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SURFACE CONTRIBUTIONS TO EMF AND HALF CELL POTENTIALS OF NONISOTHERMAL ELECTRODE CONCENTRATION CELLS

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Abstract

Nonequilibrium thermodynamics for surfaces is used to obtain general formulae for electrochemical cells. This theory gives boundary conditions for all thermodynamic variables at surfaces, enabling us to integrate the electric field across the electrode surface. Half cell potentials are obtained by integration half way through the cell. The electrode surface is seen as a two-dimensional, polarized, electroneutral, and open thermodynamic system. The electric potential jump across the surface gives significant contributions to the cell *emf* compared to the electrolyte contribution to the cell *emf*. The theory reduces to the classical *emf* values for certain conditions, and imposes conditions on experimental designs and interpretations.

Keywords: surface contribution, nonisothermal electrode concentration cells.

1. Introduction

We have recently used the theory of nonequilibrium thermodynamics for surfaces [1] to describe electrode surfaces of galvanic cells [2] – [4]. We have predicted temperature jumps [2] and formulated new equations for overpotentials [3] for some selected single electrodes. We have analyzed surface conditions at the anode and cathode in the aluminium electrolysis cell [4]. These cases all concern cells in operation, e.g., cells with a sizable current density, j. We shall now see in more detail how the *emf* measurement can be described and understood in terms of nonequilibrium thermodynamics for surfaces and bulk materials.

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A simple example is used to bring out the features of the theory: a cell with sodium amalgam electrodes and the ceramic material $Na_2O{\cdot}6Al_2O_3$, β''-alumina, as electrolyte. In common notation this is given by:

$$\mathrm{Na(Hg)} \mid \beta'' - \text{alumina} \mid \mathrm{Na(Hg)}. \tag{1}$$

Sodium is dissolved in mercury, in different amounts on the two sides. The temperatures of the two sides are also different. A negligible positive current is passing from left to right in the cell during the *emf* measurement; here carried by Na^+ in β''-alumina. The *emf* (in Volts) of the concentration cell (1) is, at constant temperature, according to classical thermodynamics:

$$\Delta\varphi = -\frac{1}{F}(\mu^c_{\mathrm{Na}} - \mu^a_{\mathrm{Na}}), \tag{2}$$

where μ_{Na} is the chemical potential of Na (in J mol^{-1}), F is Faraday's constant, and superscripts ^{c} and ^{a} indicate cathode and anode, respectively. The thermoelectric power of the same cell is, for small $\Delta T = T^c - T^a$ and constant μ_{Na}:

$$\Delta\varphi = -\frac{1}{F}(S^*_{\mathrm{Na}^+} - S^*_{e^-} - S^m_{\mathrm{Na}})(T^c - T^a). \tag{3}$$

Here S^m_{Na} is the entropy of Na in the metal, $S^*_{e^-}$ and $S^*_{\mathrm{Na}^+}$ are the transported entropies in the metal and the ceramic material, respectively, and T is the temperature. In this context we aim to answer the following questions: where do the contributions to the cell *emf* come from, how do they vary and what are their likely magnitudes? The exact solution for potential and temperature profiles will be given for $j = 0$ when we have stationary state conditions in the cell.

Knowledge of energy changes during reversible transformation of chemical to electric energy gives a basis for understanding the electrochemical cell in operation. Our long range aim is to understand how energy changes can be made efficient, that is without more entropy production than necessary, in cells in operation, i.e., when $j \neq 0$. As premises for the derivation we use that the cell is everywhere electroneutral, and that the surface polarization is constant in time.

On this background we derive first the *emf* contributions from the bulk materials, and next the (significant) contributions from the electrode surfaces. The potential differences across the surfaces of the electrodes are given a completely new meaning through this analysis. The general expression for *emf* defines the conditions for the *emf* experiment and show relations between different properties of the cell. A strict new expression can be given for evaluation of cell *emfs* for large temperature gradients.

Nonequilibrium thermodynamics for surfaces [1] assumes that the surface is capable of storing so much energy and/or matter that one may define the surface as a separate system in the thermodynamic sense. This was already done by GIBBS [5]; see BOCKRIS and KHAN for a recent reference in electrochemistry [6]. Hence, we can have temperatures and chemical potentials at the surface which are different from those of the bulk materials if the system is not in equilibrium. A cell notation which illustrates this is:

$$\mathrm{Na(Hg)}|^{s,a}|\beta''\text{-alumina }|^{s,c}|\mathrm{Na(Hg)}. \tag{4}$$

The separate, open thermodynamic systems defined by the anode and cathode metal| electrolyte interfaces are given the notation $|^{s,a}|$ and $|^{s,c}|$.

Sodium is consumed in the anode surface according to

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^- \tag{5}$$

In the cathode surface, sodium is produced by the reverse of reaction (5). The density of Hg is expected to drop to zero faster than that of Na, because β''-alumina prefers the presence of Na. There is an excess of Na in the surface relative to the equimolar surface of mercury, see *Fig. 1.* The extension of the surface is given by the polarized Na. The surface thickness, δ, is thus the distance between Na^+ on the electrolyte side of the surface and the electron (its image charge) on the metal side of the surface. The surface thickness is naturally of molecular order. This means that the electrode surface is two-dimensional on a macroscopic length scale.

The cell is divided into five open subsystems when the surfaces are separated from the remaining parts in this manner. The five subsystems, coupled in series, are the bulk anode (m,a), the anode surface (s,a), the bulk electrolyte (e), the cathode surface (s,c) and the bulk cathode (m,c). The surface thickness δ, is usually one or a few nanometers. The electrode and electrolyte have thicknesses in the cm range. The *emf* of the cell, $\Delta\varphi$, is then composed of five parts:

$$\Delta\varphi = \Delta\varphi^{m,a} + \Delta\varphi^{s,a} + \Delta\varphi^{e} + \Delta\varphi^{s,c} + \Delta\varphi^{m,c}. \tag{6}$$

The surface potential jumps are denoted by $\Delta\varphi^{s,a}$ and $\Delta\varphi^{s,c}$, while the other potential differences refer to the extension of the metal anode, of the electrolyte and of the metal cathode, respectively. According to the nonequilibrium theory of surfaces, we may have jumps in the temperature to the surface and across the surface. The cell *emf* is measured between the temperatures, $T^{o,c}$ and $T^{o,a}$.

