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The Diffusion Process and the Diffusion Potential in Relation to the E.M.F. of Concentration Cells

TORMOD FÖRLAND

N.T.N.F.'s Institute of Silicate Science, N.T.H., Trondheim, Norway

Equations are given for the E.M.F. of a concentration cell with transference and for the electrostatic potential drop over the concentration gradient. The change in electrostatic energy by charge transfer is calculated and found to be very small. It is shown that the diffusion process does not interfere with the cell reaction.

In a previous paper Förland and Krogh-Moe[1] calculated the E. M. F. of a concentration cell with transference. For a cell

$$\mathrm{A};\ (\mathrm{A,B})_{\mathrm{I}}\ \mathrm{Y} : (\mathrm{A,B})_{\mathrm{II}}\ \mathrm{Y};\ \mathrm{A}$$

with an electrolyte of the two components A^+Y^- and B^+Y^- and with electrodes reversible to A only, the E.M.F. may be expressed by the equation:

$$\begin{aligned} E \cdot \mathcal{F} = {} & t_{\mathrm{B}+(\mathrm{I})}(\Delta \overline{F}_{\mathrm{AY(I)}} - \Delta \overline{F}_{\mathrm{BY(I)}}) \\ & - t_{\mathrm{B}+(\mathrm{II})}(\Delta \overline{F}_{\mathrm{AY(II)}} - \Delta \overline{F}_{\mathrm{BY(II)}}) - \int_{N_{\mathrm{A}+(\mathrm{I})}}^{N_{\mathrm{A}+(\mathrm{II})}} \frac{\mathrm{d}\,\Delta F}{\mathrm{d}\,N_{\mathrm{A}^+}} \, \frac{\mathrm{d}\,t_{\mathrm{A}^+}}{\mathrm{d}\,N_{\mathrm{A}^+}} \, \mathrm{d}\,N_{\mathrm{A}^+} \end{aligned} \tag{1}$$

Here E is the E.M.F., $\mathcal{F}$ is Faradays number, the index (I) and (II) refer to the two compartments of the concentration cell, t_{A^+} and t_{B^+} are transport numbers for the ions A^+ and B^+ referring to the Y^- ions as a reference frame, N_{A^+} and N_{B^+} are the ionic fractions of the two kinds of ions. $\Delta \overline{F}$ with index is partical molar free energy of mixing and ΔF with index is free energy of mixing per mole mixture. The first and second term of the equation are the free energy changes taking place in the electrolyte close to the two electrodes. The last term is the free energy change over the region of the concentration gradient.

The above equation can be rearranged to the more convenient form:

$$E \cdot \mathscr{F} = \Delta\overline{F}_{\mathrm{AY(I)}} - \Delta\overline{F}_{\mathrm{AY(II)}} + \int_{\Delta\overline{F}_{\mathrm{AY(I)}}}^{\Delta\overline{F}_{\mathrm{AY(II)}}} \frac{t_{\mathrm{A}^+} - N_{\mathrm{A}^+}}{N_{\mathrm{B}^+}} \, \mathrm{d}\, \Delta\overline{F}_{\mathrm{AY}}$$

From the equation in the differential form:

$$\mathrm{d}E \cdot \mathscr{F} = -\mathrm{d}\Delta\overline{F}_{\mathrm{AY}} + \frac{t_{\mathrm{A}^+} - N_{\mathrm{A}^+}}{N_{\mathrm{B}^+}} \, \mathrm{d}\, \Delta\overline{F}_{\mathrm{AY}}$$

one can also derive:

$$\Delta\overline{F}_{\mathrm{AY(II)}} = \Delta\overline{F}_{\mathrm{AY(I)}} - \frac{1}{\mathscr{F}} \int_{\mathrm{I}}^{\mathrm{II}} \frac{N_{\mathrm{B}^+}}{t_{\mathrm{B}^+}} \, \mathrm{d}\, E \tag{2}$$

Thus by plotting corresponding values of $N_{\mathrm{B}^+}/t_{\mathrm{B}^+}$ and E as coordinates the partial free energy of the component AY is obtained as an area.

In the derivation of eqn. (1) it was assumed that dipol layers in the concentration gradient will not change their electrostatic energy significantly when an electrical charge is transported through the cell. It was further assumed that the diffusion process did not interfere with the cell reaction so the two processes could be treated separately.

It is the object of this paper to show that these assumptions are valid.

