Local Properties of a Formation Cell as Described by Nonequilibrium Thermodynamics

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Abstract

The current description of a formation cell using nonequilibrium thermodynamics gives an overall picture. It does not consider the behaviour of the temperature, chemical potential and electric potential locally. Thus it is unclear where temperature and potential change in the cell. Are these quantities discontinuous at the electrode surfaces, and if yes: how this should be described. Using methods developed in our earlier work we present such a local description. A differential equation is derived and solved for the transference coefficient of the salt in the electrolyte between the electrodes. Boundary conditions are essential for this purpose.

1. Introduction

The aim of this paper is to determine the currentless cell potential of a formation cell using irreversible thermodynamics. The currentless potential is the electric potential difference between two electrodes measured in the limit of zero electric current. (Other names of the currentless potential are the electromotive force and the open circuit potential.) In classical electrochemistry, the currentless potential is given by the Nernst equation, \( \Delta \phi = -\Delta_r G/F \) where \( \Delta_r G \) is the Gibbs energy of the electrochemical cell reaction. The equation, that applies when the temperature and concentrations are constant, serves as the background for lists of standard reduction potential. Liquid junction potentials inside the cell are handled by Henderson’s or Nernst-Planck’s methods. Discussions of liquid junctions and further references can be found in Kotyk and Janaček [6], and Förland et al. [3]. Contributions to the cell potential due to variations in temperature, are usually of the order of mV, and can be neglected when compared to the contribution from \( \Delta_r G \). Thermocells were first treated thoroughly by Agar [1].

An electrochemical cell converts chemical, but also thermal and mechanical energy into electrical energy or vice versa. This occurs in many common-place systems, such
as batteries, fuel cells and electrolysis cells. An accurate description of the currentless potential is important for work that aims to improve efficiency of energy conversion, that is to optimise the cell potential when a sizable current is running. The purpose of this work is to derive an accurate and general expression for the currentless potential of a formation cell, that includes contributions from concentration gradients and temperature gradients across the cell. The expression can later be generalized to include the effect of a non-zero electric current, and is therefore fit to deal with practical situations of energy conversion.

The way we approach the problem is to first divide the cell into five open subsystems. There are three bulk systems with extensions in three dimensions, and two surfaces that are two-dimensional systems according to Gibbs [4]. The direction of transport is perpendicular to the surface areas. From left to right, the subsystems are the bulk anode material, denoted (a), the anode surface, denoted (s,a), the bulk electrolyte, denoted (e), the cathode surface, denoted (s,c) and the bulk cathode, denoted (c). The cell potential, $\Delta \phi$, between the contact points of the potentiometer (a,o) and (c,o) are (see Figure 1):

$$
\Delta \phi = \phi^{c,o} - \phi^{a,o} = (\phi^{c,o} - \phi^{c,e}) + (\phi^{c,e} - \phi^{c,c}) + (\phi^{c,c} - \phi^{c,a}) + (\phi^{c,a} - \phi^{a,e}) + (\phi^{a,e} - \phi^{a,o}) = \Delta_a \phi + \Delta_{a,e} \phi + \Delta_c \phi + \Delta_{c,c} \phi + \Delta_c \phi
$$

(1)

The first superscript indicates the region and the second a specific position in that region. Thus (c,e) is, for instance, in the bulk cathode next to the surface of the...
electrolyte. One subscript for $\Delta$ gives the difference across that region, while two subscripts give the difference across the surface between the corresponding regions. All such differences are, always given by the value on the right hand side minus the value on the left hand side. The electric potential difference across the surface is due to the surface polarization. Kjelstrup et al. [5] have given a more detailed discussion of the surface as a thermodynamic system. In the bulk regions, the electric potential varies smoothly.

The profiles of $\phi(x)$, of chemical potential, pressure and temperature, $\mu_i(x)$, $p(x)$ and $T(x)$, depend on one another because the fluxes of heat, mass and charge are coupled. There is therefore a set of flux equations for each region, that must be solved simultaneously, to find the contribution to the electric potential from that region. We shall find solutions of $\phi(x)$, $\mu_i(x)$, and $T(x)$ for a formation cell that has a steady increase or decrease in its components, superimposed on gradients in concentration and temperature. The thermostating of the system is assumed to be such that the temperatures of the five regions are independent of the time. We use the fact that the system is electroneutral in all its parts.

To illustrate the theory, we consider as an example the formation cell:

$$\text{Na(Hg)}|^{s,a}\text{NaCl(aq)}|^{s,c}\text{Cl}_2(g)(Pt)$$

There is an amalgam electrode of Na to the left, and a Cl$_2$(g) electrode to the right. The purpose of mercury is to keep the activity of sodium down and make it less reactive. The electron carrier to chlorine is Pt. The electrolyte is an aqueous solution of NaCl. The electrode reaction at the left side is normally written as

$$\text{Na} \rightarrow \text{Na}^{+}(aq) + e^-$$

At this electrode, one mole of Na disappears from the bulk reservoir, per mole of electrons passing the external circuit from right to left. One mol of Na$^+$ is produced close to the electrode. The right electrode reaction is written as

$$\frac{1}{2}\text{Cl}_2(g) + e^- \rightarrow \text{Cl}^-(aq)$$

One mol of Cl$^-$ is produced at the electrode surface.

A time independent electric current $j$ leads to an increase of the salt content in the electrolyte of $j/F$ moles of NaCl per unit of time and per unit of cross sectional area. The ionic strength in the formation cell is usually so large that the surfaces of the electrodes are saturated with adsorbed salt. A very small change in the adsorption, $\Gamma_{\text{NaCl}}$, is enough to adjust the chemical potential of the salt in the surface to the chemical potential in the adjacent electrolyte. When this equilibration occurs rapidly, we may use that

$$\mu_{\text{NaCl}}^{s,a}(t) = \mu_{\text{NaCl}}^{e,a}(t) \quad \text{and} \quad \mu_{\text{NaCl}}^{s,c}(t) = \mu_{\text{NaCl}}^{e,c}(t)$$
In the bulk anode the concentration of sodium, and in the cathode the concentration of the chlorine, are independent of time. At the anode surface the absorptions of sodium and salt, and at the cathode surface the concentration of chlorine and salt, are in good approximation independent of the time. The system is thermostated in such a way that the temperature is everywhere independent of the time.

In Sections 2–6 we will derive the contribution to the currentless potential of the five different subsystems, the bulk anode material, the anode surface, the bulk electrolyte, the cathode surface, and the bulk cathode. We give first the entropy production rate of the subsystem using independent variables. The electric potential difference then follows by integrating the flux equations for proper boundary conditions.