We aim to give the functional relationships between $\Delta\varphi$ and the gradients in temperature and chemical potential across the cell. These relationships are derived from the entropy production rates, or the dissipation functions for each part of the cell.

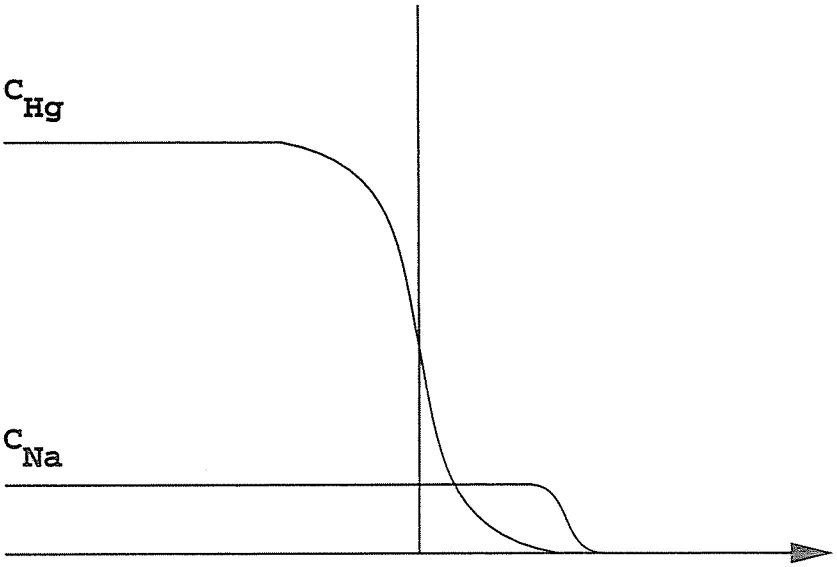

Fig. 1. The concentration variation of Hg and Na across the anode surface, and the equimolar surface of Hg between Na (Hg) and β''-alumina

2. Dissipation Functions

The dissipation function $T\Theta$, determines the fluxes and forces of the cell (see de GROOT and MAZUR [7], Ch. XIII. eq. 169). For the two bulk electrodes, the most convenient form of the dissipation function is:

$$T^m\Theta^m = -J_s^m\frac{\partial T}{\partial x} - J_{\mathrm{Na}}^m\frac{\partial \mu_{\mathrm{Na}}^m}{\partial x} - j\frac{\partial \varphi}{\partial x}. \tag{7}$$

Here $-dT/dx$ is the conjugate force of the absolute entropy flux J_s^m. The absolute mass flux, J_{Na}^m, which is sodium diffusion flux and sodium flow, has the conjugate force $-d\mu_{\mathrm{Na}}^m/dx$ and the electric current has as the conjugate force the electric field, $-d\varphi/dx$. The dissipation function, $T^e\Theta^e$, for the bulk electrolyte is:

$$T^e\Theta^e = -J_s^e\frac{\partial T}{\partial x} - j\frac{\partial \varphi}{\partial x}. \tag{8}$$

The dissipation function for a surface is found in terms of excesses of the various densities in the layer of thickness δ. Gradients are integrated across δ, so all forces are therefore given as differences between the larger and smaller x-values of the variables. The expression for the anode surface is [2, 3]:

$$T^a\Theta^a = -J_s^{m,a}\Delta T^{m,a} - J_s^{e,a}\Delta T^{e,a} - J_{\mathrm{Na}}^{m,a}\Delta\mu_{\mathrm{Na}}^{m,a} - j\Delta\varphi^{s,a}. \tag{9}$$

The driving forces for $J_s^{m,a}$ and $J_s^{e,a}$ are $-\Delta T^{m,a}$ and $-\Delta T^{e,a}$, respectively, where $\Delta T^{m,a} = T^{s,a} - T^{m,a}$ is the difference between the surface temperature and the temperature close to the surface on the metal side, and $\Delta T^{e,a} = T^{e,a} - T^{s,a}$ is the difference between the temperature close to the surface on the electrolyte side and the surface temperature. The mass flux, $J_{\mathrm{Na}}^{m,a}$, is finite out of the metal, with the conjugate force $-\Delta\mu_{\mathrm{Na}}^{m,a} = -(\mu_{\mathrm{Na}}^{s,a} - \mu_{\mathrm{Na}}^{m,a})$. The electric force at the surface is $-\Delta\varphi^{s,a}$.

For the cathode the variables are defined similarly [2, 3]:

$$T^c\Theta^c = -J_s^{m,c}\Delta T^{m,c} - J_s^{e,c}\Delta T^{e,c} - J_{\mathrm{Na}}^{m,c}\Delta\mu_{\mathrm{Na}}^{m,c} - j\Delta\varphi^{s,c}. \qquad (10)$$

We have chosen the same positive direction for the forces for both electrodes, so there is a sign shift in the forces of *Eq.* (10) compared to those of *Eq.* (9), giving $\Delta T^{m,c} = T^{m,c} - T^{s,c}$, $\Delta T^{e,c} = T^{s,c} - T^{e,c}$, $\Delta\mu_{\mathrm{Na}}^{m,c} = \mu_{\mathrm{Na}}^{m,c} - \mu_{\mathrm{Na}}^{s,c}$.

