Relaxation behavior in a bistable chemical system. Plateau behavior

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The relaxation behavior of the bistable iodate-arsenous acid reaction near a hysteresis limit has been investigated. Outside the bistability region, relaxations to the unique stable steady state may exhibit a plateau in concentration as a function of time, corresponding to a local minimum in rate of reaction. Very close to the saddle-node bifurcation defining the bistability limit, the relaxing system remains in the plateau for long periods of time. Experimental measurements of plateau behavior are compared to behavior predicted by a one-variable model of the iodate-arsenous acid system.

I. INTRODUCTION

A qualitative change in dynamic behavior occurs when a system undergoes a bifurcation. In anticipation of the bifurcation, the quantitative features of the system may also undergo dramatic change. For example, as the saddle-node bifurcation point corresponding to a hysteresis limit of a bistable system is approached, relaxations to the steady state about to lose its stability require longer and longer times. The apparent divergence of relaxation time, known as "critical slowing down," has been characterized in a number of bistable chemical systems.1-5

The iodate oxidation of arsenous acid is a useful model system for detailed studies of the bistability phenomenon. Although the mechanism of the reaction in terms of elementary steps is somewhat complicated,6 it can be accurately described in terms of a simple empirical rate law model. A four-variable model based on a component process description was developed by De Kepper, Kustin, and Epstein7 for the buffered reaction in a CSTR. Rate and conservation considerations allow a reduction of this model to a description in terms of a single variable for reactions with arsenous acid in stoichiometric excess.2,4,8-10 A two-variable model describes the system when the conservation conditions no longer apply.1,2,10

Using the one-variable model, Dewel et al.11,12 studied the relaxation behavior of the system in terms of an analytical relaxation function. In addition to critical slowing down, they found anomalous behavior beyond the hysteresis limits defining the region of bistability. Outside the bistability region, relaxations to the unique steady state may exhibit "plateau behavior," where the rate passes through a local minimum. Plateau behavior in an illuminated thermochemical system (o-cresolphthealine) has been studied by Kramer and Ross3 and retarded ignitions near a saddle-node bifurcation point in a nonisothermal system have been theoretically investigated by Gray and Kordylewski.13

In this paper, we report on experimental measurements of plateau behavior in the CSTR iodate-arsenous acid system. Relaxations to the flow branch steady state were monitored just beyond the saddle-node bifurcation point defining the upper bistability limit (high flow rate, low residence time). The general features of the iodate-arsenous acid system in terms of the one-variable model are described in Sec. II, and the experimental procedures and results are described in Sec. III. The experimental behavior is compared with that predicted by the one-variable model of the system in Sec. IV, and in Sec. V plateau behavior is compared to other types of critical behavior.

II. IODATE-ARSENOUS ACID SYSTEM

We consider reaction mixtures with arsenous acid in stoichiometric excess, described by the net reaction

\[
\text{IO}_3^- + 3\text{H}_2\text{AsO}_3 = \text{I}^- + 3\text{H}_3\text{AsO}_4. \tag{1}
\]

Providing there is no input into the CSTR other than the reactant flow stream, the dynamics of the system are governed by the one-variable differential equation

\[
\frac{dX}{dt} = (k_u + k_o)(S_0 - X)X + k_o(X_0 - X), \tag{2}
\]

where \(X = [\text{I}^-], X_0\) and \(B_0\) are the feedstream concentrations of iodide and iodate with \(S_0 = X_0 + B_0, k_o\) is the reciprocal residence time, and \(k_u\) and \(k_o\) are rate constants.4,8,10 This one-variable description is based on the assumption that \(\text{I}^-\) and \(\text{IO}_3^-\) are the only stoichiometrically significant iodine containing species, which is valid provided that the concentration of \(\text{H}_2\text{AsO}_3\) is sufficiently in stoichiometric excess.14 The description also requires that hydrogen ion concentration be maintained constant by buffering the reaction mixture.

