The Electric Work Method. II. Applications to Concentration, Formation and Membrane Cells

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The electric work method is applied to isothermal electrochemical systems of increasing complexities; the cell with transference, the transference number being constant or variable, with one or two electrolytes, the simple formation cell, and systems with membranes. The EMF of the system is developed from analyses of local mass and energy changes. Contributions to the EMF are additive, and physically and operationally identifiable. No introduction of electrostatic field is necessary, neither is the concept of charge. Thus the electric work method gives a different interpretation of electrochemical systems from that of conventional electrochemistry. End formulas are, however, the same. It is shown that less severe assumptions are required in the new method.

1. Introduction

The principles of the electric work method were presented in the preceding article.[1] The conversion of chemical and mechanical energy into electric energy or vice versa was analysed[1] and non-isothermal cells were studied.[2-4] Here we shall apply the electric work method to some common isothermal cell systems. The electric work method brings out a new physical understanding of the systems. Some phenomena, such as electrokinetic effects, are still not treated. These will be the topic of a future paper (part III).

Relevant cases in the literature are so numerous that we have found it impossible to give a comprehensive list of references. For the simple examples treated here, most modern textbooks may serve as a reference for the method which here is called "the conventional method". The historic development of this method dates back to the first three decades of this century. Arrhenius, Nernst, Debye, and Guggenheim are central, to mention a few names. In recent years it appears[5] that the textbooks of Bockris are important (e.g. Ref. 6). There has been criticism of conventional basic concepts such as electrochemical potential.[7-9] Many authors, e.g. Newman,[10] have taken great care to avoid ambiguities, and errors to which the conventional method has led. Several authors of textbooks claim that an objective of their book is to make electrochemistry clear to the student (e.g. Ref. 5). As we have explained already,[1] we do not see that the inherent difficulties in conventional electrochemistry can be circumvented.

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2. The fundamental equation of electrochemistry

It is our purpose to build a new fundamental base for electrochemistry. The fundamental equation must then first be presented.

From the preceding article we have seen in sections 6 and 7 that the production of certain mass and energy fluxes determine the EMF of the electrochemical system in the absence of pressure gradients. We choose as an example the electrolyte solution of NaCl, for which a concentration gradient $\partial c_{NaCl}/\partial x$ exists (Fig. 1). We shall consider first the mass flux, j_{NaCl}. In the present treatment and example this is the only flux we need consider explicitly. A concentration gradient may be anywhere in the cell, in particular at the electrodes. Owing to the concentration gradient, there is diffusion. Diffusion can be described by Fick's second law in isothermal, isobaric systems [eqn. (1)].

$$\partial c_{NaCl}/\partial t = D(\partial^2 c_{NaCl}/\partial x^2) \tag{1}$$

where D is Fick's diffusion constant and t denotes the time. An electric current, I, is now passing through the solution. The current density is $j = I/A$ where A is the cross-sectional area. At a given location, x, an excess mass flux j'_{Na} results for the constituent Na. (The charge of the atom is irrelevant in this respect, but Na is a constituent of the compound NaCl.) From eqns. (20) and (25) of part I[1] the excess mass flux is given by eqn. (2), where t_{Na} is the transference number of Na and F is Faraday's constant. For the other constituent Cl, the corresponding equation is eqn. (3).