3. The Cell EMF

3.1. The emf Contributions from the Bulk of the Electrodes

The flux equations for the bulk metal are according to *Eq.* (7):

$$\begin{aligned} J_s^m &= -L_{ss}^m\frac{dT}{dx} - L_{s\mu}^m\frac{d\mu_{\mathrm{Na}}}{dx} - L_{s\varphi}^m\frac{d\varphi}{dx}, & (11)\\ J_{\mathrm{Na}}^m &= -L_{\mu s}^m\frac{dT}{dx} - L_{\mu\mu}^m\frac{d\mu_{\mathrm{Na}}}{dx} - L_{\mu\varphi}^m\frac{d\varphi}{dx}, & (12)\\ j &= -L_{\varphi s}^m\frac{dT}{dx} - L_{\varphi\mu}^m\frac{d\mu_{\mathrm{Na}}}{dx} - L_{\varphi\varphi}^m\frac{d\varphi}{dx}. & (13)\end{aligned}$$

The transference coefficient of Na, t_{Na}^m, is defined by:

$$t_{\mathrm{Na}}^m = \left(\frac{J_{\mathrm{Na}}^m}{j}\right)_{dT/dx=0,\ d\mu_{\mathrm{Na}}/dx=0} = \frac{L_{\mu\varphi}^m}{L_{\varphi\varphi}^m}. \qquad (14)$$

Electrons conduct charge in the bulk of the electrode. After Na is produced in the cathode surface, it flows into the Hg, at a rate proportional to the electric current. This leads to t_{Na}^m (in mol C^{-1}):

$$t_{\mathrm{Na}}^m = \frac{1}{F}. \qquad (15)$$

The Peltier coefficient of the metal, π^m, is defined by [7, 8]:

$$\pi^m = T\left(\frac{J_s^m}{j}\right)_{dT/dx=0,\ d\mu_{\mathrm{Na}}/dx=0} = T\frac{L_{s\varphi}^m}{L_{\varphi\varphi}^m}. \qquad (16)$$

This Peltier coefficient (given in Volts) is given by the reversible heat transported by the electrons and the Na flow

$$\pi^m = T(S^*_{e^-} + S^m_{\mathrm{Na}})\frac{1}{F}. \tag{17}$$

The transported entropy of the electrons, $S^*_{e^-}$, is small. The contribution to the cell *emf* from the anode is obtained by integrating *Eq.* (13) for $j = 0$. We integrate from the contact point of the potentiometer $T^{o,a}$ to $T^{m,a}$ and $\mu^{o,a}_{\mathrm{Na}}$ to $\mu^{m,a}_{\mathrm{Na}}$. The chemical potentials have been given the same superscripts as their corresponding temperature. By introducing *Eqs.* (14)–(17) we obtain for the anode:

$$\begin{aligned} F\Delta\varphi^{m,a} &= -S^*_{e^-}(T^{m,a} - T^{o,a}) \\ &\quad -S^{m,a}_{\mathrm{Na}}T^{m,a} + S^{m,*,a}_{\mathrm{Na}}T^{o,a} - (\mu^{m,a}_{\mathrm{Na}} - \mu^{o,a}_{\mathrm{Na}}) \end{aligned} \tag{18}$$

Onsager's reciprocal relations, $L^m_{ji} = L^m_{ij}$, were applied. In the cathode metal phase we have accordingly:

$$\begin{aligned} F\Delta\varphi^{m,c} &= -S^*_{e^-}(T^{o,c} - T^{m,c}) \\ &\quad -S^{m,*,c}_{\mathrm{Na}}T^{o,c} + S^{m,c}_{\mathrm{Na}}T^{m,c} - (\mu^{o,c}_{\mathrm{Na}} - \mu^{m,c}_{\mathrm{Na}}). \end{aligned} \tag{19}$$

In the case of pure sodium metal, the entropy term will cancel out the chemical potential term and we are left with the small contribution from the transported entropy of the electrons. The potential profile in the electrodes will then be essentially flat.

3.2. The emf Contribution from the Electrolyte

The flux equations from the dissipation function (8) are next written for β''-alumina:

$$J^e_s = -L^e_{ss}\frac{dT}{dx} - L^e_{s\varphi}\frac{d\varphi}{dx}, \tag{20}$$

$$j = -L^e_{\varphi s}\frac{dT}{dx} - L^e_{\varphi\varphi}\frac{d\varphi}{dx}. \tag{21}$$

The phenomenological coefficients for the electrolyte have superscript e. The Peltier coefficient for the electrolyte, π^e, is defined by:

$$\pi^e = T\left(\frac{J^e_s}{j}\right)_{dT/dx=0} = T\frac{L^e_{s\varphi}}{L^e_{\varphi\varphi}}. \tag{22}$$

The Peltier coefficient is given by the temperature times the entropy transported by Na^+ away from the surface:

$$\pi^\epsilon = TS^*_{\mathrm{Na}^+}\frac{1}{F}. \tag{23}$$

We integrate *Eq.* (21) for $j \approx 0$, from the temperature at the anode side, $T^{a,\epsilon}$, to the temperature at the cathode side, $T^{c,\epsilon}$ using Eq. (22) and Onsager's reciprocal relation. The result is the contribution to the *emf* from the electrolyte:

$$F\Delta\varphi^\epsilon = -S^{*,c}_{\mathrm{Na}^+}T^{\epsilon,c} + S^{*,a}_{\mathrm{Na}^+}T^{\epsilon,a}. \tag{24}$$

The transported entropy in *Eq.* (24) is positive. The electric potential contribution to the *emf* from the transport of Na^+ through β''-alumina from a low temperature $T^{\epsilon,a}$ to a high temperature $T^{\epsilon,c}$ is then negative from *Eq.* (24).