The steady states of the system, defined by the condition \(dX/dt = 0\), are given by the resulting cubic equation in \(X\). The three roots fall into two categories depending on the values of the constraints. The roots may be positive and real, with two corresponding to stable steady states and one to an unstable steady state. At other values of the constraints, one root is positive real and the other two complex conjugates; the system now has only one stable steady state. For particular values of \(k_u, k_o, \) and \(B_0\), bistability occurs only when \(X_0 < X_c, \) when \(X_0 > X_c, \) the system is monostable for all values
of \(k_0\). Here, \(X'_0\) represents the critical iodide concentration, or critical isocron, separating the two types of behavior. Shown in Fig. 1 are the steady states calculated from Eq. (2) for a particular \(X_0 < X'_0\). The solid curves show the stable steady states and the dashed curve shows the unstable steady state. The real and imaginary parts of the complex roots above the upper limit of the bistability region are indicated by the solid and open circles. Complex roots (not shown) also emanate from the lower limit of the bistability region. The solid triangles show inflection points in the relaxation curves, discussed below.

### III. EXPERIMENTAL RESULTS

#### A. Procedure

A description of the experimental apparatus and procedures has appeared elsewhere. In this work, two reagent solutions were pumped into the CSTR, one containing io
date in a sulfate/bisulfate buffer and the other containing arsenous acid and iodide in the same buffer. Two peristaltic pumps were used, allowing the flow rate of each stream to be independently adjusted. The flow rate of each stream was measured by a volume flow meter before and after each relaxation experiment. A single set of reactant concentrations, given in Table I, was used in all the experiments. Each experiment was initiated by stopping the flow and allowing the reaction to reach equilibrium as a closed system. The pumps were then switched on with the desired flow rates preset and the relaxation of the system to the stable steady state was monitored with an iodide selective electrode.

#### B. Relaxation experiments

Relaxations from an initial state corresponding to the equilibrium composition to a final state corresponding to the flow branch steady state are shown in Fig. 2 for seven values of reciprocal residence time. The overall relaxation time significantly increases as the hysteresis limit is approached. When \(k_0\) is close to \(k'_0\), the reciprocal residence time corresponding to the upper hysteresis limit, the system lingers at an iodide concentration close to that of the upper branch of steady states in the bistable region (see Fig. 1).

Examination of the relaxation curves in Fig. 2 shows that the plateau is characterized by an inflection point corresponding to a local minimum in rate. Plots of rate as a function of time, obtained from successive concentration differences at 30 s intervals, are shown in Fig. 3. The local minimum and maximum in Fig. 3(a) correspond to the first and second inflection points of curve A in Fig. 2. The extrema move toward each other in the successive curves until they coalesce at a value of \(k_0\) close to that for Fig. 3(f), corresponding to curve F in Fig. 2. Beyond that point, the rate curve is monotonic as in Fig. 3(g). We define plateau behavior by the presence of a local minimum in the relaxation rate.

The behavior in Fig. 2 suggests that the time for complete relaxation diverges as \(k_0\) approaches \(k'_0\). Since the initial state is defined by \(X = S_0\), corresponding to the equilibrium composition, the initial displacement from the steady

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**TABLE I. Experimental conditions, combined reactant stream concentrations and rate constants.**

| \([\text{IO}_3^-]_0\) | \(2.69 \times 10^{-3} \text{ M}\) | \([\text{I}^-]_0\) | \(4.48 \times 10^{-3} \text{ M}\) |
|---------------------|---------------------|---------------------|

\[
\begin{align*}
\text{k}_a &= (4.5 \times 10^3 \text{ M}^{-3} \text{s}^{-1}) \left[\text{H}^+\right]^2 = 1.966 \times 10^{-1} \text{ M}^{-1} \text{s}^{-1} \\
\text{k}_b &= (4.5 \times 10^3 \text{ M}^{-3} \text{s}^{-1}) \left[\text{H}^+\right]^2 = 1.966 \times 10^4 \text{ M}^{-2} \text{s}^{-1} \\
\end{align*}
\]

Acidity maintained constant with sulfate/bisulfate buffer at \(p\text{H} = 2.18\) ([\(\text{H}^+\]) = 6.61 \times 10^{-3} \text{ M}). CSTR volume = 35.2 mL. Temperature = 25.0 \pm 0.1 \text{ °C}.
state $\Delta x_0$ is given by $S_0 - X_0$, where $X_0$ is the steady state iodide concentration. In order to avoid the uncertainty in determining relaxation times that include the asymptotic approach to the stable steady state, we define relaxation time as the time required for the system to relax from the initial state to a state defined by $X = X_0 + 0.01 \Delta x_0$. Thus, the perturbation is allowed to decay to 1% of its initial value, corresponding to a 99% relaxation. Any definition of relaxation time that corresponds to nearly complete relaxation would be equally satisfactory, however, conventional definitions like half-life are unsatisfactory because the major contribution to the relaxation time may not be included.

