

# Mesoscopic Nonequilibrium Thermodynamics Gives the Same Thermodynamic Basis to Butler–Volmer and Nernst Equations

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Mesoscopic nonequilibrium thermodynamics is used to derive the Butler–Volmer equation, or the stationary state nonlinear relation between the electric current density and the overpotential of an electrode surface. The equation is derived from a linear flux–force relationship at the mesoscopic level for the oxidation of a reactant to its charged components. The surface was defined with excess variables (a Gibbs surface). The Butler–Volmer equation was derived using the assumption of local electrochemical equilibrium in the surface on the mesoscopic level. The result was valid for an isothermal electrode with reaction-controlled charge transfer and with equilibrium for the reactant between the adjacent bulk phase and the surface. The formulation that is used for the mesoscopic level is consistent with nonequilibrium thermodynamics for surfaces and, thus, with the second law of thermodynamics. The Nernst equation is recovered in the reversible limit. The reversible/dissipative nature of the charge-transfer process is discussed on this basis.

## 1. Introduction

The theory of reaction kinetics<sup>1</sup> has been used successfully to give also electrode kinetics a broader basis. By introducing the law of mass action, the concepts of unidirectional rates, and the transition state, the Butler–Volmer equation is derived, and it has been shown to contain also the Nernst equation, see, for example, refs 2–4. Also, the Marcus theory uses the concepts of unidirectional rates and the transition state.<sup>5</sup>

The Butler–Volmer equation, the central equation in electrode kinetics, gives the current density  $j$  as a nonlinear function of the overpotential  $\eta$ :

$$j = j_0 [e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}] \quad (1)$$

Here  $j_0$  is the equilibrium exchange current density, the rate of formation of products or reactants in equilibrium, and  $\alpha$  is the transfer coefficient, that describes how the electric potential alters the activation energy barrier of the reaction. The symbols  $F$ ,  $R$ , and  $T$  are Faraday's constant, the gas constant, and the absolute temperature. The exchange current density is a function of the activation energy  $E_a$  and the height of the barrier

$$j_0 = Be^{-E_a/RT} \quad (2)$$

where  $B$  is a pre-exponential factor.

At equilibrium, one can derive the Nernst equation from this equation in a similar way as one derives the equilibrium constant in reaction kinetic theory. The Nernst equation

$$(\Delta\phi)_{j \rightarrow 0} = -\Delta_r G/F \quad (3)$$

describes the reversible conversion of the reaction Gibbs energy  $\Delta_r G$  into electric energy  $\Delta\phi$ , when one mole of charge is

transferred in the outer circuit. For large overpotentials, one of the exponential terms in the Butler–Volmer equation can be neglected, and one obtains the Tafel equation. The system is then considered to be far from equilibrium. More complicated expressions than eq 1 are available; see, for example, ref 3.

The Nernst equation has its firm basis also in thermodynamics, but the Butler–Volmer equation has so far a kinetic basis only. Far from chemical and thermodynamic equilibrium, it is relevant to ask: Is there really a basis for using thermodynamic functions to describe energy conversion at the electrode surface? In this work, we show that a *thermodynamic* basis can be established for the Butler–Volmer equation and that the Nernst equation is contained in the same formulation.

The aim of this work is to establish a well defined thermodynamic basis for the description of energy conversion during electrode reactions. Such a basis can be found from a branch of thermodynamics that has not yet been applied to electrochemistry, namely mesoscopic nonequilibrium thermodynamics.<sup>6</sup> The theory has so far been applied to chemical reactions<sup>7</sup> and particle motion with inertial effects.<sup>8</sup>

Through the application of mesoscopic nonequilibrium thermodynamics to energy conversion processes at the electrode, we shall derive eq 1, but with a different set of assumptions than usual. The surprising finding is that we shall need the assumption of *local electrochemical equilibrium* in the reaction coordinate space. In reaction kinetics, one normally assumes equilibrium between the reactants and the activated species, but this assumption is not needed here. We shall also see that the rate equation in eq 1 originates from an expression that starts with the *net* rate of reaction, similar to well-known rate equations such as Fourier's and Fick's law. A thermodynamic basis for the equation can thus be given, using nonequilibrium thermodynamic theory for the mesoscopic level.

We shall accomplish this by putting together well-known concepts in a new way. We shall first define the electrode surface following Gibbs,<sup>9</sup> using his excess variables (section

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2). In section 3 we give the entropy production rate for the surface. This was done already for several cases<sup>10–13</sup> and also for a polarized electrode. The internal coordinate from mesoscopic nonequilibrium thermodynamics is in this context the reaction coordinate. The reaction coordinate is introduced in section 4, and the particulars of the mesoscopic nonequilibrium thermodynamics are given. By using this theory, we can arrive at an expression for the entropy production rate at the mesoscopic level under certain conditions. The overpotential of an electrode is defined from its measurement<sup>14</sup> in section 5. Under isothermal, stationary state conditions, with equilibrium for the reactant at the surface and with local electrochemical equilibrium along the reaction coordinate, we obtain the Butler–Volmer equation in section 6 without considering the unidirectional rates in the electrode reaction. The flux–force relationship on the mesoscopic level is *linear* and conforms completely to nonequilibrium thermodynamic theory. However, at the integrated level, the level that is related to measurements, the relationship becomes nonlinear.

