Relaxation behavior in a bistable chemical system near the critical point and hysteresis limits

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Relaxation half-times have been measured in the bistable iodate-arsenous acid reaction near a hysteresis limit and the critical point. A one-variable empirical rate law model is used to examine the apparent divergence in the relaxation times at these points. Relaxation behavior vary close to, and exactly at the critical point and hysteresis limits is considered.

I. INTRODUCTION

Multistable systems maintained far from equilibrium by pumping with radiant energy, high energy chemicals, or some other energy source exhibit features reminiscent of the changes of state found in equilibrium systems. As a constraint such as the pumping rate is varied, a multistable system may undergo a transition from one stationary state to another, just as a pure substance may undergo a phase transition upon variation of pressure or temperature. One-variable descriptions of bistability like the Schröd model¹ bear a striking resemblance to the van der Waals description of the gaseous and liquid states of a pure substance. Nonequilibrium "phase transitions" have been investigated from a variety of theoretical viewpoints over the past decade.²⁻⁴

In a bistable system carried out in a continuous flow stirred tank reactor (CSTR), the transition from one steady state to another and the reverse transition occur at different values of the pumping constraint; between these values the system may exist in either state. At a particular value of the constraint in the bistable region, the system remains indefinitely in one of the two possible steady states in the absence of perturbations exceeding some critical magnitude. The threshold for perturbation induced transitions between steady states is readily measured and characterized in simple one- and two-variable systems.⁵ In a system described by one variable, the threshold occurs at the unstable steady state; in a two-variable steady system, the basins of attraction associated with the stable states are partitioned by a separatrix. Nucleation effects have been observed in imperfectly stirred reactors⁶ and nucleation induced transitions in a bistable reaction-diffusion system have been theoretically investigated.⁷ Thermal and experimental fluctuations in a well mixed CSTR may result in premature transitions near a hysteresis limit, but in the limit of an ideal reactor, premature transitions will occur only when the perturbations are of sufficient magnitude to move the system beyond the deterministic transition threshold.

In analogy to equilibrium systems, the behavior of a bistable system near the hysteresis limits and critical point is of special interest. The correspondence between equilibrium and nonequilibrium systems was developed in detail by Ross and co-workers² and more recently Heinrichs and Schneider⁸ focused on the relaxation behavior of model systems. Their linear analysis predicted a divergence in relaxation time as a hysteresis limit or critical point is approached upon variation of a constraint. A dramatic increase in relaxation times near a hysteresis limit has been observed in the bistable iodate-arsenous acid reaction.⁹ The slowing down was explained by one of the linear stability eigenvalues of a two-variable empirical rate law model vanishing at the transition point. Dewel et al.¹⁰ subsequently developed an analytical relaxation function from this model and showed that, in the limit of divergence, divergent behavior is expected at the hysteresis limits and the critical point with critical exponents of -1/2 and -2/3, respectively. Gray and Scott¹¹ have recently shown with a model for cubic autocatalysis that relaxation times exactly at the hysteresis limits are finite for finite perturbations and are governed by second-order kinetics.

In this paper, we investigate the relaxation behavior of the bistable iodate-arsenous acid system near the critical point and hysteresis limits. Features of an empirical rate law model for the system are developed in Sec. II. Relaxation experiments near a hysteresis limit and the critical point are described in Sec. III and corresponding modeling results are presented in Sec. IV. Experiment and theory are analyzed in Sec. V and conclusions are drawn in Sec. VI.

II. CHEMICAL SYSTEM AND MODEL

The iodate oxidation of arsenous acid is accurately described by a one-variable empirical rate law model⁵ when arsenous acid is sufficiently¹² in stoichiometric excess. The one-variable model is a reduction of a four-variable empirical rate law model proposed by Epstein and co-workers¹³ and has been used to describe the propagating fronts¹⁴⁻¹⁶ and bistability⁵⁻⁶ exhibited by this system. The chemical basis of the model will be only outlined here; a more detailed description relevant to this study can be found in Ref. 5.

The iodate-arsenous acid reaction with arsenous acid in stoichiometric excess is described by the net reaction

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

(I)

In a CSTR, the concentration of iodide is described by

\[ \frac{dX}{dt} = (k_x + k_{2a}X)(X_0 + B_0 - X)X + k_0(X_0 - X) \]  

(R)

where \( X = [\text{I}^-] \), \( k_x = k_1[\text{H}^+]^2 \), \( k_{2a} = k_3[\text{H}^+] \), \( B_0 \) and \( X_0 \) are the concentrations of iodate and iodide in the combined reactant stream, and \( k_0 \) is the reciprocal residence time (flow

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rate/reactor volume). Buffered reaction mixtures allow hydrogen ion concentration to be considered constant. Values of reactant concentrations are given in Table I and rate constants are given in the caption of Fig. 1.

The steady state concentration of iodide \( X_b \) as a function of \( k_o \) is readily obtained from Eq. (R) for the steady state condition \( dX_b/dt = 0 \) by calculating \( k_o \) for various \( X_b \), according to

\[
k_o = \frac{(k_e + k_p X_b)(X_b + B_0 - X_e)X_e}{X_b - X_o}.
\]

Shown in Fig. 1 are steady state iodide concentrations calculated from Eq. (1) for five different concentrations of iodide in the feed stream. Equation (1) is triple valued in \( X_b \) over a range of \( k_o \) in curves (a)–(c) and is single valued in curves (d) and (e). The turning points in curves (a)–(c) may be found from the first derivative \( dk_o/dX_b = 0 \) according to

\[
0 = 2k_eX_e^2 + (k_o - 4k_eX_o - k_pB_0)X_e^2 + [2k_e(X_o + B_0)X_o - 2k_eX_o] \times X_e + k_o(X_o + B_0)X_o
\]

The positive real roots of this equation define the hysteresis limits for various values of \( X_o \) and \( B_0 \). The dashed curve in Fig. 1 shows the locus of the turning points as a function of \( k_o \) as \( X_o \) is varied; unstable steady states lie within the area enclosed by the curve and stable steady states lie outside this area.

