On the Nonequilibrium Thermodynamics of Large Departures from Butler−Volmer Behavior

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Large deviations from the behavior predicted by the Butler−Volmer equation of electrochemistry are accounted for using mesoscopic nonequilibrium thermodynamics. The nonequilibrium thermodynamic hypotheses are extended to include velocity space and cope with imperfect reactant transport leading to departures from Butler−Volmer behavior. This results in a modified Butler−Volmer equation in good agreement with experimental data. The distinct advantages of the method and its applicability to analyze other systems are briefly discussed.

Activated processes are ubiquitous in nature and constitute a basic mechanism in the evolution of many systems. Chemical reactions, adsorption, nucleation, surface growth, elastoplasticity, and crossing of energy gaps in semiconductors are, to name a few, examples of activated processes. These processes obey a rate law often expressed as two Arrhenius terms accounting for the forward and the reverse rates, as is the case of the Butler−Volmer equation of electrochemistry.[1−3] The Butler−Volmer equation describes the rate of an electrochemical reaction as a function of the departure from the equilibrium voltage of the electrochemical cell. This equation, however, fails to reproduce the behavior of the system at high reaction rates, where nonideal effects in transport become significant (see, e.g., refs 4−6).

The purpose of this letter is to show a formalism capable of describing experimentally observed departures from Butler−Volmer behavior to greater agreement than more elaborate phenomenological models found in the electrochemistry literature (see, e.g., refs 4 and 5). Given the essentially nonlinear nature of activated processes, a classical nonequilibrium thermodynamic description[7] is not feasible. However, using mesoscopic nonequilibrium thermodynamics (MNET),[8−10] a description of activated dynamics is accessible while preserving the postulates of the classical theory. MNET has been successfully used to describe a wide variety of ideal activation phenomena including nucleation,[11] aggregation and agglomeration,[12,13] evaporation and condensation,[14] and charge transfer through electrode surfaces.[2,3]

The local equilibrium postulate of non-equilibrium thermodynamics is applicable to systems that, although far from equilibrium, may be approximated as a collection of equilibrium subsystems.[7] When changes in the spatial density occur simultaneously with changes in the velocities of the constituent elements, both the spatial and the velocity coordinates must be independently partitioned by the local equilibrium hypothesis.[9,10,15] Then, using the Gibbs entropy postulate, we may write

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an equilibrium chemical potential in the spatial and velocity coordinates as follows:[7]

$$\mu(\gamma, \nu) = k_B T \ln n(\gamma, \nu) + \frac{1}{2} m\nu^2 + C(\gamma) \quad (1)$$

where γ and ν are, respectively, the spatial and velocity coordinates, T is the absolute temperature, k_B is Boltzmann's constant, and $n(\gamma, \nu)$ is the density of particles, which have mass m and potential energy $C(\gamma)$. Constant temperature and volume were assumed in eq 1.

From mass conservation in (γ, ν)-space, the local linearity postulate of nonequilibrium thermodynamics results.[9] This postulate prescribes that each flux is a linear combination of all the different forces driving the evolution of the system. Hence, the particle fluxes in γ and ν spaces are, respectively, given by

$$j_\gamma = -L_{\gamma\gamma} \frac{\partial \mu}{\partial \gamma} - L_{\gamma\nu} \frac{\partial \mu}{\partial \nu} \quad (2)$$

