

Thermal effects in a modified law of mass action

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Abstract

Non-isothermal effects in activated processes are considered by means of mesoscopic non-equilibrium thermodynamics. Charge transfer through electrode surfaces is used as a model problem. It is shown that as a generalization of classical non-equilibrium thermodynamics, the theory is capable of incorporating thermal effects into a non-linear description of activated processes. This results in a modified law of mass action accounting for non-isothermal conditions. Generalized versions of Nernst and Butler–Volmer equations allowing for thermal gradients are presented as a consequence of the modified rate law. Some distinct advantages of the formalism over its classical counterpart are discussed.

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1. Introduction

Activated processes are ubiquitous in nature and constitute a basic mechanism in the evolution of many systems. Chemical reactions, nucleation, surface growth, elastoplasticity, and crossing of energy gaps in semiconductors are, to name a few, examples of activated processes.

The traditional treatment of Arrhenius-type laws for activated processes [1,2] has limited itself to the description of systems in isothermal heat baths, thereby neglecting the possible existence of thermal gradients hindering or enhancing the rate of the process. The presence of such temperature gradients may lead to significant effects as in the case of evaporation and condensation [3,4], nucleation [5], growth [6,7], polymer crystallization [8] and chemical vapor deposition [9].

A classical non-equilibrium thermodynamic [10] treatment of activated processes is not possible due to

their intrinsically non-linear nature. When these processes are analyzed at shorter time scales as done by mesoscopic non-equilibrium thermodynamics (MNET) [11,12] it is possible to obtain a description for the non-linear kinetics. MNET has been successfully used to describe a wide variety of isothermal activation phenomena including nucleation [13], aggregation and agglomeration [14,15], evaporation and condensation [16] and charge transfer through an electrode surface [17].

As a generalization of classical linear non-equilibrium thermodynamics, mesoscopic non-equilibrium thermodynamics should be capable of incorporating all the different thermodynamic forces into its non-linear description. The present work intends to extend the treatment of activated processes to non-isothermal regimes. For this purpose the framework of MNET is used to analyze charge transfer through electrode surfaces beyond the work of Rubi and Kjelstrup [17] who, assuming isothermal conditions, showed that MNET can be used to obtain the law of mass action and the Butler–Volmer equation for an anodic electrochemical reaction.

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For the sake of generality the anode and the cathode are given separate consideration at an initial stage. The electrode surfaces are described using Gibbs' excess variables. The central assumption of local equilibrium is taken along an internal mesoscopic space describing the advancement of the chemical reaction. It is not only the chemical potential of the reacting species that is assumed to vary along this internal space; the electric potential and the temperature are also argued to obey some functionality with respect to this coordinate. The resulting activated expression for the current density is a modified law of mass action and its direct off-spring a modified Butler–Volmer equation.

The organization of the present paper is as follows. In Section 2 the system under consideration is described and the relation between different reacting species is identified. In Section 3 the entropy production for the polarized electrode surface is presented, the reaction coordinate is introduced and the resulting flux–force relations are written in this space; a modified law of mass action results. Section 4 contains the derivation of the current–overpotential relation; the electrode overpotential is defined and a modified equation of the Butler–Volmer type results. The method and the results are discussed in Section 5.

2. The system

Reaction controlled charge transfer through an electrode surface will be considered as a typical example of an activated process. The system under consideration is an electrode surface which is thought to be an autonomous, open system, fully described by its excess variables. The fuel cell anode and cathode are used as examples capturing the nature of typical oxidation and reduction-type electrochemical reactions. The following reactions take place at the anode and the cathode, respectively:



The surface extends in space over a thickness $\delta_s \rightarrow 0$ containing both the product(s) and the reactant(s) (see Fig. 1). The extension of the surface is chosen so that it is electroneutral. The excess densities of the different species reacting are Γ_i ($i = \text{H}_2, \text{H}^+, \text{e}^-, \text{H}_2\text{O}$) and they obey the relations:

$$\Gamma_{\text{H}^+} = \Gamma_{\text{e}^-}, \quad (3)$$

$$r_a = -\frac{1}{2} \frac{d\Gamma_{\text{H}_2}}{dt} = \frac{d\Gamma_{\text{H}^+}}{dt}, \quad (4)$$

$$r_c = -\frac{d\Gamma_{\text{H}^+}}{dt} = -\frac{1}{4} \frac{d\Gamma_{\text{O}_2}}{dt} = \frac{1}{2} \frac{d\Gamma_{\text{H}_2\text{O}}}{dt}, \quad (5)$$