A plot of relaxation time $\tau$ as a function of the displacement from the hysteresis limit $k^*_a$ is shown in Fig. 4, where $k^*_a = k_a - k_0$. The dependence of $\tau$ on $k^*_a$ is given by

$$\tau = c(k^*_a)^x,$$

where $c$ is a proportionality constant and $x$ is the critical dynamical exponent characterizing the plateau behavior. Equation (3) describes relaxation times within the "plateau region," defined by those relaxations exhibiting a local minimum in rate. A least-squares fit of the straight line defined by a plot of $\ln \tau$ vs $\ln k^*_a$ yields a value of $x = -0.50(\pm 0.09)$. The solid curve in Fig. 4 was calculated from Eq. (3) with this value of $x$ along with the value of $c$ (3.91) obtained from the least-squares fit. Only the first five points were used in the fit because the last two points corresponding to curves $F$ and $G$ in Fig. 1 were outside the plateau region.

**IV. MODELING RESULTS**

**A. Plateau region**

Defining plateau behavior by the presence of a local minimum in rate permits a rigorous description of the plateau region in terms of the one-variable model. Relaxation curves in this region are characterized by two inflection points, one corresponding to the local minimum in rate and the other to the local maximum in rate that occurs as the system leaves the plateau.

The solid triangles in Fig. 1 show the inflection points as a function of $k_0$, calculated from the quadratic equation

$$\frac{d}{dt} \frac{dX}{dt} = -3k_S X^2$$

$$+ (2k_nS_0 - 2k_0)X + k_nS_0 - k_0 = 0. \quad (4)$$

Equation (4) is simply the derivative of rate Eq. (2) with respect to iodide concentration set to zero, giving iodide concentration at the inflection points. The limit of the plateau region occurs when the two inflection points coalesce, at a value of $k_0$ given by

$$k_0 = \frac{1}{3} \left[ \frac{k^2_a}{k_0} + k_nS_0 + k_nS_0^2 \right]. \quad (5)$$

The upper branch of the parabolic curve, which corresponds to the local minimum in rate, intersects the steady state curve at the saddle-node bifurcation point. The plateau region is defined by the $k_0$ values between the knee of the steady-state curve and the coalescence of the inflection points given by Eq. (5).

**B. Relaxation times**

The decay of a perturbation is conveniently described in terms of a Taylor series based on rate Eq. (2). Following the earlier treatment in Ref. 4, we have

$$\frac{d(\Delta x)}{dt} = \lambda (\Delta x) + \frac{1}{2} \mu (\Delta x)^2 + \frac{1}{6} \gamma (\Delta x)^3, \quad (6)$$

where

$$\lambda = -3k_S X^2 + (2k_nS_0 - 2k_0)X + k_nS_0 - k_0,$$

$$\mu = -6k_S X - 2k_nS_0,$$

$$\gamma = -6k_n,$$

and $\Delta x$ is the displacement from the steady state. Integration of Eq. (6) by partial fractions leads to an expression for the relaxation time,
\[
\frac{\mu}{2\lambda \sqrt{\beta}} \left( \tan^{-1} \left( \frac{1}{3} \frac{\gamma \Delta x_0 + \frac{1}{2} \mu}{\sqrt{\beta}} \right) - \tan^{-1} \left( \frac{1}{3} \frac{\gamma \Delta x_0 + \frac{1}{2} \mu}{\sqrt{\beta}} \right) \right)
\]  

(7)

where \( \alpha = 0.01 \), corresponding to 99\% relaxation, and \( \beta = \frac{3 \lambda}{\gamma} - \frac{1}{4} \mu^2 \). Equation (7) with \( \alpha = 0.5 \), corresponding to 50\% relaxation, is the same as Eq. (11) in Ref. 4.