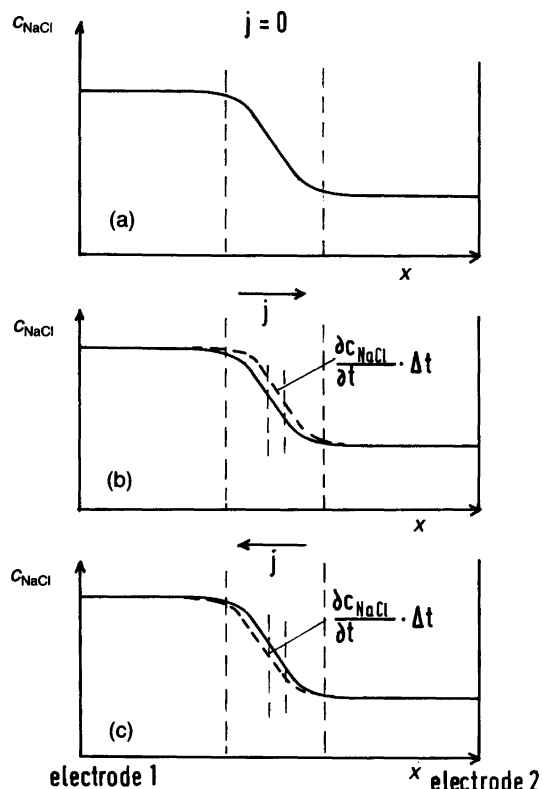$$j'_{Na} = t_{Na}\, j/F \tag{2}$$

$$j'_{Cl} = -t_{Cl}\, j/F \tag{3}$$

Fig. 1. Concentration profiles of NaCl(aq) in the cases of (a) pure diffusion and (b,c) diffusion and electrical current.

Thus with div $j = 0$, we get eqns. (4a) and (4b) for the divergences of the excess mass fluxes.

$$\text{div } j'_{Na} = \text{div}(t_{Na} j/F) = -\partial c_{Na}/\partial t = (j/F)(dt_{Na}/dx) \quad (4a)$$

$$\text{div } j'_{Cl} = -\text{div}(t_{Cl} j/F) = -\partial c_{Cl}/\partial t = (j/F)(dt_{Na}/dx) \quad (4b)$$

The relationship $t_{Cl} = 1 - t_{Na}$ has been used. We see that concentrations of both constituents change with time in the same way in the volume element $dV = A dx$. The contribution from the excess mass flux, eqn. (4a), must be added to eqn. (1) to obtain the change in time of NaCl content, eqn. (5).

$$\partial c_{NaCl}/\partial t = D(\partial^2 c_{NaCl}/\partial x^2) - (j/F)(dt_{Na}/dx) \quad (5)$$

This equation, which is purely phenomenological, is a simple form of our fundamental equation of electrochemistry. The second term on the right-hand side of eqn. (5) describes the reversible production or consumption of NaCl (Fig. 1). The most basic change of t_{Na} happens at the electrodes, where necessarily $dt_{Na}/dx \neq 0$. These are the discontinuities exemplified in part I, Fig. 9, by the contacts A|AB and AB|B. Ekman *et al.*[11] also consider eqn. (5) to be a basic equation. However, these authors do not take the full consequence of the choice, since they return to

calculations of local electric potentials from this starting point.

In the case of multicomponent solutions, the fundamental equation includes ternary or higher-order diffusion as well as mass production for all components.[7]

Transference numbers generally depend on concentration [eqn. (6)].

$$(dt_{Na}/dx) = (dt_{Na}/dc_{NaCl})(dc_{NaCl}/dx) \quad (6)$$

By introducing eqn. (6) into eqn. (5) we obtain eqn. (7)

$$\partial c_{NaCl}/\partial t = D(\partial^2 c_{NaCl}/\partial c^2) \quad (7)$$
$$-(j/F)(dt_{Na}/dc_{NaCl})(dc_{NaCl}/dx)$$

The equation tells that we have mass production of NaCl for positive j, and mass consumption for negative j at any given location between the electrodes provided $dc_{NaCl}/dx < 0$. Eqn. (7) has a direct proof in the moving boundary method, a standard method for measuring transference numbers of ions.[7,12]

3. The Hittorf experiment

The Hittorf method is the second main method for determination of transference numbers.[12] We apply the fundamental equation of electrochemistry to this case. Consider a cell with electrodes made of Na(Hg) and a NaCl solution as electrolyte. The transference number of Na is 1 at the electrode and t_{Na} in the bulk. The variation between these values is illustrated in Fig. 2. Mathematically it is given by eqn. (8).

$$t_{Na}(x) = 1 - [(1 - t_{Na})x/\delta x], \quad 0 < x < \delta x \quad (8)$$

Introduction of eqn. (8) into eqn. (5), and integration from 0 to δx gives eqn. (9).

$$\int_0^{\delta x} (\partial c_{NaCl}/\partial t)dx = -j_{NaCl}$$
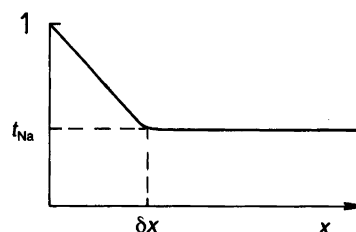$$- (j/F)\int_0^{\delta x} [(t_{Na} - 1)/\delta x]dx \quad (9)$$

Fig. 2. Variation in transference number of the left-hand side electrode in the Hittorf experiment.

