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Determination of Thermodynamic and Stochastic Potentials in Nonequilibrium Systems from Macroscopic Measurements[†]

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For systems far from equilibrium, a potential determines the fluctuations from stable attractors, such as stationary states, and the thermodynamic approach to such states (Lyapunov function). For a reaction system with ionic reactions in a stationary state far from equilibrium, the imposition of a current displaces the system from that state. For such systems, we show that an electrochemical potential due to the imposed current, consisting of both a Nernstian term and a non-Nernstian term, directly yields the stochastic potential around its maximum to a good approximation, without knowledge of the reaction mechanism of the system. The approximation is good to the order of the percent difference between the Nernstian and non-Nernstian terms and can be used for evaluating the stochastic potential. For general systems, the imposition of a flow of intermediates also displaces the system from its stationary state to a new stationary state, which is a nonstationary state of the system without flow. The concentrations of the chemical species can be measured without time restraints, and by repeating various such displacements, sufficient data can be obtained to determine rate coefficients for a solution of a stationary master equation and its stochastic potential for a known or assumed reaction mechanism. Several experiments are suggested to test the consistency of the results with predictions of the master equation and, thus, to test that equation itself.

I. Introduction

The determination of equilibrium thermodynamic quantities, for example, an electrochemical potential or a Gibbs free energy difference, ΔG, must be done from measurements carried out reversibly, with a " balance of active tendencies" according to Gibbs.[1] Intensive variables must be continuous across the boundary of the system, say the pressure in an expansion process or the electrode potential in an electrochemical experiment.[2] Fluctuations of concentrations in a system at equilibrium and constant temperature and pressure are given by the stationary solution of a master equation;[3] the probability of a fluctuation at constant temperature, T, and pressure, p, is proportional to the exponential of the Gibbs free energy change, ΔG

$$P \approx \exp(-\Delta G/RT) \tag{1}$$

Fluctuations of concentrations (or numbers of species) in a stationary state of a nonequilibrium system are also determined by the stationary solution of a master equation. The probability of a fluctuation from this stationary state is proportional to the exponential of a potential function, labeled here $-\Phi/RT$. We have shown in theoretical and experimental studies[4−10] that Φ is an excess work of removing the system from its stationary state, that it is a Lyapunov function for the deterministic path returning the system to its stationary state, that it provides necessary and sufficient conditions for stability of the stationary state, and that it provides measures of relative stability of stationary states in systems with multiple stationary states. Extensive prior work has been performed by many investigators on the master equation and its stationary probability distribution.[3]

We have several purposes in mind for the present study: (1) a discussion of the determination of the stochastic potential Φ/RT from macroscopic measurements, (2) suggestions for testing the consistency of the master equation with such measurements, and (3) an application of our prior work on electrochemical systems in nonequilibrium stationary states.[11,12]

For the suggestion of a direct method of determining the stochastic potential of a chemical system in a stationary state far from equilibrium, we choose a reaction system with ionic reactants, section II. An (ion-selective) electrode is inserted into the chemical system and connected to a reference electrode. The imposition of a current flow through the electrode connection drives the chemical system (CS) away from its initial stationary state to a new stationary state of the combined chemical and electrochemical system (CCECS), analogous to driving the CS away from equilibrium in the same manner. A potential difference is generated by the imposed current, which consists of a Nernstian term and a non-Nernstian term dependent on the kinetics; this potential difference is directly related to the stochastic potential for systems with detailed balance, and it is related with small error to that potential for all systems around nonequilibrium stationary states. (This is an easier realization of the determination of the stochastic potential by macroscopic measurements than suggested in ref 4.) In these cases, for the electrochemical method suggested, we need to know the ionic species in the chemical system, but we do not need to know the reaction mechanism of the system. For systems

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without detailed balance and displaced sufficiently from nonequilibrium stationary states, the potential difference generated by an imposed current is still closely related to the stochastic potential, as we show in Appendix B.

For reaction systems with or without ionic species, we offer a suggestion for an indirect method of determining the stochastic potential from macroscopic measurements (section IV): impose a flow of any of the stable intermediate chemical species on the CS, and thus displace the CS from its initial stationary state to a new stationary state of the combined CS and inflow that is not a stationary state of the chemical system for the fixed constraints. If, in repeated experiments for different imposed flow rates of the different species, the concentrations of the reacting species are measured in each new stationary state, then the rate coefficients and the stochastic potential can be evaluated numerically from an assumed master equation and an assumed reaction mechanism.

In section V, we present further suggestions for testing the master equation.

II. Change of Chemical System into Coupled Chemical and Electrochemical System. A Simple Example

Consider a simple model system

$$\mathrm{R_+ + Q_+ \xrightleftharpoons[k_{+1}^{-}]{k_{+1}^{+}} A_1 + B_2 \xrightleftharpoons[k_{0}^{-}]{k_{0}^{+}} B_1 + A_2 \xrightleftharpoons[k_{-1}^{-}]{k_{-1}^{+}} R_- + Q_-} \qquad (2)$$

where R_+, Q_+, R_-, and Q_- are each held at given constant concentrations of R_+, Q_+, R_-, and Q_-, respectively. The species A_1, A_2, B_1, and B_2 (at concentrations A_1, A_2, B_1, and B_2, respectively) are uniformly distributed (mixed) in a reaction vessel. For values of R_+Q_+/R_-Q_- not equal to the equilibrium constant for the overall reaction, a nonequilibrium stationary state is achieved asymptotically in time.

The deterministic kinetic equations are

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = \frac{\mathrm{d}B_2}{\mathrm{d}t} = k_{+1}^{+}R_+Q_+ + k_0^{-}B_1A_2 - (k_{+1}^{-} + k_0^{+})A_1B_2$$

$$\frac{\mathrm{d}A_2}{\mathrm{d}t} = \frac{\mathrm{d}B_1}{\mathrm{d}t} = k_{-1}^{-}R_-Q_- + k_0^{+}A_1B_2 - (k_{-1}^{+} + k_0^{-})B_1A_2 \qquad (3)$$

We assume that the constant concentrations of R_+, Q_+, R_-, and Q_- are known and that the concentrations of A_1, A_2, B_1, and B_2 can be measured, at least at the stationary state. Radioactive tracer experiments might help to determine some rate coefficients, although such methods are complicated by the reversibility of the chemical reactions. In principle, further measurements can be made on this system in nonstationary states to obtain rate coefficients, but there might be serious time constraints in doing so.

To overcome the difficulties cited in the previous paragraph, we need to devise a method of removing the CS from its stationary state at the fixed external constraints, R_+Q_+ and R_-Q_-. This can be achieved in several ways. For reactions with ionic species, electrodes can be inserted into the chemical system, which thus becomes coupled to an electrochemical system. Such cases are discussed in section III. Another method involves the introduction of a flux of an intermediate species into the reaction chamber of the chemical system, and such cases are discussed in section IV.