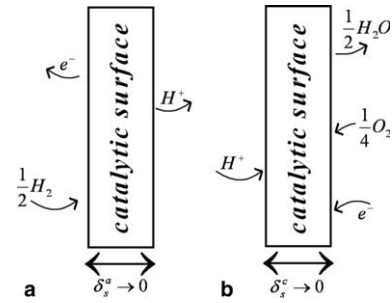


Fig. 1. The reaction is taking place at the catalytic surface. (a) Anode: Hydrogen is arriving to the surface from the gas diffusion backing. Electrons are leaving toward the load. Protons are going into the proton exchange membrane. (b) Cathode: The protons are arriving from the proton exchange membrane (left of surface). The electrons and the oxygen are coming into the surface from the load and the gas diffusion backing, respectively (both at the other side of the surface). The water produced is expelled towards the right. The surface thicknesses of the anode and the cathode are δ_s^a and δ_s^c , respectively.

where r_a and r_c are the rates of reactions (1) and (2), respectively.

Reactions (1) and (2) can be understood as activated processes, where the state of the reactant(s) and the state of the product(s) are connected through an activated state along an internal reaction space with coordinate γ [2].

3. The entropy production rate and flux equations for the electrode surface: a modified law of mass action

When current flows through an electrode, the system departs from equilibrium and the chemical reaction takes on a dominant direction. The entropy production of a polarized electrode surface is given by

$$\sigma^s = J_q^{i'} \left(\frac{1}{T^s} - \frac{1}{T_i} \right) + J_q^{o'} \left(\frac{1}{T_o} - \frac{1}{T^s} \right) - \frac{1}{T^s} j \left(\frac{\Delta G^s}{F} + \Delta\phi \right). \quad (6)$$

The expression for the entropy production is equally valid for the anode and the cathode. Details on the derivation of expression (6) and the meaning of the symbols therein may be found in Appendix A. In Eq. (6), Δ in $\Delta\phi$ refers to the positions at each side of the surface while Δ in ΔG^s refers to the state of the products and the state of the reactants at the surface. Considering that the chemical potential at the left lateral limit of the surface is dominated by the reactants and at the right lateral limit by the products, we may make an identification between both sides of the surface and both wells in reaction space γ [16]. Assuming a continuous reaction path [17], we may then write

$$\int_{\gamma_i}^{\gamma_o} \frac{\partial \mu}{\partial \gamma} d\gamma = \mu(r^s) - \mu(l^s), \quad (7)$$

where r^s and l^s are the right and left lateral limits of the surface, respectively. Then, changes occurring across the surface may be regarded as occurring in internal reaction space, which allows us to establish a correspondence between temperature and electric potential gradients across the electrode surface and their variation across internal reaction space. See Fig. 2.

The chemical potential of the species at the surface is given by

$$\mu^s(\gamma) = C(\gamma) + RT(\gamma) \ln \Gamma(\gamma), \quad (8)$$

where $C(\gamma)$ is the height of the potential barrier that the reactant must pass in its way to the product state.

By looking at the last term in Eq. (6), we may regard the following expressions as the electro-chemical potentials of the reactants and the products, respectively:

$$\tilde{\mu}_i^{\text{anode}} = \frac{1}{2} \mu_{\text{H}_2}^s(\gamma_i^a) + F\varphi(\gamma_i^a), \quad (9)$$

$$\tilde{\mu}_i^{\text{cathode}} = \mu_{\text{H}^+}^s(\gamma_i^c) + \frac{1}{4} \mu_{\text{O}_2}^s(\gamma_i^c) + \mu_{\text{e}^-}^s(\gamma_i^c) + F\varphi(\gamma_i^c), \quad (10)$$

$$\tilde{\mu}_o^{\text{anode}} = \mu_{\text{H}^+}^s(\gamma_o^a) + \mu_{\text{e}^-}^s(\gamma_o^a) + F\varphi(\gamma_o^a), \quad (11)$$

$$\tilde{\mu}_o^{\text{cathode}} = \frac{1}{2} \mu_{\text{H}_2\text{O}}^s(\gamma_o^c) + F\varphi(\gamma_o^c). \quad (12)$$

