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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · APRIL 1987

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The latter two results suggest stabilization of the collision complex by the aromatic ring and reduced opportunity for the migration of the  $^{11}\text{C}$  atom or the reactive intermediate. If the collision complex involves a symmetrical intermediate involving the  $^{11}\text{C}$  atom in the benzene  $\pi$ -complex, the intermediate must be sufficiently stabilized to permit rearrangement. The yield of  $^{(11)}\text{C}_2\text{D}_2$  arising from insertion decomposition on the dideuterioalkyl carbon adjacent to the phenyl ring is 10–11% whereas the mixed acetylene yield  $^{(11)}\text{C}_2\text{HD}$  is as noted: 1,1,2,2,3,3,3-deuterio-propylbenzene (22%); 1,1,2,2,2-deuterioethylbenzene (21%); and 1,1,1-deuteriomethylbenzene (25%). Therefore, we concluded there must either be rearrangement or formation of a symmetrical intermediate over the aromatic ring (Figure 2). Visser's data<sup>13</sup> would favor the argument for rearrangement.<sup>16</sup>

(16) Rather recently Gaspar, P. P., et al. concluded that the reaction of either triplet and singlet carbon-11 atoms with toluene can lead to benzo-cyclobutene formation through insertion into C–H bonds. Styrene was formed presumably by insertion of singlet carbon-11 atoms into a C–H bond on the methyl substituent, followed by rearrangement of the resulting benzyl-methylene (unpublished).

The same considerations for the collision complex and its lifetime apply to the product yielding steps for  $^{(11)}\text{C}_2$  or  $^{(11)}\text{C}_2\text{H}$  as high-energy intermediates leading to formation of mixed acetylene  $^{(11)}\text{C}_2\text{HD}$  via the intermolecular mechanism. High-energy stripping and abstraction reactions appear to account for acetylene formed by an intermolecular pathway.

The observation that the intermolecular mechanism is more pronounced in aromatics than alkanes is not unexpected due to the expected stabilization of a  $\pi$ -system compared to a  $\sigma$ -system. After correction for the intermolecular mechanism, the remaining acetylene is formed mainly by direct insertion ( $\pi$  or  $\sigma$ ) plus a small contribution from a mechanism involving random selection of H or D in the phenyl ring.

**Acknowledgment.** This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

**Registry No.** Carbon-11, 14333-33-6; benzene, 71-43-2; acetylene, 74-86-2.

## Relaxation Kinetics near the Hysteresis Limit of a Bistable Chemical System: The Chlorite–Iodide Reaction in a CSTR

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We report the results of an investigation of the relaxation kinetics in the bistable chlorite–iodide reaction in a continuous stirred tank reactor (CSTR). Critical slowing down is observed in the vicinity of the upper marginal stability point (flow branch). The dynamical exponent that characterizes the relaxation time as one gets closer to the hysteresis limit is found to be equal to  $0.45 \pm 0.10$ . This value is similar to the experimental value obtained by Ganapathisubramanian and Showalter in their study of the iodate–arsenous acid system. The value is also in good agreement with previous theoretical predictions of a universal value of  $1/2$  for this exponent. Our results are compared with a model of the relaxation kinetics in the vicinity of a saddle-node bifurcation. The model shows good qualitative agreement with the experimental results.

### Introduction

The study of relaxation kinetics in bistable chemical systems has recently attracted some attention. In a pioneering study of the bistable iodate–arsenous acid reaction in a CSTR, Showalter and Ganapathisubramanian first reported the anomalous increase in the relaxation time that takes place as an hysteresis limit<sup>1</sup> or a critical point<sup>2</sup> is approached. This unusual phenomenon, known as “critical slowing down”, is well documented in equilibrium phase transitions.<sup>3</sup> In analogy with equilibrium critical phenomena, one can define a dynamical exponent that characterizes the sin-

gularity of the linear response near the hysteresis limits or the critical point.<sup>4,5</sup> On the basis of model calculations, it has been predicted that these exponents should be fairly independent of the mechanistic details of the reactions and therefore have a universal character.<sup>4,5</sup> Values of  $1/2$  and  $2/3$  were respectively predicted for the dynamical exponents near the hysteresis limits and the critical point.<sup>5</sup> These values were found to agree quite well with experimental values obtained in the iodate–arsenous acid reaction.<sup>2,6</sup> The accurate experimental determination of these exponents is, however, difficult, as emphasized by a recent reinvestigation of the iodate–arsenous acid system.<sup>6</sup> The phenomenon of critical slowing down was also observed and characterized to

(1) Ganapathisubramanian, N.; Showalter, K. *J. Phys. Chem.* **1983**, *87*, 1098–9.

(2) Pifer, T.; Ganapathisubramanian, N.; Showalter, K. In *Non-Equilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer-Verlag: West Berlin, 1984; pp 50–4.

(3) See for example: Binder, K.; Kalos, M. N. In *Topics in Current Physics*; Binder, K., Ed.; Springer-Verlag: West Berlin, 1979; Vol. 7, pp 225–60.