Consider the introduction of an electrochemical system to the chemical system, run in solution, eq 1. Reaction 1 is run in an open, isothermal reactor, and for given constraints, R_+Q_+ and R_-Q_-, a stationary state of the chemical system will be established. We next insert an electrode into the reaction system (see Fig.1 in ref.12) and connect that electrode to a reference electrode. The electrode reactions are

$$\mathrm{A_1 + e^- \rightleftarrows A_2, \quad B_1 + e^- \rightleftarrows B_2} \qquad (4a)$$

We also consider a combination of the electrode reactions in eqs 4a and buffer chemical reactions involving the species R_+, Q_+, R_-, and Q_-

$$\mathrm{R_+ \rightleftarrows A_1 + e^- \rightleftarrows A_2 \rightleftarrows R_-;\ Q_+ \rightleftarrows B_1 + e^- \rightleftarrows B_2 \rightleftarrows Q_-} \qquad (4b)$$

We notice that the sum of the two sets of reactions (eqs 4a and 4b) is the chemical reaction in eq 2. Upon insertion of the electrode into the reacting system, there is a change in the concentrations of the species away from their values in the stationary state prior to the electrode insertion. If a current flow is imposed through the external circuit connecting the electrode in the system and the reference electrode, then a stationary state of the CCECS is attained. The CS now is not in a stationary state. The electrochemical system is a device for removing the chemical system, for given inflow conditions, from its stationary state to different values of concentrations and maintaining these new concentrations in a stationary state of the CCECS. The stationary state is maintained by a balance of fluxes. In ref 11, we present a derivation of an electrochemical potential in a nonequilibrium system and show that the potential measured in a stationary state of a combined reaction and electrochemical system differs from the equilibrium expression for the Nernst potential; for experiments, see ref 12. In ref 13, we illustrate these differences with calculations for the minimal bromate oscilliatory reaction system in a nonequilibrium stationary state.

Experiments were performed on the displacement of the minimum bromate reaction from stationary states far from equilibrium and from equilibrium as outlined here, and the $\mathrm{Ce^{IV}/Ce^{III}}$ electrode potential was measured for various imposed currents.[14]

The expression for a given imposed current j is given by the Butler−Volmer equations (see eq 4 in ref 11) and repeated here in a slightly different notation

$$j = j_1^{-} - j_1^{+} + j_2^{-} - j_2^{+} + j_3^{-} - j_3^{+} + j_4^{-} - j_4^{+} + j_5^{-} - j_5^{+} + j_6^{-} - j_6^{+} \qquad (5)$$

where

$$j_1^{+} = \mathscr{F} C_{\mathrm{R}_+} R_+ \exp[-\Delta G^{\ddagger}_{\mathrm{R}_+\mathrm{A}_1}(0)/RT] \exp(-\alpha_{\mathrm{R}_+\mathrm{A}_1} fE)$$

$$j_1^{-} = \mathscr{F} C_{\mathrm{A}_1} A_1 \exp[-\Delta G^{\ddagger}_{\mathrm{R+A}_1}(0)/RT] \exp[(1 - \alpha_{\mathrm{R}_+\mathrm{A}_1}) fE], \text{ etc.} \qquad (6)$$

In these equations, E is the potential difference between the two electrodes; $\mathscr{F}$ is the Faraday constant; C_{R_+},C_{A_1}, etc., are Arrhenius prefactors; R_+, A_1, B_2, etc., are concentrations; $\Delta G^{\ddagger}_{\mathrm{R}_+\mathrm{A}_1}(0)$ is the Gibbs free energy of activation for the electrode reaction $\mathrm{R_+ = A_1 + e^-}$ when the potential difference between the electrode and the reacting solution vanishes (and similarly for the other activation energies); $\alpha_{\mathrm{R+A_1}}$ is the transfer coefficient for the $\mathrm{R_+/A_1}$ reaction and similarly for the other reactions; and finally $f = \mathscr{F}/RT$.

In eq 5, the first term is the current due to the half-cell reaction

$$R_+ \rightarrow A_1 + e^- \qquad (7)$$

the second term due to

$$A_1 + e^- \rightarrow R_+ \qquad (8)$$

and similarly for the other reactions (eq 4b).

Now consider a stationary state of the combined chemical and electrochemical systems with a given imposed current j in the external circuit, which can be positive, negative, or zero. The chemical flux in the forward direction, which produces A_2 and B_1, can be thought of as being opposed by the sum of the electrode reactions $A_1 + e^- \rightarrow A_2$ and $B_2 \rightarrow B_1 + e^-$. The chemical flux in the backward reaction, which produces A_1 and B_2, can be thought of as being opposed by the sum of the electrode reactions $A_2 \rightarrow A_1 + e^-$ and $B_1 + e^- \rightarrow B_2$.

The chemical composition of the CCECS can be described by a set of modified evolution equations that contain chemical terms, present in eq 3, and electrochemical terms depending on the currents $j_u^{\pm}$, $u = 1, ..., 6$

$$\frac{dA_1}{dt} = k_{+1}^{+} R_+ Q_+ + k_0^{-} B_1 A_2 - (k_{+1}^{-} + k_0^{+}) A_1 B_2 + \frac{1}{\mathcal{F}}(j_1^{+} - j_1^{-} + j_2^{-} - j_2^{+})$$

$$\frac{dA_2}{dt} = k_{-1}^{-} R_- Q_- + k_0^{+} A_1 B_2 - (k_{-1}^{+} + k_0^{-}) B_1 A_2 + \frac{1}{\mathcal{F}}(j_2^{+} - j_2^{-} + j_3^{-} - j_3^{+})$$

$$\frac{dB_1}{dt} = k_{-1}^{-} R_- Q_- + k_0^{+} A_1 B_2 - (k_{-1}^{+} + k_0^{-}) B_1 A_2 + \frac{1}{\mathcal{F}}(j_4^{+} - j_4^{-} + j_5^{-} - j_5^{+})$$

$$\frac{dB_2}{dt} = k_{+1}^{+} R_+ Q_+ + k_0^{-} B_1 A_2 - (k_{+1}^{-} + k_0^{+}) A_1 B_2 + \frac{1}{\mathcal{F}}(j_6^{-} - j_6^{+} + j_5^{+} - j_5^{-}) \qquad (9)$$

For a stationary state of the CCECS, the stationary concentrations of the species A_2, A_1, B_2, and B_1 are the solutions of the equations

$$\frac{dA_1}{dt} = \frac{dA_2}{dt} = \frac{dB_1}{dt} = \frac{dB_2}{dt} = 0 \qquad (10)$$

The stationary concentrations of the species A_2, A_1, B_2, and B_1 in the CCECS are altered from those in the CS to satisfy eqs 9 and 10; they can be measured without time restrictions. For the CS, these concentrations correspond to a nonstationary state for the given constraints. Thus, by varying the input current j, we obtain stationary (without electrodes) and nonstationary (with electrodes) states of the CS, all time-independent.

III. Determination of the Stochastic Potential Φ in Coupled Chemical and Electrochemical Systems

In prior studies,[4] we showed that the differential of the stochastic potential for the chemical system in the stationary state, $d\Phi_c$, can be written as

$$d\Phi_c = \sum_i (\mu_i - \mu_i^0)\, dn_i \qquad (11)$$

with

$$i = A_1, B_1 \text{ taken to be neutral}$$

$$i = A_2, B_2 \text{ taken to be singly negatively charged}$$

where n_i denotes the number of moles of species i.

The differential $d\Phi_c$ is exact, and hence, choices of paths of integration are arbitrary; the path could be a most probable fluctuational path or an anti-deterministic path, etc. The chemical potentials μ_i^0 are those of the species in a reference state; the reference state concentration x_j for species X_j is obtained from the momentum canonically conjugate to x_j along the fluctuational trajectory (see eqs 42–44 in ref 4). Alternatively, the exponential of the integral in eq 11 can be viewed as a formal representation of the eikonal solution to first order for the stationary solution of the master equation for the chemical system; differentiation yields the master Hamilton–Jacobi equation that, in the eikonal approximation, is equivalent to the master equation.