We assume that expressions (9)–(12) for the lateral limits of the surface are valid everywhere in the internal reaction space γ , thereby converting in these equations all the γ_i^χ and γ_o^χ into unevaluated γ^χ (where $\chi = \text{anode, cathode}$). Furthermore, if local electro-chemical equilibrium is assumed in γ -space so that $\tilde{\mu}(\gamma) = \tilde{\mu}_i(\gamma) = \tilde{\mu}_o(\gamma) = \mu^s(\gamma) + F\varphi(\gamma)$, then

$$\tilde{\mu}(\gamma) = \mu^s(\gamma) + F\varphi(\gamma) = RT(\gamma) \ln (f(\gamma)\Gamma(\gamma)), \quad (13)$$

where $f(\gamma) \equiv e^{\frac{C(\gamma)+F\varphi(\gamma)}{RT(\gamma)}}$.

Noting that $\Delta G^s = \mu^s(\gamma_o) - \mu^s(\gamma_i)$ we may now insert the electro-chemical potential (13) in expression (6) to rewrite the entropy production as follows:

$$\sigma^s = J_q^i \left(\frac{1}{T^s} - \frac{1}{T_i} \right) + J_q^o \left(\frac{1}{T_o} - \frac{1}{T^s} \right) - \frac{1}{T^s} j \frac{\Delta \tilde{\mu}}{F}. \quad (14)$$

The theory of non-equilibrium thermodynamics postulates that the irreversible fluxes present in the entropy production are locally linear functions of the thermodynamic forces [10]. The linear flux–force relations governing transport across the surface are:

$$j = -L_{\varphi\varphi}(\gamma) \frac{\Delta \tilde{\mu}}{T^s F} + L_{\varphi o}(\gamma) \left(\frac{1}{T_o} - \frac{1}{T^s} \right) + L_{\varphi i}(\gamma) \left(\frac{1}{T^s} - \frac{1}{T_i} \right), \quad (15)$$

$$J_q^u = -L_{u\varphi}(\gamma) \frac{\Delta \tilde{\mu}}{T^s F} + L_{uo}(\gamma) \left(\frac{1}{T_o} - \frac{1}{T^s} \right) + L_{ui}(\gamma) \left(\frac{1}{T^s} - \frac{1}{T_i} \right), \quad (16)$$

where $u = o, i$.

We may further manipulate expression (15) for the electric current by making use of Eq. (13):

$$j \frac{T^s F f \Gamma}{RTL_{\varphi\varphi}} = \frac{\tilde{\mu}}{R} e^{\frac{\tilde{\mu}}{RT}} \Delta \frac{1}{T} - \Delta e^{\frac{\tilde{\mu}}{RT}} + \frac{T^s f \Gamma}{RT} \pi_o \left(\frac{1}{T_o} - \frac{1}{T^s} \right) + \frac{T^s f \Gamma}{RT} \pi_i \left(\frac{1}{T^s} - \frac{1}{T_i} \right). \quad (17)$$

In (17) π_i and π_o are the Peltier coefficients at the reactant(s) and the product(s) side of the surface, respectively. The Peltier coefficients describe the heat transferred reversibly with the electric current, and are defined as follows:

$$\pi_u = \left(\frac{J_q^u}{j} \right)_{T_i=T^s=T_o} = F \frac{L_{\varphi u}}{L_{\varphi\varphi}}, \quad \text{where } u = o, i. \quad (18)$$

The Peltier coefficients π_i and π_o are defined only at the lateral limits of the surface, and they could be included in Fig. 2 as a parameter having different values at γ_i and γ_o in a fashion similar to the electric and chemical potentials: $\pi_i = \pi(\gamma_i)$ and $\pi_o = \pi(\gamma_o)$. The Peltier coefficient need not be defined anywhere else in γ -space as it will only be evaluated at γ_i and γ_o as we shall see later.