First it should be emphasized that an electrostatic potential in the concentration gradient of a concentration cell will in itself not affect the E.M.F. of the cell, since the process taking place is a transport of a neutral component from one side of the cell to the other. Only a change in the electrostatic energy in the concentration gradient may be observed in the outer circuit by the E.M.F. measurement.

THE ELECTROSTATIC POTENTIAL GRADIENT

The electrostatic potential gradient in a concentration gradient has been calculated by Sundheim [2]. As Sundheims reference system seems to be less practical for the present problem, a slightly different derivation of the electrostatic potential gradient (grad φ) will be given below.

We will consider the transports taking place in the gradient of the concentration cell:

$$\mathrm{A};(\mathrm{A}^+, \mathrm{B}^+)_{\mathrm{I}}\, \mathrm{Y}^- : (\mathrm{A}^+, \mathrm{B}^+)_{\mathrm{II}}\, \mathrm{Y}^- ; \mathrm{A}$$

As a reference for the velocities of the particles in the system we will choose the average velocity of the Y^- ions. We designate by $\vec{J}_{\mathrm{A}^+}$ ($\vec{J}_{\mathrm{B}^+}$) the flux in moles/cm²sec of ions A^+(B^+) and by $\vec{I}$ the electric current density in Faradays/cm²sec, all measured with respect to the average velocity of the Y^- ions. Thus $\vec{J}_{\mathrm{A}^+} + \vec{J}_{\mathrm{B}^+} = \vec{I}$.

The forces corresponding to the above fluxes are grad $\Delta\overline{F}_{AY}(\Delta\overline{F}_{BY})$ and grad φ, respectively. Here $\Delta\overline{F}_{AY}$ $(\Delta\overline{F}_{BY})$ is the partial free energy of the component AY (BY) in cal/moles and φ is the electrostatic potential in cal/Faradays.

The fluxes and forces are connected by the following linear equations:

$$\vec{J}_{A^+} = -L_{11}\text{grad } \Delta\overline{F}_{AY} - L_{12}\text{grad } \Delta\overline{F}_{BY} - L_{13}\text{grad } \varphi \tag{3}$$

$$\vec{J}_{B^+} = -L_{21}\text{grad } \Delta\overline{F}_{AY} - L_{22}\text{grad } \Delta\overline{F}_{BY} - L_{23}\text{grad } \varphi \tag{4}$$

$$\vec{I} = -L_{31}\text{grad } \Delta\overline{F}_{AY} - L_{32}\text{grad } \Delta\overline{F}_{BY} - L_{33}\text{grad } \varphi \tag{5}$$

According to Onsager's theory for microscopically reversible processes, we have the following relations between coefficients:

$$L_{12} = L_{21};\ L_{31} = L_{13};\ L_{23} = L_{32}$$

The coefficient L_{33} is the specific elecrical conductance, $\varkappa$, measured in Faradays ^{2}/cal cm sec. By defining $L_{13} = \varkappa t_1$ and $L_{23} = \varkappa t_2$ and further introducing the Gibbs-Duhem equation

$$N_{A^+} \text{ grad } \Delta F_{AY} + N_{B^+} \text{ grad } \Delta F_{BY} = 0 \tag{6}$$

(in which it is assumed that the partial free energy of a neutral component is not changed when the system is electrically charged) we obtain:

$$\vec{J}_{A^+} = -\left(L_{11} - L_{12}\frac{N_{A^+}}{N_{B^+}}\right) \text{grad } \Delta\overline{F}_{AY} - \varkappa t_1 \text{ grad } \varphi \tag{7}$$

$$\vec{J}_{B^+} = -\left(L_{21} - L_{22}\frac{N_{A^+}}{N_{B^+}}\right) \text{grad } \Delta\overline{F}_{AY} - \varkappa t_2 \text{ grad } \varphi \tag{8}$$

$$\vec{I} = -\varkappa\left(t_1 - t_2\frac{N_{A^+}}{N_{B^+}}\right) \text{grad } \Delta\overline{F}_{AY} - \varkappa \text{ grad } \varphi \tag{9}$$

Dividing eqns. (7) and (8) by (9) for the case that the composition is uniform we have:

$$t_1 = \left[\frac{\vec{J}_{A^+}}{\vec{I}}\right]_{\Delta\overline{F}_{AY}} = t_{A^+} \text{ and } t_2 = \left[\frac{\vec{J}_{B^+}}{\vec{I}}\right]_{\Delta\overline{F}_{AY}} = t_{B^+}$$

where t_{A^+} and t_{B^+} are the transport numbers of the cations referring to the anions as a reference frame.

