_{A+\ (x)} + \frac{\partial\ t_{A+}}{\partial\ x}\ dx = t_{A+\ (x)} + t'_{(N_A+)} \frac{\partial\ N_{A+}}{\partial\ x}\ dx \qquad (3)$$

The change in the content of A^+ in the volume of thickness dx by the transport of electrical charge will be:

$$\frac{\partial\ n_{A+}}{\partial\ Q} = \frac{1}{F}\ (t_{A+\ (x)} - t_{A+\ (x\ +\ dx)}) \qquad (4)$$

and as $n_{A+} = \dfrac{dx \cdot q}{V} \cdot N_{A+}$ where q is the crossection of the electrolyte and V is the volume of one mole of $(A,B)Y$, the change in the ionic fraction of A^+ will be:

$$\frac{\partial\ N_{A+}}{\partial\ Q} = -\frac{V}{q \cdot F}\ t'_{(N_A+)} \frac{\partial\ N_{A+}}{\partial\ x} \qquad (5)$$

One may notice that if $\partial N_{A+}/\partial Q$ is proportional to the concentration gradient $\partial N_{A+}/\partial x$, then the curve showing N_{A+} as a function of x will not change its slope by the transport of electricity. It will only be shifted in a parallel way towards right. From eqn. (5) one can see that this will be the case when

$$t'_{(N_A+)} = \text{constant} \qquad (6)$$

in the concentration interval in question, or if the transport number can be expressed by an equation

$$t_{A+} = a\ N_{A+} + b \qquad (7)$$

where a and b are constants. One may further notice that the shift of the concentration gradient is equal to:

$$\left(\frac{\partial\ x}{\partial\ Q}\right)_{N_{A+}\ =\ \text{const.}} = -\frac{V}{q \cdot F}\ t'_{(N_A+)} \qquad (8)$$

which shows that it is independent of the gradient $\partial N_{A+}/\partial x$.

One may now calculate all changes taking place in the cell by the transfer of a small electrical charge ΔQ.

At the left side electrode $\Delta Q/F$ mole of A^+ ions will form and $t_{A+\ (I)} \cdot \Delta Q/F$ mole of A^+ ions and $t_{B+\ (I)} \cdot \Delta Q/F$ mole of B^+ ions will leave this side of the cell. This change is equivalent to the introduction of $\dfrac{t_{B+\ (I)}}{N_{B+\ (I)}} \cdot \Delta Q/F$ mole of AY, and the simultaneous removal of $\dfrac{t_{B+\ (I)}}{N_{B+\ (I)}} \cdot \Delta Q/F$ mole of $(A,B)_I Y$ with the same A/B ratio as the electrolyte on this side of the cell.

The change at the right side of the cell is equivalent to removal of $\dfrac{t_{B+\,(II)}}{N_{B+\,(II)}} \cdot \Delta Q/F$ mole of AY and the simultaneous introduction of $\dfrac{t_{B+\,(II)}}{N_{B+\,(II)}} \cdot \Delta Q/F$ mole of $(A, B)_{II}$ Y with the same A/B ratio as the electrolyte on the right side of the cell.

At the same time the concentration gradient will be shifted according to eqn. (7). The changes taking place are schematically shown in Fig. 1.

The free energy change taking place in the region of the concentration gradient, when a charge ΔQ is transported through the cell, is equal to

$$\Delta F_1 = \int \frac{q \cdot dx}{V} \cdot \frac{d\Delta F}{dN_{A+}} \cdot \Delta N_{A+} \tag{9}$$

where ΔF is the free energy of mixing per one mole of the mixture AY—BY, and ΔN_{A+} is the change in the ionic fraction of A^+:

$$\Delta N_{A+} = \frac{\partial N_{A+}}{\partial Q} \cdot \Delta Q = - \frac{V \cdot \Delta Q}{q \cdot F} t'_{(N_{A+})} \frac{\partial N_{A+}}{\partial x} \tag{10}$$