The left-hand side in the limit of $\delta x = 0$ is zero, and we obtain eqn. (10).

$$j_{\text{NaCl}} = (1 - t_{\text{Na}})j/F \tag{10}$$

Eqn. (10) is a consequence of the fundamental law of electrochemistry. By integrating first over a larger range, $0 < x < x_{\text{bulk}}$ where x_{bulk} is a position of constant composition, and next over time we get eqn. (11), where Δm_{NaCl} is the mass of NaCl accumulated during the time t within the range $0 < x < x_{\text{bulk}}$. The result for determination of t_{Na} has thus been derived using the same fundamental equation as in the moving boundary experiment.

$$\Delta m_{\text{NaCl}} = [1 - t_{\text{Na}}] \int_0^t (I/F) dt \tag{11}$$

4. The simple concentration cell with transference

In the simplest possible case the cell with transference has identical electrodes, say of Na(Hg) and a one-component electrolyte solution with a liquid junction. By junction we mean any form of contact between the half cells, a diaphragm, a porous plug or merely a diffusion field. Concentration gradients occur in the junction. The system is illustrated in Fig. 3. The chemical reaction which corresponds to the scheme $A + B \Rightarrow AB$ in Fig. 9. of part I^1 is now reduced to $AB \Rightarrow AB'$, that is

$$\text{Na(Hg)} + \text{NaCl(aq, } c_1) \Rightarrow \text{Na(Hg)} + \text{NaCl(aq, } c_2).$$
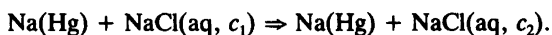
In order to determine the EMF E of this cell, we record all mass changes in the cell as prescribed by Fig. 11 of part I^1. These in turn lead to changes in Gibbs energy which are additive and make up the EMF from the total Gibbs energy change, $(dG/dt)_{\text{tot}}$ [eqns. (16)–(18) of part I].[1] From eqn. (26) of part I we obtain eqn. (12).
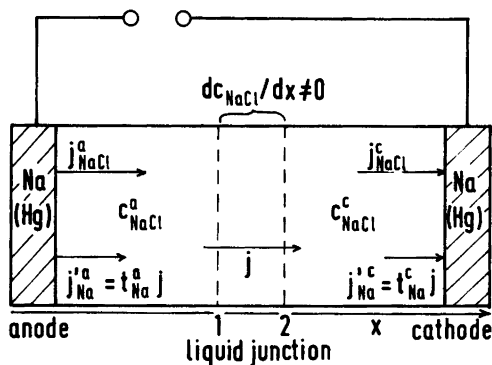

Fig. 3. A concentration cell with transference. The electrodes are both reversible with respect to Na^+. The two electrolytes of different compositions are separated by a liquid junction. The mass flux $j_{\text{NaCl}} = t_{\text{Cl}} j/F$ (a, anode; c, cathode).

$$EAj = - (dG/dt)_{\text{tot}} = -[(dG/dt)^c + (dG/dt)^a + (dG/dt)_{\text{jnct}}] \tag{12}$$

A modified form of this equation was also used by Førland et al.[9] At the cathode, given by superscript c, the Gibbs energy change, given by the mass flux of NaCl leaving the solution, follows from eqn. (10) (see also Fig. 11 of part I), and is given by eqn. (13a)

$$(dG/dt)^c = - (1 - t_{\text{Na}}^c)\mu_{\text{NaCl}}^c \, jA/F \tag{13a}$$

At the anode, (superscript a), the Gibbs energy change is accordingly given by eqn. (13b).

$$(dG/dt)^a = (1 - t_{\text{Na}}^a)\mu_{\text{NaCl}}^a \, jA/F \tag{13b}$$

The contributions due to metal removed or deposited at the electrodes are zero, since the cathode and anode are under the same conditions. The work in the junction according to eqn. (5) is given by eqn. (14).

$$(dG/dt)_{\text{jnct}} = - \int_1^2 \mu_{\text{NaCl}}(dt_{\text{Na}}/dx) \, (jA/F) dx \tag{14}$$

In the uniform ranges the integrand of eqn. (14) vanishes. (In part I this contribution was not discussed.) Eqn. (14) can be generalized[7,9] to describe any multicomponent system.