For the electrochemical system, we choose the same variables as for the chemical system. The reactions at the electrodes are assumed to be sufficiently fast that the measured potential is the equilibrium potential at the electrode, and fluctuations in it and in the imposed current are neglected. This is a commonly used approximation, analogous to neglecting fluctuations in concentrations of species in equilibrium with mass reservoirs. For systems with detailed balance, for example all systems with the concentration state space for which equilibrium is the only stable attractor, we can write the electrochemical potential of each ionic species, say A_2, as

$$\mu_{A_2} + E_{A_2}\mathcal{N}\mathcal{F} \qquad (12)$$

where E_{A2} is the potential for a given imposed current, $\mathcal{N}$ is the number of equivalents of electrons in the half-cell reaction for A_2, and $\mathcal{F}$ is the Faraday constant. We postulate that we can write $d\Phi$ of the combined chemical and electrochemical system, $d\Phi_E$, for small deviations from a stationary state far from equilibrium as

$$\begin{aligned} d\Phi_E = {} & (\mu_{A_1} - \mu_{A_1}^0)\, dn_{A_1} + (\mu_{B_1} - \mu_{B_1}^0)\, dn_{B_1} \\ & + (\mu_{A_2} + E_{A_2}\mathcal{N}\mathcal{F} - \mu_{A_2}^0 - E_{A_2}^0\mathcal{N}\mathcal{F})\, dn_{A_2} \\ & + (\mu_{B_2} + E_{B_2}\mathcal{N}\mathcal{F} - \mu_{B_2}^0 - E_{B_2}^0\mathcal{N}\mathcal{F})\, dn_{B_2} \\ = {} & d\Phi_c + (E_{A_2} - E_{A_2}^0)\mathcal{N}\mathcal{F} dn_{A_2} + (E_{B_2} - E_{B_2}^0)\mathcal{N}\mathcal{F} dn_{B_2} \end{aligned} \qquad (13)$$

The postulate is consistent with an expansion of the master equation or an equivalent Hamilton–Jacobi equation (see Appendix B).

At a stationary state of the combined system, the differential $d\Phi_E = 0$, and therefore, we obtain for $d\Phi_c$

$$\begin{aligned} d\Phi_c = {} & -\mathcal{N}\mathcal{F}[(E_{A_2} - E_{A_2(s)}) - (E_{A_2}^0 - E_{A_2(s)})]\, dn_{A_2} \\ & - \mathcal{N}\mathcal{F}[(E_{B_2} - E_{B_2(s)}) - (E_{B_2}^0 - E_{B_2(s)})]\, dn_{B_2} \end{aligned} \qquad (14)$$

where we have added and subtracted $E_{A_2(s)}$ and $E_{B_2(s)}$, the potentials of A and B, respectively, in the stationary state of the chemical system. The imposition of electrodes and a current moves the chemical system away from that stationary state. The first term in each square bracket depends on concentrations, say A_2 and $A_{2(s)}$, only and thus is the Nernstian contribution to the measured electrochemical potential. The second term in each bracket depends on the kinetics of the chemical system and is the non-Nernstian contribution to the measured electrochemical potential. The measurements of the electrochemical potentials, say with ion-specific electrodes, yield $(\partial\Phi_c/\partial n_{A_2})$ and $(\partial\Phi_c/\partial n_{B_2})$, respectively. Thus, we obtain the important result that from these macroscopic measurements of potentials and macroscopic concentrations of A_1, A_2, B_1, and B_2 at a sufficient number of displacements from the stationary state of the chemical system, the stochastic potential Φ_c of the chemical system can be determined in some regions around stationary states.

If the chemical system approaches equilibrium rather than a stationary state (nonequilibrium), then the non-Nernstian terms vanish, and $d\Phi_c$ becomes $d(\Delta G)$.

No direct use has been made of the master equation itself in obtaining the stochastic potential Φ_c from the measurements described, and no knowledge of the reaction of the chemical system is required; hence, the measurements provide a direct determination of the stochastic potential in a limited range around a stationary state of the chemical system.

For systems without detailed balance, that is, for most systems, in the domain of concentration state space with a nonequilibrium stable attractor such as a node or focus, the relation of the electrochemical potential induced by a given imposed current flow into the stochastic potential is, in general, not as simple as for cases with detailed balance. Near a stationary state far from equilibrium, the electrical potential is still, to good approximation, linearly related to the stochastic potential around its maximum, as we show in Appendix B. Hence, if we are interested in determining the stochastic potential near a stationary state far from equilibrium, we can do so directly, again without the use of a master equation or knowledge of the reaction mechanism. If, however, the stochastic potential must be known in the domain of concentration state space around a given stationary state extending to regions where the lowest-order approximation does not suffice, then it is necessary to gather sufficient data of concentrations, currents, and voltages at several displacements from the stationary state and to use these data to evaluate the rate coefficients and the stochastic potential by numerical solution of the master equation for a given model of the reaction mechanism.

IV. Chemical Systems with Imposed Fluxes.

Consider the chemical system in eq 1, with species A_1, A_2, B_1, and B_2 being either ions or neutrals, in a reaction chamber in a nonequilibrium stationary state. If we impose a flux of species A_1, $J = k'A_1'$, into the reaction chamber with Q_+ and Q_- unchanged, we move the chemical system to a different, nonequilibrium stationary state with different concentrations of the reacting species. This procedure allows the sampling of different combinations of A_1, A_2, B_1, and B_2 values at fixed Q_+ and Q_- by means of the imposition of different fluxes of any of these reactants. These combinations represent nonstationary states in the absence of the imposed flux, but with the imposed flux, they are stationary states, and hence, the measurements of concentrations can be made without constraints of time. If we were to attempt to measure concentrations in nonstationary states, then the measurement technique would have to be fast compared to the time scale of change of the concentrations.

In an electrochemical system (section IV), we impose a change in chemical potential; here we impose a flux of a species. This imposition must be added to the deterministic kinetic equations of the elementary steps in a known or assumed reaction mechanism. The problem then is to deduce the effect of this imposition on the stochastic potential. For that, we need to go from the deterministic kinetic equations to a stochastic equation, say the lowest-order eikonal approximation of the master equation. Hence, the measurements provide an indirect determination of the stochastic potential, one that depends on the use of the master equation and an assumed reaction mechanism.

For one-variable systems, this procedure is easy because we know the stationary solution of the master equation to that order. For example, for the Schlögl model, we have the elementary reaction steps

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3X, \quad X \underset{k_4}{\overset{k_3}{\rightleftarrows}} B \tag{15}$$

where the concentrations of A and B are fixed; the kinetic equation with imposed flux $J = k'X'$ is

$$\frac{dX}{dt} = k_1AX^2 + k_4B - (k_2X^3 + k_3X) \equiv t^+ - t^- \tag{16}$$

The stationary solution of the lowest-order eikonal approximation of the master equation corresponding to the chemical reactions in eqs 15 is

$$P(X) \approx \exp\left(-\frac{\Phi'}{k_BT}\right) \tag{17}$$

where

$$-\frac{1}{k_BTV}\frac{\partial\Phi'}{\partial X} = \ln\left(\frac{t^+ + J}{t^-}\right) = \ln\left(\frac{t^+}{t^-}\right) + \ln\left(1 + \frac{J}{t^-}\right) \tag{18}$$

In the absence of an external flux, this solution reduces to

$$P(X) \approx \exp\left(-\frac{\Phi}{k_BT}\right) \tag{19}$$

where

$$-\frac{1}{k_BTV}\frac{\partial\Phi}{\partial X} = \ln\left(\frac{t^+}{t^-}\right) \tag{20}$$

At a stationary state of the system with imposed flux $\partial\Phi'/\partial X = 0$, the first term on the rhs of eq 18 is

$$-\frac{1}{k_BTV}\frac{\partial\Phi}{\partial X} = \ln\left(\frac{t^+}{t^-}\right) = -\ln\left(1 + \frac{J}{t^-}\right) \tag{21}$$

which is proportional to the derivative of the stochastic potential Φ for the system without imposed flux. We see that this derivative is given not by the imposed flux alone but by the ratio J/t^+ . Therefore we need to know the rate coefficients in t^+.