2. Bulk Anode

The entropy production rate per unit time and volume in the nonisothermal anode is given by

\[
T \sigma^a = -j^a_q \frac{1}{T} \frac{\partial T}{\partial x} - J^a_{Na} \frac{\partial}{\partial x} \mu^a_{Na,T} - \frac{\partial \phi}{\partial x}
\]

\[
= -j^a_q \frac{1}{T} \frac{\partial T}{\partial x} - \frac{j}{T} \left( \frac{\partial}{\partial x} \left[ \phi + \frac{1}{F} \mu^a_{Na,T} \right] \right)
\]

where we used that the sodium flux, \( J^a_{Na} \), is equal to the electric current divided by Faraday’s constant, \( j/F \). Furthermore \( j^a_q \) is the measurable heat flux, \( \mu^a_{Na} \) the chemical potential of sodium and \( \phi \) the electric potential. The subscript \( T \) indicates that the derivative is taken with the temperature constant. The resulting linear force-flux relations are

\[
J^a_q = -L^a_{qq} \frac{1}{T} \frac{\partial T}{\partial x} - L^a_{q\phi} \frac{\partial}{\partial x} \left[ \phi + \frac{1}{F} \mu^a_{Na,T} \right]
\]

\[
j = -L^a_{\phi\phi} \frac{1}{T} \frac{\partial T}{\partial x} - L^a_{\phi\phi} \frac{\partial}{\partial x} \left[ \phi + \frac{1}{F} \mu^a_{Na,T} \right]
\]

The ratio of the heat flux and the electric current defines the Peltier coefficient

\[
\pi^a \equiv F \left( \frac{J^a_q}{j} \right)_{\partial T/\partial x = 0} = F \frac{L^a_{q\phi}}{L^a_{\phi\phi}} = T(S^a_{Na} - S^e_{Na})
\]

In the last equality we wrote the Peltier coefficient in terms of the entropy of the sodium and the transported entropy of the electrons. The entropy of sodium has a positive sign, since sodium is consumed in the electrode reaction and liberates the heat \( T S^a_{Na} \), Forland et al. [3]. The sign before the transported entropy is chosen negative because the electrons move in the direction opposite to the electric current. This convention results in a positive transported entropy for the electrons. For a zero
electric current, we have, using that the conductivity matrix is symmetric, $L_{\phi q}^a = L_{q\phi}^a$, for the electric potential gradient

$$
\frac{\partial \phi}{\partial x} = -\frac{1}{F} \left[ \frac{\partial}{\partial x} \mu_{Na,T}^a + \frac{\pi^a}{T} \frac{\partial T}{\partial x} \right]
$$

(9)

Integration across the electrode gives

$$
\Delta_{a\phi} = \int_{a,o}^{a,c} d\phi = -\frac{1}{F} \left[ \int_{a,o}^{a,c} d\mu_{Na,T}^a + \int_{a,o}^{a,c} (S_{Na}^a - S_{e^{-}}^a) dT \right]
$$

$$
= -\frac{1}{F} \left[ \mu_{Na}^{a,c} (T^{a,o}) - \mu_{Na}^{a,o} + (S_{Na}^a - S_{e^{-}}^a) (T^{a,c} - T^{a,o}) \right]
$$

$$
= -\frac{1}{F} \left[ \mu_{Na}^{a,c} (T^{a,o}) - \mu_{Na}^{a,o} + \frac{\pi_{a,c}}{T_{e,c}} (T^{a,c} - T^{a,o}) \right]
$$

(10)

where we referred the chemical potential to the temperature $T^{a,o}$ at the beginning of the electrode and where we took the entropy and the transported entropy independent of the temperature. For constant temperature this reduces to

$$
\Delta_{a\phi} = -\frac{1}{F} (\mu_{Na}^{a,c} - \mu_{Na}^{a,o})
$$

(11)

An electrode made of pure Na does not have any drop in electric potential. An amalgam electrode with consumption of Na at the anode surface, has probably a smaller amount of Na close to the surface than away from the surface. This means that the difference $(\mu_{Na}^{a,c} - \mu_{Na}^{a,o})$ is negative, and that the potential difference, $\Delta_{a\phi}$, is positive. This situation is illustrated in Figure 1.

3. Anode Surface

The situation in the left surface is illustrated in Figure 2. Before reaction, Na must migrate from the bulk of the electrode into the surface: There is a flow of sodium, $J_{Na}$, into the surface. The state of Na in the surface, may be different from that of the bulk phase. The energy of the metal (the chemical potential of sodium) is lower in the surface than in the bulk, if sodium prefers to be in the surface. (Na is a reactive metal). We denote the chemical potential of Na in the amalgam by $\mu_{Na}^a$, and in the surface by $\mu_{Na}^{s,a}$. The reaction takes place at the surface of the anode:

$$
Na(s,a) \rightarrow Na^+(s,a) + e^- (s,a)
$$

(12)

The Gibbs energy change of the reaction is

$$
\Delta G^{s,a} = \mu_{Na}^{s,a} + \mu_{e^-}^{s,a} - \mu_{Na}^{s,a}
$$

(13)

with the reaction rate, $r^{s,a}$. After the reaction, the electron is transferred to the conduction band in the metal, and the sodium ion is transferred to the ionic
atmosphere in the electrolyte. The entropy production rate per unit time and area in the nonisothermal anode surface becomes:

\[
\sigma^{s,a} = J_{q}^{a,e} \left( \frac{1}{T_{s,a}} - \frac{1}{T_{a,e}} \right) + J_{q}^{e,a} \left( \frac{1}{T_{a,e}} - \frac{1}{T_{s,a}} \right) - J_{NaCl}^{e,a} \frac{\mu_{NaCl}(T_{s,a}) - \mu_{NaCl}^{s,a}}{T_{s,a}} \\
- J_{Na}^{a,e} \frac{\mu_{Na}^{s,a} - \mu_{Na}^{e,a}(T_{s,a})}{T_{s,a}} - r^{s,a} \frac{\Delta G_{a}^{s,a}}{T_{s,a}} - j \frac{\Delta a,e \phi}{T_{s,a}}
\]