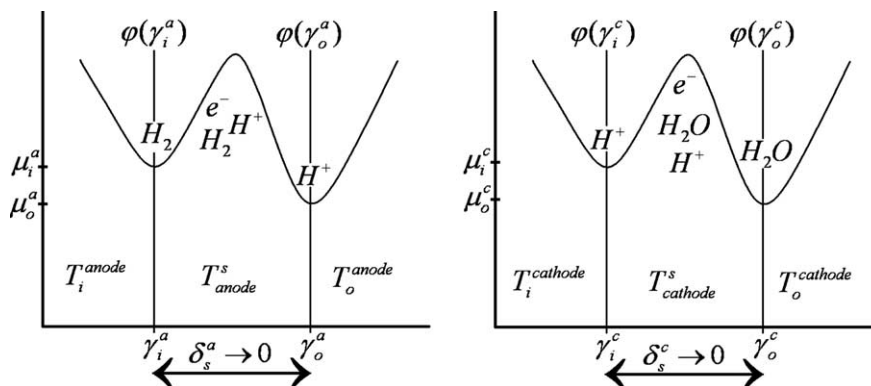


Fig. 2. The interval (γ_i, γ_o) in γ -space is identified with δ_s , the surface thickness. The chemical potential drop across the surface may be identified with a chemical potential difference in γ -space. The same will be true for electric potential differences and temperature differences which may be related to gradients in γ -space as discussed.

Expression (17) may be further rewritten:

$$j \frac{\kappa^{-1}}{R} = -\Delta e^{\frac{\tilde{\mu}}{RT}} - \Delta \left(\pi \frac{e^{\frac{\tilde{\mu}}{RT}}}{RT} \right) + \pi \Delta \frac{e^{\frac{\tilde{\mu}}{RT}}}{RT} + \Delta \left(\frac{\pi}{T^2} \frac{T^s e^{\frac{\tilde{\mu}}{RT}}}{R} \right) - \frac{\pi}{T} \Delta \frac{T^s e^{\frac{\tilde{\mu}}{RT}}}{RT} + \Delta \left(\frac{\tilde{\mu}}{RT} e^{\frac{\tilde{\mu}}{RT}} \right) - \frac{1}{T} \Delta \left(\frac{\tilde{\mu}}{R} e^{\frac{\tilde{\mu}}{RT}} \right), \quad (19)$$

where κ is a transport coefficient assumed independent of γ and defined as follows

$$\kappa \equiv \frac{T(\gamma)L_{\phi\phi}(\gamma)}{FT^s f(\gamma)\Gamma(\gamma)}. \quad (20)$$

This coefficient may be interpreted as the electric mobility for the motion of protons in the surface.

Before we proceed any further we need to define the temperature more precisely in reaction space. On the reactant(s) side of the surface the temperature is T_i , and on the product(s) side it is T_o . There is a temperature jump across the surface. We may assume that the surface, where the reaction is taking place, has a temperature T^s (see Fig. 2). Thus, the temperature's functional dependence on γ is:

$$T(\gamma) = \begin{cases} T_i, & \gamma \leq \gamma_i, \\ T^s, & \gamma_i < \gamma < \gamma_o, \\ T_o, & \gamma_o \leq \gamma. \end{cases} \quad (21)$$

Because the reaction is occurring between γ_i and γ_o every temperature that is not part of a difference will be equal to T^s as given by expression (21). Thus, the third and fifth terms in the right-hand side of Eq. (19) cancel. By replacing the differences with definite integrals over the reaction interval in γ -space, Eq. (19) becomes

$$j = -L \left(a_o e^{\frac{\tilde{\mu}_o}{RT_o}} - a_i e^{\frac{\tilde{\mu}_i}{RT_i}} \right), \quad (22)$$

where $L = \kappa R$ and

$$a_u \equiv 1 + \frac{\pi u}{RT_u} \left\{ \frac{T_u - T^s}{T_u} \right\} - \frac{\tilde{\mu}_u}{R} \left(\frac{1}{T_u} - \frac{1}{T^s} \right), \quad (23)$$

where $u = o, i$.

It is worth noting that from the local linearity postulate in expression (15) a non-linear equation for the current is obtained. This equation is a modified version of the law of mass action and reduces to it once isothermal conditions ($T_i = T^s = T_o$) are assumed.