$$j_\nu = -L_{\nu\gamma} \frac{\partial \mu}{\partial \gamma} - L_{\nu\nu} \frac{\partial \mu}{\partial \nu} \quad (3)$$
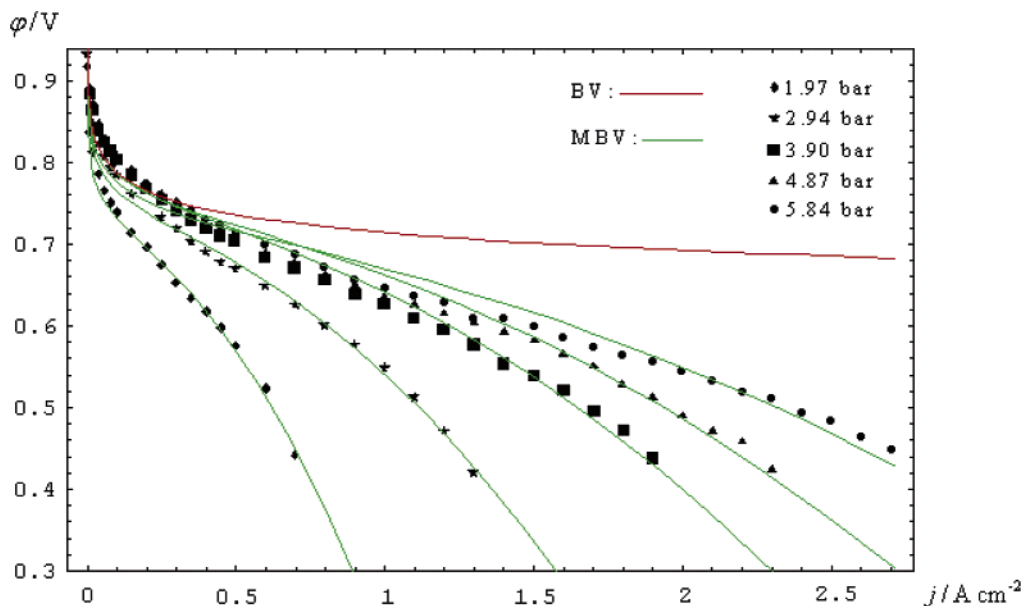
where the L_{ij} with $i, j \in \{\gamma, \nu\}$ are the phenomenological coefficients, and they obey Onsager's reciprocity relations.[7] These coefficients may, in first approximation, be assumed proportional to the density n

$$L_{ij}(\gamma, \nu) = k_{ij} n(\gamma, \nu) \quad (4)$$

If sufficiently fast relaxation in velocity space is assumed, then the spatial and velocity coordinates are decoupled. As a result $n(\gamma, \nu)$ can be separated, and it obeys a Gaussian distribution in velocity space[9]

$$n(\gamma, \nu) = n_\gamma(\gamma) \exp\left(\frac{-\kappa}{k_B T} \nu^2\right) \quad (5)$$

Figure 1. Voltage−current curves for a polymer electrolyte fuel cell for indicated values of oxygen partial pressure. When more oxygen (a reactive) is present at the cathode, the rate of the electrochemical reaction increases and ideal behavior is approached. The dots represent experimental data taken from ref 4, and the green lines alongside are the fit given by the modified Butler−Volmer expression (eq 12). The operating temperature of the cell is 90 °C. The exchange current j_0 is taken to be $14.3 \cdot 10^{-6}$ A cm^{-2} for all curves.[4] φ_0 is the offset voltage close to 1 V in all cases. The parameter α decreases with the oxygen partial pressure and takes values between $3.3 \cdot 10^{-2}$ cm^4 A^{-2} and $4.6 \cdot 10^{-1}$ cm^4 A^{-2}. A sample $\alpha = 0$ (and, consequently, $v^2 \ll k_B T/\kappa$) Butler−Volmer curve is shown (red) that fails to capture the inflection toward a limiting current due to imperfect oxygen transport in the feeding layer of the electrode.[5]

where κ is inversely related to the variance of the particle velocity distribution. In these conditions, the system is close to mechanical equilibrium, and we may effectively neglect the cross term in eq 2.[14] Inserting eqs 1, 4, and 5 into eq 2, we obtain for the current in the spatial dimension γ

$$j_\gamma \exp\!\left(\frac{C(\gamma)}{k_B T}\right) = -k_{\gamma\gamma} k_B T \exp\!\left(\frac{-mv^2}{2k_B T}\right) \frac{\partial}{\partial \gamma} \exp\frac{\mu(\gamma, v)}{k_B T} \quad (6)$$

From conservation of mass flux, we may infer that $j_\gamma = j$ is a constant function of γ.[14] Integrating eq 6 from the initial spatial configuration γ_1 to the final γ_2 results in

$$j = -k_1 k_B T \exp\!\left(\frac{-\kappa}{k_B T} v^2\right)\!\left(1 - \exp\frac{-\Delta_\gamma \mu(\gamma, v)}{k_B T}\right) \quad (7)$$

where

$$k_1 \equiv \frac{k_{\gamma\gamma} n_\gamma(\gamma_2)\, e^{C(\gamma_2)/k_B T}}{\int_{\gamma_1}^{\gamma_2} d\gamma\, e^{C(\gamma)/k_B T}}$$

and

$$\Delta_\gamma \mu(\gamma, v) \equiv \mu(\gamma_2, v) - \mu(\gamma_1, v)$$

If relaxation in velocity space were infinitely fast, then κ would be exactly equal to $m/2$ (Maxwell's velocity distribution) and, as a result, the chemical potential a function of γ only as results from inserting eq 5 into eq 1. In the limiting case when $v^2 \ll k_B T/\kappa$, the law of mass action and the Nernst equation can be recovered from eq 7.[2,3]