For $\vec{I} = 0$ eqn. (9) gives:

$$\text{grad } \varphi = \left(t_{B^+}\frac{N_{A^+}}{N_{B^+}} - t_{A^+}\right) \text{grad } \Delta\overline{F}_{AY} \tag{10}$$

To simplify calculations we introduce

$$m = t_{B^+}\frac{N_{A^+}}{N_{B^+}} - t_{A^+} = -\frac{t_{A^+} - N_{A^+}}{N_{B^+}}$$

The electrostatic diffusion potential is equal to

$$\Delta\, \varphi = \int m \text{ grad } \Delta \overline{F}_{\mathrm{AY}} \,\mathrm{d}x = -\int_{\Delta \overline{F}_{\mathrm{AY(I)}}}^{\Delta \overline{F}_{\mathrm{AY(II)}}} \frac{t_{\mathrm{A}^+} - N_{\mathrm{A}^+}}{N_{\mathrm{B}^+}} \,\mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}} \text{ cal/Faraday}$$

where x is the distance from one side of the cell. This integral is finite over the whole concentration interval from $N_{\mathrm{A}^+} = 0$ to $N_{\mathrm{A}^+} = 1$ as long as the $\frac{t_{\mathrm{A}^+}}{N_{\mathrm{A}^+}}$ or $\frac{t_{\mathrm{B}^+}}{N_{\mathrm{A}^+}}$ is finite for small values of N_{A^+} and N_{B^+}, respectively. It appears that the expression for the diffusion potential does not contain the concentration gradient. This also implies that the electrostatic potential is not changed when a small charge is transported through the cell.

If we express the E.M.F. of the cell in cal/Faraday and count it positive from left to right, we see that the E.M.F. can also be expressed by the equation:

$$E' = \Delta F_{\mathrm{AY(II)}} - \Delta F_{\mathrm{AY(I)}} + \Delta \varphi \tag{12}$$

THE ELECTROSTATIC ENERGY CHANGE

Knowing the gradient of the electrostatic potential, grad φ, the electrostatic energy (U) in the concentration gradient can be calculated

$$U = \tfrac{1}{2} \int_{v} \varepsilon \text{ (grad } \varphi)^2 \,\mathrm{d}\, v \tag{13}$$

where ε is the absolute dielectric constant of the medium measured in Faraday^2/cal cm, and v is a volume covering the concentration gradient. The change in this electrostatic energy by the transport of electrical charge (Q measured in Faradays) through the gradient is given by

$$\frac{\partial U}{\partial Q} = \frac{\partial}{\partial Q} \left(\tfrac{1}{2} \int_{v} \varepsilon m^2 \text{ (grad } \Delta \overline{F}_{\mathrm{AY}})^2 \,\mathrm{d}v\right) = \frac{q}{2} \frac{\partial}{\partial Q} \int_{\overline{F}_{\mathrm{AY(I)}}}^{\overline{F}_{\mathrm{AY(II)}}} \varepsilon\, m^2 \text{grad } \Delta \overline{F}_{\mathrm{AY}} \,\mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}} \tag{14}$$

where q is the cross-section of the cell. The only factor of the integral which is changed by the transfer of dQ is grad ΔF_{AY}. We thus have

$$\frac{\partial U}{\partial Q} = \frac{q}{2} \int \varepsilon m^2 \left[\frac{\partial \text{ grad } \Delta \overline{F}_{\mathrm{AY}}}{\partial\, Q}\right]_{\Delta\, \overline{F}_{\mathrm{AY}}} \mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}} \tag{15}$$

Here

$$\left[\frac{\partial \text{ grad } \Delta \overline{F}_{\mathrm{AY}}}{\partial\, Q}\right]_{\Delta \overline{F}_{\mathrm{AY}}} = \frac{\mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}}}{\mathrm{d}\, N_{\mathrm{A}^+}} \left[\frac{\partial}{\partial Q} \left(\frac{\partial\, N_{\mathrm{A}^+}}{\partial\, x}\right)\right]_{N_{\mathrm{A}^+}}$$

$$= \frac{\mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}}}{\mathrm{d}\, N_{\mathrm{A}^+}} \left[\frac{\partial}{\partial Q} \left(\frac{1}{\partial x / \partial N_{\mathrm{A}^+}}\right)\right]_{N_{\mathrm{A}^+}}$$