4. The overpotential and the current density: a modified Butler–Volmer equation

The overpotential, η , of an electrode is the difference between its equilibrium potential – the potential across the electrode when there is no net current – and the potential across the electrode when it is polarized and there is current flowing through it:

$$\eta = |\Delta\phi - \Delta\phi_{j=0}|. \quad (24)$$

By making Eq. (15) equal to zero we obtain the zero-current electric potential, which is given by

$$\Delta\phi_{j=0} = \frac{1}{F} \left(-\Delta G_{j=0}^s + \pi_o \left\{ \frac{T^s - T_o}{T_o} \right\} - \pi_i \left\{ \frac{T^s - T_i}{T_i} \right\} \right). \quad (25)$$

Expression (25) may be regarded as a generalized version of Nernst equation allowing for thermal gradients. Rubi and Kjelstrup showed that Nernst equation has indeed a non-equilibrium thermodynamic basis [17], and this result is now expanded into the non-isothermal case.

Inserting expression (13) for the electro-chemical potential and expression (25) into Eq. (24) we obtain for the overpotential:

$$\eta = \frac{1}{F} \left| \Delta\tilde{\mu} - \left(\Delta G^s - \Delta G_{j=0}^s \right) + \pi_o \left(\frac{T_o - T^s}{T_o} \right) - \pi_i \left(\frac{T_i - T^s}{T_i} \right) \right|. \quad (26)$$

One of the assumptions that must be made to derive the Butler–Volmer equation is that of uniform concentration around the electrode surface so that the overpotential is not affected by concentration changes in the vicinity of the electrode [18], which is one of the assumptions made in the derivation of the entropy production given by Eq. (6). One way to accomplish this ideal situation is by vigorously stirring the electrolytic solution [19]. Another way to accomplish uniformity of concentration near the electrode is by having a low current density flowing through electrode surfaces so that the passage of current does not significantly affect the concentration of ionic species just outside the double layer. Taking this low current density assumption, Eq. (26) reduces to

$$\eta = \frac{1}{F} \left| \Delta\tilde{\mu} + \pi_o \left(\frac{T_o - T^s}{T_o} \right) - \pi_i \left(\frac{T_i - T^s}{T_i} \right) \right|. \quad (27)$$

Assuming that the thermal gradients do not reverse the directions of reactions (1) and (2), we can identify the overpotential with an effective driving force for the chemical reaction:

$$\eta = \frac{-1}{F} \left(\tilde{\mu}_o + \pi_o \left\{ \frac{T_o - T^s}{T_o} \right\} - \tilde{\mu}_i - \pi_i \left\{ \frac{T_i - T^s}{T_i} \right\} \right). \quad (28)$$

We can now write a corrected version of the Butler–Volmer equation. Expression (22) may be restated as follows:

$$j = -L \left(a_o e^{\frac{\tilde{\mu}_{eq}}{RT_o}} e^{\frac{\tilde{\mu}_o - \tilde{\mu}_{eq}}{RT_o}} - a_i e^{\frac{\tilde{\mu}_{eq}}{RT_i}} e^{\frac{\tilde{\mu}_i - \tilde{\mu}_{eq}}{RT_i}} \right), \quad (29)$$

where $\tilde{\mu}_{eq}$ is the effective electrochemical potential at equilibrium, which has a value between $\tilde{\mu}_i$ and $\tilde{\mu}_o$.

We may now make the following identifications in agreement with Eq. (28):

$$\tilde{\mu}_i - \tilde{\mu}_{\text{eq}} = (1 - \alpha)F\eta - \pi_i \left(\frac{T_i - T^s}{T_i} \right), \quad (30)$$

$$\tilde{\mu}_o - \tilde{\mu}_{\text{eq}} = -\alpha F\eta - \pi_o \left(\frac{T_o - T^s}{T_o} \right). \quad (31)$$

These identities allow us to rewrite Eq. (29) as follows:

$$j = j_i \left(e^{\frac{(1-\alpha)F\eta}{RT_i}} \right) - j_o \left(e^{\frac{-\alpha F\eta}{RT_o}} \right), \quad (32)$$

where the pre-exponential factors are given by

$$j_u(T_u, T^s) = La_u e^{\frac{\tilde{\mu}_{\text{eq}}}{RT_u}} \\ = Ja_u e^{\tau \left(\frac{1}{T_u} - \frac{1}{T^s} \right)} e^{\frac{\tilde{\mu}_u}{RT_u} \left(\frac{T^s - T_u}{T_u} \right)}, \quad \text{where } u = o, i \quad (33)$$

and $\tau = \frac{\tilde{\mu}_{\text{eq}}}{R}$, $J = Le^{\frac{\tau}{T^s}}$.

