

Kinetic and Thermodynamic Information Derived from Electrochemical Measurements on Stationary States

Allen Hjelmfelt and John Ross*

Department of Chemistry, Stanford University, Stanford, California 94305-5080

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Experiments are reported on the electrochemical displacement of the nonlinear minimum bromate reaction from stationary states far from equilibrium and from equilibrium. We measure the $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ electrode potential V at a given displacement effected by an imposed current clamp, I . The variation of the excess power $(V - V_s)I$, where V_s is the electrode potential at a stationary state, versus the imposed current is of the same form as the time derivative of an excess work, related in prior theoretical analyses to the thermodynamics of systems far from equilibrium.

We study the electrochemical displacement of a nonlinear reaction system from nonequilibrium stationary states and from equilibrium. Consider a chemical reaction run in an open system. If there is a redox couple that interacts with an electrode, then we can use this electrode to measure the redox potential by allowing the couple to equilibrate with the electrode. This potential is measured versus a reference potential generated by a reference reaction. In this measurement zero current flows between the working and reference electrodes. We can measure the potential whether the overall chemical reaction run in the open system is in equilibrium or not, if the redox couple equilibrates with the electrode [i.e., the equilibration with the electrode is fast compared to other processes.]

We can use another electrode to displace the concentrations of the redox couple from their autonomous states. In this experiment a nonzero current flows between the working and counter electrodes. We can displace the concentrations of the redox couple whether the overall chemical reaction run in the open system is in equilibrium or not. The redox couple will not be in equilibrium with the working electrode, and the difference may be expressed in terms of overvoltages.

From the measurements of applied currents and potentials of the redox couple we can calculate an excess power. This quantity plays a central role in the thermodynamic theory developed and tested in refs 1–15 (see Discussion).

In this article we report on electrochemical measurements on the nonlinear multivariable minimum bromate reaction in an open, isothermal reactor. We measure the $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ electrode potential at an electrode in equilibrium with the reacting solution first in a stationary state, which may be at equilibrium or at nonequilibrium. Then we impose a current clamp of a given current I at a different working electrode, which displaces the system from its autonomous stationary state (no current clamp) to a new stationary state, with a different $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ ratio and hence a voltage difference V different from that in the autonomous stationary state, V_s ; we measure that new voltage. If the current clamp is removed, then the system relaxes back to its autonomous stationary state.

From these measurements we find that a plot of the excess power $(V - V_s)I$, necessary to sustain the nonequilibrium state with a current clamp, versus the imposed current is of

the expected form for the overall reaction at equilibrium: it shows the extremum at equilibrium (zero current clamp) and the decrease on either side of equilibrium with increasing and decreasing imposed currents. The excess work for that case reduces to the Gibbs (at constant T, p) or Helmholtz (at constant T, V) free energy change for the displacement.

For the imposition of a current clamp on a stationary state other than equilibrium, a plot of the excess power $(V - V_s)I$ vs the imposed current clamp, with both positive and negative current clamps, is similar to that at equilibrium: there is an extremum at the stationary state with zero current clamp and a decrease on either side of the extremum with increasing and decreasing currents. This plot for stationary states is significantly flatter for those away from equilibrium than that for equilibrium. Thus, in this system stationary states away from equilibrium seem to respond less to external forcing (imposed current) than the equilibrium state, and we see an interesting buffering effect.

The measurements reported here are the first step on electrochemical experiments on and near a stable stationary state. The interpretation of such experiments will be given in a following article and requires more information than obtained here. Nonetheless, we show here that our measurements are related to the time derivative of an excess work, which is a Liapunov function (an evolution criterion in time) for the deterministic kinetics of the transient relaxation to a stationary state.