3.3. The *emf* Contribution from the Anode Surface

There are four independent fluxes at each electrode surface, according to the dissipation functions. For the anode, the flux equations from *Eq.* (9) are:

$$\begin{aligned}
J_s^{m,a} &= -L^a_{mm}\Delta T^{m,a} - L^a_{m\epsilon}\Delta T^{\epsilon,a} - L^a_{m\mu}\Delta\mu^{m,a}_{\mathrm{Na}} - L^a_{m\varphi}\Delta\varphi^{s,a}, && (25)\\
J_s^{\epsilon,a} &= -L^a_{\epsilon m}\Delta T^{m,a} - L^a_{\epsilon\epsilon}\Delta T^{\epsilon,a} - L^a_{\epsilon\mu}\Delta\mu^{m,a}_{\mathrm{Na}} - L^a_{\epsilon\varphi}\Delta\varphi^{s,a}, && (26)\\
J_{\mathrm{Na}}^{m,a} &= -L^a_{\mu m}\Delta T^{m,a} - L^a_{\mu\epsilon}\Delta T^{\epsilon,a} - L^a_{\mu\mu}\Delta\mu^{m,a}_{\mathrm{Na}} - L^a_{\mu\varphi}\Delta\varphi^{s,a}, && (27)\\
j &= -L^a_{\varphi m}\Delta T^{m,a} - L^a_{\varphi\epsilon}\Delta T^{\epsilon,a} - L^a_{\varphi\mu}\Delta\mu^{m,a}_{\mathrm{Na}} - L^a_{\varphi\varphi}\Delta\varphi^{s,a}, && (28)
\end{aligned}$$

where $\Delta\varphi^{s,a}$ is the contribution that we are seeking. The interpretations of the phenomenological coefficients, L^a_{ij}, for the surface follow those of the bulk coefficients [6]. Their dimensionality is the dimensionality of the corresponding bulk coefficient divided by m. The transference coefficient for Na is defined by:

$$t^{m,a}_{\mathrm{Na}} = \left(\frac{J^{m,a}_{\mathrm{Na}}}{j}\right)_{\Delta T^{m,a}=\Delta T^{\epsilon,a}=0,\ \Delta\mu^{m,a}_{\mathrm{Na}}=0} = \frac{L^{m,a}_{\mu\varphi}}{L^{m,a}_{\varphi\varphi}}. \tag{29}$$

The definition of $t^{m,a}_{\mathrm{Na}}$ differs from that of t^m_{Na}. The bulk flux of sodium enters both definitions, but the conditions for the coefficient determination vary, as indicated by the subscripts of definitions (14) and (29). Nevertheless the value of the transference coefficient, is the same as for the bulk metal:

$$t^{m,a}_{\mathrm{Na}} = \frac{1}{F}. \tag{30}$$

The Peltier coefficients of the surface are defined by:

$$\pi^{\epsilon,a} = T^{\epsilon,a}\left(\frac{J_s^{\epsilon,a}}{j}\right)_{\Delta T^{\epsilon,a}=\Delta T^{m,a}=0,\ \Delta\mu_{\mathrm{Na}}^{m,a}=0} = T^{\epsilon,a}\frac{L^a_{\epsilon\varphi}}{L^a_{\varphi\varphi}} \tag{31}$$

and

$$\pi^{m,a} = T^{m,a}\left(\frac{J_s^{m,a}}{j}\right)_{\Delta T^{m,a}=\Delta T^{\epsilon,a}=0,\ \Delta\mu_{\mathrm{Na}}^{m,a}=0} = T^{m,a}\frac{L^a_{m\varphi}}{L^a_{\varphi\varphi}}. \tag{32}$$

These Peltier coefficients have the values:

$$\pi^{m,a} = T^{m,a}(S^*_{\epsilon^-} + S^{m,a}_{\mathrm{Na}})\frac{1}{F} \tag{33}$$

and

$$\pi^{\epsilon,a} = T^{\epsilon,a}S^{a,*}_{\mathrm{Na}^+}\frac{1}{F}. \tag{34}$$

The contribution to the cell *emf* from the anode surface is now, from *Eq.* (28) for $j = 0$, using *Eqs.* (29–34):

$$\Delta\varphi^{s,a} = -\frac{\pi^{m,a}}{T^{m,a}}\Delta T^{m,a} - \frac{\pi^{\epsilon,a}}{T^{\epsilon,a}}\Delta T^{\epsilon,a} - t^{m,a}_{\mathrm{Na}}\Delta\mu^{m,a}_{\mathrm{Na}},$$

$$F\Delta\varphi^{s,a} = -(S^*_{\epsilon^-} + S^{m,a}_{\mathrm{Na}})(T^{s,a} - T^{m,a}) - S^{*,a}_{\mathrm{Na}^+}(T^{\epsilon,a} - T^{s,a}) - (\mu^{s,a}_{\mathrm{Na}} - \mu^{m,a}_{\mathrm{Na}}). \tag{35}$$

This equation shows that thermal and chemical equilibrium between the surface and the bulk materials give zero surface potential for $j \approx 0$, as expected.

3.4. The emf Contribution from the Cathode Surface

The flux equations for this surface have the same form as those for the anode. The transference coefficient for sodium is defined by:

$$t^{m,c}_{\mathrm{Na}} = \left(\frac{J^{m,c}_{\mathrm{Na}}}{j}\right)_{\Delta T^{m,c}=\Delta T^{\epsilon,c}=0,\ \Delta\mu^{m,c}_{\mathrm{Na}}=0} = \frac{L^{m,c}_{\mu\varphi}}{L^{m,c}_{\varphi\varphi}}. \tag{36}$$

Sodium does not conduct charge into the electrode, but flows into the electrode, at a rate proportional to the current density, so the transference coefficient of Na equals:

$$t^{m,c}_{\mathrm{Na}} = \frac{1}{F}. \tag{37}$$

The Peltier coefficients of the cathode are:

$$\pi^{m,c} = T^{m,c}(S^*_{\epsilon^-} + S^{m,c}_{\mathrm{Na}})\frac{1}{F} \tag{38}$$

and

$$\pi^{\epsilon,c} = T^{\epsilon,c} S^{*,c}_{\mathrm{Na}^+} \frac{1}{F}. \tag{39}$$

The same expressions for the transport coefficients are obtained for both surfaces. The electric potential contribution from the cathode surface is accordingly:

$$\Delta\varphi^{s,c} = -\frac{\pi^{m,c}}{T^{m,c}}\Delta T^{m,c} - \frac{\pi^{\epsilon,c}}{T^{\epsilon,c}}\Delta T^{\epsilon,c} - t^{m,c}_{\mathrm{Na}}\Delta\mu^{m,c}_{\mathrm{Na}},$$

$$F\Delta\varphi^{s,c} = -(S^{*}_{e^-} + S^{m,c}_{\mathrm{Na}})(T^{m,c} - T^{s,c}) - S^{*,c}_{\mathrm{Na}^+}(T^{s,c} - T^{\epsilon,c}) - (\mu^{m,c}_{\mathrm{Na}} - \mu^{s,c}_{\mathrm{Na}}). \tag{40}$$

Expressions (35) and (40) for the surface contributions to the *emf* are valid in stationary state or not.