Curve (a) represents the special case of zero iodide concentration in the reactant stream. In this case, iodide concentration is zero in one of the stable steady states, corresponding to no chemical reaction. We note that according to Eq. (R), the system may exist in the other stable steady state only if it is perturbed from the zero state by a finite addition of iodide. This feature of the model holds even for \( k_o < k_pB_0 \) where the zero root switches from stable to unstable. Thus, in a batch reaction with \( k_o = 0 \), the system remains in the zero state unless a finite amount of iodide is introduced to the reaction mixture, even though that state is unstable. Of course, it is not possible to completely eliminate iodide from iodate reagent, making this special case experimentally unrealistic. In addition, an otherwise insignificant uncatalyzed reaction between iodate and arsonous acid may occur to provide the iodide necessary to initiate autocatalysis.

Curves (b) and (c) represent more realistic bistability behavior. In these curves, we see the steady state iodide concentration approach the iodide concentration in the reactant stream at high flow rates; at low flow rates the steady state concentration approaches the sum of the iodate and iodide concentrations in the reactant stream, corresponding to the complete conversion of iodate to iodide according to net reaction (1). The conversion of iodate to iodide in (1) is essentially complete since the equilibrium constant for the reaction is about 2 × 10^{53}.

Curve (d) in Fig. 1 corresponds to the critical concentration of iodide in the reactant stream where bistability disappears. The critical point occurs where \( dk_o/dX_e = k_0 k_o/dX_e = 0 \). The second derivative of Eq. (1) is

\[
0 = 2k_eX_e^2 + (k_o - 4k_eX_o - k_pB_0)X_e^2 + [2k_e(X_o + B_0)X_o - 2k_eX_o] \times X_e + k_o(X_o + B_0)X_o
\]

and the critical reactant concentration \( X_e^c \) and critical steady state concentration \( X_e^c \) are found by solving Eqs. (2) and (3) for \( X_e \) and \( X_e \) with a particular value of \( B_0 \). The position of the critical point in the \( X_e - k_o \) constraint plane is a function of \( B_0 \); the disappearance of bistability is therefore characterized by a locus of critical points in \( B_0 - X_e - k_o \) constraint space.

The critical point may also be found by noting that the three roots of Eq. (1) are identical at this point.\(^{10}\) The triple root \( X_e^c \), corresponding to the steady state iodide concentration at the critical point, is found by equating coefficients of like powers of \( X_e \) in Eq. (1) and \( (X_e - X_e^c)^3 = 0 \), yielding the relations

\[
X_e^c = \frac{[k_p(X_o + B_0) - k_e]}{3k_e}, \quad X_e^c = \frac{[k_o - k_e(X_o + B_0)]}{3k_e}, \quad X_e^c = \frac{k_oX_e^c}{k_e}
\]

where \( k_o \) is the reciprocal residence time corresponding to the critical point. These equations may be solved to give unique values of \( X_e^c, X_e^c, \) and \( k_o^c \) for any particular \( B_0 \).

Throughout this work we consider only a single value of \( B_0 \).

Curve (e) in Fig. 1 corresponds to an iodide concentration in the reactant stream larger than the critical concentration. For values of \( X_o > X_e^c \), Eq. (1) gives rise to only one

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**Table I. Experimental conditions and combined reactant stream concentrations.**

<table>
<thead>
<tr>
<th></th>
<th>([\text{IO}_3^-]_0)</th>
<th>([\text{I}^-]_0)</th>
<th>([\text{H}_2\text{AsO}_4]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7.10 \times 10^{-4}) M</td>
<td>(2.02 - 9.90 \times 10^{-3}) M</td>
<td>(2.97 \times 10^{-3}) M</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{Acidity maintained constant with sulfate/bisulfate buffer at [H}^+\text{]} = 6.9 \times 10^{-3} \text{ M. CSTR volume} = 34.9 \text{ ml. Temperature} = 25.0 \pm 0.1 \text{ °C.}\)**
positive real root and the system is monostable over the entire range of $k_0$.

Stable steady states in Fig. 1 are shown as solid lines and unstable steady states by dotted lines. Steady state stability is readily determined by the sign of the linear stability eigenvalue $\lambda$, according to

$$\lambda = -3k_2X_0^2 + [2k_4(X_0 + B_0) - 2k_2]X_1 + k_6(X_0 + B_0) - k_6.$$  (5)

The sign of $\lambda$ is positive for the branch of unstable steady states between the hysteresis limits in curves (a)--(c). All other steady states in Fig. 1 are stable with negative values of $\lambda$ except in curve (a), where the zero root is unstable for $k_0 < k_4 B_0$ and stable for $k_0 > k_4 B_0$. The peculiar behavior in curve (a) arises because model (R) contains both quadratic and cubic autocatalysis.