The contribution to EMF from the liquid junction according to the electric work method can be determined by introducing the concentration dependences of chemical potentials and transference numbers. In the trivial case that t_{Na} is constant, no work is done in the junction. A simple formal expression for the concentration dependence of ion transference numbers is eqn. (15a)[9,12]

$$t_j = u_j c_j / \sum_k u_k c_k \tag{15a}$$

where subscript j denotes an ion in the system and u_j is the ion mobility. (Usually the mobilities are defined as drift velocities per unit driving force.) The summation is carried out over all k ions present. Mobilities are defined by eqn. (2), $j'_{\text{Na}} = t_{\text{Na}}j/F = u_{\text{Na}}c_{\text{Na}}$ and $\Sigma t_k = 1$. In the present case eqn. (2) leads to eqn. (15b)

$$t_{\text{Na}} = [u_{\text{Na}}c_{\text{Na}}/(u_{\text{Na}}c_{\text{Na}} + u_{\text{Cl}}c_{\text{Cl}})] \tag{15b}$$

and, since $c_{\text{Na}} = c_{\text{Cl}}$ everywhere, t_{Na} reduces to the constant $t_{\text{Na}} = [u_{\text{Na}}/(u_{\text{Na}} + u_{\text{Cl}})]$ when we neglect the concentration dependence of u_i. There is thus no contribution from the junction to EMF when all the u_i are constant. Constant transference numbers lead to a total EMF of the cell equal to the sum of electrode contributions only, eqn. (16a) or (16b), where a denotes the mean activity defined by $a_{\text{NaCl},\pm} = c_{\text{NaCl}}\gamma_\pm$, and $\gamma_\pm$ is the mean activity coefficient.

$$EjA = [-(1-t_{\text{Na}})\mu_{\text{NaCl}}^a + (1+t_{\text{Na}})\mu_{\text{NaCl}}^c]jA/F \tag{16a}$$

$$EF = t_{Cl}(\mu_{NaCl}{}^c - \mu_{NaCl}{}^a)$$
$$= t_{Cl} RT \ln(a^c_{NaCl,\pm}/a^a_{NaCl,\pm}) = E_1F \qquad (16b)$$

The result of eqn. (16b) is the same as that derived by the conventional method.[5,6] The important difference between the electric work method and the conventional method is that the former eliminates, for example, the need to have charge separation in the liquid junction in order to explain the EMF. The EMF is not explained as a sum of electrostatic potentials.[6] The EMF is, rather, explained by observable mass changes in a neutral system. This gives a dynamic or process-dependent, not static, description of the electric or other energy conversion. The only conditions are that the system is of a specific topological structure, here A|AB||(AB)'|A, and materials used must be electric conductors (part I, Fig. 9).

Further characteristics are that the EMFs in eqns. (16) and (14) have not been derived from flux equations, which is common in irreversible thermodynamic theories using the Onsager reciprocal relations.[9,13] In the electric work method, the transference numbers obtained from the Hittorf experiment are the same as those used in the expression for EMF. In the irreversible thermodynamic theories mentioned above, it is only according to Onsager's proof of his reciprocity relations that this is so. It can be shown, however, that the validity of the Onsager reciprocal relations leads to an equation of the same form as eqn. (5).[9] Validity of the Onsager reciprocal relations is thus consistent with the electric work method, but the validity of these relations cannot be deduced from the electric work method.