3.5. *The Total emf of the Cell*

The five separate contributions to the cell *emf* have now been identified and discussed. It remains to combine them.

$$\begin{aligned} F\Delta\varphi = &-(\mu^{s,a}_{\mathrm{Na}} - \mu^{o,a}_{\mathrm{Na}}) - (\mu^{o,c}_{\mathrm{Na}} - \mu^{s,c}_{\mathrm{Na}}) - S^{*}_{e^-}(T^{o,c} - T^{s,c} + T^{s,a} - T^{o,a}) \\ &-S^{m,a}_{\mathrm{Na}}T^{s,a} + S^{m,a}_{\mathrm{Na}}T^{o,a} - S^{m,c}_{\mathrm{Na}}T^{o,c} + S^{m,c}_{\mathrm{Na}}T^{s,c} - S^{*,c}_{\mathrm{Na}^+}T^{s,c} + S^{*,a}_{\mathrm{Na}^+}T^{s,a}. \end{aligned} \tag{41}$$

This is the general expression for the *emf* in the stationary as well as in the non-stationary case.

Eq. (41) can be reduced to classical expressions for the *emf* when the chemical potential of Na in the surface is known. The present cell has a fixed electrolyte, the Na^+-conductor β''-alumina. At a given oxygen pressure, the surface state for Na in contact with the electrolyte is uniquely defined through the equilibrium:

$$\mathrm{Na_2O}(s) = 2\mathrm{Na}(l) + \frac{1}{2}\mathrm{O_2}(g). \tag{42}$$

This equilibrium was recently discussed by NÄFE [10] in relation to the stability of β''-alumina as an ion conductor. The electrolyte, as well as the surface, have no compositional degrees of freedom (at a given oxygen pressure) according to this equilibrium. We may therefore anywhere in the electrolyte take out a cross-section of the material and obtain the same surface state for adsorbed Na in equilibrium with the ceramic material. It is likely that a temperature difference has a negligible influence on the different surface states over a certain temperature interval. This leads to the relation:

$$\mu^{s,a}_{\mathrm{Na}} = \mu^{e}_{\mathrm{Na}} = \mu^{s,c}_{\mathrm{Na}}. \tag{43}$$

When the oxygen pressure is changed, a new chemical potential of Na results. It is *not* likely that this condition changes, when the electric current density through the system is small. (The presence of a large electric current may, however, alter the value of the chemical potential in the surface. This was one of our assumptions for the derivation of the overpotential of an electrode surface [3].) With this condition we see that *Eq.* (41) reduces to *Eq.* (2) in an isothermal cell. *Eq.* (3) is obtained in the absence of temperature jumps at the electrode surfaces, when $T^{o,a} = T^{o,c}$, but with a temperature difference between the electrode surfaces.

Our cell potential is obtained by integrating the electric field of Maxwell's equations across the electrode, electrode surface and part of the electrolyte [1]. It is as such uniquely defined. The results shown for the simple case chosen here can of course be generalized. Concepts like inner and outer potentials [9] are not needed for the calculation of the electric field given by the Maxwell equations, which are the basis of our derivation [1, 7].

3.6. Half Cell Potentials

Classical electrochemistry uses the half cell potential for electrochemical tables. *Eq.* (41) contains variables which are suitable for a division into half cell potentials. The half cell potential of our cell, is first determined by dividing the *emf* contribution of the electrolyte into two parts, separated by the temperature T^h. We then define:

$$\Delta\varphi^{\epsilon} = -\Delta\varphi^{h,a} + \Delta\varphi^{h,c} \tag{44}$$

with

$$F\Delta\varphi^{h,a} = -S^{*,h}_{\mathrm{Na}^+} T^{\epsilon,h} + S^{*,a}_{\mathrm{Na}^+} T^{\epsilon,a} \tag{45}$$

and

$$F\Delta\varphi^{h,c} = -S^{*,h}_{\mathrm{Na}^+} T^{\epsilon,h} + S^{*,c}_{\mathrm{Na}^+} T^{\epsilon,c}. \tag{46}$$

Eq. (44) gives the cell *emf* as the right hand side potential minus the left hand side potential, as is common in electrochemistry. By adding the potential contributions from o to h, we have the anode half cell potential.

$$\begin{aligned} F\Delta\varphi^{a} \equiv -F(\Delta\varphi^{m,a} + \Delta\varphi^{s,a} + \Delta\varphi^{h,a}) = -(\mu^{o,a}_{\mathrm{Na}} - \mu^{s,a}_{\mathrm{Na}}) \\ -S^{*}_{e^-}(T^{o,a} - T^{s,a}) - S^{m,*,a}_{\mathrm{Na}} T^{o,a} + S^{m,a}_{\mathrm{Na}} T^{s,a} - S^{*,a}_{\mathrm{Na}^+} T^{s,a} + S^{*,h}_{\mathrm{Na}^+} T^{h,a}. \end{aligned} \tag{47}$$

The cathode half cell potential is similarly:

$$F\Delta\varphi^{c} \equiv F(\Delta\varphi^{m,c} + \Delta\varphi^{s,c} + \Delta\varphi^{h,c}) = -(\mu^{o,c}_{\mathrm{Na}} - \mu^{s,c}_{\mathrm{Na}}) \tag{48}$$

$$-S^{*}_{e^{-}}(T^{o,c}-T^{s,c})-S^{m,*,c}_{\mathrm{Na}}T^{o,c}+S^{m,c}_{\mathrm{Na}}T^{s,c}-S^{*,c}_{\mathrm{Na}^{+}}T^{s,c}+S^{*,h}_{\mathrm{Na}^{+}}T^{h,e}.$$

Eqs. (47) and (48) represent reduction potentials according to *Eq.* (44). Half cell potentials can, according to this procedure, be computed accurately. For a critical analysis of the concepts of absolute electrode potentials we refer to REISS [9] and references therein.