## 2. The System

The electrode surface is here regarded as an open, autonomous thermodynamic system, fully described by its excess variables. Its description is standard in equilibrium<sup>3</sup> and originates from Gibbs.<sup>9</sup>

As an example we choose the electrochemical (anodic) oxidation of the metal A at an anode:



The surface has an extension in space that contains A, A<sup>+</sup>, and e<sup>−</sup>. The surface contains A in the amount  $\Gamma_{\text{A}}$  and the charged particles in the amounts  $\Gamma_{\text{A}^+}$  and  $\Gamma_{\text{e}^-}$ . We choose the extension of the surface so that it is electroneutral. For the excess densities, this gives

$$\Gamma_{\text{A}^+} = \Gamma_{\text{e}^-} \quad (5)$$

Since the electrons are predominantly present in the conduction band of the metal and the cations are predominantly facing the electrolyte double layer, the surface is polarized. Most likely there is therefore also a specific adsorption of electrolyte from the solution to the polarized surface. The surface excess densities are determined according to the prescription of Gibbs<sup>9</sup> and are given for instance in units of mol/m<sup>2</sup>. The charged species give the surface a polarization  $P^s$  (in C/m). The additional extensive variables of the surface are the entropy density  $s^s$  and the internal energy density  $u^s$ .

Mass conservation for A gives

$$r_{\text{A}} = \frac{d\Gamma_{\text{A}^+}}{dt} = -\frac{d\Gamma_{\text{A}}}{dt} \quad (6)$$

where  $r_{\text{A}}$  is the rate of the anodic reaction.

Chemical energy is transformed into electrical energy in the electrochemical reaction in eq 4. In order for A to separate into charges, A<sup>+</sup> and e<sup>−</sup>, A goes through an activated state. The beginning and final states in this process are normally, and also here, thought of as being connected by a path. The distance along the path is measured by a reaction coordinate  $\gamma$ . The coordinate is in state space and is called an internal variable in

mesoscopic nonequilibrium thermodynamics. There is no possible external control for this type of variable.

The derivation that follows can be carried out for other cases than our example (eq 4), following the procedure that is outlined below.

## 3. Entropy Production Rate for an Electrode Surface

The entropy balance for the surface is

$$\frac{ds^s}{dt} = J_{\text{s}}^i - J_{\text{s}}^o + \sigma^s \quad (7)$$

where  $s^s$  is the surface excess entropy and  $J_{\text{s}}$  is the entropy flux; see, for example, ref 15

$$J_{\text{s}} = \frac{1}{T} J_{\text{q}}' + J_{\text{A}} S_{\text{A}} \quad (8)$$

The superscripts i means into the surface, and o means out of the area element. The area element is now called the thermodynamic surface or simply the surface. The entropy flux contains the measurable heat flux,  $J_{\text{q}}'$ , and the thermodynamic entropies times their corresponding mass flux, here for A only. The transported entropy of A<sup>+</sup>,  $S_{\text{A}^+}^*$ , is included in  $J_{\text{q}}'$  in this choice of fluxes.

The excess entropy production rate of a polarized electrode surface,  $\sigma^s$ , was given by Bedeaux and Kjelstrup Ratkje.<sup>10</sup> It is found in each case from the Gibbs equation and the first law for the surface. In this system, the Gibbs equation is

$$T^s ds^s = du^s - (\mu_{\text{A}^+}^s + \mu_{\text{e}^-}^s - \mu_{\text{A}}^s) d\Gamma_{\text{A}^+} - \frac{D_{\text{eq}}}{\epsilon_0} dP^s \quad (9)$$

where  $\epsilon_0$  is the dielectric constant of the vacuum,  $D_{\text{eq}}$  is the displacement field of the adjacent phases, and  $\mu_i$  is the chemical potential. The time rate of change in the excess variables in the Gibbs equation gives

$$T^s \frac{ds^s}{dt} = \frac{du^s}{dt} - \Delta G^s r_{\text{A}} - \frac{D_{\text{eq}}}{\epsilon_0} \frac{dP^s}{dt} \quad (10)$$

with the reaction Gibbs energy for the reaction that takes place in the surface

$$\Delta G^s = (\mu_{\text{A}^+}^s + \mu_{\text{e}^-}^s - \mu_{\text{A}}^s) \quad (11)$$

The first law for the surface is

$$\frac{du^s}{dt} = J_{\text{q}}^i + J_{\text{A}}^i H_{\text{A}} - J_{\text{q}}^o - j\Delta\phi + \frac{D}{\epsilon_0} \frac{dP^s}{dt} \quad (12)$$

The fluxes are determined by their values in the homogeneous phases adjacent to the surface. There is a heat flux into the surface,  $J_{\text{q}}^i$ , and out of the surface,  $J_{\text{q}}^o$ , and a flux of A into the surface,  $J_{\text{A}}^i$ , that carries enthalpy  $H_{\text{A}}$ . The electrical potential jump  $\Delta\phi$  times the electric current density  $j$  gives the electric energy delivered by the surface, and  $D$  is the displacement field when the system is out of equilibrium. The first law describes how supplied electric energy is transformed into internal energy (enthalpy) and heat, and how the state of polarization is changed or, vice versa, how fluxes of enthalpy, heat, and polarization can give electric energy.