The current in γ-space is given by the velocity averaged with the density in γ-space. Hence, the velocity can be taken to be proportional to the current

$$j = \rho v \quad (8)$$

Inserting eq 8 into eq 7 yields

$$j \exp(k_2 j^2/k_B T) = -k_1 k_B T[1 - \exp(-\Delta_\gamma \mu(\gamma, v)/k_B T)] \quad (9)$$

where $k_2 \equiv \kappa/\rho^2$.

For positive currents, the quantity $\exp(-\Delta_\gamma \mu(\gamma, v)/k_B T)$ is always greater or much greater than 1. Hence, we may approximate eq 9 as follows:

$$j \exp(k_2 j^2/k_B T) \simeq j_0 \exp(-\Delta_\gamma \mu(\gamma, v)/k_B T) \quad (10)$$

where $j_0 \equiv k_1 k_B T$. Furthermore, in regimes where $j \gg j_0$, the exponential on the right-hand side of eq 10 is much greater than the one on the left, which entails

$$\ln \frac{j + j_0}{j_0} \simeq -\frac{\Delta_\gamma \mu(\gamma, v)}{k_B T} - \frac{k_2 j^2}{k_B T} \quad (11)$$

In an electrochemical reaction, the potential energy function $C(\gamma)$ that one proton must overcome to move through γ-space is given by $C(\gamma) = e \cdot \varphi(\gamma)$, where e is the proton's charge and $\varphi(\gamma)$ is the electrostatic potential. Inserting this expression into eq 11 yields

$$\varphi = -\frac{k_B T}{e} \ln \frac{j + j_0}{j_0} - \alpha j^2 + \varphi_0 \quad (12)$$

where $\alpha \equiv k_2/e$ is inversely proportional to the variance of the velocity distribution and, as such, a measure of the departure from perfect transport; $\varphi_0 \equiv k_B T/e \ln n_\gamma(\gamma_1)/n_\gamma(\gamma_2)$ is an offset voltage; and j_0 is the equilibrium exchange current density.

Large deviations in the current−voltage behavior predicted by the Butler−Volmer equation of electrochemistry have been observed (see, e.g., refs 4−6). The Butler−Volmer equation

fails at large currents, which affect the uniformity of reactive concentrations assumed to exist in the vicinity of the electrode.[1] Equation 12 presented here does not suffer from the restrictions bounding the applicability of the Butler−Volmer equation, but instead reduces to it when low electric currents are assumed such that $j^2 \ll k_B T/k_2$.[2,3]

Figure 1 shows the performance of eq 12 against current−voltage data from a polymer electrolyte fuel cell cathode with different oxygen partial pressures.[4,5] While the physical meaning of the fitting parameters remains to be investigated, the theory presented here offers better agreement with the data than kinetic models previously used for its analysis.[4,5]

We have shown how by using the tools of nonequilibrium thermodynamics a simple expression can be obtained to account for saturation effects in the rate of electrochemical reactions. Imperfect transport of the reacting species to the catalytic surface causes these nonideal effects that are beyond the reach of a simple Arrhenius−Kramers description such as the Butler−Volmer equation. The velocity coordinate has to be brought into the local-state description of the system in order to cope with the possibility of delayed relaxations. While no additional complexity is caused by adding this coordinate, the applicability of the results is extended to a wider range of regimes. This formalism has already been used to account for inertial effects in nucleation[16] and evaporation,[14] and it offers a possibility to analyze other activated processes exhibiting departures from Arrhenius−Kramers behavior, such as viscoplasticity[17] and protein folding.[18]

Note Added after ASAP Publication. This article was published ASAP on March 18, 2006. Data were corrected in eqs 9−11 and paragraphs 8−11 of the main text. The revised version was reposted on March 23, 2006.

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