(14)

where \( T_{a,e} \) is the temperature in the bulk anode close to the surface, \( T_{s,a} \) the temperature of the surface and \( T_{e,a} \) the temperature of the electrolyte close to the anode surface. The temperature, at which an evaluation of a property is done, is indicated by the superscript. The chemical potential at the surface, \( \mu_{Na}^{s,a} \), is thus evaluated at the surface temperature, \( T_{s,a} \). If the quantity is evaluated at a different temperature, however, this is explicitly indicated. Thus the chemical potential of the sodium in the bulk anode close to the surface, \( \mu_{Na}^{e,a}(T_{s,a}) \), is evaluated at the temperature of the surface. All fluxes are here taken as independent of time. For such a stationary state, the sodium current and the reaction rate are equal to the electric current divided by Faraday’s constant. This results in

\[
T_{s,a} \sigma^{s,a} = -J_{q}^{a,e} \left( \frac{T_{s,a} - T_{a,e}}{T_{a,e}} \right) - J_{q}^{e,a} \left( \frac{T_{e,a} - T_{s,a}}{T_{s,a}} \right) \\
- J_{NaCl}^{e,a} \left( \frac{\mu_{NaCl}(T_{s,a}) - \mu_{NaCl}^{s,a}}{T_{s,a}} \right) \\
- j \left[ \Delta a,e \phi + \frac{1}{e} (\mu_{Na}^{s,a} + \mu_{e}^{s,a} - \mu_{Na}^{e,a}(T_{s,a})) \right]
\]

(15)

Fig. 2. Concentration profiles at the surface.
The resulting linear force-flux relations are

\[
J_{q}^{a,e} = -L_{aa}^{s,a} \left( \frac{T_{c,a}^{a} - T_{a,c}^{a}}{T_{a,c}} \right) - L_{ae}^{s,a} \left( \frac{T_{c,a}^{c} - T_{a,c}^{a}}{T_{c,a}} \right) - \frac{1}{F} \left( \mu_{NaCl}^{e,a} \left( T_{c,a}^{a} - T_{a,c}^{a} \right) - \mu_{NaCl}^{s,a} \right) \\
- L_{a,e}^{s,a} \left[ \Delta_{a,e}^{a,e} \phi + \frac{1}{F} \left( \mu_{Na}^{e,a} + \mu_{Na}^{c,a} - \mu_{Na}^{a,e} \left( T_{a,c}^{a} \right) \right) \right]
\]

\[
J_{q}^{e,a} = -L_{ea}^{s,a} \left( \frac{T_{c,a}^{a} - T_{a,c}^{a}}{T_{a,c}} \right) - L_{ae}^{s,a} \left( \frac{T_{c,a}^{c} - T_{a,c}^{a}}{T_{c,a}} \right) - \frac{1}{F} \left( \mu_{NaCl}^{e,a} \left( T_{c,a}^{a} - T_{a,c}^{a} \right) - \mu_{NaCl}^{s,a} \right) \\
- L_{e,e}^{s,a} \left[ \Delta_{e,e}^{a,e} \phi + \frac{1}{F} \left( \mu_{Na}^{e,a} + \mu_{Na}^{c,a} - \mu_{Na}^{a,e} \left( T_{a,c}^{a} \right) \right) \right]
\]

\[
J_{NaCl}^{c,a} = -L_{aa}^{s,a} \left( \frac{T_{c,a}^{a} - T_{a,c}^{a}}{T_{a,c}} \right) - L_{ae}^{s,a} \left( \frac{T_{c,a}^{c} - T_{a,c}^{a}}{T_{c,a}} \right) - \frac{1}{F} \left( \mu_{NaCl}^{e,a} \left( T_{c,a}^{a} - T_{a,c}^{a} \right) - \mu_{NaCl}^{s,a} \right) \\
- L_{a,a}^{s,a} \left[ \Delta_{a,a}^{a,e} \phi + \frac{1}{F} \left( \mu_{Na}^{e,a} + \mu_{Na}^{c,a} - \mu_{Na}^{a,e} \left( T_{a,c}^{a} \right) \right) \right]
\]

\[
J_{NaCl}^{e,a} = -L_{aa}^{s,a} \left( \frac{T_{c,a}^{a} - T_{a,c}^{a}}{T_{a,c}} \right) - L_{ae}^{s,a} \left( \frac{T_{c,a}^{c} - T_{a,c}^{a}}{T_{c,a}} \right) - \frac{1}{F} \left( \mu_{NaCl}^{e,a} \left( T_{c,a}^{a} - T_{a,c}^{a} \right) - \mu_{NaCl}^{s,a} \right) \\
- L_{a,a}^{s,a} \left[ \Delta_{a,a}^{a,e} \phi + \frac{1}{F} \left( \mu_{Na}^{e,a} + \mu_{Na}^{c,a} - \mu_{Na}^{a,e} \left( T_{a,c}^{a} \right) \right) \right]
\]

(16)

The salt flux is a bulk flux and its ratio with the electric current defines the transference coefficient [3]:

\[
i_{NaCl}^{c,a} = F \left( \frac{J_{NaCl}^{c,a}}{j} \right)_{\Delta_{a}T=\Delta_{a} \mu_{NaCl}=0} = \frac{F L_{s,a}}{L_{s,a}} L_{\phi,a}^{s,a}
\]

(17)

In the following section we will show that

\[
i_{NaCl}^{c,a} = i_{NaCl}^{c,a} (\chi = 0) = i_{Na}^{c,a}
\]

(18)

The origin of the coordinate axis is the anode surface.

The heat fluxes are also bulk fluxes. Their ratios with the electric current define the Peltier coefficients for these bulk fluxes at the anode surface:

\[
\pi_{a}^{a,c} = F \left( \frac{J_{a,c}^{a,c}}{j} \right)_{\Delta_{a}T=\Delta_{a} \mu_{NaCl}=0} = \frac{F L_{s,a}}{L_{\phi,a}^{s,a}}
\]

\[
\pi_{a}^{c,a} = F \left( \frac{J_{c,a}^{a,c}}{j} \right)_{\Delta_{a}T=\Delta_{a} \mu_{NaCl}=0} = \frac{F L_{s,a}}{L_{\phi,a}^{s,a}}
\]

(19)

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The Peltier coefficients can be written in terms of the transported entropies of electrons, of sodium ions, and thermodynamic entropies in the following way:

\[ \pi^{a,\text{e}} = T^{a,\text{e}}(S_{\text{Na}}^{\text{Na}} - S_{\text{Na}}^{\text{e},a,e}) \]

\[ \pi^{e,a} = \pi^e(x = 0) = T^{e,a}\text{f}_{\text{Na}^+}(S_{\text{Na}}^{\text{e}} + S_{\text{Na}^+}^{\text{e},a,a}) \]