III. EXPERIMENTAL RESULTS

A. Procedure

Relaxation experiments were carried out following a procedure which preserves the one-variable characteristics of the iodate-arsenous acid system, allowing iodide concentration at any time to be described by Eq. (R). The system was perturbed away from a particular steady state by temporarily increasing or decreasing the reactant flow rate, thereby decreasing or increasing iodide concentration, respectively. Upon attaining the desired iodide concentration, continuously monitored by an iodide electrode and associated instrumentation (Orion 901), the original flow rate was resumed in order to restore the reciprocal residence time of interest. The relaxation of the system at this value of $k_0$ was monitored until no further change in concentration was apparent. This perturbation procedure, involving input into the reactor from the reactant stream only, ensures that the conservation of iodine atoms according to $[I^-]_0 + [IO_3^-]_0 = [I^-] + [IO_3^-]$ is maintained, allowing a one-variable description of the system.

The above procedure proved to be inadequate for establishing steady state iodide concentrations in the very slow relaxations. Iodide concentration changed extremely slowly in the final approach to steady states near a hysteresis limit or the critical point and even when the concentration appeared to be constant, significant concentration changes occurred over very long periods of time. Therefore, steady state concentrations were determined after an apparent steady concentration was established by subjecting the system to small positive and negative perturbations and monitoring the subsequent evolution of the system. This additional procedure allowed the steady state concentrations to be determined within a concentration bracket of about $\pm 0.2\%$.

Two peristaltic pumps (Gilson Minipuls 2) were utilized throughout this work, one channel pumping buffered $H_2AsO_3/KI$ solution and the other pumping buffered $KIO_3$ solution. Peristaltic pumps suffer from pump-head tubing degradation which results in a drift in flow rate; therefore, each pump was calibrated before and after each relaxation experiment using a volume-measurement flow meter (Phase Separation, Ltd.). Because the tubing in multichannel
degraded at different rates, it was necessary to use two pumps so that the channels could be independently calibrated and adjusted. Even with our best efforts to measure and control flow rate, errors in reciprocal residence time were as high as $\pm 2\%$ for the very long relaxation experiments.

B. Steady state concentrations

Shown in Fig. 2 are steady state iodide concentrations as a function of $k_0$ for six different values of $[I^-]_0$. Experiments at the lowest value of $[I^-]_0$, in curve (a) were carried out to measure relaxation times near the transition point of the high iodide branch. The remaining experiments, shown in curves (b) -- (f), were carried out to determine the value of $[I^-]_0$ and to measure relaxation times near the critical point. In an iterative sequence of experiments, hysteresis limits were located for different reactant iodide concentrations. No hysteresis was found in curve (d) with $[I^-]_0 = 9.45 \times 10^{-5}$ M compared to curve (c) with $[I^-]_0 = 9.30 \times 10^{-5} M$ which exhibited bistability; therefore, the reactant iodide concentration in curve (d) is within $1.6\%$ of the critical value. Relaxation experiments were carried out near the critical point along curve (d).

C. Relaxation experiments

Relaxation behavior near the critical point and hysteresis limit was investigated by monitoring the time evolution of the system perturbed away from steady states near these points according to the procedure described in Sec. III A. Relaxation times near a hysteresis limit were determined in an earlier study by finding the approximately linear slope in plots of $\ln([I^-] - [I^-]_0)$ vs time. Relaxation times obtained by this procedure must be viewed with caution since the treatment is appropriate only for first-order relaxation behavior. In this work, in order to avoid a bias in the data treatment, simple relaxation times were measured. Relaxation half-times were determined for a variety of perturbation magnitudes and relaxation times for various extents of relaxation were determined for a particular perturbation magni-
ed to give low values for the exponent \( y \) due to unavoidable scatter in the experimental measurements (see Sec. IV B).

The relaxation experiments for Fig. 3 utilized positive perturbations from the steady state, with the initial amplitudes defined by \( \Delta x_0 = X_\text{eq} - X_1 \). Positive perturbations were used in these experiments since even small negative perturbations very close to the hysteresis limit resulted in transitions to the other steady state.

Figure 4 shows relaxation half-times near the critical point along curve (d) in Fig. 2. The circles show half-times for positive perturbations, corresponding to increases in iodide concentration; the triangles show half-times for negative perturbations, corresponding to decreases in iodide concentration. For \( k_0 < k_0^* \) and \( \Delta x_0 > 0 \), the half-times are shorter than those with \( \Delta x_0 < 0 \); for \( k_0 > k_0^* \) the opposite behavior is found. The solid curves show fits of the half-times for positive perturbations as a function of the displacement from the critical point according to

\[
\tau = A \ |k_0 - k_0^*|^z \ ,
\]

where \( A \) is a constant, \( k_0^* \) is the reciprocal residence time at the critical point, and \( z \) is the least-squares slope of a plot of \( \ln(\tau) \) vs \( \ln(k_0 - k_0^*) \). The dashed curves show fits for negative perturbations. The value of \( k_0^* (5.620 \times 10^{-3} \text{ s}^{-1}) \) was arbitrarily taken as the average of the \( k_0 \) values for the longest half-time with \( \Delta x_0 > 0 \) and the longest half-time with \( \Delta x_0 < 0 \). No attempt was made to determine the value of \( k_0^* \) by optimizing the fit according to the least-squares correlation coefficient as was done for the value of \( k_0^* \) in Fig. 3 since the critical point in Fig. 4 lies between four different curves. Values of the critical exponent \( z \) for positive and negative perturbations before and after the critical point are listed in Table II.