The classical Butler–Volmer equation of electrochemistry is a special case of expression (32) in which isothermal conditions ($T_i = T^s = T_o$) are assumed. This serves as an example for how thermal gradients may hinder or enhance the rate of an activated process; in this case temperature differences across the surface affect the rate of charge transfer through the electrode.

5. Discussion and conclusion

In this paper a framework to analyze activated dynamics under non-isothermal conditions has been presented. In particular, charge transfer through non-isothermal electrode surfaces has been discussed by means of mesoscopic non-equilibrium thermodynamics.

The central assumptions of MNET are the same as those of classical non-equilibrium thermodynamics: local equilibrium within small elements of the system, and local linearity between the independent fluxes and the thermodynamic forces appearing in the entropy production [10]. However, even though the same systematic procedure is used, the inclusion of mesoscopic variables turns MNET into a more powerful and comprehensive non-linear theory. These internal variables provide a space in which to practice the assumptions of the classical theory even in systems far from equilibrium. A more proper definition for the driving force is ensured by introducing an internal space in which to conceive an effective potential energy surface to account for all the forces. An example of such effective potential is the electro-chemical potential $\tilde{\mu}(\gamma)$ given by expression (13). This construction of an effective potential could be taken one step further by rewriting (22) as follows:

$$j = -L \left(e^{\frac{\tilde{\mu}_o}{RT_o}} - e^{\frac{\tilde{\mu}_i}{RT_i}} \right). \quad (34)$$

Now the effective thermo-electro-chemical potential $\tilde{\mu}$ is given in terms of the chemical and electric potentials as well as the temperature and Peltier coefficients in configuration space:

$$\tilde{\mu}_u \equiv \tilde{\mu}(\gamma_u) \equiv \tilde{\mu}(\gamma_u) + RT(\gamma_u) \ln a(\gamma_u) \\ = C(\gamma_u) + RT(\gamma_u) \ln \{ a(\gamma_u) \Gamma(\gamma_u) \} + F\varphi(\gamma_u) \\ = \mu^s(\gamma_u) + F\varphi(\gamma_u) + RT(\gamma_u) \\ \times \ln \left\{ 1 + \frac{\pi(\gamma_u)}{RT(\gamma_u)} \left\{ \frac{T(\gamma_u) - T^s}{T(\gamma_u)} \right\} \right. \\ \left. - \frac{\mu^s(\gamma_u) + F\varphi(\gamma_u)}{R} \left(\frac{1}{T(\gamma_u)} - \frac{1}{T^s} \right) \right\}. \quad (35)$$

The concept of an effective thermo-electro-chemical potential was not introduced earlier in order to retain the more familiar electro-chemical potential during the derivation of the result. However, we can see in Eq. (26) how the overpotential presents non-isothermal contributions from the thermal gradient across the surface. These are also present in (25), which is a generalized Nernst-type equation. The thermal contributions appear as an entropic barrier in the effective thermo-electro-chemical potential (35).

Under isothermal conditions, Eq. (22) reduces to the law of mass action. The presence of thermal gradients induces asymmetry in this equation by causing on one hand the pre-exponential factors, and on the other hand the temperatures in the exponents, to be different from one another. These asymmetries are carried into a modified Butler–Volmer equation, which is a direct off-spring of the law of mass action. Asymmetries in the pre-exponential factors are commonly introduced as phenomenological modifications to rate equations [20,21]. Asymmetries in the temperatures were recently suggested by Sieniutycz [22], who pointed out that reaction rates are not only a function of chemical affinity, but also of temperature and concentrations. The result presented here comprises both asymmetries as obtained from MNET, which presents an insightful and systematic framework to include non-zero contributions from thermal and other forces into the description of rate processes. For instance, according to classical non-equilibrium thermodynamics [10], the presence of large concentration gradients in the vicinity of the region where the reaction is taking place would cause additional forces inducing non-chemical mass transport to be coupled with the electrochemical and thermal fluxes (15) and (16). The effect of these concentration gradients in the activated dynamics, which is typically accounted for with phenomenological asymmetries in the pre-exponential factors of the rate law [20,21], could also be analyzed by means of mesoscopic non-equilibrium thermodynamics, which combines the descriptive power of the classical theory with its own accessibility to the description of non-linear processes.