By introducing the first law into eq 10, rearranging the terms, and comparing the result with the entropy balance (eqs 7 and 8), one finds the excess entropy production rate (see ref 10 for more details):

$$\sigma^s = J_q^i \left( \frac{1}{T^s} - \frac{1}{T^i} \right) + J_q^o \left( \frac{1}{T^o} - \frac{1}{T^s} \right) - \frac{1}{T^s} [\mu_{A,T}^s - \mu_{A,T}^m] J_A^o - \frac{r_A}{T^s} \Delta G^s - \frac{1}{T^s} j \Delta \phi + \frac{1}{T^s} \frac{(D - D_{eq})}{\epsilon_0} \frac{dP^s}{dt} \quad (13)$$

The chemical potentials,  $\mu_{A,T}^s$  and  $\mu_{A,T}^m$ , are taken at the same temperature, here the temperature of the electrolyte. The superscript m refers to the electrolyte. To compare with experiments, we shall introduce the conditions of an *isothermal* surface, with the same chemical potential of A as that of its adjacent bulk phase ( $\mu_{A,T}^s = \mu_{A,T}^m$ ).

The deviation of the displacement field from its equilibrium value is equal and opposite to the electric potential difference across the surface

$$\frac{(D - D_{eq})}{\epsilon_0} = - \frac{\Delta \phi}{d_s} \quad (14)$$

with  $d_s$  being the surface thickness. The expression  $1/d_s \, dP^s/dt$  is the displacement current  $j_{displ}$ , and

$$j_{tot} = j + j_{displ} \quad (15)$$

By introducing these relations, we are left with two terms in the excess entropy production rate

$$\sigma^s = - \frac{1}{T^s} j_{tot} \Delta \phi - \frac{r_A}{T^s} \Delta G^s \quad (16)$$

This entropy production rate gives two fluxes in the system, linearly related to their forces.

$$j_{tot} = -L_{11} \Delta \phi - L_{12} \Delta G^s \quad (17)$$

$$r_A = -L_{21} \Delta \phi - L_{22} \Delta G^s \quad (18)$$

Relations such as these were used to find the surface impedance<sup>13</sup> and Randle's equivalent circuit. The surface impedance is found by applying an oscillation potential to the surface and recording the corresponding oscillating electric current density. The chemical force in this experiment is independent of the electrical force if the surface can accumulate reactants or products.

For a surface with constant polarization, like here, the term containing  $dP^s/dt$  disappears, and  $j = j_{tot}$ . Under constant polarization, the two driving forces are no longer independent and

$$r_A = j_{tot}/F = j/F \quad (19)$$

Charge conservation in the surface means that the electric current density  $j$  is constant through the surface and equal to the flux of electrons or the flux of positive ions. All derivations from now on are made for this condition. The entropy production rate is reduced to

$$\sigma^s = - \frac{1}{T^s} j \left[ \Delta \phi + \frac{\Delta G^s}{F} \right] \quad (20)$$

The well-known limiting value of this expression for zero electric current can now be found:

$$\lim(\sigma^s)_{j \rightarrow 0} = - \frac{j}{T^s} \left[ \Delta \phi + \frac{\Delta G^s}{F} \right] = 0 \quad (21)$$

The Nernst equation results in

$$(\Delta \phi)_{j \rightarrow 0} = - \frac{\Delta G^s_{j \rightarrow 0}}{F} \quad (22)$$

Here  $\Delta$  refers to the state of the products and the state of the reactant in the surface. With respect to the reactant and products, we speak of a *two-state description* on the macroscopic thermodynamic level.

Equation 22 expresses that the chemical energy is completely transformed into electrical energy. The potential jump across the surface is defined by a reversible transformation of (all) chemical energy in the surface into electrical energy. Under a reversible transformation, there is a balance between the electrical force and the chemical force. The surface is not in *chemical equilibrium* as long as  $\Delta G^s$  is different from zero, but it may be regarded as being in *electrochemical equilibrium*, when eq 22 applies. This is in agreement with the common perception of electrochemical equilibrium.

According to nonequilibrium thermodynamic theory,<sup>15</sup> the excess entropy production rate (eq 20) gives the following flux–force relationship:

$$j = -L \left[ \Delta \phi + \frac{\Delta G^s}{F} \right] \quad (23)$$

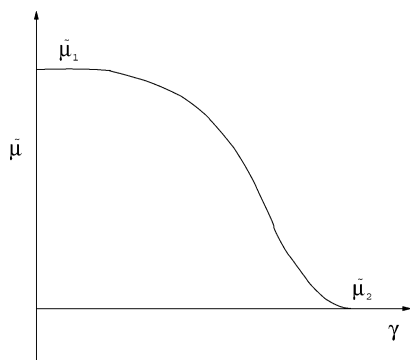
The problem to be solved is now how we can reconcile this seemingly linear relation with the common Butler–Volmer equation. We shall see that this can be done by introducing the variable that changes continuously between the two chemical states, the reaction coordinate or the internal coordinate, mentioned in the preceding section.