The relaxation behavior near the critical point or hysteresis limits is not only dependent on the direction of the perturbation, but also on the perturbation magnitude and on the extent of relaxation defining the relaxation time. Shown in Fig. 5 are relaxation times (\( \tau \)) for positive perturbations along the critical curve corresponding to three different extents of relaxation. The solid curves show least-squares fits of the relaxation times according to Eq. (7). The value of \( k_0^* \) in Eq. (7) was the same as that used in Fig. 4. We see that the curves become more symmetrical around the critical point as the extent of relaxation increases. The critical exponents for the six curves are listed in Table III. The values of \( z \) before and after the critical point for a particular perturbation mag-

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**TABLE II. Critical exponents for experimental and calculated half-times near the critical point.**

<table>
<thead>
<tr>
<th>( \Delta x_0 &gt; 0 )</th>
<th>( \Delta x_0 &lt; 0 )</th>
<th>( k_0 &lt; k_0^* )</th>
<th>( k_0 &gt; k_0^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt ( ^a )</td>
<td>(-0.47 \pm 0.08)</td>
<td>(-0.58 \pm 0.06)</td>
<td>(-0.61 \pm 0.06)</td>
</tr>
<tr>
<td>Calc ( ^b )</td>
<td>(-0.73 \pm 0.01)</td>
<td>(-0.68 \pm 0.00)</td>
<td>(-0.80 \pm 0.01)</td>
</tr>
</tbody>
</table>

\(^a\) Perturbation amplitude \( \Delta x_0 = \pm 2.0 \times 10^{-3} \text{ M} \).

\(^b\) Values correspond to Fig. 4.

\(^c\) Values correspond to Fig. 7; least-squares fits of 100 points obtained from integrating Eq. (R) with 10 s increments.
FIG. 5. Relaxation time \( \tau \) as a function of \( k_0 \) for steady states in curve (d) of Fig. 2. Experimental conditions and reactant concentrations in Table I and Fig. 2. Extent of relaxation 50\% (\( \bullet \)), 75\% (\( \triangle \)), and 90\% (\( \square \)). Curves show least-squares fits of relaxation times to Eq. (7). Initial perturbation amplitude \( \Delta x_0 = 1.0 \times 10^{-4} \) M.

IV. MODELING RESULTS

The relaxation behavior of the system near the critical point and hysteresis limits can be conveniently modeled with Eq. (R). Steady state concentrations, hysteresis limits, and the critical point are readily obtained from the one-variable model as described in Sec. II. The time dependent evolution of the system perturbed away from a steady state can be investigated by numerically integrating Eq. (R) or by examining an analytical solution of the equation.

A. Analytical solution

Following Gray and Scott,\(^{11} \) we write a Taylor series in \( \Delta x = X - X_s \) to describe the time evolution of a relaxation,

\[
\frac{d\Delta x}{dt} = \lambda \Delta x + \frac{1}{2} \mu \Delta x^2 + \frac{1}{6} \gamma \Delta x^3,
\]

where \( \lambda = d\dot{X} / dX, \mu = d^2\dot{X} / dX^2 \), and \( \gamma = d^3\dot{X} / dX^3 \), with each derivative evaluated at the steady state. The first term only is considered in the linear stability analysis, with the eigenvalue \( \lambda \) given by Eq. (5). The second derivative of Eq. (R) yields

\[
\mu = -6k_0 X_s - 2k_0 + 2k_0 (X_0 + B_0).
\]

The third derivative yields a constant given by

\[
\gamma = -6k_0.
\]

Since Eq. (R) is a cubic in \( X \), the three-term Taylor series is complete and may be integrated to yield an analytical expression for the time evolution of \( \Delta x \). Integrating Eq. (8) by partial fractions and solving for the half-time yields

\[
\tau = -\frac{1}{\lambda} \ln 2 - \frac{1}{2\lambda} \ln \left[ \frac{1}{\Delta x_0^2} + \frac{(\mu / \gamma) \Delta x_0 + 6\lambda / \gamma}{\Delta x_0^2 + (3\mu / \gamma) \Delta x_0 + 6\lambda / \gamma} \right] - \frac{3}{2} \frac{\mu}{\lambda \gamma} \left[ \tan^{-1} p - \tan^{-1} q \right],
\]

where

\[
b = \left[ \frac{6\lambda}{\gamma} - \left( \frac{3}{2} \frac{\mu}{\gamma} \right)^2 \right]^{1/2},
\]

\[
p = \frac{1}{b} \left( \frac{1}{2} \Delta x_0 + \frac{3}{2} \frac{\mu}{\gamma} \right),
\]

\[
q = \frac{1}{b} \left( \Delta x_0 + \frac{3}{2} \frac{\mu}{\gamma} \right),
\]

and \( \Delta x_0 \) is the initial amplitude of the displacement from the steady state. Half-times evaluated by numerically integrating Eq. (R) are identical to those obtained from Eq. (11). While Eq. (8) conveniently groups terms of like powers in \( \Delta x \), it should be recognized that this expression is nothing more than Eq. (R) with \( X = X_s + \Delta x \). The resulting expression is that obtained in a stability analysis when higher order terms are retained.

B. Hysteresis limit

Shown in Fig. 6 are relaxation half-times predicted by Eq. (R) for the conditions of Fig. 3. No effort was made to obtain a quantitative fit to the experimental behavior by adjusting rate constants. Even with no adjustments, the calculated hysteresis limit agrees reasonably well with the experimental determination [compare curve (b) in Fig. 1 to curve (a) in Fig. 2]. The calculated half-times increase as the value of \( k_0 \) approaches \( k_\phi \) much like the increase exhibited by the experimental half-times.