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Appendix A. The entropy production of a polarized electrode surface. The fuel cell anode and the fuel cell cathode

A detailed justification of Eq. (6) for the entropy production of a polarized electrode is given in this section. A similar derivation was done in [17], and more detailed work may be found in [23]. The entropy balance for the surface shown in Fig. 1 is

$$\frac{ds^s}{dt} = J_s + \sigma^s, \quad (\text{A.1})$$

where s^s is the surface excess entropy, σ^s is the entropy production rate at the surface, and J_s is the net entropy flux into the surface (the difference between the entropy flux into and out of the surface). The net entropy flux J_s is given by:

$$\text{Anode: } J_s = \frac{1}{T_i} J_q^i + J_{\text{H}_2}^i S_{\text{H}_2} - \frac{1}{T_o} J_q^o, \quad (\text{A.2})$$

$$\text{Cathode: } J_s = \frac{1}{T_i} J_q^i - J_{\text{O}_2}^o S_{\text{O}_2} - \frac{1}{T_o} J_q^o - J_{\text{H}_2\text{O}}^o S_{\text{H}_2\text{O}}. \quad (\text{A.3})$$

The net entropy flux contains the measurable heat flux, J_q^i , and the thermodynamic entropy S_k times the corresponding mass flux J_k for each of the species k . The transported entropy of the ions is included in J_q^i . The superscripts i and o stand for the left- and the right-hand side of the surface, respectively, as do the temperatures T_i and T_o . Fluxes going from left to right in Fig. 1 are positive.

The excess entropy production rate of a polarized electrode surface, σ^s , can be found from the Gibbs equation and the energy conservation for the surface. In these systems, the Gibbs equations are:

$$\begin{aligned} \text{Anode: } T^s ds^s \\ = du^s - \left(\mu_{\text{H}^+}^s + \mu_{\text{e}^-}^s - \frac{1}{2} \mu_{\text{H}_2}^s \right) d\Gamma_{\text{H}^+} - \frac{D_{\text{eq}}}{\varepsilon_0} dP^s, \end{aligned} \quad (\text{A.4})$$

$$\begin{aligned} \text{Cathode: } T^s ds^s \\ = du^s + \left(\frac{1}{2} \mu_{\text{H}_2\text{O}}^s - \frac{1}{4} \mu_{\text{O}_2}^s - \mu_{\text{e}^-}^s - \mu_{\text{H}^+}^s \right) d\Gamma_{\text{H}^+} - \frac{D_{\text{eq}}}{\varepsilon_0} dP^s, \end{aligned} \quad (\text{A.5})$$

where T^s is the surface temperature, u^s is the excess internal energy of the surface, μ_k^s is the chemical potential of species k at the surface, D_{eq} is the electric displacement due to the free charge at the adjacent phases, P^s is the polarization due to charges bound to the surface and ε_0 is the electric permittivity of the vacuum. The time rate of change in the excess variables in the Gibbs equation gives:

$$T^s \frac{ds^s}{dt} = \frac{du^s}{dt} - r \Delta G^s - \frac{D_{\text{eq}}}{\varepsilon_0} \frac{dP^s}{dt}, \quad (\text{A.6})$$

where r is the reaction rate and ΔG^s is the free energy for the reaction taking place at the surface, given by $\mu_{\text{H}^+}^s + \mu_{\text{e}^-}^s - \frac{1}{2} \mu_{\text{H}_2}^s$ for the anode and $\frac{1}{2} \mu_{\text{H}_2\text{O}}^s - \frac{1}{4} \mu_{\text{O}_2}^s - \mu_{\text{e}^-}^s - \mu_{\text{H}^+}^s$ for the cathode.