For multivariable systems, this approach is more difficult; the determination of the stochastic potential requires sufficient measurements to determine the rate coefficients and the numerical solution of the stationary form of the master equation, as detailed in Appendix A

V. Suggestions for Experimental Tests of the Master Equation

One direct test of the master equation for a nonequilibrium system in a stationary state involves a comparison of the

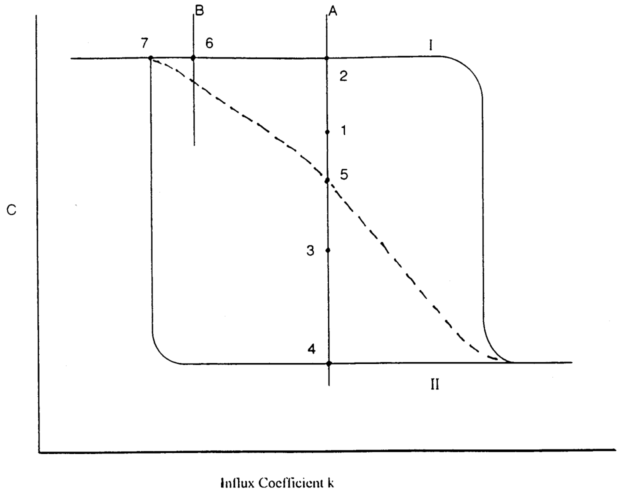

Figure 1. Typical hysteresis loop for a one-variable system with a cubic kinetic equation: plot of concentration c vs influx coefficient. Solid lines, stable stationary states (nodes); broken line, unstable stationary state. For a discussion of lines A and B and numbers, see the text.

probability of a fluctuation with measured fluctuations. Such measurements have not yet been made. However, another direct test is made possible by the developments presented here. In sections II and III, we described direct macroscopic measurements of the stochastic potential in a stationary state of chemical systems with detailed balance and for any system at and near a stationary state far from equilibrium. In section IV, we discussed the displacement of a system in a nonequilibrium stationary state by an imposed flux as a means of generating additional and sufficient data for the determination of the rate coefficients. In Appendix A we outline several methods of calculating that stochastic potential from the necessary rate coefficients determined in macroscopic experiments and from the numerical solution of an assumed master equation. Comparison of the direct measurement of the stochastic potential with the indirect method of calculating the stochastic potential from macroscopic measurements and the master equation provides a test of the measurements and of the master equation itself. Such tests have also not yet been made.

There are other, indirect tests of the master equation. Consider a chemical reaction system with one (or effectively one) variable stationary state and multiple stationary states, for example, the iodate−arsenous acid reaction in an open system.[15] A schematic drawing of the hysteresis loop in such a system is shown in Figure 1. Several macroscopic experiments can be performed that can test predictions of the master equation, in particular predictions concerning the stationary stochastic potential Φ_c.

A. Relative Stability and Equistability of Two Stable Stationary States in the Homogeneous Reaction System. We label the concentration of a given variable by c and assume that we can measure it as the influx into the system, denoted by the influx coefficient k, is varied; thus, we trace out the solid lines of the hysteresis loop shown in Figure 1. If next we can form a combined chemical and electrochemical system as discussed in section III, then we can locate the combined system at point 1 on line A, say, by imposing a given current flow. This point is a stable stationary state of the combined system. If the electrochemical system is suddenly disconnected, the chemical system will return deterministically to the stable stationary state 2 on the solid line in Figure 1. If this kind of experiment is repeated to locate the combined system on point 3, then on disconnection of the electrochemical system, the chemical system will return to the stable stationary state 4. By means of such experiments, the separatrix, which is the branch of unstable stationary states shown by the dotted line in Figure 1, can be determined. The same approach works for a system displaced from a stationary state by an influx of a species.

The condition of equistability of a homogeneous stationary state on the upper branch of the hysteresis loop, labeled I, with a homogeneous stationary state on the lower branch, labeled II, occurs at one value of the inflow coefficient k within the hysteresis loop. If the deterministic rate equation for the concentration c is

$$\mathrm{d}c/\mathrm{d}t = F(c) \tag{22}$$

then the deterministic condition of equistability is[16]

$$\int_{\mathrm{I}}^{\mathrm{II}} F(c)\,\mathrm{d}c = 0 \tag{23}$$

Alternatively, if line A is at the value of k at equistability, then we have

$$\int_4^5 F(c)\,\mathrm{d}c = \int_2^5 F(c)\,\mathrm{d}c \tag{24}$$

If these two integrals are not equal, then one stable stationary state, the one with the large value of the integral in eq 24, is said to be more stable than the other.

The predictions of the stationary solution of the stochastic master equation, to be compared with measurements, are that (a) the minimum of the bimodal stationary probability distribution in the hysteresis region must be located on the separatrix and (b) at equistability, the probability of fluctuations $P(c)\,\mathrm{d}c$ must obey[17]

$$\int_4^5 P(c)\,\mathrm{d}c = \int_2^5 P(c)\,\mathrm{d}c \tag{25}$$

Approximately, the height of the probability peak at 2 is equal to that at 4. To either side of the value of k at equistability, one peak, that of the more stable stationary state, is higher than the other.[16]

A comparison of deterministic and stochastic calculations (but not experiments) has been discussed in a different context, that of viewing the stochastic potential as an excess work.[4]

B. Critical Slowing. In Figure 1, one of the two marginal stability points is labeled 7. Near such points, for example 6 on line B, a critical slowing occurs: on perturbation of the chemical system initially at point 6, the system decays back to 6 more slowly than for values of k to the right of 6 and faster than for values of k to the left of 6 but still to the right of 7. Similar slowing occurs to the left of 7, but only for a small range of k. This effect has been observed experimentally in several systems.

Critical slowing manifests itself also in the stationary solutions of the master equation. In ref 16, we discuss a simple example with a cubic deterministic rate equation. Linearization of a perturbation away from a stationary state yields the relaxation time within one branch of stationary states, which increases on the approach to a marginal stability point. A quantitative comparison with experiments with the predictions based on the potential Φ, without any linearization, needs to be made.

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Appendix A

To calculate the potential Φ_c for a chemical system, such as in eq 3, we first need to determine the rate coefficients. There are six rate coefficients, but only three are independent if three equilibrium constants are known. The rate coefficients can be measured in standard kinetic experiments. Second, the concentrations of the species A_1, A_2, B_1, and B_2 can be measured in sufficient numbers of stationary states achieved by varying the known ratios of R_- and Q_- to R_+ and Q_+, and the rate coefficients are obtained by fitting these concentrations to the equations for the stationary states, eq 3, with dA_1/dt, dA_2/dt, dB_1/dt, and dB_2/dt set equal to 0. Third, the rate coefficients can be determined by fitting measurements made by removing the chemical system with an imposed flux, as described.