The signs of all the entropic contributions are positive if the corresponding component moves with the current and negative when it moves in the opposite direction. It is common to define the Peltier coefficient for the surface in terms of the amount of heat needed to assure that the temperature of the electrode surface does not change when a positive electric current is passing the surface:

\[ \pi^{s,a} \equiv F \left( \frac{J_{\text{f},\text{a}} - J_{\text{a},\text{e}}}{j} \right) \Delta_{s,\text{a}}T = \Delta_{s,\text{e}}T = \Delta_{s,\text{e}}\text{f}_{\text{Na}^+} = 0 = -\pi^{a,\text{e}} + \pi^{e,a} \]  

(21)

Substituting the expressions for the bulk Peltier coefficients gives

\[ \pi^{s,a} = F \left( \frac{L_{\text{f},\text{a}} - L_{\text{a},\text{e}}}{L_{\phi,\phi}^{a}} \right) = -T^{a,\text{e}}(S_{\text{Na}}^{\text{s}} - S_{\text{Na}}^{\text{e},a,e}) + T^{e,a}\text{f}_{\text{Na}^+}(S_{\text{Na}^+}^{\text{s}} + S_{\text{Na}^+}^{\text{e},a,a}) \]

(22)

Using the Onsager symmetry relations for the conductivity matrix, the currentless potential across the anode surface becomes

\[ \Delta_{a,\text{e}} \phi = -\frac{1}{F} \left[ \mu_{\text{Na}^+}^{s,a} + \mu_{\text{e}^+}^{s,a} - \mu_{\text{Na}^+}^{a,\text{e}}(T^{s,a}) + \pi^{a,\text{e}}(T^{s,a} - T^{a,\text{e}}) \right] 
+ \pi^{e,a} \left( \frac{T^{e,a} - T^{s,a}}{T^{e,a}} \right) \text{f}_{\text{Na}^+}(\mu_{\text{Na}^+}^{e,a}(T^{s,a}) - \mu_{\text{Na}^+}^{a,\text{e}}) \]  

(23)

For a constant temperature and equilibrium for the salt at the surface, this expression reduces to its first three terms. The chemical potentials are evaluated at the location given by the superscript if a different temperature is not explicitly given. It is likely that the combination of the chemical potentials gives the largest contribution to the surface potential drop, since it is relatively easy to thermostate well a metal electrode interface. The potential between a sodium (anode) and a standard hydrogen electrode is 2.7 V [2]. We have therefore indicated a jump upwards in electric potential at the anode surface of Figure 1. This means that \( \mu_{\text{Na}^+}^{s,a} + \mu_{\text{e}^+}^{s,a} - \mu_{\text{Na}^+}^{a,\text{e}} < 0 \), and is consistent with high-energy (reactive) sodium.

One may extract the contribution due to temperature differences. For this we consider the case that \( \mu_{\text{Na}^+}^{s,a} + \mu_{\text{e}^+}^{s,a} - \mu_{\text{Na}^+}^{a,\text{e}}(T^{s,a}) = 0 \), and \( \mu_{\text{Na}^+}^{e,a}(T^{s,a}) - \mu_{\text{Na}^+}^{a,\text{e}} = 0 \). This results in

\[ \Delta_{a,\text{e}} \phi = -\frac{1}{F} \left[ \pi^{a,\text{e}}(T^{s,a} - T^{a,\text{e}}) + \pi^{e,a} \left( T^{e,a} - T^{s,a} \right) \right] \]  

(24)
If we write this using the Peltier coefficients given above, we find

\[
\Delta_{a,e} \phi = -\frac{1}{F} \left[ (S_{Na}^{a,e} - S_{e}^{*,a,e}) (T_{Na}^{a,a} - T^{a,e}) + \kappa_{NaCl}^{e,a} (S_{NaCl}^{e,a} + S_{Na}^{*,e,a}) (T^{e,a} - T_{Na}^{s,a}) \right]
\]

(25)

There are two contributions, one from each side of the surface.

4. Electrolyte

The entropy production rate in the electrolyte is given by

\[
T \sigma^e = -J_q^e \frac{1}{T} \frac{\partial T}{\partial x} - J_{NaCl}^e \frac{\partial}{\partial x} \mu_{NaCl,T}^e - j \frac{\partial \phi}{\partial x}
\]

(26)

The resulting linear force-flux relations are

\[
J_q^e = -L_{q \mu q}^e \frac{1}{T} \frac{\partial T}{\partial x} - L_{q \mu}^e \frac{\partial}{\partial x} \mu_{NaCl,T}^e - L_{q \phi}^e \frac{\partial \phi}{\partial x}
\]

\[
J_{NaCl}^e = -L_{\mu q}^e \frac{1}{T} \frac{\partial T}{\partial x} - L_{\mu}^e \frac{\partial}{\partial x} \mu_{NaCl,T}^e - L_{\phi}^e \frac{\partial \phi}{\partial x}
\]

(27)

The transference coefficient is defined by

\[
t_{NaCl}^e (x) \equiv F \left( \frac{J_{NaCl}^e (x)}{j} \right) \frac{\partial T}{\partial x} = \frac{F L_{\phi}^e (x)}{L_{q \phi}^e}
\]

(28)

The ratio of the heat flux and the electric current defines the Peltier coefficient

\[
\pi^e (x) \equiv F \left( \frac{J_q^e (x)}{j} \right) \frac{\partial T}{\partial x} = F \frac{L_{q \phi}^e (x)}{L_{\phi}^e}
\]

(29)

As we shall see below the transference and the Peltier coefficient are not a property of the electrolyte alone. Boundary conditions and in particular the exchange of salt and heat with the environment, are found to be decisive in determining these coefficients.