A least-squares fit of the half-times as a function of the displacement from the transition point according to Eq. (6) yields a value of \( \gamma \) equal to \(-0.60 \pm 0.04\), about 54\% higher than the experimental value. This calculation was carried out using 30 half-times determined to four significant figures in order to simulate the experimental results in Fig. 3. The value of \( k_\phi (3.112 11 \times 10^{-3} \text{s}^{-1}) \) used in these calculations is readily determined analytically from Eq. (2). The value of
the exponent \( y \) is apparently quite sensitive to error in the half-time values. A second calculation using 100 half-times determined to 16 significant figures yielded a value of \( y \) equal to \( -0.69 \pm 0.01 \). This sensitivity represents a deficiency in the procedure for determining critical exponents from experimental measurements and should be considered when comparing the experimental results to the predictions of the model calculations. The primary experimental error in the measurements occurred in determining the value of \( k_0 \) for each relaxation (\( \pm 2\% \)). Two 30 point calculations like the one above were carried out except that every other point was increased by 2% in \( k_0 \) and the remaining points were decreased by 2%. These calculations yielded values of \( y \) equal to \(-0.38 \pm 0.09 \) and \(-0.55 \pm 0.06 \) for the two possible sets of half-times. While these calculations do not represent a rigorous error analysis, they do show that the fitting procedure is sensitive to scatter in the half-times and low values of the critical exponent may result.

The linear eigenvalue \( \lambda \) is simply related to the apparent relaxation rate constant for the decay of an infinitesimal perturbation \( (\lambda = -k_{\text{app}}) \). As in equilibrium relaxation experiments, this approximation is useful for describing the system in its final approach to the steady state. The linear half-times \( [\tau = -(\ln 2)/\lambda] \) predicted by Eq. (5) are also proportional to the displacement from the transition point according to Eq. (6). These half-times over the experimental range in Fig. 3 generate a value of \( y \) equal to \(-0.56 \pm 0.01 \). The value of \( y \) predicted by Eq. (R) approaches the linear value as the size of the perturbation decreases. The value of \( y \) also depends on the proximity of the system to the transition point. In the limit of infinitesimal perturbations, \( y \) approaches \(-1/2 \) as the displacement from the transition point becomes vanishingly small.

C. Critical point

Shown in Fig. 7 are calculated half-times near the critical point corresponding to the conditions in Fig. 4. The solid curves show half-times for positive perturbations; the dashed curves show half-times for negative perturbations. We see that the half-times before the critical point are shorter for positive perturbations than for negative perturbations and after the critical point just the opposite behavior is exhibited, much like the experimental curves in Fig. 4. The increase in half-times as the value of \( k_0 \) approaches \( k_0^c \) is described by Eq. (7). Values of the critical exponent \( z \), listed in Table II, were calculated by determining the least-squares slope in plots of \( \ln(\tau) \) vs \( \ln|k_0 - k_0^c| \). The value of \( k_0^c \) \((4.557 \times 10^{-3} \text{ s}^{-1}) \) in these calculations is readily determined analytically from Eqs. (2) and (3) or Eqs. (4). We see in Table II that the calculated values of \( z \) are higher than the experimental values. The scatter in the measured half-times apparently results in low experimental values.

Linear half-times predicted by Eq. (5) form nearly symmetrical curves on either side of \( k_0^c \), falling between the curves for positive and negative perturbations predicted by Eq. (R). The linear half-times give rise to values of \( z \) before and after the critical point of \(-0.78 \pm 0.00 \) and \(-0.66 \pm 0.00 \) for the \( k_0 \) range and resolution of the critical point in Fig. 7. As the perturbation size is decreased, the curves calculated from Eq. (R) approach the curves predicted by the linear eigenvalue \( \lambda \).

While half-times are a convenient measure of experimental and calculated relaxation behavior, extents of relaxation other than 50% are readily measured. Listed in Table III are values of the exponent \( z \) predicted by Eq. (R) for 50%, 75%, and 90% relaxation corresponding to the experiments shown in Fig. 5. We see that as the extent of relaxation increases, the curves become more symmetrical around the critical point. The corresponding values of \( z \) approach the values predicted by the eigenvalue \( \lambda \).

The value of the critical exponent \( z \) also depends on the proximity to the critical point. The linear half-times yield a value of \( z \) that approaches \(-2/3 \) as the displacement from the critical point becomes vanishingly small. Thus, the value of \(-2/3 \) is recovered in the limit of infinitesimal perturbations and a vanishing displacement from the critical point.
V. DISCUSSION

The simplicity of the iodate-arsenous acid reaction allows a detailed examination of relaxation behavior in a bistable system near the critical point and hysteresis limits. Many of the features exhibited by this simple system are generally applicable to more complex systems.

A. Hysteresis limit

Relaxation half-times significantly lengthen as the hysteresis limit is approached. We see good agreement between the measured half-times in Fig. 3 and the calculated half-times in Fig. 6. In both experiment and calculation, the increase in half-time is well described by Eq. (6) over this range of \( k_0 \) and resolution of the transition point. This description fails for finite perturbations as the displacement from the transition point becomes very small.

As the size of the perturbation is reduced or the extent of relaxation increased, half-times predicted by Eq. (R) approach those predicted by the linear eigenvalue \( \lambda \). Higher order terms in Eq. (8) become negligible as \( \Delta \lambda \) becomes very small and the relaxation is described by simple first-order decay. However, the relative magnitudes of the terms in Eq. (8) also depend on the values of \( k_0 \) and \( X_0 \) according to Eqs. (5), (9), and (10). Shown in Fig. 8 are the coefficients \( \lambda, \mu \), and \( \gamma \) as a function of \( k_0 \), corresponding to the steady states in curve (b) of Fig. 1. The turning points of the \( \lambda \) and \( \mu \) curves correspond to the hysteresis limits of curve (b). We see that \( \lambda \) is negative for both branches of stable steady states and positive for the branch of unstable steady states.