To calculate the stochastic potential for the chemical system, we assume the validity of the stochastic version of mass-action law,[3] and with that, we can derive a Markovian master equation for the state probability of the system. In the following, rather than considering the particular example considered in this article, we consider a reaction network of the type

$$\sum_{j=1}^{\mathrm{S}_1}\alpha_{ji}^{+}S_j + \sum_{j=1}^{\mathrm{S}_2}\beta_{ji}^{+}X_j \underset{k_i^-}{\overset{k_i^+}{\rightleftharpoons}} \sum_{j=1}^{\mathrm{S}_1}\alpha_{ji}^{-}S_j + \sum_{j=1}^{\mathrm{S}_2}\beta_{ji}^{-}X_j, \quad i = 1, ..., R \tag{A.1}$$

which include the reaction network in eq 2 as a particular case. Here, $\alpha_{ji}^{\pm}$ and $\beta_{ji}^{\pm}$ are stoichiometric coefficients, and $k_i^{\pm}$ represents the rates of the forward and backward steps. To prevent the approach of the system to chemical equilibrium, one assumes that the numbers of species S_j are controlled by interaction with a system of reservoirs connected to the system by means of semipermeable walls. If the numbers of the S_j species are known a simplified description of the system is possible. By removing from eqs A.1 the stable substances A_j, we obtain a set of reduced reactions[19]

$$\sum_{j=1}^{\mathrm{S}_2}\beta_{ji}^{+}X_j \underset{\kappa_i^-}{\overset{\kappa_i^+}{\rightleftharpoons}} \sum_{j=1}^{\mathrm{S}_2}\beta_{ji}^{-}X_j, \quad i = 1, ..., R \tag{A.2}$$

where

$$\kappa_i^{\pm} = k_i^{\pm}\left\{\prod_{j=1}^{\mathrm{S}_1}\left[\frac{S_j(S_j - 1)\cdots(S_j - \alpha_{ji}^{\pm} + 1)}{V^{\alpha_{ji}^{\pm}}}\right]\right\} \tag{A.3}$$

are reduced rate constants, S_j represents the number of molecular species S_j, and V is the volume of the system.

We introduce the composition vector of the system $\mathbf{X} = (X_1, X_2, ...)$ where X_1, X_2, ... are the numbers of the species X_1, X_2, ..., respectively. We can derive a Markovian master equation for the probability $P_{\mathbf{X}}(t)$ of the state vector at time t

$$dP_{\mathbf{X}}(t)/dt = \sum_{\mathbf{X}'}[W_{\mathbf{X}'\mathbf{X}}P_{\mathbf{X}'}(t) - W_{\mathbf{X}\mathbf{X}'}P_{\mathbf{X}}(t)] \tag{A.4}$$

where the transition rates $W_{\mathbf{X}\mathbf{X}'}$ can be determined from the deterministic rate constant $k_j^{\pm}$. We define the concentration vector $\mathbf{x} = \mathbf{X}/V$ and the vector ξ of the reaction extents attached to the reduced reactions in eq 2

$$\mathbf{x}(t) = \mathbf{x}(0) + \mathbf{F}\xi \tag{A.5}$$

where $\mathbf{F}$ is the matrix of the net stoichiometric coefficients for the reduced reactions in A.2, $\mathbf{F} = [\beta_{ji}^{-} - \beta_{ji}^{+}]$.

In the thermodynamic limit

$$\mathbf{X} \rightarrow \infty,\ V \rightarrow \infty, \text{ with } \mathbf{x} = \mathbf{X}/V \text{ constant} \tag{A.6}$$

we introduce the probability densities of the concentration vector $P(\mathbf{x},t)$ and of the reaction extents $P(\xi,t)$. These two probabilities are related to each other by the relationship

$$P(\mathbf{x},t) = \int_{\xi}\prod_{u}\delta[x_u - x_u(0) - \sum_{b}f_{ub}\xi_b]P(\xi,t)\, d\xi \tag{A.7}$$

Starting from eq A.4, we can derive a master equation for the probability density $P(\xi,t)$ that can be written in a form similar to a Schrödinger equation

$$-\frac{\partial}{\partial t}P(\xi,t) = \mathbb{H}P(\xi,t) \tag{A.8}$$

where the Hamiltonian operator $\mathbb{H}$ is given by

$$\mathbb{H}[\xi,\nabla_{\xi}]\cdots = \sum_{i}\left\{\left[1 - \exp\left(-V^{-1}\frac{\partial}{\partial\xi_i}\right)\right][r_i^{+}(\xi)\cdots] + \left[1 - \exp\left(+V^{-1}\frac{\partial}{\partial\xi_i}\right)\right][r_i^{-}(\xi)\cdots]\right\} \tag{A.9}$$

and $r_j^{\pm}(\xi)$ represents the rates of the reduced reactions in eq A.2, expressed in terms of the vector ξ of the reaction extents.

In the thermodynamic limit, eq A.8 can be solved by using the eikonal approximation

$$P(\xi,t) = \text{const} \times \exp[VJ(\xi;t)] \qquad \text{as } V \rightarrow \infty \text{ with } \xi \text{ constant} \tag{A.10}$$

where $P(\xi,t) = \mathcal{O}(V^0)$ is a chemical action. In the particular case of a stochastic stationary regime, both the probability of concentration fluctuations and the chemical action are time-independent, i.e., $P(\xi,t) = P(\xi)$, $J(\xi;t) = J(\xi)$, and the stationary action $J(\xi)$ is related to the stochastic potential Φ_c by

$$J(\xi) = -\Phi_c/RTV \tag{A.11}$$

By inserting eq A.11 into eq A.8 and keeping the dominant terms in V, we come to a Hamilton−Jacobi equation for the chemical action $J(\xi)$

$$\frac{\partial}{\partial t}J(\xi) + H[\xi,\nabla_{\xi}J(\xi)] = 0 \tag{A.12}$$

where

$$H[\xi,\mathbf{p}] = \sum_{i}\{[1 - \exp(-p_i)]r_i^{+}(\xi) + [1 - \exp(p_i)]r_i^{-}(\xi)\} \tag{A.13}$$

is a Hamiltonian function attached to the operator $\mathbb{H}$ and $\mathbf{p}$ is the vector of generalized impulses attached to the state vector ξ.

By solving the Hamilton−Jacobi equation (eq A.6), we can evaluate the stochastic potential Φ_c. This can be achieved in several ways, and we outline two methods: (1) the direct numerical solution of eq A.12 and (2) the reduction of the Hamilton−Jacobi equation to a system of Hamiltonian equations. The most direct approach is the numerical solution of the Hamilton−Jacobi equation; however, because this approach does not provide any useful physical insight, we are not going to discuss it. In the following, we give a short presentation of approach 2.

For the purpose of this article, it is enough if we manage to evaluate the stochastic potential for a stationary stochastic regime, Φ_c, that emerges for large times. However, the method chosen for obtaining Φ_c is based on the solution of Hamiltonian equations of motion, which provides the action, $J(\xi;t)$, at all times, including Φ_c for the stationary regime (eq A.11). We represent an initial probability distribution, say a Gaussian distribution

$$P(\xi,0) = \text{const} \times \exp[VJ^0(\xi)] \tag{A.14}$$

by a cloud of characteristic points in the phase space. The state vector ξ attached to a point is randomly selected from the probability distribution (eq A.14), and the corresponding impulse vector $\mathbf{p}$ is computed from the initial action

$$\mathbf{p} = \nabla_{\xi} J^0(\xi) \tag{A.15}$$

where the initial action $J^0(\xi)$ is evaluated from the initial probability density (eq A.14). Each point in the cloud is the starting point of a trajectory in the phase space. All trajectories, taken together, represent the flow of the probability fluid in phase space. Each individual trajectory is described by a system of Hamiltonian equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi = \nabla_{\mathbf{p}} H(\xi,\mathbf{p}), \quad \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{p} = -\nabla_{\xi} H(\xi,\mathbf{p}) \tag{A.16}$$