#### 4. A Continuous Reaction Path with Local Electrochemical Equilibrium

The entropy production rate given above refers to the Gibbs surface. The electric potential was the integral across the surface, and the chemical reaction was given as the difference between two chemical states, the state of the products and the state of the reactant. It is possible to find another expression, if we introduce the reaction coordinate  $\gamma$  from reaction kinetic theory<sup>1</sup> and replace the differences by integrals. The different values of the  $\gamma$  coordinate correspond to the different configurations that the system adopts during its evolution from the initial to the final state. By doing this, we change to a mesoscopic level in the description. The variables at this level cannot be controlled from the outside of the system. The thermodynamic theory dealing with this level is therefore called mesoscopic nonequilibrium thermodynamics.

Since  $j$  and  $r_A$  are constants, we are seeking a variation in  $\phi(\gamma)$  and  $G(\gamma)$  that obeys

$$\sigma^s = - \frac{j}{T^s} \int_{\gamma_1}^{\gamma_2} \left[ \frac{\partial \phi(\gamma)}{\partial \gamma} + \frac{1}{F} \frac{\partial G^s(\gamma)}{\partial \gamma} \right] d\gamma \quad (24)$$



**Figure 1.** Effective chemical potential as a function of the internal coordinate  $\gamma$ . This variation gives a positive driving force and a positive entropy production at any location in  $\gamma$  space.

The electric potential difference is thus

$$\Delta\phi = \int_{\gamma_1}^{\gamma_2} \frac{\partial\phi(\gamma)}{\partial\gamma} d\gamma = \phi(\gamma_2) - \phi(\gamma_1) \quad (25)$$

and the reaction Gibbs energy is likewise recovered by

$$\Delta G^s = \int_{\gamma_1}^{\gamma_2} \frac{\partial G^s(\gamma)}{\partial\gamma} d\gamma = \mu_{A^+}(\gamma_2) + \mu_{e^-}(\gamma_2) - \mu_A(\gamma_1) \quad (26)$$

The difference sign in the above two equations is now referring to differences in state space. We can define the effective chemical potential of the reactant in state 1

$$\tilde{\mu}_A(\gamma_1) = \mu_A(\gamma_1) + F\phi(\gamma_1) \quad (27)$$

and the effective chemical potential for the products in state 2

$$\tilde{\mu}_{A+e^-}(\gamma_2) = \mu_{A^+}(\gamma_2) + \mu_{e^-}(\gamma_2) + F\phi(\gamma_2) \quad (28)$$

This effective chemical potential is equal to the electrochemical potential of  $A^+$ , when the chemical potential of electrons is small. To make possible a distinction from the electrochemical potential, we introduce the name “effective chemical potential”.

In the next step, we assume that these expressions are valid at any location in the internal coordinate space, that is, that the normal thermodynamic relations apply in  $\gamma$ -space:

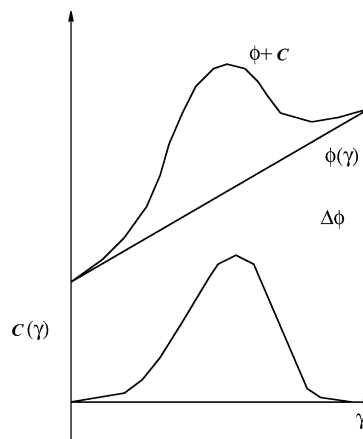
$$\begin{aligned} \tilde{\mu}_A(\gamma) &= \mu_A(\gamma) + F\phi(\gamma) \\ \tilde{\mu}_{A+e^-}(\gamma) &= \mu_{A^+}(\gamma) + \mu_{e^-}(\gamma) + F\phi(\gamma) \end{aligned} \quad (29)$$

We then move one step further and introduce the assumption of *local electrochemical equilibrium* in the internal coordinate space. With local equilibrium along the coordinate  $\gamma$ , we have

$$\mu_{A^+}(\gamma) + \mu_{e^-}(\gamma) + F\phi(\gamma) = \mu_A(\gamma) + F\phi(\gamma) = \tilde{\mu}(\gamma) \quad (30)$$

The effective chemical potential of the reactant is always equal to the effective chemical potential of the products. In other words, there is local equilibrium at any coordinate by this criterion for equilibrium. The physical meaning of this condition is as follows: At each coordinate, along the continuous path between the product and the reactant states, there is an ensemble of particles of a particular energy and state of polarization. The energy of any state along the reaction path is now expressed simply by  $\tilde{\mu}(\gamma)$ .