The increase or decrease of the salt concentration in the electrolyte is due to the exchange of ions, and possibly salt, with the surface. In the electrolyte, the concentration satisfies

\[
\frac{\partial}{\partial t} c_{NaCl}^e (x, t) = - \frac{\partial}{\partial x} J_{NaCl}^e (x, t)
\]

(30)
By integrating this equation from $x = 0$ to $x = d_e$, one obtains

$$\frac{\partial}{\partial t} \int_0^{d_e} c^{e}_{NaCl}(x,t)dx = -J^{e}_{NaCl}(d_e,t) + J^{e}_{NaCl}(0,t) = J^{e,a}_{NaCl}(t) - J^{e,c}_{NaCl}(t)$$

(31)

The accumulation of salt in the electrolyte per unit of cross-sectional area, is the difference in the salt fluxes at the two electrodes, when, as we will assume, there is no accumulation of salt at the surfaces. The increase in the salt content in the electrolyte is also given by the electric current density:

$$\frac{\partial}{\partial t} \int_0^{d_e} c^{e}_{NaCl}(x,t)dx = \frac{j(t)}{F}$$

(32)

To solve equations (27), we need the transference coefficient of the salt. In the calculation of this coefficient we can use that the temperature and the chemical potential of the salt, and therefore also the concentration of the salt, are by definition independent of the position in the electrolyte. It then follows that

$$\frac{\partial}{\partial t} c^{e}_{NaCl}(x,t) = \frac{\partial}{\partial t} c^{e}_{NaCl}(t) = \frac{j}{Fd_e}$$

(33)

For the gradient of the transference coefficient we find

$$\frac{\partial}{\partial x} r^{e}_{NaCl}(x) = \frac{F}{j} \frac{\partial}{\partial x} J^{e}_{NaCl}(x) = \frac{F}{j} \frac{\partial}{\partial t} c^{e}_{NaCl}(t) = -\frac{1}{d_e}$$

(34)

The solution of this equation is

$$r^{e}_{NaCl}(x) = r^{e}_{Na} - \frac{x}{d_e} = r^{e}_{Na} \left(1 - \frac{x}{d_e}\right) - r^{e}_{Cl} \frac{x}{d_e}$$

(35)

The integration constant has been chosen such that the transference coefficient is equal to the transport number of the sodium ion, $r^{e}_{Na^+}$, at the anode surface. At the cathode surface it then becomes equal to minus the transfer number of the chloride ion, $-r^{e}_{Cl^-} = -(1 - r^{e}_{Na^+})$.

Above we have seen that the transference coefficient of the salt is found, using the knowledge that the salt enters, or leaves, the system through the anode and cathode surface, while there is at most a negligible absorption at these surfaces. Also the Peltier coefficient is found, using the analogy between heat and mass exchange with the environment. The divergence of the heat flux leads to local cooling. The derivative of the Peltier coefficient

$$\frac{\partial \pi^{e}(x)}{\partial x} = \frac{F}{j} \left( \frac{\partial J^{e}_q(x)}{\partial x} \right) \frac{\partial T/\partial x = 0}{\partial^{e}_{NaCl}/\partial x = 0}$$

(36)
is therefore the amount of heat that must be supplied per unit of time, length and cross section, for a mole of charge carrier passed, in order to keep the temperature constant as a function of time. The essential assumption at this point is now that this heat is indeed supplied without restriction. What remains to be done is to add the heat that is carried along by the salt and by the ions. This gives

\[ \pi^e(x) = T \left[ \left(1 - \frac{x}{d_e}\right) \tau_{Na^+}^e (S_{NaCl}^e + S_{Na^+}^e, e) - \frac{x}{d_e} \tau_{Cl^-}^e (S_{NaCl}^e + S_{Cl^-}^e, e) \right] \]

\[ = T \left[ \tau_{NaCl}^e (x) S_{NaCl}^e + \left(1 - \frac{x}{d_e}\right) \tau_{Na^+}^e (S_{Na^+}^e, e) - \frac{x}{d_e} \tau_{Cl^-}^e (S_{Cl^-}^e, e) \right] \]  

(37)

where \( S_{NaCl}^e \) is the entropy of the salt per unit of volume and \( S_{Na^+}^e, e \) and \( S_{Cl^-}^e, e \) are the so-called transported entropies of the ions. Note that as a consequence of the definition of the Peltier coefficient all these (transported) entropies are taken at a constant temperature and salt concentration. In general they will depend on the temperature, however. Substitution of this expression for the Peltier coefficient in the previous equation gives the needed heat source

\[ \frac{\partial \pi^e(x)}{\partial x} = -T \frac{d_e}{d_e} \left[ \tau_{Na^+}^e (S_{NaCl}^e + S_{Na^+}^e, e) + \tau_{Cl^-}^e (S_{NaCl}^e + S_{Cl^-}^e, e) \right] \]

\[ = -T \frac{d_e}{d_e} \left[ S_{NaCl}^e + \tau_{Na^+}^e S_{Na^+}^e, e + \tau_{Cl^-}^e S_{Cl^-}^e, e \right] \]  

(38)

This is a position- and time independent heat source.

Using the Onsager symmetry relations for the conductivity matrix, the zero electric current potential gradient is therefore

\[ \frac{\partial \phi}{\partial x} = -\frac{1}{F} \left[ \tau_{NaCl}^e (x) \frac{\partial}{\partial x} \mu_{NaCl,T}^e + \frac{\pi^e(x)}{T} \frac{\partial T}{\partial x} \right] \]  

(39)

Integration across the electrolyte, using integration by parts, gives

\[ \Delta \phi = \int_{c,a} d\phi = -\frac{1}{F} \left[ \int_{c,a} \tau_{NaCl}^e d \mu_{NaCl,T}^e + \int_{c,a} \frac{\pi^e}{T} dT \right] \]

(40)

By taking the temperature and the chemical potential, or alternatively the concentration profiles linear, and the entropy of the salt constant, one obtains

\[ \Delta \phi = -\frac{1}{2F} \left[ (\tau_{Na^+}^e - \tau_{Cl^-}^e) (\Delta \mu_{NaCl}^{c,a} (T^{c,a}) + S_{NaCl}^e \Delta T) \right] \]

\[ + (\tau_{Na^+}^e S_{Na^+}^{*,a} - \tau_{Cl^-}^e S_{Cl^-}^{*,e}) \Delta e T \]  

(41)
By using the Peltier coefficient given above, this can be written as

\[ \Delta_e \phi = -\frac{1}{2F} \left[ \left( \mathcal{F}_{\text{Na}^+}^{e} - \mathcal{F}_{\text{Cl}^-}^{e} \right) \Delta_e \mu_{\text{NaCl}}^{e} (T^{e,a}) + \left( \frac{\mathcal{F}_{\text{e}}^{e,a}}{T^{e,a}} + \frac{\mathcal{F}_{\text{e}}^{e,c}}{T^{e,c}} \right) \Delta_e T \right] \]  \hfill (42)

This is the most general expression for the electric potential drop across the electrolyte. We see immediately, that in the absence of differences in chemical potential of salt, and of temperature, the electric potential is zero. The first contribution is always zero, if the transport number of the cation and anion are the same, as is the case of KCl. In an aqueous solution of NaCl, the transport number of Na\(^+\) is smaller than 0.5. The difference \( \mathcal{F}_{\text{Na}^+}^{e} - \mathcal{F}_{\text{Cl}^-}^{e} \) is therefore negative. When the electric current runs in this system, NaCl will tend to accumulate on the left hand side of the cell, giving \( \Delta_e \mu_{\text{NaCl}}^{e} \) < 0. Given that the product of these terms dominate the potential contribution from the electrolyte, we have a negative potential difference across the electrolyte (cf. Fig. 1). The cell, left to itself when the current is running, yields a smaller potential due to concentration polarisation.