By solving eqs A.10 numerically with the initial conditions

$$\xi(0) = \xi^0, \quad \mathbf{p}(0) = \nabla_{\xi} J^0(\xi^0) \tag{A.17}$$

we know the dependences

$$\xi(\tau) = \xi_{1,2}(\xi^0;\tau), \quad \mathbf{p}(\tau) = \mathbf{p}(\xi^0;\tau) \tag{A.18}$$

where τ is an intermediate time variable that can take any value between the initial moment $\tau = 0$ and the current time $\tau = t$. Equations A.18 express a "characteristic flow" in the phase space. In terms of this characteristic flow, we can express the chemical action at time t. To each trajectory in the characteristic flow, we can attach a Lagrangian chemical action $\tilde{J}(\xi^0;t)$, which depends on the initial position vector ξ^0 and the time t. We have

$$\tilde{J}(\xi^0;t) = J^0(\xi^0) + \int_0^t \mathrm{d}\tau \left[\mathbf{p}(\tau)\cdot\frac{\mathrm{d}}{\mathrm{d}\tau}\xi(\tau) - H(\xi(\tau),\mathbf{p}(\tau))\right] \tag{A.19}$$

Equation A.19 gives the action $\tilde{J}(\xi^0;t)$ at time t attached to a given point with the initial coordinate ξ^0. The action $\tilde{J}(\xi^0;t)$ gives a Lagrangian representation of the motion of characteristic points in the phase space. We are, however, also interested in the value of the Eulerian chemical action $J(\xi;t)$, which depends on the current vector ξ at time t. To compute the Eulerian chemical action $J(\xi;t)$, we must express the initial vector ξ^0 as a function of the current value ξ at time $\tau = t$. We can express these dependences from the solutions

$$\xi(t) = \vartheta(\xi^0;t) \tag{A.20}$$

of the Hamiltonian equations (eqs A.16)

$$\xi^0 = \zeta(\xi(t);t) \tag{A.21}$$

where $\zeta(\xi(t);t)$ is the inverse function of $\vartheta(\xi^0;t)$, that is, it fulfills the identities

$$\zeta(\vartheta(\xi^0;t);t) = \xi^0, \quad \vartheta(\zeta(\xi(t);t);t) = \xi(t) \tag{A.22}$$

The chemical action $J(\xi;t)$, which enters the eikonal approximation (eq A.10), can be expressed as

$$J(\xi;t) = \tilde{J}(\zeta(\xi(t);t);t) \tag{A.23}$$

In particular, the stationary chemical action and the stochastic potential Φ_c can be obtained from eq A.23 for large times.

The physical significance of this method of solving the chemical Hamilton–Jacobi equation (eq A.11) is straightforward. The temporal evolution of the probability density of concentration fluctuations in the composition space can be viewed as the flow of a probability fluid. The flow of the probability fluid can be represented either by a single partial differential equation, eq A.12, or by a set of coupled ordinary differential equations, eqs A.16, which have a structure similar to that of the Hamiltonian equations in classical mechanics. The Hamilton–Jacobi equation (eq A.12) describes the probability fluid as a scalar field (Eulerian representation), whereas the Hamiltonian equations (eqs A.16) describe the probability fluid as a bundle of trajectories that represent the motion of the probability fluid in time (Lagrangian representation). In terms of the Eulerian representation, we describe the motion of the probability fluid with respect to a fixed frame of reference, whereas in the case of Lagrange representation, we use a mobile frame of reference that moves together with the probability fluid. By solving the Hamiltonian equations, we can compute the value of the chemical action for each trajectory, expressed in terms of the Lagrange variables. On the other hand, to compute the probability of concentration fluctuations, we need to express the chemical action in terms of the Eulerian variables. The passage from the Lagrange to the Euler representation can be done by using eqs A.20–A.23.

Appendix B

The derivation presented in Appendix A can be easily extended to a compound chemical and electrochemical system. We consider that, in addition to the chemical processes in eq A.1, the following electrochemical processes occur

$$\sum_{j=1}^{S_1}\bar{\alpha}_{ji}^{+}S_j + \sum_{j=1}^{S_2}\bar{\beta}_{ji}^{+}X_j + \bar{\nu}_i e^{-} \underset{\bar{k}_i^{-}}{\overset{\bar{k}_i^{+}}{\rightleftharpoons}} \sum_{j=1}^{S_1}\bar{\alpha}_{ji}^{-}S_j + \sum_{j=1}^{S_2}\bar{\beta}_{ji}^{-}X_j, \quad i = 1,...,\bar{R} \tag{B.1}$$

which include the reaction network in eq 4b as a particular case. In these equations, $\alpha_{ji}^{\pm}$, $\bar{\beta}_{ji}^{\pm}$, and $\bar{\nu}_i$ are stoichiometric coefficients and

$$\bar{k}_i^{\pm} = \bar{k}_i^{\pm}(E) = \bar{k}_i^{\pm}(0)\exp\left[\left(\frac{1 \pm 1}{2} - \alpha_c\right)\frac{\bar{\nu}_i\mathscr{F}E}{RT}\right] \tag{B2a}$$

$$\bar{k}_i^{\pm}(0) = \mathscr{G}_i^{\pm}\exp[-\Delta G_{i,\pm}^{\ddagger}(0)/RT] \tag{B2b}$$

are electrochemical rate coefficients that are exponential functions of the potential difference E that are described by equations of the type of eq 6, $\mathscr{G}_i^{\pm}$ denotes preexponential factors, and $\Delta G_{i,\pm}^{\ddagger}(0)$ denotes Gibbs free energies of activation for the direct and reverse reactions at zero potential. By removing from eqs B.1 the stable substances S_j, we obtain a set of reduced reactions similar to eqs A.2

$$\sum_{j=1}^{S_2}\bar{\beta}_{ji}^{+}X_j + \bar{\nu}_i e^- \underset{\bar{\kappa}_i^-}{\overset{\bar{\kappa}_i^+}{\rightleftharpoons}} \sum_{j=1}^{S_2}\bar{\beta}_{ji}^{-}X_j, \quad i = 1, ..., \bar{R} \tag{B.3}$$

where

$$\bar{\kappa}_i^{\pm}(E) = \bar{k}_i^{\pm}(E)\left\{\prod_{j=1}^{S_1}\left[\frac{S_j(S_j-1)\cdots(S_j-\bar{\alpha}_{ji}^{\pm}+1)}{V^{\bar{\alpha}_{ji}^{\pm}}}\right]\right\} \tag{B.4}$$

are reduced electrochemical rate coefficients.

We can derive a compound master equation that includes the contribution of the reduced chemical and electrochemical processes (eqs A.2 and B.3, respectively). We can express the concentration vector $\mathbf{x}(t)$ in terms of the reaction extent vectors ξ and η attached to the reduced reactions A.2 and B.3, respectively. We have

$$\mathbf{x}(t) = \mathbf{x}(0) + \mathbf{F}\xi + \bar{\mathbf{F}}\eta \tag{B.5}$$

where $\mathbf{F} = [\beta_{ji}^- - \beta_{ji}^+]$ and $\bar{\mathbf{F}} = [\bar{\beta}_{ji}^- - \bar{\beta}_{ji}^+]$.