For certain values of the constraints, \( \beta < 0 \) in Eq. (7) and relaxation time must be calculated using an alternate solution of Eq. (6) given by

\[
\tau = \frac{1}{2\lambda} \ln \left( \frac{\alpha^2 - \frac{1}{2} \mu \Delta x_0 + \frac{1}{6} \gamma (\Delta x_0)^2}{\lambda + \frac{1}{2} \mu \Delta x_0 + \frac{1}{6} \gamma (\alpha \Delta x_0)^2} \right) - \frac{\mu}{4\lambda \sqrt{-\beta}} \ln \left( \frac{1}{3} \frac{\gamma \alpha \Delta x_0 + \frac{1}{2} \mu - \sqrt{-\beta}}{\frac{1}{3} \frac{\gamma \alpha \Delta x_0 + \frac{1}{2} \mu + \sqrt{-\beta}}{\sqrt{\beta}} - \tan^{-1} \left( \frac{1}{3} \frac{\gamma \alpha \Delta x_0 + \frac{1}{2} \mu - \sqrt{-\beta}}{\sqrt{\beta}} \right) - \tan^{-1} \left( \frac{1}{3} \frac{\gamma \alpha \Delta x_0 + \frac{1}{2} \mu - \sqrt{-\beta}}{\sqrt{\beta}} \right) \right)
\]  

(8)

Incorporating Eqs. (7) and (8) into a single algorithm allows relaxation times to be easily calculated for any values of the constraints. Equation (7) is adequate for the constraints used here, and a plot of calculated relaxation times as a function of \( k_o^* \) is shown in Fig. 5. The initial state in these calculations was defined as the equilibrium composition as in the experimental measurements. The range of \( k_o^* \) was matched to the experimental range in Fig. 3. While the curves in Figs. 3 and 5 are very similar, they are not in quantitative agreement. The discrepancy results from the slightly different values of \( k_o^* \) determined in the measurements and calculated by Eq. (2). No effort was made to obtain quantitative agreement by adjusting the rate constants. A least-squares fit of \( \ln \tau \) vs \( \ln k_o^* \) for relaxations in the plateau region, corresponding to the upper hysteresis limit and the \( k_0 \) given by Eq. (5), gives a value for the critical exponent \( x = -0.504 \) (±0.002). The relaxation behavior was also computed by simply numerically integrating rate Eq. (2). These calculations resulted in a value for \( x \) of \(-0.504 \) (±0.002), identical to that given by Eq. (7).

V. DISCUSSION

The bistable iodate–arsenous acid system exhibits three types of critical behavior, each characterized by a critical dynamical exponent.\(^4\,11\)\(^1\)\(^2\) The relaxation of a bistable system to a steady state about to lose its stability at a hysteresis limit requires increasingly longer times as the limit is approached. The steady state loses its stability when it coalesces with the unstable steady state, corresponding to a saddle-node bifurcation. This bifurcation is characterized by a vanishing linear stability eigenvalue, given by \( \lambda \) in Eq. (6) for the iodate–arsenous acid system. Because \( -\lambda \) is the pseudo first-order rate constant for the final approach to the steady state, an apparent divergence in relaxation time is exhibited as the eigenvalue approaches zero. The apparent divergent behavior is described by an expression like Eq. (3) with a critical dynamical exponent \( y = -\frac{1}{2} \). The relaxation time at the bifurcation point is finite, however, because the \( \mu \) and \( \gamma \) terms in Eq. (6) become important as \( \lambda \) approaches zero.\(^4\,16\)\(^1\)\(^2\) The final approach to the steady state exactly at the bifurcation point occurs with second-order kinetics. Bistable systems that are described by more than one variable exhibit a similar apparent divergence in relaxation time on approaching the saddle-node bifurcation point because the slowest relaxation process is determined by the vanishing eigenvalue.

As a constraint such as iodide concentration in the reactant feed stream is appropriately varied, the range of the bistability region decreases as the hysteresis limits approach each other. At the critical value \( X_o^* \), the saddle-node bifurcation points coalesce and bistability disappears. In a one-variable system like the iodate–arsenous acid reaction, this point
is analogous to the critical point in the van der Waals description of the liquid–gas phase transition.\textsuperscript{17} It is a codimension-two bifurcation because two constraints, in this case $k_k$ and $X_0$, must be varied to determine it. Both $\lambda$ and $\mu$ in Eq. (6) vanish at this bifurcation point.\textsuperscript{4} The apparent divergence in relaxation time on approaching the codimension-two bifurcation point is described by an expression like Eq. (3) with a critical dynamical exponent $z = -\frac{1}{2}$. Relaxation times remain finite, however, because the $\gamma$ term in Eq. (6) becomes important as $\lambda$ and $\mu$ approach zero.\textsuperscript{4} Exactly at the bifurcation point, relaxations occur with third-order kinetics.