In the limit of infinitesimal perturbations, half-times diverge as the transition point is approached since \( \lambda \) goes to zero at that point. In the linear limit, the value of \( \gamma \) in Eq. (6) depends on the displacement from the transition point; in the limit of a vanishing displacement, the value is \(-1/2\). This limiting value is readily seen by examining Eq. (5). It is convenient to consider the case of \( X_0 = 0 \), corresponding to curve (a) in Fig. 1, since in this case the reciprocal residence time at the transition point is given by the simple expression

\[
k'_0 = (k_k_0)(k_s - k_s B_0)^2 + k_s B_0.
\]

Defining the displacement from the transition point as \( \delta = k'_0 - k_0 \) and substitution of Eq. (12) into Eq. (5) yields

\[
\lambda = -k_0^{1/2} (k_s B_0 - k_s) (k_s)^{1/2} - 2k_s.
\]

In the limit of a vanishing displacement from the transition point, Eq. (13) predicts the half-time \( \tau \) to be a function of \( k_s \)

\[
\tau(\lim k_s \rightarrow 0) = C(k_s)^y,
\]

where \( C = (\ln 2)(k_0^{1/2}/k_s B_0 - k_s) \) and \( y = -1/2 \). Equation (14) is in accord with Eq. (6) predicting divergent relaxation behavior in the limit of infinitesimal perturbations and a vanishing displacement from the transition point. This result was shown earlier by Dewel et al., with an analytical relaxation function obtained by integrating Eq. (R).

Although relaxation rates dramatically decrease as the hysteresis limit is approached, half-times for finite perturbations must remain finite. As Gray and Scott have pointed out, the higher order terms in Eq. (8) govern the relaxation behavior for finite perturbations as \( \lambda \) approaches zero. We see in Fig. 8 that as \( \lambda \) vanishes, \( \mu \) remains negative at the hysteresis limit of the high iodide branch and at the hysteresis limit of the low iodide branch, \( \mu \) remains positive. The coefficient \( \gamma \) is negative for all values of \( k_0 \).

Half-times exactly at the hysteresis limit may be calculated for various perturbation magnitudes. When \( \lambda = 0 \), Eq. (8) is readily integrated by partial fractions, yielding

\[
\tau = -\frac{2}{\mu \Delta x_0} + 2\gamma \frac{\ln(\Delta x_0 \gamma + 6\mu)}{3\mu},
\]

(15)

The first term in Eq. (15) results from the second-order relaxation according to the \( \mu \) term in Eq. (8); the second term represents a mixture of second- and third-order kinetics. The coefficient \( \mu \) is negative at the high iodide hysteresis limit and therefore the first term of Eq. (15) is positive for positive perturbations; the second term is always negative because \( \gamma \) is negative. When \( \Delta x_0 < 0 \), negative half-times are predicted, corresponding to a perturbation induced transition to the other stable steady state. Since unstable and stable steady states coalesce at the hysteresis limit, even an infinitesimal negative perturbation is sufficient to induce the transition. At the hysteresis limit of the low iodide branch of curve (b) in Fig. 1, the value of \( \mu \) is positive and the first term in Eq. (15) is positive for positive perturbations. Again, the second term is always negative, diminishing the half-time from that predicted by purely second-order kinetics. At this hysteresis limit, a positive perturbation results in a negative half-time, corresponding to a transition to the other steady state. As \( \Delta x_0 \) becomes very small, the second term in Eq. (15) becomes negligible compared to the first term and the relaxation to either hysteresis limit follows second-order kinetics. Relaxation behavior at the transition point in the limit of second-order kinetics has been considered by Gray and Scott. Since \( \mu \) is a function of \( X_0 \) according to Eq. (9), half-times calculated from Eq. (15) for a particular perturbation magnitude will vary along the locus of hysteresis limits in Fig. 1. At the hysteresis limit of the high iodide branch of


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curve (b) in Fig. 1, Eq. (15) predicts a half-time of 6.94 x 10^7 s for \( \Delta x_0 = 2.0 \times 10^{-5} \) M. A simple second-order relaxation with the same values of \( \mu \) and \( \Delta x_0 \) predicts \( \tau = 7.23 \times 10^3 \) s; therefore, the relaxation is close to second order for this perturbation magnitude.

Because the relaxation behavior is determined largely by the linear eigenvalue except very near the hysteresis limit, the experimental half-times in Fig. 3 and half-times predicted by Eq. (R) in Fig. 6 are well described by Eq. (6). This description fails as the transition point is approached except for infinitesimal perturbations. The divergence of half-times at the hysteresis limit for infinitesimal perturbations is consistent with Eq. (15) since the value of \( \tau \) approaches infinity as \( \Delta x_0 \) approaches zero.

**B. Critical point**

Relaxation half-times significantly increase as the critical point is approached along the critical curve. Measured half-times in Fig. 4 and half-times predicted by Eq. (R) in Fig. 7 exhibit an apparent divergence according to Eq. (7). The half-times are shorter with positive perturbations than with negative perturbations for \( k_0 < k_0^* \) and the trend is reversed for \( k_0 > k_0^* \). In the limit of infinitesimal perturbations, half-times predicted by the linear eigenvalue \( \lambda \) fall between the curves for positive and negative perturbations in Fig. 7.