Chemical System

For our experiments we use the minimal bromate oscillatory^{16,17} (MBO) in the bistable regime in which its deterministic kinetics has third-order terms. The reaction, which is the inorganic skeleton of the Belousov–Zhabotinsky reaction, is the oxidation by bromate ions of Ce^{III} to Ce^{IV} . The NFT¹⁸ mechanism for this reaction consists of seven elementary steps with the species Br , Br_2 , HBrO_2 , HOBr , BrO_2 , Ce^{III} , Ce^{IV} , and BrO_3 .

Experimental Section

A schematic drawing of the apparatus is shown in Figure 1. The left vessel is a continuous stirred tank reactor (CSTR), volume 30 mL, an open system equipped with two inlet flows and one outlet flow (aspirated). The CSTR has indentations to improve mixing and is stirred at 250 ± 10 rpm with a 2 cm

* To whom correspondence should be addressed.

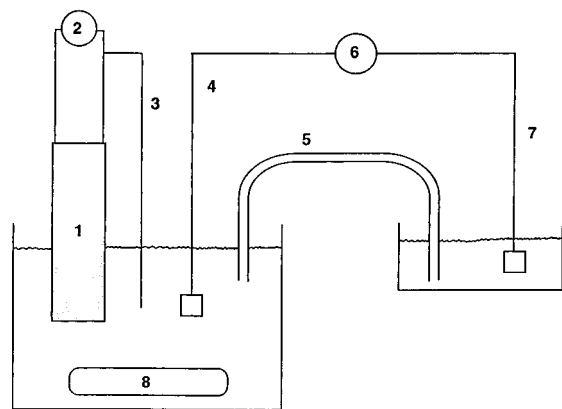


Figure 1. Schematic drawing of apparatus: 1, combination electrode Pt, Ag–AgCl; 2, voltmeter; 3, Br^- electrode; 4, Pt electrode; 5, salt bridge; 6, constant current source; 7, Pt electrode; 8, stirrer bar. The inlet flow and aspiration outlet on the CSTR (left vessel) are not shown.

Teflon stir bar. Variations in stirring rates of ± 30 rpm produce no change in the measurements. The CSTR is connected to an H_2SO_4 cell by an H_2SO_4 bridge, with the same concentration of H_2SO_4 as that in the MBO reaction. Both vessels are thermostated at 25°C . Large area (6.25 cm^2) Pt electrodes are placed in the CSTR and the H_2SO_4 cell, and between these electrodes a current may be imposed. These electrodes, at which there exist overvoltages, are used to displace electrochemically the MBO reaction from its autonomous steady state. Also placed in the CSTR is a combination Pt–Ag/AgCl electrode (Orion) which is electrically isolated from the two large area Pt electrodes. This combination electrode is used to measure the potential of the $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ redox couple; no overvoltage is present at this electrode which is in equilibrium with the reacting solution. We may relate the potential of the $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ electrode to cerium concentrations by means of the Nernst equation, which applies approximately (better than 1% error);¹⁹ however, that relation is not used in the interpretation of the results. A Br^- -specific electrode (Orion) is also placed in the CSTR; we do not use its measurements for the thermodynamic calculations.

To run the MBO reaction at a nonequilibrium steady state, the contents of the three reservoirs are pumped separately into the CSTR by a three-channel peristaltic pump (Ismatec model 7919-30); see ref 19. The three reservoirs contain $0.00450\text{ M Ce}^{\text{III}}$, 0.0100 M BrO_2^- , and $1.00 \times 10^{-6}\text{ M Br}^-$ (to obtain inlet reactor concentrations divide by 3). Additionally, each reservoir contains $0.72\text{ M H}_2\text{SO}_4$. To run the reaction at equilibrium, the contents of the three reservoirs are mixed and allowed to react for at least 1 day. The mixture is pumped into the CSTR to create an equilibrium steady state. The H_2SO_4 bridge and the H_2SO_4 cell also contain $0.72\text{ M H}_2\text{SO}_4$. The readings from the Pt–Ag/AgCl electrode may be used to determine the Ce^{III} concentrations in the CSTR with the use of a prior calibration. The calibration is established by measuring the potential developed by at least five solutions with different ratios of $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$. (The total cerium concentration was 0.0015 M ; see ref 19.) These calibration points are then used to determine experimentally the slope and intercept of the Nernst equation. These values are not used for thermodynamic calculations but do indicate the monotonicity of the change of the Ce^{III} concentrations as the current is applied. Additionally, Ce^{IV} appears yellow in the solution, and visual inspection can be used to verify the existence of high concentrations of Ce^{IV} on the thermodynamic branch.