4. Numerical Calculations and Results

Transport coefficients of the bulk materials and of the surfaces are needed to do the calculations described above. While the transport coefficients for the bulk materials were obtained from the literature (for data, see below), the surface coefficients must be guessed. The coefficients of the surface are given per unit surface area. They deviate from the coefficients for the bulk materials if they deviate from the bulk value divided by the surface thickness.

One way to circumvent the guess of the diffusion coefficient from the metal to the surface is to assign a value for the chemical potential of Na in the surface. We have chosen:

$$\mu^{s,a}_{\mathrm{Na}}=\mu^{s,c}_{\mathrm{Na}}=\frac{\mu^{m,a}_{\mathrm{Na}}+\mu^{m,c}_{\mathrm{Na}}}{2}. \tag{49}$$

We have this freedom because the surface chemical potentials do not affect the *emf* and the temperature profiles in the present case. In the metal, the chemical potential is given by:

$$\mu^{m}_{\mathrm{Na}}=\mu^{o,m}_{\mathrm{Na}}+RT\ln a^{m}_{\mathrm{Na}}, \tag{50}$$

where $\mu^{o,m}_{\mathrm{Na}}$ is the standard chemical potential (at 1 bar) and $a^{o,m}_{\mathrm{Na}}$ is the sodium activity. The data compiled by NÄFE [10] indicate that the sodium activity is smaller than one for β''-alumina in air for a range of temperatures when sodium is in the liquid state. This means that the assumption given by *Eq.* (49) probably overestimates the value of the surface chemical potential. It remains true, however, that the difference between the sodium chemical potential at the surface and in the bulk of the electrode is large, and that our values, though qualitative, still give a realistic illustration of the size of these jumps.

The following model was used for the surface heat conductivities:

$$\lambda^{\mathrm{surf}}=\frac{k}{\delta}\lambda^{\mathrm{bulk}}. \tag{51}$$

The relative conductivity factor k was taken to be unity in the first case. This means that the surface behaves as the adjacent bulk phase. In the second and third case, the surface conductivities were multiplied by $k=10^{-5}$

and $k=10^{-9}$, respectively. The second choice was motivated by excess coefficients from earlier work [4]. The electric resistance of the surface is not needed for *emf* calculations (the current density is zero). The cross coupling coefficients l_{me}, $l_{\mu e}$ and $l_{\mu m}$ for the surfaces were always neglected in the calculations.

We took the temperature in the cathode constant. The temperature profile was otherwise allowed to change according to the flux equations (11)–(13), (20), (21) and (25)–(28). This situation can be compared to the case where heat is flowing from a thermostatted cathode and cathode surface, through the electrolyte to the anode. The energy flux through the cell leads to a variation in the temperature of the surfaces and their adjacent temperatures. We used the surface thickness $\delta = 1$ nm, and an energy flux $J_e=-10^3$ J m^{-2} s^{-1}.

The thermal conductivities of Na and of β''-alumina were taken from Janaf and V. Sharivker, 78 and 2.3 J s^{-1} K^{-1} m, respectively. When $T^{o,a}=$ 433 K and $(T^{c,o} - T^{a,o})$ is 140 K, the *emf* is equal to 29.40 mV [11]. The Thomson coefficient is unknown for Na$^+$ transport, and was mostly set equal to the heat capacity of Na, 4.3 J K^{-1} mol^{-1} (JANAF).

Table 1. Effect of heat storage at the anode surface on *emf* contributions – determination of transported entropy.
The surface heat conductivity relative to the bulk heat conductivity is k for both sides of the anode surface, the *emf* is 29.40 mV, $T^{o,c} - T^{o,a} =$ 140 K, $\tau = c_{p,\mathrm{Na}}$. The electrodes are pure sodium.

Set	k	Electrolyte contribution mV	Surfaces contribution mV	$S^*_{\mathrm{Na}^+}$ JK^{-1}mol^{-1}
1	1	−78.06	107.45	54.14
2	10^{-5}	−77.53	106.93	54.13
3	10^{-9}	− 1.12	30.52	53.56

Backup effects of heat at the anode surface on the *emf* contributions were first investigated, see *Table 1*. Such backup may take place when the surface has a large excess resistance to heat conduction (bad material contact). The temperature profile across the cell and the transported entropy, $S^*_{\mathrm{Na}^+}$, and the contributions to the *emf* were calculated, for $k = 1$, 10^{-5} and 10^{-9}, see *Figs. 2, 3* and *Table 1*. *Fig. 2* gives a typical profile for data set 2, while *Fig. 3* is a close-up of the temperature profile in the anode for sets 1–3 (see *Table 1*).

Further calculations were performed to see whether the Thomson coefficient (the derivative of the transported entropy with respect to the temperature), could be obtained from the functional relationship between the *emf* and $(T^{c,o} - T^{a,o})$. The *emf* contributions were *not* sensitive to doubling the value of the Thomson coefficient and the transported entropy changed from 54.13 to 54.21 J K^{-1} mol^{-1} upon this change. This is small compared to experimental uncertainties.

Mercury was introduced into the sodium electrodes to change the activity of sodium in the electrodes. A small contribution to the *emf* from the Soret effect in the metal, between 0.006 and 0.010 mV, resulted. Also, we found that introduction of mercury into the electrode lowers the entropy and increases the contributions from the electrode to the *emf.*

5. Discussion

The numerical results, which show the new method at work, will be discussed first. After this we shall compare our method to classical nonequilibrium thermodynamics methods, and comment the new theoretical insights.