$$= \frac{\mathrm{d}\,\varDelta\overline{F}_{\mathrm{AY}}}{\mathrm{d}\,N_{\mathrm{A}^+}} \left[-\left(\frac{\partial\,N_{\mathrm{A}^+}}{\partial x}\right)^2 \frac{\partial}{\partial Q}\left(\frac{\partial\,x}{\partial\,N_{\mathrm{A}^-}}\right)\right]_{N_{\mathrm{A}^+}}$$

$$= -\frac{\mathrm{d}\,\varDelta\overline{F}_{\mathrm{AY}}}{\mathrm{d}\,N_{\mathrm{A}^+}} \left(\frac{\partial N_{\mathrm{A}^+}}{\partial\,x}\right)^2 \frac{\partial}{\partial\,N_{\mathrm{A}^+}} \left(\frac{\partial x}{\partial Q}\right)_{N_{\mathrm{A}^+}} \tag{16}$$

According to derivations (eqn. (8)) in the previous paper[1] (compare the present eqn. (26)), we have

$$\left(\frac{\partial x}{\partial Q}\right)_{N_{\mathrm{A}^+}} = -\frac{V}{q}\,t'_{(N_{\mathrm{A}^+})} \tag{17}$$

where V is the molar volume of the mixture and $t'_{(N_{\mathrm{A}^+})} = \dfrac{\mathrm{d}\,t_{\mathrm{A}^+}}{\mathrm{d}\,N_{\mathrm{A}^+}}$.

Introducing eqn. (17) into (16) we have:

$$\left(\frac{\partial\,\mathrm{grad}\,\varDelta\overline{F}_{\mathrm{AY}}}{\partial\,Q}\right)_{\varDelta\overline{F}_{\mathrm{AY}}} = \frac{\mathrm{d}\,\varDelta\overline{F}_{\mathrm{AY}}}{\mathrm{d}\,N_{\mathrm{A}^+}} \left(\frac{\partial\,N_{\mathrm{A}^+}}{\partial\,x}\right)^2 \cdot \frac{V}{q}\,t''_{(N_{\mathrm{A}^+})} \tag{18}$$

neglecting changes in V with changes in composition, and introducing this into eqn. (15) we obtain

$$\frac{\partial\,U}{\partial\,Q} = \frac{V}{2}\int\limits_{N_{\mathrm{A}^+_{\mathrm{I}}}}^{N_{\mathrm{A}^+_{\mathrm{II}}}} \varepsilon\,m^2\,t''_{(N_{\mathrm{A}^+})} \left(\frac{\mathrm{d}\,\varDelta\overline{F}_{\mathrm{AY}}}{\mathrm{d}\,N_{\mathrm{A}^+}}\right)^2 \left(\frac{\partial\,N_{\mathrm{A}^+}}{\partial\,x}\right)^2 \mathrm{d}\,N_{\mathrm{A}^+} \quad \text{or}$$

$$\frac{\partial\,U}{\partial\,Q} = \frac{V}{2}\int\limits_{N_{\mathrm{A}^+_{\mathrm{I}}}}^{N_{\mathrm{A}^+_{\mathrm{II}}}} \varepsilon\,m^2\,t''_{(N_{\mathrm{A}^+})}\,(\mathrm{grad}\,\varDelta\overline{F}_{\mathrm{AY}})^2\,\mathrm{d}\,N_{\mathrm{A}^+} \tag{19}$$

The absolute dielectric constant ε may be expressed by the absolute dielectric constant of vacuum ε_0 and the relative dielectric constant of the medium ε_{r}:

$$\varepsilon = \varepsilon_0 \cdot \varepsilon_{\mathrm{r}}$$

where $\varepsilon_0 = \dfrac{1}{\pi \cdot 36} \times 10^{-9}\,(\text{coulomb}^2/\text{joule} \cdot \text{m}) = 3.98 \times 10^{-23} \left(\dfrac{\text{Faraday}^2}{\text{cal} \cdot \text{cm}}\right)$

Due to the small numerical value of ε_0, one may expect to find that the change in electrostatic energy in the region of the concentration gradient is negligible compared to the other free energy changes in the cell.

EFFECT OF THE CURRENT DENSITY

In eqn. (14) it is assumed that the current density is zero. However, in a real measurement a small current will generally be drawn. The transport of charge is therefore connected with a loss in electric energy as joule heat. This energy loss will be symmetrical with respect to the sign of the current density, and it will usually not disturb the E.M.F. measurement.