By following the procedure presented in Appendix A, in the thermodynamic limit, we can reduce the determination of the stochastic potential to the evaluation of the stationary solution of a Hamilton−Jacobi equation. We have

$$P = \text{const} \times \exp[VJ(\xi,\eta;t)] \tag{B.6}$$

where the action function $J(\xi,\eta;t)$ is the solution of a Hamilton−Jacobi equation similar to eq A.12

$$\frac{\partial}{\partial t}J(\xi,\eta;t) + H[\xi,\eta,\nabla_\xi J(\xi,\eta;t),\nabla_\eta J(\xi,\eta;t)] = 0 \tag{B.7}$$

where the Hamiltonan function

$$H[\xi,\eta,\mathbf{p},\mathbf{q}] = H_{\text{chem}}[\xi,\eta,\mathbf{p}] + H_{\text{electro}}[\xi,\eta,\mathbf{q}] \tag{B.8}$$

is made up of a chemical term

$$\begin{aligned} H_{\text{chem}}[\xi,\eta,\mathbf{p}] &= \sum_i H_{\text{chem}}^{(i)}[\xi,\eta,p_i] \\ &= \sum_i [1-\exp(-p_i)]r_i^+(\xi,\eta) + \\ &\qquad [1-\exp(p_i)]r_i^-(\xi,\eta) \end{aligned} \tag{B.9}$$

which expresses the contribution of the reduced chemical reactions in eq A.2, and an electrochemical term

$$\begin{aligned} H_{\text{electro}}[\xi,\eta,\mathbf{q}] &= \sum_i H_{\text{electro}}^{(i)}[\xi,\eta,q_i] \\ &= \sum_i \frac{\mathcal{N}}{\bar{\nu}_i\mathcal{F}}\{[1-\exp(-q_i)]j_i^+(\xi,\eta;E) + \\ &\qquad [1-\exp(q_i)]j_i^-(\xi,\eta;E)\} \end{aligned} \tag{B.10}$$

which expresses the contribution of the reduced electrochemical reactions B.3. Here, $\mathbf{q} = [q_i]$ is the impulse vector conjugate to the electrochemical extent vector η; $j_i^+(\xi,\eta;E)$ and $j_i^-(\xi,\eta;E)$ are the electrical currents generated by the forward and backward *i*th electrochemical reduced reaction in eq B.3, respectively, expressed as functions of the extent vectors ξ and η and of the potential difference E; $\mathcal{N}$ is Avogadro's number; and the other symbols have the same significance as before.

In this paper, we are mainly interested in the stationary solutions $J = J(\xi,\eta;t)$ of the compound Hamilton−Jacobi equation (eq B.7). These stationary solutions are related to the stochastic potential Φ by a relation similar to eq A.11, introduced in Appendix A for chemical systems

$$J(\xi,\eta) = -\Phi/RTV \tag{B.11}$$

For a stochastic stationary regime, the Hamilton−Jacobi equation becomes

$$\sum_i H_{\text{chem}}^{(i)}\left[\xi,\eta,\frac{\partial J}{\partial \xi_i}\right] + \sum_i H_{\text{electro}}^{(i)}\left[\xi,\eta,\frac{\partial J}{\partial \eta_i}\right] = 0 \tag{B.12}$$

We first consider the particular case where the reduced electrochemical reactions in eqs B.3 are in detailed balance, even though the reduced chemical reaction might be far from detailed balance. From the theory of chemical Hamilton−Jacobi equations,[19] it follows that, under these circumstances, each term of the electrochemical part of eq B.12 is equal to 0

$$H_{\text{electro}}^{(i)}\left[\xi,\eta,\frac{\partial J}{\partial \eta_i}\right] = 0, \quad i = 1, 2, ... \tag{B.13}$$

Equations B.13 are quadratic equations in $\exp(\partial J/\partial\eta_i)$; by solving these equations and keeping the physically significant roots, we find

$$\frac{\partial}{\partial \eta_i}J = \ln\left(\frac{j_i^+}{j_i^-}\right) = \Gamma_i - \bar{\nu}_i f E, \quad i = 1, 2, ... \tag{B.14}$$

where K_i^{eq} is the apparent chemical equilibrium constant of the *i*th reduced electrochemical process, C_{X_j} is the concentration of the species X_j, and

$$\Gamma_i = \ln\left(\frac{K_i^{\text{eq}}}{\prod_j (C_{X_j})^{\bar{\beta}_{ji}^- - \bar{\beta}_{ji}^+}}\right) \tag{B.15}$$

We express the chemical action as the sum of a term independent of the potential difference E, $J(0)$, and an E-dependent term, $\Delta J(E)$

$$J = J(0) + \Delta J(E) \tag{B.16}$$

By assuming the validity of eqs B.14, we have

$$\frac{\partial}{\partial \eta_i}\Delta J(E) = \Gamma_i - \bar{\nu}_i f E \tag{B.17}$$

which shows that, for electrochemical systems at detailed balance, $\Delta J(E)$ is a linear function of the potential difference E, which is consistent with what is known from equilibrium studies. To calculate the stochastic potential Φ, we have to pass from reaction extents to concentrations. By expressing eqs B.17 in terms of concentrations, we obtain a set of expressions for $(\partial\Delta J/\partial C_{X_j}) = \chi_j$ that fulfill the Schwartz condition, $\partial\chi_j/\partial C_{X_u} = \partial\chi_u/\partial C_{X_j}$. It follows that eqs B.17 can be used to construct the component $\Delta J(E)$ starting from eq B.16 (for details, see ref 19). After standard but lengthy computations, we have

$$\Delta J(E) = \Delta J(0) + fE\mathcal{F}\sum_j z_j C_{X_j} + \text{const} \tag{B.18}$$

where z_j is the charge number of species X_j. By combining eqs

B.11, B.16, and B.18, we obtain

$$\Phi = \Phi(E{=}0) - VE\mathscr{F}\sum_j z_j C_{X_j} - VRT \times \text{const} \qquad \text{(B.19)}$$

where

$$\Phi(E{=}0) = -VRT[J(0) + \Delta J(0)] \qquad \text{(B.20)}$$

is the stochastic potential in the case where the difference of electrical potentials is equal to 0. Because the electrochemical reactions do not take place for $E = 0$, we have

$$\Phi_c = \Phi(E{=}0) = -VRT[J(0) + \Delta J(0)] \qquad \text{(B.21)}$$

and thus, eq B.19 justifies the conjecture made in section III (eqs 13 and 14).

Rigorously speaking, eq 19 is valid only if the electrochemical reactions are at detailed balance. However, it can be used as an approximation for other systems for which the detailed balance does not hold. For a system that is not at detailed balance, eqs B.13 become

$$H^{(i)}_{\text{electro}}\left[\xi,\eta,\frac{\partial J}{\partial \eta_i}\right] = \mathscr{R}^{(i)}_{\text{electro}}, \quad i = 1, 2, ... \qquad \text{(B.22)}$$

where $\mathscr{R}^{(i)}_{\text{electro}}$, $i = 1, 2, ...$, represents the components of the action flux vector.[19] $\mathscr{R}^{(i)}_{\text{electro}}$ is a measure of the departure of the ith electrochemical reaction from detailed balance; in particular, at detailed balance, $\mathscr{R}^{(i)}_{\text{electro}} = 0$. We solve eqs B.22 for $\partial J/\partial \eta_i$, resulting in

$$\frac{\partial}{\partial \eta_i}J = \Gamma_i - \bar{\nu}_i fE + \ln\left\{\frac{1}{2}[1 + e^{-(\Gamma_i - \bar{\nu}_i fE)} - \sqrt{(1 - e^{-(\Gamma_i - \bar{\nu}_i fE)})^2 - 4\sigma_i e^{-2(\Gamma_i - \bar{\nu}_i fE)}}]\right\} \qquad \text{(B.23)}$$