5.1. Numerical Results

The results of the investigation of heat storage in the anode are shown in *Table 1* and in *Figs. 2* and *3*. The temperature gradient across the electrolyte is always linear. In the anode bulk, the temperature is (nearly) constant because of the high conductivity of the metal. The temperature jumps at the surface are negligible for $k = 1$ as expected. They remain insignificant for $k = 10^{-5}$. For $k = 10^{-9}$ a large jump is seen. This means that surface coefficients which have excess values of the order of 10^{-5} are not able to give substantial excess heat in the surface. We have chosen $k = 10^{-5}$, which is probably more realistic, for the further calculations.

The chemical potential difference of the metals between the two sides is due to the different temperatures (the entropic contribution), and, as the model *Eq.* (49) prescribes, the difference is divided equally between the surfaces. The electric potential profile varies across the cell according to the temperature profile and the changes in the chemical potentials. The electric potential profile is thus linear in the electrolyte, (nearly) constant in the metal and has jumps at the surfaces, see *Fig. 2*. The chemical potential differences between the surfaces and the electrodes give the main part of the electric potential jump across the surfaces. The numerical results for the electric potential profile are as expected; the Soret effect gives a small contribution, changes in the activity of the bulk electrodes alter the surface contributions.

Table 1 also shows that the determination of $S^*_{\mathrm{Na}^+}$ is not sensitive to the temperature profile across the electrolyte. This is so because the Peltier

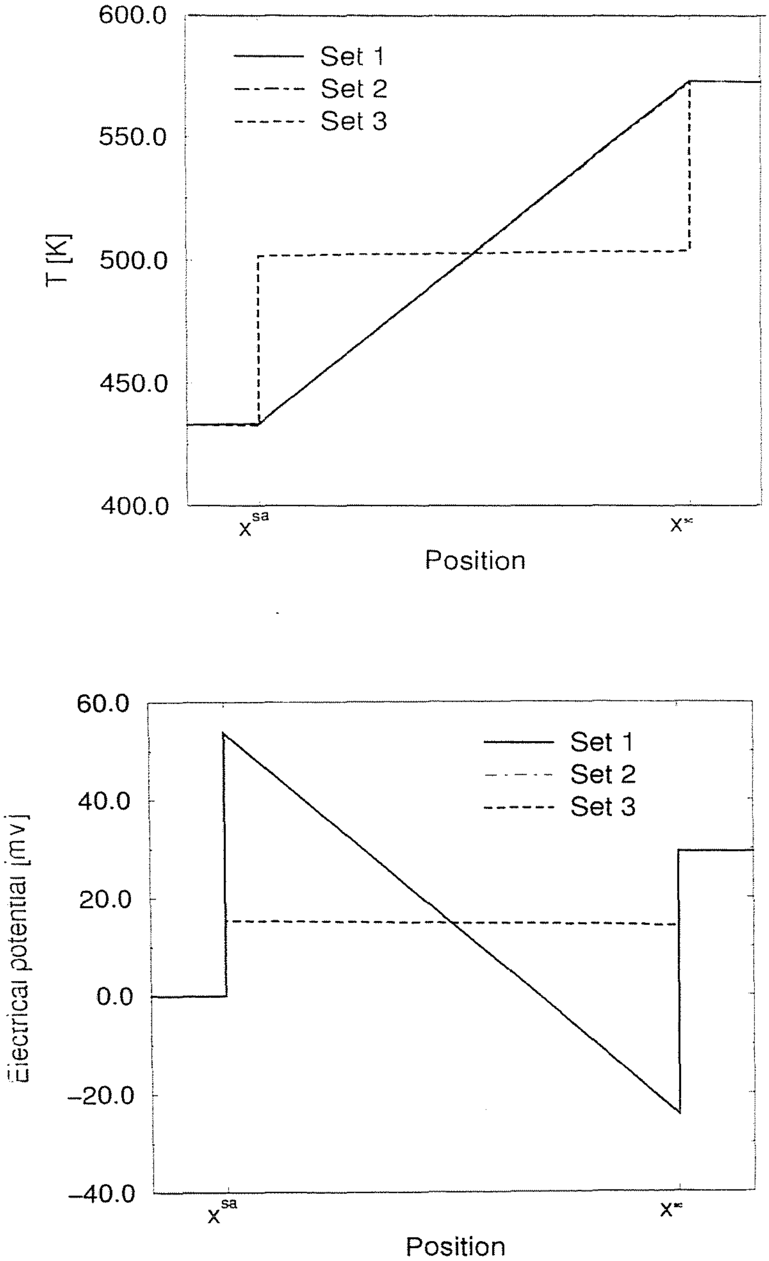

Fig. 2. Numerical results for cell temperature, chemical potential of Na and electric potential with data from *Table 1*

coefficients for the bulk materials and the surface are always the same. The temperatures $T^{o,c}$ and $T^{o,a}$ are normally measured inside the electrodes of the cell, as close to the interface as possible [11]. We see that the position is not critical when $S^*_{\mathrm{Na}^+}$ is not sensitive to the temperature profile.

The change obtained in $S^*_{\mathrm{Na}^+}$ by changing the Thomson coefficient is well within the experimental uncertainties. As a consequence, a seemingly linear relationship between $\Delta\varphi$ and $(T^{c,o} - T^{a,o})$ does not contain accurate information about the Thomson coefficient, at least for the temperatures chosen here. A straight line observed when the *emf* is plotted against ΔT, up to ΔT as large as maybe 100 K, can be explained by these features.

In order to use *Eq.* (3) as a simplification of *Eq.* (41) we found that it is imperative that the entropies are evaluated at the mean temperature of the cell, however. AGAR [13], and KEUNING and KETELAAR [14] recommended that ΔT should not be too large, so that $\Delta\varphi/\Delta T$ can be related to the mean temperature of the cell. With our expression (41), there are no limitations on the magnitude of the experimental temperature difference that is used. Empirical fits, used so far for thermoelectric powers, can be replaced by *Eq.* (41).