Introducing this into eqn. (9) one has:

$$\Delta F_1 = - \frac{\Delta Q}{F} \int_{N_{A+\,(I)}}^{N_{A+\,(II)}} \frac{d\Delta F}{dN_{A+}} \cdot t'_{(N_{A+})} \, dN_{A+} \tag{11}$$

The total change in free energy associated with the transport of the charge ΔQ is equal to

$$\Delta F_{total} = \left[\frac{t_{B+\,(I)}}{N_{B+\,(I)}} (\Delta \overline{F}_{AY(I)} - \Delta F_{(I)}) - \frac{t_{B+(II)}}{N_{B+(II)}} (\Delta \overline{F}_{AY(II)} - \Delta F_{(II)}) \right.$$
$$\left. - \int_{N_{A+\,(I)}}^{N_{A+\,(II)}} \frac{d\Delta F}{dN_{A+}} \cdot t'_{(N_{A+})} \, dN_{A+} \right] \frac{\Delta Q}{F} \tag{12}$$

where $\Delta F_{(II)}$ and $\Delta F_{(I)}$ are the free energy changes by mixing AY and BY to give one mole of the two electrolytes $(A,B)_{II}Y$ and $(A,B)_{I}Y$, respectively.

The liquid junction may form a dipol layer whose energy is changed by the cell reaction. However, in a system of fused salts it is reasonable to assume that this energy change is insignificant, and it will be omitted here.

Since the transfer of the charge ΔQ is not connected with any other changes in the cell than what is expressed by eqn. (12) (it can not depend on any time-dependent process as the transfer of the charge is time-independent), the E.M.F. of the cell is given by

$$E \cdot \Delta Q = \Delta F_{total}$$

or

$$E \cdot F = \frac{t_{B+\,(I)}}{N_{B+\,(I)}}\, \Delta \overline{F}_{AY(I)} - \frac{t_{B+\,(II)}}{N_{B+\,(II)}}\, \Delta \overline{F}_{AY(II)}$$

$$+ \frac{t_{B+\,(II)}}{N_{B+\,(II)}}\, \Delta F_{(II)} - \frac{t_{B+\,(I)}}{N_{B+\,(I)}}\, \Delta F_{(I)} - \int_{N_{A+\,(I)}}^{N_{A+\,(II)}} \frac{\mathrm{d}\Delta F}{\mathrm{d}N_{A+}} \cdot t'_{(N_{A+})}\mathrm{d}N_{A+} \quad (13)$$

The correlation between E.M.F. of the cell and the partial free energy of one component is thus rather complicated in the general case.

For the special case when $t_{A+} = N_{A+}$ and $t_{B+} = N_{B+}$ over the concentration interval in question one obtains

$$E \cdot F = \Delta \overline{F}_{AY\,(I)} - \Delta \overline{F}_{AY\,(II)}$$

Further one will see that the E.M.F. is zero if $t_{B+} = 0$.

If the electrodes were reversible to Y, the E.M.F. would be zero if the relative transport numbers of the cations were proportional to their ionic fractions ($t_{A+} = N_{A+}$, $t_{B+} = N_{B+}$ and $t_{Y-} = 0$ equivalent to $t_{A+} = 0$, $t_{B+} = 0$ and $t_{Y-} = 1$). If the electrodes are reversible to Y, and $t_{B+} = -t_{Y-} = -1$ and $t_{A+} = 1$, E.M.F. will be given by the equation

$$E \cdot F = \Delta \overline{F}_{AY\,(II)} - \Delta \overline{F}_{AY\,(I)}$$

An electrolyte of sodium silicate can formally be described as consisting of the ions Na^+. Si^{4+} and O^{2-}. A cell with two oxygen electrodes and an electrolyte of an acid sodium silicate would thus be of the latter type.

It has come to our knowledge that Sundheim [3,4] has recently derived an expression for the liquid junction potential. His derivation is based on the equations of the thermodynamics of irreversible processes, and the result is in a form different from that given above.

REFERENCES

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3. Sundheim, B. R. *Ibid.* **61** (1957) 485.
4. Sundheim, B. R. *J. Chem. Phys.* **27** (1957) 791.