One may extract the contribution due to the temperature differences. For this we consider the case that \( \Delta_e \mu_{\text{NaCl}}^{e} (T^{e,a}) = 0 \). This results in

\[ \Delta_e \phi = \frac{1}{2F} \left( \frac{\mathcal{F}_{\text{e}}^{e,a}}{T^{e,a}} + \frac{\mathcal{F}_{\text{e}}^{e,c}}{T^{e,c}} \right) \Delta_e T \]  \hfill (43)

If we write this using the Peltier coefficients given above, one obtains

\[ \Delta_e \phi = -\frac{1}{2F} \left[ \mathcal{F}_{\text{Na}^+}^{e} (S_{\text{NaCl}}^{e} + S_{\text{Na}^+}^{*,e,a}) - \mathcal{F}_{\text{Cl}^-}^{e} (S_{\text{NaCl}}^{e} + S_{\text{Cl}^-}^{*,e,c}) \right] \Delta_e T \]  \hfill (44)

5. Cathode Surface

The entropy production rate for the cathode surface is:

\[ \sigma_{s,c} = J_q^{e,c} \left( \frac{1}{T_{s,c}} - \frac{1}{T_{e,c}} \right) + J_q^{e,c} \left( \frac{1}{T_{e,c}} - \frac{1}{T_{s,c}} \right) - J_{\text{NaCl}}^{e,c} \mu_{\text{NaCl}}^{s,c} - \mu_{\text{NaCl}}^{e,c} (T^{s,c}) \]

\[ - J_{\text{Cl}_2}^{e,c} \mu_{\text{Cl}_2}^{s,c} (T^{s,c}) - \mu_{\text{Cl}_2}^{e,c} \]

\[ - j \frac{\Delta G^{s,c}}{T_{s,c}} - j \frac{\Delta_e \phi}{T_{s,c}} \]  \hfill (45)

For the stationary state condition, the chlorine current and the reaction rate are again given in terms of the electric current. The result is

\[ T_{s,c} \sigma_{s,c} = -J_q^{e,c} \left( \frac{T_{s,c} - T_{e,c}}{T_{e,c}} \right) - J_q^{e,c} \left( \frac{T_{e,c} - T_{s,c}}{T_{e,c}} \right) \]

\[ - J_{\text{NaCl}}^{e,c} \left( \mu_{\text{NaCl}}^{s,c} - \mu_{\text{NaCl}}^{e,c} (T^{s,c}) \right) \]

\[ - j \left[ \Delta_e \phi + \frac{1}{F} \left( \mu_{\text{Cl}_2}^{s,c} - \mu_{\text{Cl}_2}^{e,c} \right) - \frac{1}{2} \mu_{\text{Cl}_2}^{e,c} (T^{s,c}) \right] \]  \hfill (46)

J. Non-Equilib. Thermodyn. · 2000 · Vol. 25 · No. 2
The resulting linear force-flux relations are

\[
J_{q}^{c,e} = -L_{ee}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \mu_{NaCl}^{s,c} - \mu_{NaCl}^{e,c} \left(T_{c}^{s,c} \right) \right) \\
- L_{e}^{s,c} \left[ \Delta_{e,c} \phi + \frac{1}{F} \left( \mu_{Cl}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2} \mu_{Cl}^{e,c} \right) \right] \\
J_{q,c,e}^{c,e} = -L_{ec}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \mu_{NaCl}^{s,c} - \mu_{NaCl}^{e,c} \left(T_{c}^{s,c} \right) \right) \\
- L_{e}^{s,c} \left[ \Delta_{e,c} \phi + \frac{1}{F} \left( \mu_{Cl}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2} \mu_{Cl}^{e,c} \right) \right] \\
J_{NaCl}^{c,e} = -L_{e\mu}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \mu_{NaCl}^{s,c} - \mu_{NaCl}^{e,c} \left(T_{c}^{s,c} \right) \right) \\
- L_{e}^{s,c} \left[ \Delta_{e,c} \phi + \frac{1}{F} \left( \mu_{Cl}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2} \mu_{Cl}^{e,c} \right) \right] \\
j = -L_{e\phi}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \frac{T_{c}^{e,c} - T_{e,c}^{s,c}}{T_{e,c}} \right) - L_{e}^{s,c} \left( \mu_{NaCl}^{s,c} - \mu_{NaCl}^{e,c} \left(T_{c}^{s,c} \right) \right) \\
- L_{e}^{s,c} \left[ \Delta_{e,c} \phi + \frac{1}{F} \left( \mu_{Cl}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2} \mu_{Cl}^{e,c} \right) \right] \\
\tag{47}
\]

The transference coefficient of the salt is defined by

\[
f_{NaCl}^{c,e} \equiv F \left( \frac{j_{NaCl}^{c,e}}{j} \right)_{\Delta_{e}T=\Delta_{e}T=\Delta_{e}S_{NaCl}=0} = F \frac{L_{e}^{s,c}}{L_{e}^{s,c}} \left( \mu_{NaCl}^{s,c} \right) = \frac{f_{NaCl}^{c,e}}{j} = -f_{Cl}^{c}
\]

The ratio of the heat fluxes and the electric current define the bulk Peltier coefficients at the cathode surface

\[
\pi_{e}^{c,e} \equiv F \left( \frac{j_{q}^{e,c}}{j} \right)_{\Delta_{e}T=\Delta_{e}T=\Delta_{e}S_{NaCl}=0} = F \frac{L_{e}^{s,c}}{L_{e}^{s,c}} = \left( \frac{T_{c}^{e,c}}{T_{e,c}} \right) \left( \mu_{NaCl}^{s,c} - S_{e}^{c,e} \right) \\
\pi_{e}^{c,e} \equiv F \left( \frac{j_{q}^{e,c}}{j} \right)_{\Delta_{e}T=\Delta_{e}T=\Delta_{e}S_{NaCl}=0} = F \frac{L_{e}^{s,c}}{L_{e}^{s,c}} = \left( \frac{T_{c}^{e,c}}{T_{e,c}} \right) \left( \frac{1}{2} S_{Cl}^{e} + S_{e}^{c,e} \right)
\]