5.2. Electric Potential Jumps at the Electrode Surface

The central point in this work has been to show, by a theoretical method of analysis which is new in electrochemistry [2] – [4], that a more general expression for the electric potential of a cell is obtainable. This expression contains jumps in the electric potential at the electrode surfaces, mainly because there is a difference in the chemical potentials of the reactant at the surface and in the bulk of the electrode. We are building heavily on the groundbreaking work of de GROOT and MAZUR [7] in our analysis, and adding two elements to their presentation: the surface as a separate thermodynamic system with its own intensive variables, and the choice of neutral components (see separate discussion below).

The potential jumps are given for a simple cell, (1), but similar jumps are present across all electrode surfaces. In addition to the chemical potential jumps, there are also temperature jumps, although of minor significance in an *emf* experiment (see *Fig. 3* for $k = 10^{-5}$). The meaning of the jump in the variables is that the surface and the adjacent bulk materials are *not* in chemical or thermal equilibrium. The lack of equilibrium between the phases also means that we have a local driving force for the electrochemical reaction (5). This postulation of a local driving force in the surface is new.

The classical nonequilibrium thermodynamic theory [7] has *no* net driving force for transport across the surface. The classical theory uses electrochemical equilibrium across the surface. For both electrodes, we have [7]

$$\Delta_s \mu_{\mathrm{Na}^+} = -F\Delta_s \psi, \tag{52}$$

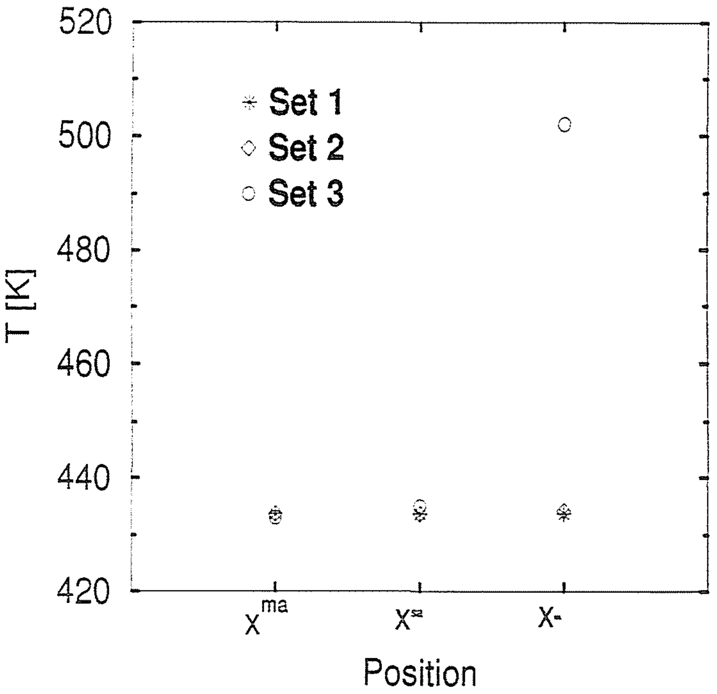

Fig. 3. The temperatures $T^{m,a}$, $T^{s,a}$ and $T^{\epsilon,a}$ close to and in the anode surface for data sets 1–3, *Table 1.*

where Δ_s refers to a difference in bulk values across the surface. *Eq.* (52) says that the chemical potential difference of sodium ion is balanced by a jump in the electrostatic potential across the surface. The temperature is taken as a continuous function across the surface. *Eq.* (52) neglects the surface as a thermodynamic system and assumes interface equilibrium. In *Eq.* (41) we have a surface which is not in equilibrium with the bulk electrolyte. The electrostatic potential difference is an equilibrium charge distribution across the junction, while our potential difference originates in the lack of equilibrium between the surface and the bulk metal. Equilibrium between the electrolyte and the surface was assumed in the special case treated here, see *Eq.* (52), but in general there may also be a lack of equilibrium between the surface and the electrolyte. The classical approach allocates one temperature to the surface region, while our method may result in three different temperatures in the same region. In spite of these seemingly different basic assumptions, our expression (41) reduces to the classical results. It is also common in theories of thermoelectricity to distinguish between interface contributions (so-called heterogeneous contributions) and bulk or homogeneous contributions, a description which dates back to HOWARD and LIDIARD [15]. Both such heterogeneous and homogeneous contributions are derived from a condition of zero net force as in *Eq.* (52).

The addition of the surface as a separate thermodynamic system offers a tool for the analysis of reversible and irreversible terms in the cell potential in greater detail than before. In the present analysis, we addressed reversible terms only. In previous works [2] – [4], we found that the overpotential of an electrode contained the presently discussed reversible cell potential contributions, in addition to irreversible terms. In these works we identified the electric potential jump at the surface, $-\Delta\varphi^{s,c}$, with the overpotential, η^c. Within the context of an *emf* experiment, it is not appropriate to use the term overpotential for the surface potential contributions, since the overpotential traditionally has been linked to a loss of energy, a dissipative process. We have therefore not used the name overpotential here.

5.3. The Choice of Components

One advantage of using a number of neutral components according to the phase rule in the description is that a mimimum representation is obtained which immediately shows the number of independent measurements to be made. It allows for a clear distinction between the thermodynamic level and the level of modelling molecular mechanisms in which all ions are crucial. The operational approach is independent of which charged species are really present, which may not be known. The minimum representation is furthermore convenient because it greatly reduces the number of Onsager coefficients.

6. Conclusion

Nonequilibrium thermodynamics theory for surfaces has been further developed for electrochemical cells by this work. The theory, which extends classical irreversible thermodynamics, gives boundary conditions for the electrode surface, which makes it possible to find a unique solution for the electric field of Maxwell's equations for the electrochemical cell. Central variables of the theory were defined for practical applications. Numerical examples were used to show that the more detailed theory gives new information, even for the very simple case chosen. The theory shows how to produce and interpret experimental results more accurately. This means that the new theory should be helpful in experimental design and understanding.

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