The effective chemical potential  $\tilde{\mu}(\gamma)$  is illustrated in Figure 1. The difference between the product and the reactant state of the effective chemical potential is negative, since the anode



**Figure 2.** Intrinsic barrier  $C(\gamma)$  (lower part of the figure). A linear potential profile is drawn in the upper part of the figure, and the combination of  $C(\gamma)$  and  $\phi(\gamma)$  is also shown. The surface potential drop is indicated to the right in the figure.

reaction is spontaneous. In *global* electrochemical equilibrium, the two state values are the same, and

$$\Delta\tilde{\mu} = 0 \quad (31)$$

This is yet another formulation of the Nernst equation (eq 22).

By introducing eq 30 into the entropy production rate (eq 24), we can now write

$$\sigma^s = -\frac{1}{T^s} \int_{\gamma_1}^{\gamma_2} \frac{j}{F} \left[ \frac{\partial\tilde{\mu}(\gamma)}{\partial\gamma} \right] d\gamma \quad (32)$$

This expression for the entropy production rate is equivalent to the expression in eq 20. It means that all equations above apply when there is local chemical equilibrium along the internal coordinate space.

The effective driving force times its flux, the electric current density, gives the dissipation of energy of the electrode surface through eq 32. Only the difference between the chemical force and the electric force, the effective driving force of the reaction, leads to dissipation of energy. Chemical reactions that take place in homogeneous phases are purely dissipative phenomena. At the electrode surface, however, the reaction can be driven backward or forward, depending on the direction of the electric current. There is thus an element of control or of reversibility in the electrochemical reaction that distinguishes it from the simple chemical reaction.

According to the second law,  $\sigma^s > 0$ . We shall make the assumption, as de Groot and Mazur also did,<sup>15</sup> that the entropy production is positive, also on the mesoscopic level:

$$\sigma(\gamma) = -\frac{j}{T^s F} \left[ \frac{\partial\tilde{\mu}(\gamma)}{\partial\gamma} \right] d\gamma > 0 \quad (33)$$

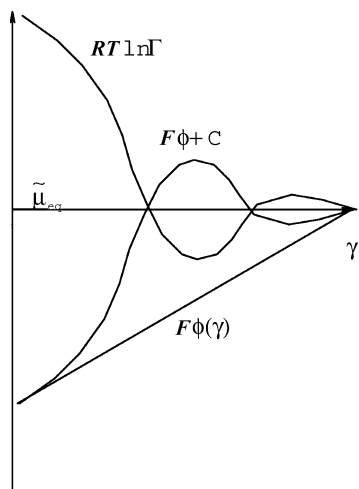
The effective chemical potential in Figure 1 agrees with this assumption. To comply with the condition in eq 33, we must have a monotone decreasing function.

We now specify the chemical contribution of eq 30 further:

$$\tilde{\mu}(\gamma) = C(\gamma) + RT^s \ln \Gamma(\gamma) + F\phi(\gamma) \quad (34)$$

The second term on the right in this equation is the normal configurational contribution to the chemical potential. The excess surface adsorption  $\Gamma$ , or the density of  $A$  or  $A^+$ , is a function of  $\gamma$ . The term  $C(\gamma)$  is the intrinsic barrier that the reactant has to pass on the way to products; see Figure 2. The





**Figure 3.** Illustration of the configurational part of the chemical potential and the electric potential plus the barrier at equilibrium. There is a symmetry around the horizontal line of constant effective chemical potential.

variation in the electric potential is here illustrated by a straight line, labeled  $\phi(\gamma)$ . The effective chemical potential can be further rewritten as

$$\tilde{\mu} = RT^s \ln f\Gamma \quad (35)$$

where  $f(\gamma)$  is the activity coefficient, defined as

$$f(\gamma) = e^{(C+F\phi)/RT^s} \quad (36)$$

The activity coefficient expresses the variation in the barrier plus the electrical potential in  $\gamma$  space.

The situation at global electrochemical equilibrium is illustrated in Figure 3. We see the variation in the sum of the barrier and the electric potential,  $C + \phi$ , as a function of  $\gamma$ . With  $F\Delta\phi = -RT^s \Delta \ln \Gamma$ , the configurational part of the chemical potential is everywhere opposite and equal to this function. The equilibrium value of the effective chemical potential is constant and appears as a line of symmetry in the figure.

### 5. The Overpotential Measurement

The overpotential is measured under stationary state conditions with the help of three electrodes; see, for example, ref 14. A net current is passed between the working electrode (the electrode of interest) and an auxiliary electrode. The current density at the working electrode is  $j$ . The potential between the working electrode and a reference electrode of the same kind that is kept at zero current density is  $\Delta\phi_j$ . When the electric current density of the working electrode is zero, the measured potential is  $\Delta\phi_{j=0}$ . The overpotential is then the difference between the potential drop at a given current density and that at zero current density:

$$\eta = |\Delta\phi_j - \Delta\phi_{j=0}| \quad (37)$$

The overpotential is defined as positive. In the present case of an anodic overpotential,  $\Delta\phi_j > \Delta\phi_{j=0}$ . By definition, when  $j = 0$ ,  $\eta = 0$ .