Energy conservation for the surface reads:

$$\begin{aligned} \text{Anode: } \frac{du^s}{dt} = J_q^i - J_q^o - j \Delta \varphi + \frac{D}{\varepsilon_0} \frac{dP^s}{dt} \\ + J_{\text{H}_2}^i H_{\text{H}_2}, \end{aligned} \quad (\text{A.7})$$

$$\begin{aligned} \text{Cathode: } \frac{du^s}{dt} = J_q^i - J_q^o - j \Delta \varphi + \frac{D}{\varepsilon_0} \frac{dP^s}{dt} \\ - J_{\text{O}_2}^o H_{\text{O}_2} - J_{\text{H}_2\text{O}}^o H_{\text{H}_2\text{O}}. \end{aligned} \quad (\text{A.8})$$

The fluxes are determined by their values measured in the homogeneous phases adjacent to the surface. There is a heat flux into the surface, J_q^i , and out of the surface, J_q^o . There is also a flux of species k into the surface, J_k^i , that carries enthalpy H_k . The electric potential difference $\Delta \varphi$ times the electric current j gives the power dissipated at the surface, and D is the electric displacement when the system is away from equilibrium.

By introducing Eqs. (A.7), (A.8), (A.1) and (A.2), (A.3) into Eq. (A.6) we obtain (see [23] for details):

$$\begin{aligned} \sigma_{\text{anode}}^s = J_q^i \left(\frac{1}{T^s} - \frac{1}{T_i} \right) + J_q^o \left(\frac{1}{T_o} - \frac{1}{T^s} \right) \\ - \frac{r}{T^s} \Delta G^s - \frac{1}{T^s} j \Delta \varphi + \frac{1}{T^s} \frac{(D - D_{\text{eq}})}{\varepsilon_0} \frac{dP^s}{dt} \\ - \frac{1}{T^s} \left(\mu_{\text{H}_2,T}^s - \mu_{\text{H}_2,T} \right) J_{\text{H}_2}^i, \end{aligned} \quad (\text{A.9})$$

$$\begin{aligned} \sigma_{\text{cathode}}^s = J_q^i \left(\frac{1}{T^s} - \frac{1}{T_i} \right) + J_q^o \left(\frac{1}{T_o} - \frac{1}{T^s} \right) - \frac{r}{T^s} \Delta G^s - \frac{1}{T^s} j \Delta \varphi \\ + \frac{1}{T^s} \frac{(D - D_{\text{eq}})}{\varepsilon_0} \frac{dP^s}{dt} + \frac{1}{T^s} \left(\mu_{\text{O}_2,T}^s - \mu_{\text{O}_2,T} \right) J_{\text{O}_2}^o \\ - \frac{1}{T^s} \left(\mu_{\text{H}_2\text{O},T}^s - \mu_{\text{H}_2\text{O},T}^s \right) J_{\text{H}_2\text{O}}^o. \end{aligned} \quad (\text{A.10})$$

We assume the chemical potential of all reactants at the surface is the same as in its adjacent phase:

$$\mu_{k,T}^s = \mu_{k,T}. \quad (\text{A.11})$$

The deviation of the displacement from equilibrium is equal and opposite to the electric potential drop across the surface [24]:

$$\frac{(D - D_{\text{eq}})}{\varepsilon_0} = - \frac{\Delta \varphi}{\delta_s}. \quad (\text{A.12})$$

Assuming the polarization P^s of the surface (i.e., the dipole moment per molecule) is constant in time—current will flow only due to the migration of charge caused by the chemical reaction, and not due to the field caused by charges adjacent to the surface (no displacement current), then the electric current and the reaction rate are related by Faraday's constant F :

$$\frac{dP^s}{dt} = 0, \quad (\text{A.13})$$

$$r = j/F. \quad (\text{A.14})$$

Inserting expressions (A.11) to (A.14) into (A.9) and (A.10) we obtain for the entropy production:

$$\sigma^s = J_q^{Ti} \left(\frac{1}{T^s} - \frac{1}{T_i} \right) + J_q^{To} \left(\frac{1}{T_o} - \frac{1}{T^s} \right) - \frac{1}{T^s} j \left(\frac{\Delta G^s}{F} + \Delta\varphi \right). \quad (\text{A.15})$$

This expression, which is equally valid for the anode and the cathode, gives the entropy increase of the system plus that of its surroundings (the heat bath). According to the second law of thermodynamics, the entropy production is positive for all irreversible transformations, and zero in the reversible limit.

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