where we take

$$\sigma_i = \mathscr{R}^{(i)}_{\text{electro}}/j_i^- \qquad \text{(B.24)}$$

as a relative measure of the departure of the ith electrochemical reaction from detailed balance. We define the percent error in the evaluation of partial derivatives

$$\mathscr{E}(\%) = 100\left[\frac{(\partial J/\partial \eta_i)_{\text{no det bal}} - (\partial J/\partial \eta_i)_{\text{det bal}}}{(\partial J/\partial \eta_i)_{\text{no det bal}}}\right] \qquad \text{(B.25)}$$

where $(\partial J/\partial \eta_i)_{\text{det bal}}$ and $(\partial J/\partial \eta_i)_{\text{no det bal}}$ are the values of the partial derivative at detailed balance and away from detailed balance, respectively. The percent error depends on only two variables: the relative measure σ_i of the deviation of electrochemical reaction i from detailed balance and the additional variable

$$\epsilon_i = \Gamma_i - \bar{\nu}_i fE \qquad \text{(B.26)}$$

For small values of ϵ_i, $\epsilon_i \approx 0$, the values of the derivatives $(\partial J/\partial \eta_i)_{\text{no det bal}}$ are close to the values of the derivatives computed by assuming the validity of detailed balance, $(\partial J/\partial \eta_i)_{\text{det bal}}$, that is

$$(\partial J/\partial \eta_i)_{\text{no det bal}} \approx (\partial J/\partial \eta_i)_{\text{det bal}} \text{ as } \epsilon_i \approx 0 \qquad \text{(B.27)}$$

For $\epsilon_i \approx 0$, $\mathscr{E}_i(\%)$ is relatively insensitive with respect to the value of the deviation σ_i from detailed balance (see Figure 2). For large values of ϵ_i, however, the error $\mathscr{E}_i(\%)$ is strongly dependent on the deviation σ_i from detailed balance and $|\mathscr{E}_i(\%)|$ becomes larger and larger as $|\sigma_i|$ increases. The deviation σ_i can take any real value between $-\infty$ and $^1/_4$. As σ_i decreases, for values of ϵ_i close to 0, the error is limited to about 8%, provided that σ_i is larger than -100. Figure 2 shows the dependence of $\mathscr{E}_i(\%)$ on σ_i for $\epsilon_i = -0.51$ and $\epsilon_i = 0.51$ (see below) in the region where the approximation developed in section III is reasonable.

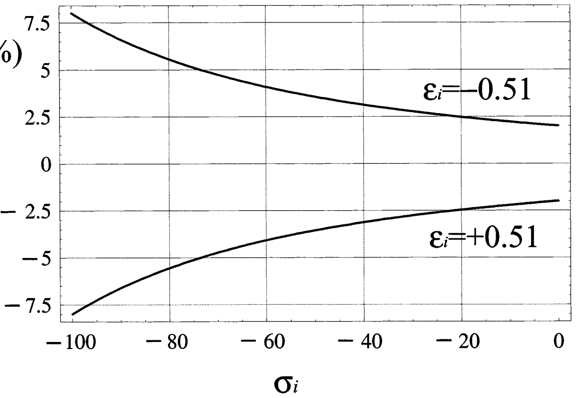

Figure 2. Graphical representation of the relative error $\mathscr{E}_i(\%)$ vs the relative deviation from detailed balance, σ_i, for $\epsilon_i = \pm 0.51$. The value $\epsilon_i = -0.51$ corresponds to the maximum deviation of the electromotive force from the equilibrium Nernstian value for the minimal bromate oscillator (ref 12).

The above analysis shows that the linear expression B.19 for the stochastic potential might hold approximately even for systems away from detailed balance, provided that the variable ϵ_i is close to 0, that is

$$\epsilon_i = \Gamma_i - \bar{\nu}_i fE \approx 0 \qquad \text{(B.28)}$$

To clarify the physical meaning of eq B.28, we recall that the reaction affinity of the reduced electrochemical reaction i is

$$\mathscr{A}_i = RT \ln\left(\frac{K_i^{\text{eq}}}{\prod_j (C_{X_j})^{\bar{\beta}_{ji}^- - \bar{\beta}_{ji}^+}}\right) \qquad \text{(B.29)}$$

By using eqs B.15 and B.28, we can rewrite the condition in eq B.28 in the form

$$\mathscr{A}_i \approx \bar{\nu}_i \mathscr{F}E \qquad \text{(B.30)}$$

which is essentially the Nernst equation for the electromotive force applied to the reduced electrochemical reaction i. Experimental studies have shown that, for nonequilibrium systems, there are deviations from the Nernst equation. However, these deviations are small, which justifies the use of the conjecture made in section III.

To evaluate the validity range of the method suggested in section III, we must establish a correspondence between the value of the parameter σ_i and the order of magnitude of the deviation from the stationary state. A crude estimation of the correspondence between σ_i and the deviation from the stationary state can be made by assuming a single couple of forward and backward electrochemical reactions and considering that the action J is approximately a biquadratic function

$$J \approx b(\eta - \langle\eta\rangle)^2 + c(\eta - \langle\eta\rangle)^4, \quad \text{with } b \approx V^2 \text{ and } c \approx V^4 \qquad \text{(B.31)}$$

where η is the reaction extent of the electrochemical process. By using eq 31, we can obtain a rough estimate of the deviation

$\delta\eta = \eta - \langle\eta\rangle$ corresponding to the extremum value of σ_i, $\sigma_i \approx -100$ for which the approximation developed in section III is reasonable. For $c/b^2 \approx 0.2$, $\langle\Delta\eta^2\rangle \approx 1/(2b^2)$, we have $\delta\eta(-100) \approx \pm 0.4\sqrt{\Delta\eta^2}$.

We illustrate our approach by considering the experimental data on the non-Nernstian potential measured for the minimal bromate oscillator.[12] The largest deviation from the Nernst potential reported in ref 12 is $\Delta E = E - E_{\text{Nernst}} = 13$ mV. It is easy to relate this difference to the value of the parameter ϵ_i. From eqs B.26 and B.29, we can compute the non-Nernstian potential, E, as a function of the parameter ϵ_i

$$E = \frac{\mathcal{A}_i - \epsilon_i RT}{\bar{\nu}_i \mathcal{F}} \tag{B.32}$$

Because the Nernst potential is given by

$$E_{\text{Nernst}} = \mathcal{A}_i/(\bar{\nu}_i \mathcal{F}) \tag{B.33}$$

it follows that ΔE is proportional to ϵ_i

$$\Delta E = E - E_{\text{Nernst}} = -\epsilon_i RT/\bar{\nu}_i \mathcal{F} \tag{B.34}$$

In the particular case of the experiments reported in ref 12, we have $RT/\bar{\nu}_i\mathcal{F} = 25.37$ mV and the deviation $\Delta E = 13$ mV corresponds to $\epsilon_i = -0.51$. According to Figure 2, for $\epsilon_i = -0.51$, the error in evaluating the partial derivative of the stochastic potential with respect to the reaction extent η is less than 8%.

In conclusion, the approach presented in this appendix suggests that, close to a steady state, the deviation from the assumption made in section III is generally small, even for systems away from detailed balance. In particular, for the experimental data reported in ref 12, this deviation is less than 8%. We emphasize that, although useful, our analysis is limited because it involves the derivatives of the stochastic potential, not the stochastic potential itself. The main advantage of our approach is its simplicity: it is a local method that does not involve the numerical solution of the Hamilton−Jacobi equation. A complete solution to the problem should be based on a global approach, which must involve the solution of the Hamilton−Jacobi equation. Such a solution must be based on the approach presented in Appendix A.

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