With no current imposed on the system, and the chosen inflow conditions, we wait for transients to disappear (about 20 min)

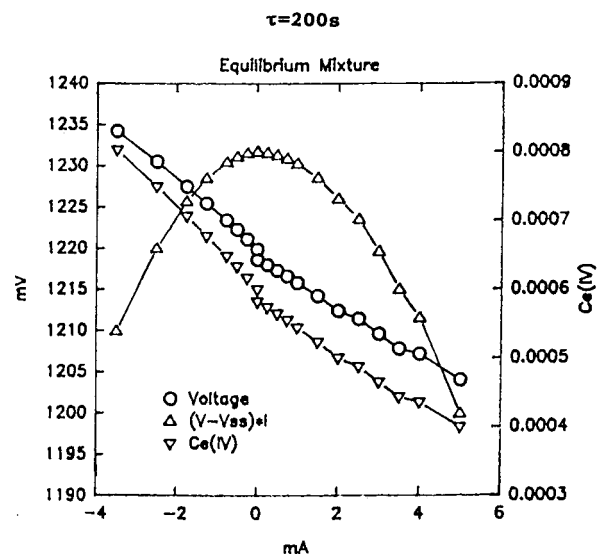


Figure 2. Plot of voltage (scale on left ordinate) as measured on voltmeter, numbered 2 in Figure 1, vs imposed current; plot of calculated Ce^{IV} concentration (scale on right ordinate) vs imposed current; and plot of the excess power $(V - V_s)I$, the measured voltage for a given imposed current minus the measured voltage with zero imposed current, all times the current I , vs imposed current, no ordinate scale shown. The residence time in the CSTR is $\tau = 200\text{ s}$. The stationary state with zero imposed current is the equilibrium state.

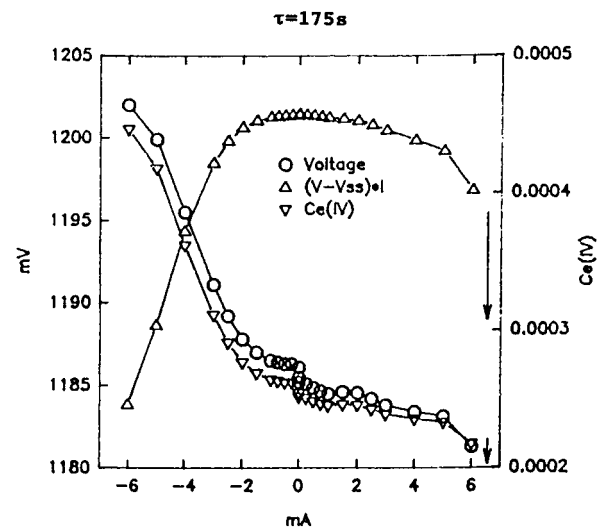


Figure 3. Same plots as in Figure 2. The residence time is $\tau = 175\text{ s}$. In this and the following like figures the stationary state with zero imposed current is a far from the equilibrium state. The arrows indicate transitions to the other stable stationary state.

and for the attainment of a stationary state. In that state we measure the voltage V_s between a platinum electrode and a silver–silver chloride electrode; see item 1 in Figure 1. Then we impose a given current (PAR model 173) between two platinum electrodes, one in the CSTR (4) and the other in the other vessel, (7) (Figure 1); again, we wait for the attainment of a stationary state and measure the voltage V in the stationary state. The last measurement is repeated for the same inlet flow conditions for a number of positive and negative currents. Then this procedure is repeated for several different inlet flow conditions (several different stationary states of the system with zero imposed current).