Suppose now that the overpotential is due to a rate-limiting reaction at the electrode surface and that we have been able to correct the measurement of  $\Delta\phi_j$  for concentration gradient contributions and ohmic resistance drops in the electrolyte. The

surface potential drop that appears in the equations of the preceding section is then equal to  $\Delta\phi_j$  in eq 37.

The reaction Gibbs energy of the electrode is  $\Delta G_j^s$ . We can add and subtract this value in eq 37. This gives, with the definition of the effective driving force,

$$\eta = |\Delta\tilde{\mu} + (\Delta G_j^s - \Delta G_{j=0}^s)| \frac{1}{F} \quad (38)$$

When, furthermore,  $\Delta G_j^s = \Delta G_{j=0}^s = -\Delta\phi_{j=0}$ , we have from this equation that the overpotential can be identified with the effective driving force defined by eq 32.

$$\eta = |\Delta\tilde{\mu}| \frac{1}{F} \quad (39)$$

The assumption  $\Delta G_j^s = \Delta G_{j=0}^s$  is true when the chemical potentials are little affected by the current density. The overpotential times the electric current is then a measure of the dissipation of energy at the electrode surface. We have also assumed that  $\Delta T = 0$  and  $\Delta\mu_i = 0$  applies to the surface.

### 6. The Butler–Volmer Equation

We are now in a position to find the conditions for which the Butler–Volmer equation appears. From the entropy production (eq 33) we can define the thermodynamic force, conjugate to the flux  $j$ :

$$X(\gamma) = -\frac{1}{FT^s} \frac{\partial \tilde{\mu}}{\partial \gamma} = -\frac{R}{Ff\Gamma} \frac{\partial f\Gamma}{\partial \gamma} \quad (40)$$

The force appears as the derivative of the density. This is normal for forces on the macroscopic level (for instance in Fick's law). The force refers to the surface temperature,  $T^s$ , by eq 24.

The central assumption in nonequilibrium thermodynamics is that of linear flux–force relationships. The assumption is normally used on the macroscopic level. We shall now use it for the mesoscopic level. The linear law that follows from the local entropy production rate in  $\gamma$  space is then

$$j = -L(\gamma) \frac{R}{F} \frac{1}{f\Gamma} \frac{\partial f\Gamma}{\partial \gamma} \quad (41)$$

We used as a condition for the derivations in the preceding sections that the electric current is constant. Since the force varies with  $\gamma$ , so will  $L(\gamma)$ . The linear law is now rewritten

$$j = -u_+ e^{-(C+F\phi)/RT^s} R \frac{\partial}{\partial \gamma} e^{\tilde{\mu}/RT^s} \quad (42)$$

with the coefficient of transport

$$u_+ = \frac{L(\gamma)}{F\Gamma} \quad (43)$$

This coefficient can be interpreted as the electric mobility for motion of the charge carrier  $A^+$  in the complex  $A^+e^-$  in the polarized electrode (the motion of the electron is not rate-limiting). Since the current has been taken constant along the internal coordinate, we obtain by integration

$$j = -l [e^{\tilde{\mu}_2/RT^s} - e^{\tilde{\mu}_1/RT^s}] \quad (44)$$

where  $l = R/I$  and

$$I = \int_1^2 u_+^{-1} e^{(C+F\phi)/RT^s} d\gamma \quad (45)$$

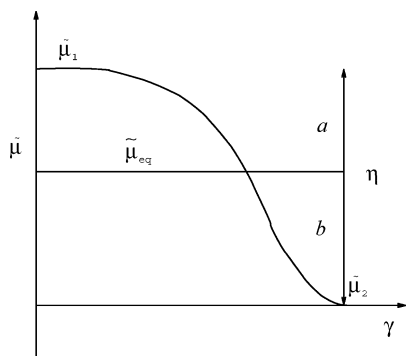


Figure 4. Effective chemical potential and the overpotential.

is the integral of the inverse mobility weighted with the proper Boltzmann factor.

The effective chemical potential at equilibrium  $\tilde{\mu}_{\text{eq}}$  must have a value between  $\tilde{\mu}_1$  and  $\tilde{\mu}_2$ . We subtract and add the factor  $\tilde{\mu}_{\text{eq}}$  in the exponentials of eq 44 and obtain

$$j = -le^{\tilde{\mu}_{\text{eq}}/RT} [e^{(\tilde{\mu}_1 - \tilde{\mu}_{\text{eq}})/RT} - e^{(\tilde{\mu}_2 - \tilde{\mu}_{\text{eq}})/RT}] \quad (46)$$

So far we have only assumed a stationary state, and eq 46 is the most general outcome of the derivation. We have seen that a process that is linear in the internal variable leads to a nonlinear process in the external variable space.