The change in electrostatic energy will, however, have terms in addition to the expression in eqn. (14) when current flows through the cell. According to eqn. (9) the potential gradient is:

$$\text{grad } \varphi = m \text{ grad } \Delta \overline{F}_{\mathrm{AY}} - R\vec{I} \qquad \text{where } R = \frac{1}{\varkappa} \tag{20}$$

and $$(\text{grad } \varphi)^2 = m^2 (\text{grad } \Delta \overline{F}_{\mathrm{AY}})^2 - 2\, R\vec{I}\, m \text{ grad } \Delta \overline{F}_{\mathrm{AY}} + (RI)^2$$

For constant I we have:

$$\frac{\partial}{\partial Q}\left[\frac{1}{2}\int_v \varepsilon\, (2\, R\vec{I}\, m \text{ grad } \Delta \overline{F}_{\mathrm{AY}})\, \mathrm{d}v\right] = \vec{I} q \frac{\partial}{\partial Q} \int \varepsilon\, R\, m \text{ grad } \Delta \overline{F}_{\mathrm{AY}}\, \mathrm{d}x$$

$$= I q \frac{\partial}{\partial Q} \int_{N_{\mathrm{A}^+(\mathrm{I})}}^{N_{\mathrm{A}^+(\mathrm{II})}} \varepsilon \cdot R\, m\, \frac{\mathrm{d}\, \Delta \overline{F}_{\mathrm{AY}}}{\mathrm{d}\, N_{\mathrm{A}^+}}\, \mathrm{d}\, N_{\mathrm{A}^+} = 0 \tag{21}$$

As the integral contains only properties of the electrolyte, it is not changed by the transport of a small charge.

The contribution by the term $(RI)^2$ to the change in electrostatic energy for a given current density is equal to:

$$\frac{\partial}{\partial Q}\left(\frac{1}{2}\int_v \varepsilon\, (RI)^2\, \mathrm{d}v\right) = \frac{1}{2} I^2 \cdot q \int \varepsilon\, 2\, R \left(\frac{\partial R}{\partial Q}\right)_x \mathrm{d}x$$

$$= I^2 \cdot q \int \varepsilon\, R\, \frac{\partial R}{\partial N_{\mathrm{A}^+}} \left(\frac{\partial N_{\mathrm{A}^+}}{\partial Q}\right)_x \mathrm{d}x \tag{22}$$

$$= - I^2\, V \int_{N_{\mathrm{A}^+(\mathrm{I})}}^{N_{\mathrm{A}^+(\mathrm{II})}} \varepsilon\, R \cdot R'_{(N_{\mathrm{A}^+})} \cdot t'_{(N_{\mathrm{A}^+})}\, \mathrm{d}\, N_{\mathrm{A}}$$

where eqn. (5) from the previous publication [1]:

$$\frac{\partial N_{\mathrm{A}^+}}{\partial Q} = - \frac{V}{q}\, t'_{(N_{\mathrm{A}^+})}\, \frac{\partial N_{\mathrm{A}^+}}{\partial x}$$

has been used (compare the present eqn. (25)). ε is considered constant. One will generally find that this contribution to the measured E.M.F. is negligible. In addition to this the current will cause polarization at the electrodes.

EFFECT OF THE DIFFUSION PROCESS

It may finally be shown that the outer electrical work carried out by the E.M.F. measurement is not influenced by the diffusion process, which is proceeding during the time of the measurement.

At the E.M.F. measurement a small charge ΔQ is transferred through the cell. This transfer is carried out over a short time period Δt. The electrical current is in average

$$I = \frac{1}{q}\,\frac{\Delta Q}{\Delta t}$$

The number of A^+ ions passing through an unit cross-section of the cell at a distance x from one side of the cell, we denote by $\vec{J}_{A^+(x)}$. The change in content of AY in a volume ranging between two unit cross-sections at the two distances x and $x + \mathrm{d}x$ is given by:

$$\Delta\, \mathrm{d}n_{A^+} = (\vec{J}_{A^+(x)} - \vec{J}_{A^+(x+\mathrm{d}x)})\, \Delta t = -\left(\frac{\partial \vec{J}_{A^+}}{\partial x}\right) \mathrm{d}x \cdot \Delta t \tag{23}$$