Representative results are shown in Figures 2–6. The reproducibility of the measurements in these figures is judged to be about 0.2%.

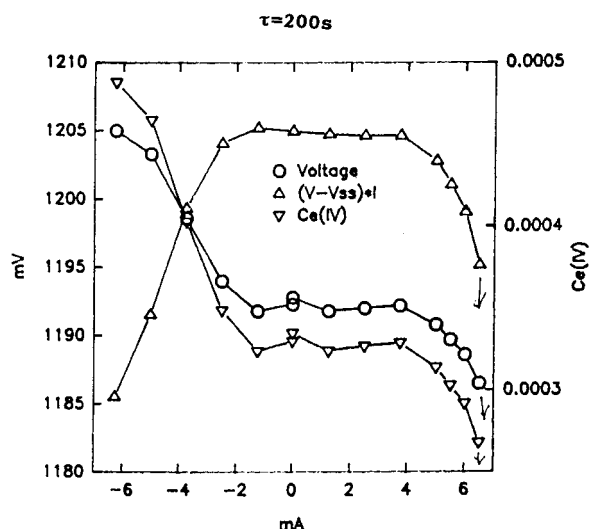


Figure 4. Same plots as in Figure 3. The residence time is $\tau = 200$ s.

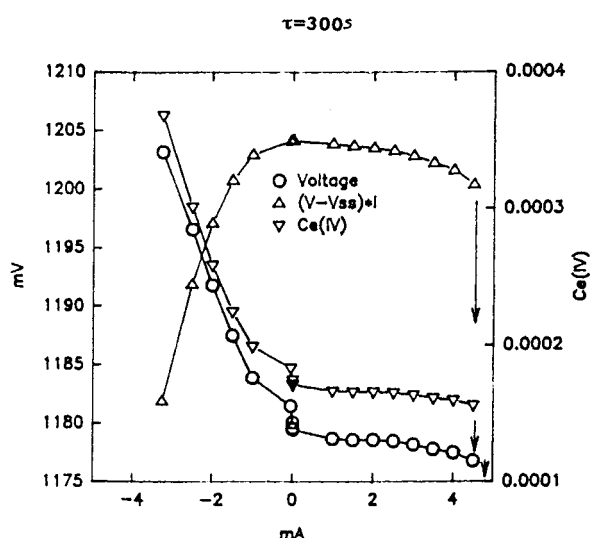


Figure 5. Same plots as in Figure 3. The residence time is $\tau = 300$ s.

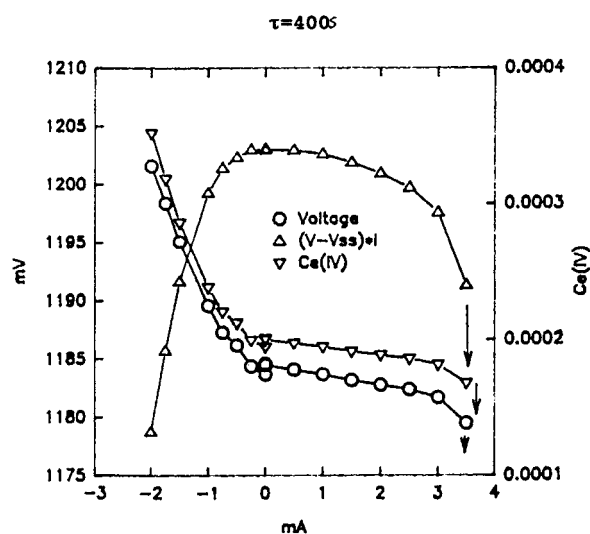


Figure 6. Same plots as in Figure 3. The residence time is $\tau = 400$ s.