The critical dynamical exponent $x$ in Eq. (3) for relaxations in the plateau region can be deduced by examining limiting cases of the analytical expression for $\tau$ given by Eq. (7). It is convenient to consider the case where $X_0 = 0$ because the reciprocal residence time corresponding to the hysteresis limit can then be described analytically by

$$k_0^* = \frac{1}{4k_k} \left( k_k - k_0 B_0 \right)^2 + k_k B_0.$$  

Writing $\lambda$ in terms of $k_0^*$ with $k_0^*$ defined by Eq. (9) considerably simplifies Eq. (7), since now $\beta = 4k_k k_0^*$. As $k_0^*$ approaches zero, the first term on the right-hand side of Eq. (7) becomes very small. The inverse tangent functions of the dominant second term change very little while the $\mu/2\lambda \sqrt{\beta}$ factor of this term varies as $(k_0^*)^{-1/2}$, in accord with Eq. (3).

At higher values of $k_k$ beyond the plateau region, the relaxation dynamics are determined by washout due to the reagent flow, with

$$\tau \propto (k_0^*)^{-1}.$$  

It should be noted that the dynamical exponent $x$ ranges from $\frac{1}{2}$ close to the hysteresis limit to $1$ at and beyond the coalescence of the inflection points defining the upper limit of the plateau region. The value of $\frac{1}{2}$ occurs in the limit as $k_0^*$ approaches zero. The values obtained by fitting $\ln \tau$ vs $\ln k_0^*$ over the entire plateau range, however, are remarkably close to $\frac{1}{2}$ for both the experimental and calculated relaxation times.

A difference between plateau behavior and the apparent divergent behavior within the bistability region is that as the saddle-node point is approached from outside the bistability region, a true divergence in relaxation time is exhibited. The relaxation curves in Fig. 2 show only a modest increase in overall relaxation time on approaching the hysteresis limit since precise control of the bifurcation parameter $k_k$ is difficult. However, it is easy to determine extremely long relaxation times by numerically integrating Eq. (2) or solving Eq. (7) as a function of $k_0$. For example, $\tau = 3.12 \times 10^4 \text{s}$ when $k_0^* = 2.5 \times 10^{-6} \text{s}^{-1}$, with the iodide concentration changing in the plateau by only about 4% in 5.5 h. The relaxation time continues to increase as $k_0^*$ approaches zero until exactly at the bifurcation point, the system relaxes to the other steady state with second-order kinetics as described above.\textsuperscript{4,16}

The iodate–arsenous acid reaction is a useful model system for examining steady state multiplicity. The behavior of the system is applicable to more complex bistable systems that are less amenable to detailed analysis. In addition, the relaxation behavior near other types of bifurcation points will exhibit similar features. For example, relaxations to a stable steady state on approaching a supercritical Hopf bifurcation will exhibit slowing down as the real part of the complex eigenvalues approaches zero.

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\textsuperscript{1}N. Ganapathisubramanian and K. Showalter, J. Phys. Chem. 87, 1098, 4014 (1983). (The $\gamma$-axis in Fig. 2 of this paper should be labeled $10^{-1}$, not $10^{-1}$).


\textsuperscript{4}N. Ganapathisubramanian and K. Showalter, J. Chem. Phys. 84, 5427 (1986) [Equation (12) in this paper should read $k_0^* = (1/4k_k)(k_k - k_0 B_0)$ + $k_0 B_0$].


\textsuperscript{15}Handbook of Chemistry and Physics, 56th ed. edited by R. C. Weast (CRC, Cleveland, 1975), pp. A119–A120.


\textsuperscript{17}A. Nitzen, P. Ortoleva, J. Deutch, and J. Ross, J. Chem. Phys. 61, 1056 (1974).