In the last equalities we expressed the Peltier coefficients in terms of the transported entropies of the chloride ion and the electron. The signs of all these entropic contributions are positive if the corresponding component moves with the current and negative when it moves in the opposite direction. The Peltier coefficient for the cathode surface is defined by

\[
\pi_{s}^{c,e} \equiv F \left( \frac{j_{q}^{e,c} - j_{q}^{e,c}}{j} \right)_{\Delta_{e}T=\Delta_{e}T=\Delta_{e}S_{NaCl}=0} = -\pi_{s}^{c,e} + \pi_{c}^{c,e}
\]

\[\text{J. Non-Equilib. Thermodyn.} \cdot 2000 \cdot \text{Vol. 25} \cdot \text{No. 2}\]
Substituting the above relations for the bulk Peltier coefficients gives

\[ \pi^{s,c} = F \frac{I_{e\phi}^{s,c} - I_{e\phi}^{e,c}}{L_{\phi\phi}^{e,c}} = T^{e,c} I_{\text{Cl}^-} (S_{\text{NaCl}}^{e,c} + S_{\text{Cl}^-}^{s,c}) - T^{e,c} \left( \frac{1}{2} S_{\text{Cl}_2}^{e,c} + S_{e}^{s,c} \right) \]  

(51)

Using the Onsager symmetry relations for the conductivity matrix, the currentless potential across the cathode surface is therefore

\[ \Delta_{e,c} \phi = -\frac{1}{F} \left[ \mu^{s,c}_{\text{Cl}^-} - \mu^{s,c}_e - \frac{1}{2} \mu^{e,c}_{\text{Cl}_2} (T^{s,c}) + \pi^{e,c} \left( \frac{T^{s,c} - T^{e,c}}{T^{e,c}} \right) \right. \\
+ \left. \pi^{e,c} \left( \frac{T^{e,c} - T^{s,c}}{T^{e,c}} \right) - \mu_{\text{NaCl}} (T^{s,c} ) \right] \]  

(52)

For a constant temperature and equilibrium for the salt at the surface, this expression reduces to the one given by the electrode reaction. A formation cell where the hydrogen electrode is measured against a chloride electrode in an aqueous solution has a cell potential of 1.40 V. We have therefore drawn a positive jump in potential at the cathode surface in Figure 1.

The contribution due to the temperature differences alone is found when \( \mu^{s,c}_{\text{Cl}^-} - \mu^{s,c}_e - \frac{1}{2} \mu^{e,c}_{\text{Cl}_2} (T^{s,c}) = 0 \), and \( \mu_{\text{NaCl}} (T^{s,c} ) = 0 \). This results in

\[ \Delta_{e,c} \phi = -\frac{1}{F} \left[ \frac{\pi^{e,c}}{T^{e,c}} (T^{s,c} - T^{e,c}) + \frac{\pi^{e,c}}{T^{e,c}} (T^{e,c} - T^{s,c}) \right] \]  

(53)

If one writes this using the Peltier coefficients given above, one has

\[ \Delta_{e,c} \phi = \frac{1}{F} \left[ \tilde{I}_{\text{Cl}^-} (S_{\text{NaCl}}^{e,c} + S_{\text{Cl}^-}^{s,c}) (T^{s,c} - T^{e,c}) + \left( \frac{1}{2} S_{\text{Cl}_2}^{e,c} + S_{e}^{s,c} \right) (T^{e,c} - T^{s,c}) \right] \]  

(54)

These are the usual two contributions, one from each side of the surface.

6. Bulk Cathode

The entropy production rate is given by

\[ T\sigma^c = -j^c_q \frac{1}{T} \frac{\partial T}{\partial x} - j^\text{Cl}_2 \frac{\partial}{\partial x} \mu^\text{Cl}_2, T - j \frac{\partial \phi}{\partial x} \]

\[ = -j^c_q \frac{1}{T} \frac{\partial T}{\partial x} - j \frac{\partial}{\partial x} \left[ \phi + \frac{1}{2F} \mu^\text{Cl}_2, T \right] \]  

(55)
where we used that \( J_{\text{Cl}_2}^c = j/2F \). The resulting linear force-flux relations are

\[
\begin{align*}
J_q^c &= -L_{qq}^c \frac{1}{T} \frac{\partial T}{\partial x} - L_{q\phi}^c \frac{\partial}{\partial x} \left[ \phi + \frac{1}{2F} \mu_{\text{Cl}_2,T}^c \right] \\
j &= -L_{\phi q}^c \frac{1}{T} \frac{\partial T}{\partial x} - L_{\phi\phi}^c \frac{\partial}{\partial x} \left[ \phi + \frac{1}{2F} \mu_{\text{Cl}_2,T}^c \right]
\end{align*}
\]

The ratio of the heat flux and the electric current defines the Peltier coefficient

\[
\pi^c \equiv F \left( \frac{J_q^c}{j} \right) = \frac{F L_{q\phi}^c}{L_{\phi\phi}^c} = -T \left( \frac{1}{2} S_{\text{Cl}_2}^c + S_e^{*,c} \right)
\]

For a zero electric current, we have, using that the conductivity matrix is symmetric, for the electric potential gradient

\[
\frac{\partial}{\partial x} \phi = -\frac{1}{F} \left[ \frac{1}{2} \frac{\partial}{\partial x} \mu_{\text{Cl}_2,T}^c + \frac{\pi^c}{T} \frac{\partial T}{\partial x} \right]
\]

Integration across the electrode gives

\[
\Delta_c \phi = \int_{c.e}^{c.o} d\phi = -\frac{1}{F} \left[ \frac{1}{2} \int_{c.e}^{c.o} d\mu_{\text{Cl}_2,T}^c \right] - \int_{c.e}^{c.o} \left( \frac{1}{2} S_{\text{Cl}_2}^c + S_e^{*,c} \right) dT
\]

\[
= -\frac{1}{F} \left[ \frac{1}{2} \left( \mu_{\text{Cl}_2}^{c.o} - \mu_{\text{Cl}_2}^{c.e} (T^{c.o}) \right) \right] - \left( \frac{1}{2} S_{\text{Cl}_2}^c + S_e^{*,c} \right) (T^{c.o} - T^{c.e})
\]

\[
= -\frac{1}{F} \left[ \frac{1}{2} \left( \mu_{\text{Cl}_2}^{c.o} - \mu_{\text{Cl}_2}^{c.e} (T^{c.o}) \right) + \frac{\pi^c}{T^{c.e}} (T^{c.o} - T^{c.e}) \right]
\]

where we referred the chemical potential to the temperature \( T^{c.o} \) at the end of the electrode. For a constant temperature this reduces to

\[
\Delta_c \phi = -\frac{1}{2F} (\mu_{\text{Cl}_2}^{c.o} - \mu_{\text{Cl}_2}^{c.e})
\]

This term is frequently zero in the experimental set-up (see Fig. 1), since there is equilibrium for the gas at the electrode.