Discussion of Results

As far as we are aware, these are the first measurements on the electrochemical displacement of a system from a stationary, nonequilibrium state. Of particular interest in Figures 2–6 are

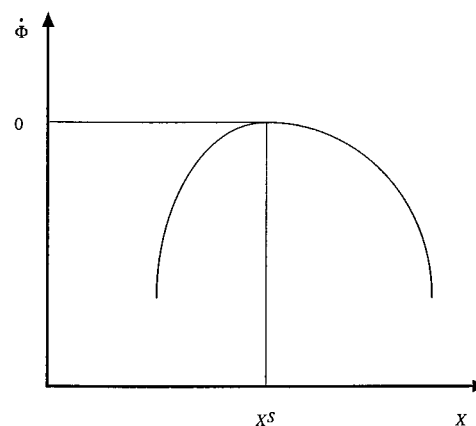


Figure 7. Schematic drawing of the time derivative of the excess work vs X ; see eq 2 for a one-dimensional linear system.

the plots of $(V - V_s)I$ vs imposed current I . The product $(V - V_s)I$ is an excess power, necessary to be expanded to maintain the system away from either a stationary nonequilibrium state or the equilibrium state.

In a series of prior articles we have formulated a thermodynamic^{1–9} and connected stochastic^{1–13} theory for linear and nonlinear chemical and physical systems far from thermodynamic equilibrium. We have treated single-variable¹ and multi-variable² chemical systems with single or multiple stationary states,^{4,8,9} single⁵ and coupled¹³ physical transport properties, and a simple hydrodynamic⁷ system and have connected light scattering experiments on fluids in a thermal gradient to the thermodynamic formulation.¹³ The theory is based on the concept of an excess work which is an extremum at a stationary state and serves as a Liapunov function for the deterministic approach to stationary states. The excess work is proportional to a thermodynamic action; both are state functions that provide a solution for the stationary probability density of a master equation in the eikonal approximation. Further, the excess work is a measure of relative stability in systems with multiple stationary states, and that concept has been tested in experiments on single¹⁴ and multiple¹⁵ variable systems. Keizer²⁰ has developed a stochastic theory of fluctuations around nonequilibrium stationary states restricted to the region of linearized kinetics. The theory presented in refs 1–13 is not thus restricted but agrees with Keizer's approach in the linearized region.

The measurements made so far are insufficient for a detailed comparison with theory and calculations made with a model of the MBO reaction. However, a qualitative comparison even with just a one-dimensional linear reaction system is instructive. For a one-dimensional linear system with concentration variable X , the excess work is defined as⁸

$$\phi = \int (\mu_x - \mu_x^s) dX \quad (1)$$

and hence

$$\dot{\phi} = (\mu_x - \mu_x^s)\dot{X} \quad (2)$$

or, with the use of Nernst's equation,

$$\dot{\phi} = -(V - V_s)I \quad (3)$$

A schematic plot of $\dot{\phi}$ vs X is shown in Figure 7; X is a measure of the displacement of the system from a stationary state X_s . Since ϕ is always positive or zero and $\dot{\phi}$ is always negative, we

see that ϕ is a Liapunov function. The plots in Figures 2–6 of $(V - V_s)I$ vs I for the experimental systems are of the same qualitative form as those of $\dot{\phi}$ vs X , and hence the quantity

$$\int (V - V_s)I \, dt \quad (4)$$

is a Liapunov function.

A comparison is interesting of the measurements plotted as power necessary to sustain a displacement of the system from its autonomous stationary state vs imposed current clamp for the autonomous system initially in equilibrium (Figure 2) and the autonomous system initially in a stationary state far from equilibrium, say Figure 5. The current clamps necessary to obtain a given change in voltage, $V - V_s$, from that in the stationary state, V_s , is significantly larger for nonequilibrium stationary states than for the system at equilibrium. Hence, we may say that in this system in nonequilibrium stationary states voltage differences are buffered to imposed current changes. Since this is a first observation, we do not know whether such buffering occurs in other systems, nor do we have a theoretical basis for this effect.

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