To find the Butler–Volmer equation, we must relate the effective chemical potential to the overpotential. We make the following identifications with the distances  $a$  and  $b$  in Figure 4:

$$\tilde{\mu}_1 - \tilde{\mu}_{\text{eq}} = a = (1 - \alpha)F\eta \quad (47)$$

$$\tilde{\mu}_2 - \tilde{\mu}_{\text{eq}} = -b = -\alpha F\eta \quad (48)$$

The difference between the equations makes the difference in effective chemical potentials equal to  $-F\eta$ . The fraction  $\alpha$  is defined by these identities. When these expressions are introduced into eq 44, we obtain the Butler–Volmer equation

$$j = j_0 [e^{(1-\alpha)\eta F/RT} - e^{-\alpha\eta F/RT}] \quad (49)$$

This completes the derivation of the Butler–Volmer equation from mesoscopic nonequilibrium thermodynamics. The equation has thus been given a thermodynamic basis. Slight differences appear in the interpretation of the variables.

The exchange current density depends on the equilibrium state through

$$j_0 = le^{\tilde{\mu}_{\text{eq}}} \quad (50)$$

In the Butler–Volmer equation there is a similar dependence on the activation energy for the barrier. The value of  $j_0$  depends here on the barrier  $C$  through the variable  $l$ . Our variable  $\alpha$  is similar to the symmetry factor  $\alpha$  in the Butler–Volmer equation, eq 1. The value of  $\alpha$  in our derivation can be related to the symmetry of the problem: It measures the difference of the first state and the final state from the equilibrium state.

The success of the Butler–Volmer equation for description of measurements is beyond doubt. We have derived this equation for stationary state conditions, making the assumption that the effective driving force can be replaced by  $\eta$ . When this assumption is not true, we can use the more general result, eq 46.

## 7. Discussion

The Butler–Volmer equation is usually derived by analysis of unidirectional processes across an activation barrier, that is, by kinetic theory; see, for example, ref 4. While there are similarities between our thermodynamic approach to the problem and the usual kinetic theory, there are also differences. The similarities and differences shall now be discussed.

Both derivations make use of the reaction coordinate in a description of the activated process. Common is that the reaction coordinate measures the progress of the chemical reaction. In mesoscopic nonequilibrium thermodynamics the reaction coordinate has also the particular status of being the internal variable that is used to describe the state of the system.

The chemical reaction is not in *global* equilibrium, nor in reaction kinetics, nor in mesoscopic nonequilibrium thermodynamics. In reaction kinetics,<sup>1</sup> one assumes equilibrium between the reactant state and the activated state. Our basic assumption is different from this. We use the assumption of local chemical equilibrium *along the whole reaction path*, and we find the Butler–Volmer equation on this basis. Therefore, we can state that processes that can be described by the Butler–Volmer equation can be regarded as happening in local equilibrium. And, there is no need to question the use of thermodynamic variables in the description of the surface reaction, in the nonlinear current–potential regime. It is of course justified to ask whether the assumption of local equilibrium is good. Some evidence is emerging that it is a good assumption in electroneutral systems and also with surfaces.<sup>16,17</sup>

The use of linear flux–force relations and local equilibrium is very different from the usual premises that are used to derive the Butler–Volmer equation. In kinetic theory, the difference between the exponentials in the Butler–Volmer equation stems from a picture of unidirectional fluxes across the barrier. Clearly, this picture describes a situation far from equilibrium. One may then rightly wonder whether, for example, the Gibbs equation holds. This doubt is eliminated by our procedure. We derive the nonlinear flux equation, by considering only the net rate, and conditions are compatible with nonequilibrium thermodynamics. We start with a linear relation in a proper variable space. By integration to the macroscopic level, the nonlinear relation is found.

Our derivation resolves the problem of the temperature of the reaction, posed by Eyring and Eyring.<sup>1</sup> It is clear from our derivation that the temperature of the reaction is the surface temperature. The surface temperature is defined by Gibbs excess variables for the surface. Reaction kinetic theory has no prescription for the temperature.

The Butler–Volmer equation and the Nernst equation have for the first time been given the same thermodynamic basis by the present work. The basis is the entropy production rate of the surface. We saw first that the reversible limit of the entropy production rate gave the well-known Nernst equation. We next used the condition of local electrochemical equilibrium to find the Butler–Volmer equation from the same entropy production rate.

The entropy production rate of the electrode surface at the stationary state was determined by the effective driving force and the electric current density. The effective driving force was the sum of the chemical and electrical forces. The overpotential, as it was defined by experiments, is not necessarily equal to this effective driving force. Since the overpotential is not necessarily equal to the effective driving force, it may not only reflect dissipative terms only. This topic deserves further attention and should be tested experimentally.

Mesoscopic nonequilibrium thermodynamics is a part of classical nonequilibrium thermodynamics.<sup>15</sup> The assumptions of a linear flux–force relation and of local chemical equilibrium are central in nonequilibrium thermodynamics. The starting point in nonequilibrium thermodynamics is always fluxes that are linear functions of their conjugate forces. Nonequilibrium thermodynamics becomes a nonlinear theory, in particular by its inclusion of variables on the mesoscopic level. Mesoscopic nonequilibrium thermodynamics uses the same systematic procedure as classical nonequilibrium thermodynamics. The crucial point, that is solved by the mesoscopic version of this theory, is that a proper definition can be found for the driving force. In our derivation, we have used a somewhat different procedure than the one originally given by de Groot and Mazur.<sup>15</sup> These authors started with the entropy change of an adiabatic system. Since the present system is not adiabatic, it is necessary to find the entropy production on the mesoscopic level from its counterpart on the macroscopic level. The proper driving force is then more easily defined.