7. The Cell Potential

The total potential difference is now obtained by adding the contributions found for the bulk electrodes, the surfaces and the electrolyte:
\[
\Delta \phi = \Delta a \phi + \Delta a,c \phi + \Delta e \phi + \Delta a,c \phi + \Delta c \phi \\
= -\frac{1}{F} \left[ (\mu_{Na+}^{s,a} + \mu_{e}^{s,a} - \mu_{Na}^{a,o}) + (\mu_{Na}^{a,c}(T^{s,a}) - \mu_{Na}^{a,o}) \\
+ \left( \mu_{Cl^-}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2}\mu_{Cl_2}^{c,e}(T^{s,c}) \right) + \frac{1}{2}(\mu_{Cl_2}^{c,o} - \mu_{Cl_2}^{c,e}(T^{c,o})) \right] \\
+ i_{Na+}^{e}(\mu_{NaCl}^{e}(T^{s,a}) - \mu_{NaCl}^{s,a}) + \frac{1}{2}(i_{Na+}^{e} - i_{Cl^-}^{e})\Delta e \mu_{NaCl}^{e}(T^{e,a}) \\
- i_{Cl^-}^{e}(\mu_{NaCl}^{e} - \mu_{NaCl}^{s,a}) + \frac{\pi_{a,e}}{T_{a,e}^{e,c}}(T^{s,a} - T^{a,o}) + \frac{\pi_{c,e}}{T_{c,e}^{e,c}}(T^{c,a} - T^{s,c}) \\
+ \frac{1}{2}\left( \frac{\pi_{c,e}}{T_{c,e}^{e,a}} + \frac{\pi_{c,e}}{T_{c,e}^{e,c}} \right) \Delta e T + \frac{\pi_{c,e}}{T_{c,e}^{e,c}}(T^{s,c} - T^{e,c}) + \frac{\pi_{c,e}}{T_{c,e}^{e,c}}(T^{c,o} - T^{s,c}) \right] 
\]

(61)

Transported entropies of the ions were taken as constant. If the temperature is everywhere constant, this expression reduces to

\[
\Delta \phi = -\frac{1}{F} \left[ (\mu_{Na+}^{s,a} + \mu_{e}^{s,a} - \mu_{Na}^{a,o}) + (\mu_{Cl^-}^{s,c} - \mu_{e}^{s,c} - \frac{1}{2}\mu_{Cl_2}^{c,o}) \right] \\
+ i_{Na+}^{e}(\mu_{NaCl}^{e} - \mu_{NaCl}^{s,a}) + \frac{1}{2}(i_{Na+}^{e} - i_{Cl^-}^{e})\Delta e \mu_{NaCl}^{e} - i_{Cl^-}^{e}(\mu_{NaCl}^{e} - \mu_{NaCl}^{s,a}) 
\]

(62)

It is the sum of the separate contributions of the five subsections of the system. If the electrolyte is stirred, and if there is equilibrium in the exchange of ions with the surface, this expression reduces to

\[
\Delta \phi = -\frac{1}{F} \left[ (\mu_{e}^{s,a} - \mu_{Na}^{a,o} - \mu_{e}^{s,c} - \frac{1}{2}\mu_{Cl_2}^{c,o}) + \mu_{NaCl} \right] 
\]

(63)

This is the classical expression, the Gibbs energy change of the reaction in an isothermal formation cell, with uniform concentrations. In contrast to equation (63), the more general equation (62) gives information on the origin of the potential difference. There are potential drops at each of the surfaces, and a gradual, continuous change through the electrolyte. The potential drop in the bulk electrodes are probably small compared to the aforementioned contributions.

In the case that the temperature is not constant, the chemical potentials in these five contributions are all referred to a temperature particular for that region. Thus for the contribution due to the surfaces, this is for instance the temperature of the surface. The potential difference due to the temperature differences alone becomes

\[
\Delta \phi = -\frac{1}{F} \left\{ \frac{\pi_{a,e}}{T_{a,e}^{a,c}}(T^{s,a} - T^{a,o}) + \frac{\pi_{c,e}}{T_{c,e}^{a,c}}(T^{e,a} - T^{s,a}) + \frac{1}{2}\left( \frac{\pi_{a,e}}{T_{a,e}^{e,a}} + \frac{\pi_{c,e}}{T_{c,e}^{e,c}} \right) \Delta e T \\
+ \frac{\pi_{c,e}}{T_{c,e}^{e,a}}(T^{s,c} - T^{e,c}) + \frac{\pi_{c,e}}{T_{c,e}^{e,c}}(T^{c,o} - T^{s,c}) \right\} 
\]

(64)
The five contributions containing the chemical potential in the previous expression are here all set equal to zero. This uses that the mass distributions in all the five subsections, though they have different temperatures, are all equilibrated. It is likely that the terms containing $\Delta \varepsilon T, (T^a - T^a.0)$ and $(T^c - T^c.0)$ are the largest terms.

8. Discussion and Conclusion

By application of irreversible thermodynamics we have found a detailed expression for the currentless potential of a formation cell. The expression was obtained by defining the entropy production rate for each subsystem in the cell, and integrating the electric potential using the corresponding flux equations. The expression that we derive is a generalisation of the common Nernst equation.

An analysis of the change in the salt concentration due to a constant electric current through the cell, gave an expression for the derivative of the transference coefficient for the salt. Together with the behaviour at the electrode surfaces it was possible to integrate this relation to obtain the transference coefficient as a function of the position. A similar analysis gave expressions for the position dependence of the Peltier coefficient in the electrolyte. The analysis brings out the importance of the exact manner in which heat and salt are exchanged with the environment.

The influence of other flux equations than that of the electric current, were not examined, however, and the electric potential difference was calculated in the limit of zero electric current only. The general set of equations, and the systematic approach has possibilities for further use. The equation set can be used to deal with more complicated situations. During operation, there is an interplay between non-zero fluxes of electricity, of heat and of mass. Irreversible thermodynamics gives a systematic description of this interaction. The flux equations for the anode and cathode surfaces give the boundary conditions that are needed to integrate across the electrode surfaces.

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