In the linear limit, half-times diverge as the critical point is approached since \( \lambda \) approaches zero at this point. The behavior of \( \lambda \) close to the critical point is shown by the solid curve in Fig. 9. For the experimental range of \( k_0 \) shown in Fig. 7, the linear half-times are unsymmetrical about the critical point. Close to the critical point, the curves become more symmetrical and as the displacement from the critical point becomes very small, the linear half-times are described by Eq. (7) with the value of \( z \) approaching \(-2/3\).

The limiting value of \(-2/3\) for the exponent \( z \) may be seen by examining the linear eigenvalue \( \lambda \) in Eq. (5). It is convenient to rewrite this equation in terms of the displacement from the critical correlation time \( k_0^* = k_0 - k_0^* \) and the displacement from the critical steady state concentration \( x = x - x^* \). With these substitutions and the expressions for \( x^*_s \), \( x^*_s^2 \), and \( x^*_s^3 \) in Eqs. (4), the eigenvalue becomes

\[
\lambda = 3k_0 x^2 - k_0^*.
\]

An expression for \( x \) in Eq. (16) may be found by carrying out the same substitutions in Eq. (1). With Eqs. (4) we find

\[
0 = k_x x^3 + k_\delta x + k_\delta (x^s - x^*_s).
\]

We may now obtain an analytical expression for the positive real root of Eq. (17) which upon substitution into Eq. (16) yields

\[
\lambda = -3k_0^{2/3}D^{2/3}k_0^{2/3} - k_0^*,
\]

where

\[
D = \left[ -\frac{G}{2} + \left( \frac{G^2}{4} + k_\delta^2/27k_0 \right)^{1/2} \right]^{1/3} + \left[ -\frac{G}{2} - \left( \frac{G^2}{4} + k_\delta^2/27k_0 \right)^{1/2} \right]^{1/3}
\]

and \( G = x^s - x^*_s \). In the limit of a vanishing displacement from the critical point, Eq. (18) predicts the half-time \( \tau \) to be a function of \( k_\delta \) according to

\[
\tau(\lim k_\delta \to 0) = A(k_\delta^*)^z,
\]

where

\[
A = (\ln 2)/(3k_0^{1/3}D^{1/2}) \quad \text{and} \quad z = -2/3.
\]

Equation (19) is in accord with the divergence of half-times according to Eq. (7) for infinitesimal perturbations and a vanishing displacement from the critical point. This result was shown earlier by Dewel et al.\textsuperscript{10} with an analytical relaxation function.

While divergent half-times are predicted by Eq. (19) for infinitesimal perturbations, half-times must be finite for finite perturbations. Shown in Fig. 10 are half-times predicted by Eq. (R) very close to the critical point. The solid curve shows half-times with \( \Delta x_0 > 0 \) and the dashed curve shows half-times with \( \Delta x_0 < 0 \). Again we see that for \( k_0 < k_0^* \), half-times are shorter with \( \Delta x_0 > 0 \) than with \( \Delta x_0 < 0 \); for \( k_0 > k_0^* \), the opposite behavior is exhibited. The two curves

![FIG. 10. Relaxation half-time \( \tau \) as a function of \( |k_0 - k_0^*| \) for curve (d) in Fig. 1 very close to the critical point. Solid curve shows half-times calculated from Eq. (R) for \( \Delta x_0 > 0 \); dashed curve shows half-times for \( \Delta x_0 < 0 \). The curves cross at the critical point (X) with the half-time given by \( \tau_0 \). Dotted curve shows half-times predicted by the linear eigenvalue \( \lambda \). Initial perturbation amplitude corresponds to experimental measurements in Fig. 4; reactant concentrations and rate constants in Fig. 1.](image)
cross at the critical point giving the half-time at that point. Thus, for finite perturbations we find that the maximum relaxation half-time occurs slightly before the critical point for $\Delta x_0 < 0$ and slightly after the critical point for $\Delta x_0 > 0$. Half-times predicted by the linear eigenvalue $\lambda$ are shown by the dotted curves in Fig. 10. As in Fig. 7, the linear half-times fall between those predicted by Eq. (R) for positive and negative perturbations except just before and just after the critical point.

The half-time at the critical point for a particular perturbation magnitude is readily obtained by integrating Eq. (8). We see in Fig. 9 that $\lambda$ and $\mu$ go to zero at the critical point; therefore, Eq. (8) reduces to a single term describing third-order kinetics. Integration of this equation yields

$$\tau = \frac{9}{\gamma \Delta x_0^2}$$  \hspace{1cm} (20)

for the half-time at the critical point. For $\Delta x_0 = 2.0 \times 10^{-5}$ M, the perturbation magnitude utilized in the experiments, we find the half-time $\tau = 1.75 \times 10^5$ s or slightly more than 48 h. This half-time is about two orders of magnitude larger than the measured half-times in Fig. 4. The half-time just before or just after the critical point is even larger by almost a factor of 4. Apparently no half-times were measured within the resolution of $k_o^*$ attained in the calculations. Divergence of the half-time at the critical point, in the limit of infinitesimal perturbations, is consistent with Eq. (20) since $\tau$ approaches infinity as $\Delta x_0$ approaches zero.