The importance of the present work lies in the systematic procedure it can give for further derivations and in the understanding it can offer. We found that certain premises must be fulfilled for the Butler–Volmer equation to apply. The surface must be isothermal, there must be equilibrium at the surface for adsorbed species, and one must be able to identify the overpotential with the effective driving force. Experiments, done for other conditions than these, may give new insight and help develop the theory further.

A derivation, starting with the second law of thermodynamics, offers insight into the dissipative nature of the process. Chemical energy is always converted into electrical energy during electrode reactions. The conversion is most clearly described in the macroscopic form in eqs 23 and 22. The central question is always: Which power is lost in the conversion; or how much energy is dissipated? In the analysis above, the effective driving force times the electric current gave the complete power loss. The effective driving force was only equal to the overpotential of the electrode for certain conditions, as defined by measurements. The reaction Gibbs energy may be a function of the state of polarization,  $\Delta G^s(P^s)$ . It is then not correct to replace  $\Delta \tilde{\mu}$  by  $\eta$ . It will be interesting to pursue this point in the future, to find all dissipative parts of the overpotential.

Nonequilibrium thermodynamics gives a systematic basis for including contributions also from nonzero heat fluxes and thermal forces. Bedeaux and Kjelstrup studied the effect of temperature gradients<sup>10</sup> and lack of equilibrium between the electrolyte and the surface.<sup>11</sup> While it is not practical to study all effects combined, it is useful to have information of the limiting cases and how they all derive from a common basis. Nonequilibrium thermodynamics for the mesoscopic level expands the possibilities further to exploit the use of internal variables and their relation with experiments. Mesoscopic

nonequilibrium thermodynamics provides a systematic way to find kinetic laws also for other conditions than the ones used here.

## 8. Conclusion

We have shown that the equation used for reaction controlled charge transfer, the Butler–Volmer equation, has a general basis in nonequilibrium thermodynamics. In the derivation we took advantage of the systematic procedure offered by mesoscopic nonequilibrium thermodynamics.

We arrived at the Butler–Volmer equation using assumptions of local electrochemical equilibrium along the reaction coordinate space, and a linear flux–force relation for this coordinate space. The derivation requires a certain identification of the overpotential with the effective driving force to be true.

By setting a more general basis for this important electrochemical equation, we open possibilities for other studies when the assumptions do not hold, that is, when there are gradients between the surface and its close surroundings, and when the stationary state condition does not apply.

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## References and Notes

- (1) Eyring, H.; Eyring, E. *Modern Chemical Kinetics*; Chapman and Hall: London, 1965.
- (2) Crow, D. R. *Principles and applications of electrochemistry*, 4th ed.; Blackie Academic & Professional: London, 1994.
- (3) Bockris, J. O. M.; Khan, S. U. M. *Surface Electrochemistry. A molecular level approach*; Plenum: 1993.
- (4) Dwayne Miller, R. J.; McLendon, G. L.; Nozik, A. J.; Schmickler, W.; Willig, F. *Surface Electron-Transfer Processes*; VCH Publishers: New York, 1995.
- (5) Marcus, R. *Can. J. Chem.* **1959**, *37*, 155.
- (6) Vilar, J. M.; Rubi, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 11081.
- (7) Perez-Madrid, A.; Pagonabarraga, I.; Rubi, J. M. *Physica A* **1997**, *237*, 205.
- (8) Rubi, J. M.; Mazur, P. *Physica A* **1999**, *276*, 477.
- (9) Gibbs, J. W. *The Scientific Papers of J. W. Gibbs*; Dover: New York, 1961.
- (10) Bedeaux, D.; Kjelstrup Ratkje, S. *J. Electrochem. Soc.* **1996**, *136*, 767.
- (11) Kjelstrup Ratkje, S.; Bedeaux, D. *J. Electrochem. Soc.* **1996**, *143*, 779.
- (12) Kjelstrup, S.; Vie, P. J. S.; Bedeaux, D. In *Surface Chemistry and Electrochemistry of Membranes*; Sørensen, T. S., Ed.; Marcel Dekker: New York, 1999; pp 483–510.
- (13) Kjelstrup, S.; Pugazhendhi, P.; Bedeaux, D. *Z. Phys. Chem.* **2000**, *214*, 895.
- (14) Atkins, P. W. *Physical Chemistry*, 6th ed.; Oxford: 1998.
- (15) de Groot, S. R.; Mazur, P. *Non-Equilibrium Thermodynamics*; Dover: London, 1984.
- (16) Røsjorde, A.; Fossmo, D. W.; Kjelstrup, S.; Bedeaux, D.; Hafskjold, B. *J. Colloid Interface Sci.* **2000**, *232*, 178.
- (17) Hafskjold, B.; Kjelstrup, S. *J. Stat. Phys.* **1995**, *78*, 463.