From eqns. (7) and (20) we have

$$\vec{J}_{A^+} = -\left(L_{11} - L_{12}\,\frac{N_{A^+}}{N_{B^+}}\right) \mathrm{grad}\, \Delta\bar{F}_{AY} - \varkappa\, t_{A^+} \cdot m\, \mathrm{grad}\, \Delta\bar{F}_{AY} + t_{A^+} \cdot \vec{I} \tag{24}$$

which will be abbreviated to

$$\vec{J}_{A^+} = -\vec{f}(N_{A^+}, \mathrm{grad}\, N_{A^+}) + t_{A^+} \cdot \vec{I}$$

which combined with eqn. (23) gives

$$\Delta\, \mathrm{d}\, n_{A^+} = f'\, (N_{A^+}, \mathrm{grad}\, N_{A^+})\, \mathrm{d}x \cdot \Delta t - t'_{(N_{A^+})}\, \frac{\partial N_{A^+}}{\partial x}\, \mathrm{d}x\, \frac{\Delta Q}{q}$$

where $f'(N_{A^+}, \mathrm{grad}\, N_{A^+})$ is the derivative of $\vec{f}(N_{A^+}, \mathrm{grad}\, N_{A^+})$ with respect to x. As $\mathrm{d}n_{A^+} = \frac{\mathrm{d}x}{V} \cdot N_{A^+}$, we obtain

$$\Delta\, N_{A^+(x = \mathrm{constant})} = V \cdot f'\, (N_{A^+}, \mathrm{grad}\, N_{A^+}) \cdot \Delta t - \frac{V}{q}\, t'_{(N_{A^+})}\, \frac{\partial N_{A^+}}{\partial x} \cdot \Delta Q \tag{25}$$

and $\Delta x_{(N_{A^+} = \mathrm{const.})} = V \cdot f'\, (N_{A^+}, \mathrm{grad}\, N_{A^+})\, \frac{\partial x}{\partial N_{A^+}} \Delta t - \frac{V}{q}\, t'_{(N_{A^+})} \cdot \Delta Q$ (26)

The free energy of the electrolyte in the region of the concentration gradient will thus change due to both the charge transfer and the diffusion process. The total free energy change is given by:

$$\Delta F_1 = \int_{\mathrm{I}}^{\mathrm{II}} \frac{q\, \mathrm{d}x}{V}\, \frac{\mathrm{d}\, \Delta F}{\mathrm{d}\, N_{A^+}}\, \Delta\, N_{A^+}$$

$$= \Delta t \cdot \int_{\mathrm{I}}^{\mathrm{II}} q \cdot \int (N_{A^+}, \mathrm{grad}\, N_{A^+})\, \frac{\mathrm{d}\, \Delta F}{\mathrm{d}\, N_{A^+}}\, \mathrm{d}\, x - \Delta Q \int_{\mathrm{I}}^{\mathrm{II}} \frac{\mathrm{d}\, \Delta F}{\mathrm{d}\, N_{A^+}}\, t'_{(N_{A^+})}\, \mathrm{d}\, N_{A^+} \tag{27}$$

where the last term is the only term considered in the previous publication [1].

Thus the equations for the change in free energy by the simultaneous diffusion process and charge transfer can be separated into two terms: one containing time and one containing the amount of charge transferred and no term containing both time and charge.

By a similar procedure using eqns. (26) and (14) one can show that the equation for the change in electrostatic energy can be separated in the same way.

It may thus be concluded that there is no interference between the diffusion process and the cell reaction.

The derivation does not contain any assumptions regarding the bonds between the three particles A^+, B^+ and Y^-. The above equation may thus be applied on a concentration cell having, *e.g.*, HCl — H_2O mixtures as electrolyte. This electrolyte can formally be describes as a mixture of the three kinds of particles Cl^-, OH^- and H^+. The fact that the OH^- particles most of the time are associated with H^+ does not affect the derivation of the above equation.

An equation similar to eqn. (1) has been derived by Wagner [3] and later in a modified way by Guggenheim [4]. Wagner's derivation is based on the assumption that the different ions move independent of each other. The more general derivation by Guggenheim is based on the electrochemical potential of a single ion, and the application of the Onsager reciprocal relations to the transfer of single ions. In the present derivation on the other hand unmeasureable quantities like the electrochemical potential of a single ion have been avoided.

Guggenheims equation has been applied to systems of fused salts by Laity [5]. Laity [6,7] has also shown that the derivation by Guggenheim is valid also in cases where the Nernst-Einstein equation connecting diffusion constant and mobility does not hold, and he has extended the treatment of single ion properties to give correlation between coefficients obtained from different kinds of transport measurements.

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