It is straight forward to include a concentration dependence of transference numbers into the expression for the junction contribution to EMF, eqn. (14). A linear approximation for t_i as a function of concentration may be used for the electrolyte; $dt_{Na}/dx = \Delta t_{Na}/\delta x$, with $\Delta t_{Na} = t^c_{Na} - t^a_{Na}$, and $\delta x = x_2 - x_1$ (Fig. 3). We also need an approximation for the mean activity, and choose a linear expansion; $a_{NaCl,\pm}(x) = a^a_{NaCl,\pm} + \Delta a_{NaCl,\pm}(x - x_1)/\delta x$ with $\Delta a_{NaCl,\pm} = a^c_{NaCl,\pm} - a^a_{NaCl,\pm}$, and $x_1 < x < x_2$. By introducing these expressions in to eqn. (14) we obtain eqn. (17) where $I_{NaCl} = -\Delta t_{Na} [(a^c_{NaCl,\pm}\ln a^c_{NaCl,\pm} - a^a_{NaCl,\pm}\ln a^a_{NaCl,\pm})/\Delta a_{NaCl,\pm} - 1]$. Addition of eqns. (12), (13) and (17) yields the final result, eqn. (18).

$$(dG/dt)_{jnct} = [-\Delta t_{Na}\mu^o_{NaCl} + 2RTI_{NaCl}](jA/F) \qquad (17)$$

$$EF = E_2F = 2RT(t^c_{Cl}\ln a^c_{NaCl,\pm} - t^a_{Cl}\ln a^a_{NaCl,\pm} - I_{NaCl}) \qquad (18)$$

By comparing eqns. (16) and (18), we see that the concentration dependence of the transference number leads to a slight modification of the original terms of eqn. (16) and the addition of one further term.
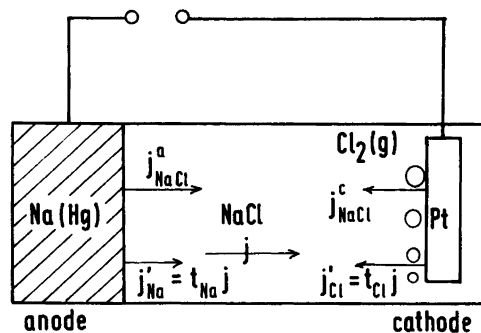

Fig. 4. A formation cell for NaCl [(aq). The cell reaction is Na(s) + ½ Cl₂(g) = NaCl(aq). The mass fluxes are $f_{NaCl} = t_{Cl} j/F$; $f^c_{NaCl} = t_{Na} j/F$.

5. The simple formation cell

Consider a system with electrodes consisting of Na(Hg) (anode) and Pt|Cl₂(g) (cathode) and the uniform electrolyte solution of NaCl as shown in Fig. 4. The only contributions to the EMF, which are given from the fundamental law of electrochemistry, eqns. (5) and (10), are from mass changes at the electrodes. In the formation cell the electrodes are different. The separate parts and the sum of these are eqn. (19) for the cathode.

$$(dG/dt)^c = [t^c_{Na}\mu^c_{NaCl} -(1/2)\mu_{Cl_2}](jA/F) \qquad (19)$$

At the anode, the chemical work is given by eqn. (20).

$$(dG/dt)^a = [(1 - t^a_{Na})\mu^a_{NaCl} - \mu_{Na}](jA/F) \qquad (20)$$

The work performed in the solution, not in contact with electrodes, is zero when c_{NaCl} (i.e. t_{Na}) is constant. The sum of the two contributions is the familiar ΔG of the chemical reaction

$$Na(Hg) + 1/2\ Cl_2(g) = NaCl(aq)$$
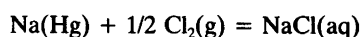
which with $\mu^a_{NaCl} = \mu^c_{NaCl} = \mu_{NaCl}$ gives eqns. (21a) and (21b).