C. Pseudo-first-order description

Equation (8) represents a differential rate law with first-, second-, and third-order terms in the perturbation $\Delta x$. Insight into the relative magnitudes of the terms may be found by considering their independent contributions to the relaxation. Integrating each of the terms and determining the corresponding half-times along the critical curve yields a surprisingly good approximation of the half-times predicted by Eq. (R). For the approximate half-time, we write

$$\tau = \frac{1}{1/\tau_\lambda + 1/\tau_\mu + 1/\tau_\gamma},$$  \hspace{1cm} (21)

where $\tau_\lambda$, $\tau_\mu$, and $\tau_\gamma$ are the half-times calculated from each of the terms in Eq. (8). With the expressions for $\lambda$, $\mu$, and $\gamma$ in Eqs. (5), (9), and (10), we have

$$\tau = \frac{1}{-\lambda / \ln 2 - (\mu / \mu_\lambda) \Delta x_0 - (\gamma / \gamma_0) \Delta x_0^2}.$$  \hspace{1cm} (22)

Equating the reciprocal of the overall half-time to the sum of the independent reciprocal half-times according to Eq. (21) is valid only if the terms of the rate law are of the same order. However, upon examination of the values of $\lambda$, $\mu$, and $\gamma$ along the critical curve, we find that the approximation is justified for a particular perturbation magnitude. Thus, we see in Fig. 9 that $|\mu|$ is near unity except very close to the critical point, $|\lambda|$ is about five orders of magnitude smaller than $|\mu|$, and $|\gamma|$ is about five orders of magnitude larger than $|\mu|$. Therefore, with an initial perturbation magnitude equal to that used in the experiments ($\Delta x_0 = 2.0 \times 10^{-5}$ M), the second and third terms in Eq. (8) become very nearly pseudo-first-order. Shown in Fig. 11 by the dashed curve are half-times close to the critical point calculated from Eq. (22) for $\Delta x_0 > 0$; the solid curve shows half-times predicted by Eq. (R). We see that the half-times are well approximated by Eq. (22) except very close to the critical point. Half-times calculated from Eq. (22) with $\Delta x_0 > 0$ and $\Delta x_0 < 0$ over the experimental range in Fig. 7 are indistinguishable from those predicted by Eq. (R).

The relative contributions to relaxations along the critical curve of the first-, second-, and third-order terms in Eq. (8) may be determined by the pseudo-first-order description of Eq. (22). As shown in Fig. 9, $\lambda$ and $\gamma$ are always negative and give rise to positive contributions in the denominator of Eq. (22) regardless of the sign of $\Delta x_0$. The coefficient $\mu$ is negative before the critical point and positive after the critical point; therefore, this term results in a positive contribution to the denominator of Eq. (22) for $k_0 < k_o^*$ with $\Delta x_0 > 0$ and a negative contribution with $\Delta x_0 < 0$. The half-times in Fig. 7 for $k_0 < k_o^*$ are shorter with $\Delta x_0 > 0$ than with $\Delta x_0 < 0$ because the $\mu$ term diminishes the half-time for positive perturbations and increases the half-time for negative perturbations. Just the opposite behavior is seen after the critical point, since $\mu$ changes sign at that point.

The relative contributions to relaxations very close to the critical point from the $\lambda$, $\mu$, and $\gamma$ terms may also be examined with Eq. (22). Figure 10 shows that half-times are shorter before the critical point for $\Delta x_0 > 0$ than for $\Delta x_0 < 0$, again because the contribution of the $\mu$ term to the denominator in Eq. (22) depends on the sign of $\Delta x_0$. As shown in Fig. 10, $\lambda$ and $\mu$ go to zero at the critical point and the half-time is therefore determined solely by the third-order $\gamma$ term. Upon changing sign at the critical point, the $\mu$ term makes a negative contribution to the denominator of Eq. (22) for $\Delta x_0 > 0$ resulting in an increase in relaxation time. The half-time reaches a maximum when the sum $(\tau_\gamma^{-1} + \tau_\mu^{-1})$ reaches its maximum negative value in Eq. (21). The half-time then decreases but remains larger than that for negative perturbations because of the negative contribution in the denominator from the $\mu$ term. The relaxation behavior around the critical point is just the opposite for $\Delta x_0 < 0$ since the $\mu$ term then takes on the opposite sign.
VI. CONCLUSION

The relaxation behavior of a perturbed bistable system is anomalously slow near the critical point and hysteresis limits. The coarse features of this slowing down result from a vanishing eigenvalue at the bifurcation points giving rise to an apparent divergence in relaxation time at these points. This behavior is general; the relaxation behavior of any system, regardless of the number of variables required to characterize the system, is governed by the slowest relaxation process at long times. Near a bifurcation point such as a hysteresis limit or critical point, a vanishing eigenvalue will dominate the relaxation behavior.

Critical slowing down has also been investigated in an illuminated thermochemical system (ortho-cresolphthalein) by Kramer and Ross. An apparent divergence in relaxation time is exhibited in this system near a hysteresis limit. Theoretical investigations of relaxation behavior in the iodate-arsenous acid system have also been carried out by Dewel et al. An analytical relaxation function was utilized to describe the system in the linear limit and recently a nonlinear analysis has been reported with results similar to our own. A recent theoretical study of a nonisothermal bistable system by Gray and Kordylewski has shown a similar apparent divergence in relaxation times near the hysteresis limits.

A simple one-variable system allows a detailed examination of relaxation behavior near a bifurcation point. We find a dependence of the half-times on the direction of the perturbation and maximum half-times near but not at the critical point. We also find that the relaxation at a hysteresis limit is described by a second-order approach to the steady state and at the critical point the final approach is described by third-order kinetics. The relaxation behavior at these points is highly unusual; relaxations to equilibrium states or to steady states always occur, except at bifurcation points, via first-order kinetics in the limit of very small displacements from these states. In systems described by many variables, contributions to the relaxation behavior by the nonvanishing linear eigenvalues may obscure the higher order contributions discernible in a one-variable system. We hope that the simple behavior found in this study might lend insight into more complicated behaviors near bifurcation points of many variable systems.

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