$$EjA = [\mu_{NaCl} - (1/2)\mu_{Cl_2} - \mu_{Na}](jA/F) \qquad (21a)$$

$$EF = [\mu_{NaCl} - (1/2)\mu_{Cl_2} - \mu_{Na}] = E_3F \qquad (21b)$$

$$(dG/dt)_{total} = [t_{Na}\mu^c_{NaCl} - (1/2)\mu_{Cl_2} + (1 - t_{Na})\mu^a_{NaCl} - \mu_{Na}](jA/F) \qquad (22)$$

$$EF = E^a_3F + t_{Na}2RT\ln (a^c_{NaCl,\pm}/a^a_{NaCl,\pm}) \qquad (23)$$

If the concentrations in the anode and cathode compartments are not equal, and t_{Na} is constant, we obtain eqn. (22) and finally eqn. (23) with $E^a_3 = [\mu^a_{NaCl} - (1/2)\mu_{Cl_2} - \mu_{Na}]$. Concentration dependences of the transference number can be taken care of by integrating eqn. (14). The result is

the addition of a third term to the right-hand side of eqn. (23).

The simple calcultions of sections 4 and 5 demonstrate some advantages of the electric work method: contributions to the EMF are additive, and the physical cause of the various contributions can be easily identified and controlled by independent means. The possible additivity of potentials need not be discussed.

6. The biionic potential

Consider next the case where the two electrolytes with a common anion are separated by a liquid junction. Assume first that the junction contains a mixture of the two electrolytes. The system is illustrated in Fig. 5. The electrodes are now reversible to chloride ion, Ag|AgCl electrodes, and the salts in solution are NaCl and KCl.

The contributions to the EMF are calculated from the mass fluxes shown in Fig. 5. The mass fluxes are all produced or absorbed at the inhomogeneities of the system as described by the fundamental equation of electrochemistry. Thus, at the cathode, c, the Gibbs energy changes are given by eqn. (24).

$$(dG/dt)^c = (-\mu_{AgCl} + \mu_{Ag} + t_K{}^c\mu_{KCl}{}^c)jA/F \qquad (24)$$

At the anode, we have eqn. (25),

$$(dG/dt)^a = (\mu_{AgCl} - \mu_{Ag} - t_{Na}{}^a\mu_{NaCl}{}^a)jA/F \qquad (25)$$

By analogy with eqn. (14), the chemical work in the junction is given by eqn. (26).

$$(dG/dt)_{jnct} = \int_1^2 [\mu_{NaCl}(dt_{Na}/dx) + \mu_{KCl}(dt_K/dx)](jA/F)dx \qquad (26)$$

The value obtained from eqn. (26) does not give the magnitude of any charge separation,[7] only the chemical work done by moving masses in the junction. Here, the total mass of NaCl expands, that of KCl contracts, c_{NaCl} decreases and c_{KCl} increases. The boundary between NaCl
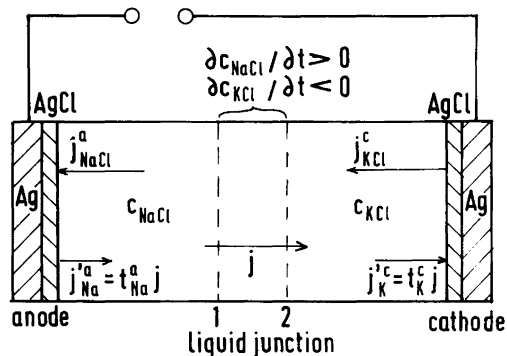

Fig. 5. A concentration cell with different electrolytes separated by a liquid junction. The mass fluxes are $j_{NaCl} = t_{Na} j/F$; $j_{KCl} = t_K j/F$.

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and KCl moves to the right. The value of the junction contribution as it stands depends on the choice of standard state for the components involved, since μ_i refers to a standard state [see also the example given by eqn. (17)]. This is so because the process describes how mass at one energy state is transferred to another state, and the energy of a state does not have an absolute value. The practical disadvantage of this is that no absolute value can be assigned to the work in the junction. However, nature behaves in this manner; we cannot demand undue localization of processes.

As in the ordinary concentation cell [eqn. (18)], when combined with the two other contributions to the EMF the terms containing the standard states will cancel. This can be seen by a simple example: by integration by parts we have eqn. (27).

$$(dG/dt)_{jnct} = \int_1^2 (\mu_{NaCl}t_{Na} + \mu_{KCl}t_K)$$

$$- \int_1^2 (t_{Na}d\mu_{NaCl} + t_K d\mu_{KCl}) \qquad (27)$$

$$= -\mu_{NaCl}{}^a t_{Na}{}^a + \mu_{KCl}{}^c t_K{}^c$$

$$+ RT\ln[(u_K + u_{Cl})/(u_{Na} + u_{Cl})]$$

In order to find a value for the integral we have used the relationships $c_K = c - c_{Na}$, where $c = c_{Cl} = $ constant, eqn. (15) with u_j constant, $j = $ Na, K, and the assumption of ideal, ternary solutions with respect to the constituents Na and K. The sum of the contributions (24)–(26) is frequently called the biionic potential. The explicit form obtained from these equations is, together with eqn. (27), given by eqn. (28).

$$EF = -RT\ln[(u_K + u_{Cl})/(u_{Na} + u_{Cl})] \qquad (28)$$

As evident and required, quantities referring to standard states do not enter the expression. Equal cation mobilities give $E = 0$. The result is independent of concentration profiles. Førland et al.[9] have used eqn. (15) to calculate the magnitude of contributions from salt bridges in reference electrodes. Further experimental work according to these lines is in progress in our laboratory.

8. The membrane potential

The conventional concept of the membrane potential deserves a special comment because this quantity is central in biology and biophysics. Any textbook on this topic can be consulted for a conventional description of the membrane potential, e.g. Ref. 14.

The presence of a membrane in the electrochemical cell does not introduce anything principally new compared to the liquid junction. We may return to Fig. 5 and replace the liquid junction by a membrane, and KCl by NaCl. The contributions to the EMF from the membrane have the

same fundamental form as the contributions from the liquid junction, eqn. (14), when local equilibrium can be assumed across the membrane. Then the work done in the membrane will be the value of the integral (14) derived for membrane variables. The membrane has particular transport properties which are reflected in the size and variation of the transference numbers. This has been discussed for ion-exchange membranes by Ratkje et al.,[15] and for glass membranes by Førland et al.[9]

The transference numbers in biological membranes are usually taken as constants. For this condition the contribution from the membrane itself to the cell EMF is zero. Assume for the sake of illustration that $t^m_{Na} = 1$ in the membrane. In the surface layer close to the membrane the transference number is reduced according to eqn. (29).

$$t^l_{Na}(x) = t^l_{Na} + (1-t^l_{Na})(x-x_1)/\delta x \qquad (29)$$

Superscript l denotes the left-hand side. The thickness of the surface layer is δx. When linear concentration profiles are assumed, eqn. (30) is the derivative of eqn. (29) within the surface layer.

$$dt^l_{Na}/dx = (1-t^l_{Na})/\delta x \qquad (30)$$

A similar expression, eqn. (31), is obtained for the right-hand side, r.

$$dt^r_{Na}/dx = -(1-t^r_{Na})/\delta x \qquad (31)$$

By introducing these expressions into eqn. (14) and integrating from x_1 to $x_1 + \delta x$, and from x_2 to $x_2 + \delta x$, we obtain eqn. (32), where m denotes the membrane surface. Addition of the cathode and anode contributions $(dG/dt)^c = (1-t^r_{Cl})\mu^r_{NaCl}$ and $(dG/dt)^a = -(1-t^l_{Cl})\mu^l_{NaCl}$ yields eqns. (33) and (34).

$$(dG/dt)_{m\pm\delta x} = -\left(\int_{x_1}^{x_1+\delta x} \mu^l_{NaCl}(dt^l_{Na}/dx)dx \qquad (32)\right.$$

$$\left. + \int_{x_2}^{x_2+\delta x} \mu^l_{NaCl}(dt^r_{Na}/dx)dx \right)(jA/F)$$

$$(dG/dt)_{total} = -[RT \ln a^l_{NaCl,\pm}/a^r_{NaCl,\pm}](jA/F) \qquad (33)$$

$$EF = RT \ln a^l_{NaCl,\pm}/a^r_{NaCl,\pm} \qquad (34)$$

At the left-hand layer at the membrane we have a consumption of NaCl, and there is a mass flux of NaCl out of solution (being converted into an excess Na flux into the membrane, and an excess Cl flux into the solution). Likewise, at the right-hand side boundary of the membrane we have a production of NaCl.

This view is in deep contrast to the commonly accepted picture that membrane fluxes are driven by the membrane potential, which is a force in these cases. The existence of the membrane is believed to cause charge separations

which constitute this force on the ions in the adjacent solutions. It should be noted that the two views are mutually shifted with respect to distinction: What exists and what happens? For the electric work method the material–geometric arrangement involving two solutions of different concentration exists, and the question answered is: where do the energy and substance changes occur? In the conventional approach, the local electric potentials are described as being something which exists even if electrodes are absent.

The electric work method is correct, since it is based on observable, well controlled parameters. It remains to be seen whether the charge separation postulated by the conventional methods exists, since the experiments described in part I[1] have not yet been carried out.

8. The Donnan potential

This membrane potential arises in a special situation where the above analyses are brought to the extremes. An electrolyte and water equilibrium is established across a semipermeable membrane. The electric potential is commonly measured with calomel electrodes, i.e. electrodes containing liquid junctions with steep concentration gradients.

In the electric work method, an equilibrium situation cannot give rise to energy conversion, so there is no contribution whatsoever from the membrane to the measured potential in this case. The result must be solely ascribed to changes in the two electrodes.[15]

In the conventional description, the situation is entirely opposite. The calomel electrodes are "believed" to have zero liquid junction potential, so that the observed EMF is ascribed to the membrane, hence the name Donnan potential and the resulting confusion in the literature as to what this potential may cause. According to Davson[17] the potential may give rise to an electric current, which of course is impossible.

This particular example thus serves to illustrate the need for an alternative theory, if for no other reason than to have an independent method to control the conclusions drawn.

9. Conclusions

The electric work method has been applied to some simple well known examples of isothermal electrochemical cells in the present article. It is shown how the EMF can be built from different localized Gibbs energy changes inside the cell. Each contribution has a well defined expression, and it can be related to particular physical phenomena. Increasing complexities than those dealt with here may be added. Hertz[7] may be consulted for the case of liquid junctions of two electrolytes without a common anion (or cation). In non-isothermal systems heat fluxes become more important. These have also been dealt with previously.[2-4] The next topic for discussion will be electrokinetic effects.

The electric work method cannot prove the conventional

method wrong, because the two methods are so far not yet mutually exclusive. The value of the new method in relation to the conventional is that it so far offers an independent control of results obtained by the other method.

Let us summarize the difference between the old and the new electrochemistry: the basic feature of the conventional treatment is the existence of non-equivalent space points in ordinary space. The particle considered has an electric charge and consequently moves in this space from points of higher to points of lower potential energy. The galvanic cell (or similar instruments) is a device to produce such regions of non-equivalent space points, i.e. the electric field. This then causes the motion of the charged bodies, the electric current.

However, the existence of the field has to be verified experimentally by an independent method, as has been explained in part I. Otherwise we have the following circular argument. The particle moves because there is a field. How do we know that there is a field? Because the particle moves.

The real driving force of the process dwells in the existence of non-uniformities of matter composition, energy and momentum distribution in macroscopic space, and the instability of sets of bodies of different materials in contact with each other (chemical reaction). To these non-uniformities in "property space" the old treatment assigns space regions with electric fields.

The new method avoids the detour of non-equivalent space points. Instead, it directly connects the regions forming the non-uniformities of properties with a system of bars, an open or a closed torus which must have two properties. (1) There must be a conduction of energy, matter and momentum without a gradient of the respective intensive property. (2) The torus must be heterogenous, composed of different materials, such that the quantities can be give off or taken up. Thus the new method offers different physical insight.

Should it not be possible to prove experimentally the existence of the electric field, then the whole procedure of using it is a burden; the old treatment carries all its arguments, having no real physical significance.

It remains to be seen whether the conventional method is built on physical concepts which are non-existant (further details were given in part I). The fact that all necessary results for electrochemical cells can be derived without

using, e.g., static electric fields, implies that electric fields are not necessary in the derivation of ordinary EMFs. However, this also means that if they are proved to be real, they will yield information in addition to that given here. The electric work method implies that only the dynamics of such fields are important.[18]

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