(4) Nitzan, A.; Ortoleva, P.; Deutch, J.; Ross, J. *J. Chem. Phys.* **1974**, *61*, 1056–64.

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some extent in the bistable thermochemical irradiated *o*-cresolphthalein (OCP) system.<sup>7</sup> In a recent study of the effect of periodic perturbation on the oscillatory combustion of acetaldehyde in a CSTR, Ross and colleagues<sup>8</sup> have also shown that a critical slowing down of the relaxation time does occur near the edge of the entrainment band. Informative model studies of the critical slowing down of the time to ignition in isothermal and non-isothermal combustion CSTR's have also been presented by Schneider<sup>9</sup> and Gray.<sup>10</sup>

In this paper, we report the results of an investigation of the relaxation kinetics near the upper marginal stability point of the bistable chlorite-iodide reaction in a CSTR. This work was initially motivated by the fact that experimental investigations of the critical slowing down in bistable chemical systems had so far been limited to the iodate-arsenous acid reaction.<sup>11</sup> It was therefore felt that theoretical predictions relative to the critical slowing down should be verified for at least one different bistable chemical system. The chlorite-iodide reaction is known to be bistable over a wide range of parameters when carried out in a CSTR.<sup>12,13</sup> Even though its detailed mechanism is still not fully understood,<sup>13</sup> this reaction appeared to be a good candidate for testing theoretical predictions of "universality" put forward by some of us.<sup>5</sup> Our experimental approach is outlined in the next section. Results are then presented with special emphasis on a quantitative analysis of the perturbation decay curves. Critical slowing down is then characterized and experimental results are compared to predictions of a theoretical model based on a one-variable generic equation describing the relaxation in the vicinity of a saddle-node bifurcation.

## Experimental Section

**The Reactor.** Experiments were carried out in an acrylic CSTR whose static volume was equal to 56.1 mL. The reactor is constructed of two pieces: a top and a bottom part. The top section is designed to accommodate a reference and an iodide selective electrode (reference: Orion double junction, Model 90-02; iodide selective: Orion Model 94-53A). The interior of the top section is machined as a cone to facilitate the escape of any gas bubbles. An opening through the apex of this cone provides room for both the stirring shaft and the outflow of solution. This outflow was continuously pumped out of the top of the reactor cap by a vacuum pump. The main body of the reactor is machined in the bottom part of the reactor and is of cylindrical shape. This section also includes a port with a Teflon septum for microliter injections of concentrated iodide solutions. The top section fits onto the bottom section as a cap. An O-ring sitting in a groove machined in the bottom part of the reactor then provides a leak-free seal once both sections are assembled. Stirring was provided by a (nylon) Marine propeller rotating at 1250 rpm. The stirring driver is a Pine Instrument Model MSR. This unit is typically used in rotating disk electrode experiments and is therefore designed to provide a very stable stirring rate ( $\pm 0.1\%$ ).

Reactant solutions were fed through 1/32-in.-i.d. Teflon capillary tubes that were stretched and force-fitted into the bottom part of the reactor. Reactants were pressure-fed from 20-L carboys. Nitrogen was used as a pressure gas. Feed rates were continuously monitored with on-line precalibrated Gilmont flowmeters and adjusted to the desired flow rates with Swagelok SS316 micrometer valves. Flow lines and connectors are all made of Teflon. This system was found to maintain a pulse-free and stable flow rate over an extended period of time. The reactor was immersed in a thermostated water bath, held at 25 °C. The output of the pH meter was connected to a Keithley Model 197 mul-

timer. A built-in IEEE-488 interface provided the link to an IBM-PC microcomputer. Data points were typically acquired at a rate of  $\approx 1$  point/s and stored for further analysis.

**The Reactants.** NaClO<sub>2</sub> and NaI reactants were fed through three separate inlet tubes, the total flow rate being kept constant at 30.0 ( $\pm 0.1$ ) mL/min ( $\tau_{\text{res}} = 112.0 \pm 0.5$  s). NaClO<sub>2</sub> was fed through the first line at a constant flow rate of 15.30 ( $\pm 0.05$ ) mL/min. Its concentration in the reactor, before any reaction takes place,  $[\text{NaClO}_2]_0$ , was kept constant at  $2.550 \times 10^{-4}$  M. The other two lines were used to feed NaI solutions at concentrations  $[\text{NaI}]_1$  and  $[\text{NaI}]_2$ , respectively. By choosing appropriate values for these two iodide solutions, we could scan any part of the bistability with the desired accuracy. This procedure was especially helpful near the marginal stability point. The two iodide lines were joined as a single line just before entering the reactor. The concentration of iodide entering the reactor,  $[\text{NaI}]_0$ , could then be varied at will by changing the flow rate of lines 2 and 3, while keeping the NaClO<sub>2</sub> and the total flow rate constant. All solutions were prepared fresh every day from reagent grade NaI and technical grade NaClO<sub>2</sub> (80%). NaOH (0.001 M) was added to the NaClO<sub>2</sub> solutions as a stabilizing agent. Iodide solutions were prepared in a pH 3.70 acetic acid/sodium acetate buffer.

**Procedure.** A typical series of runs would start by first calibrating the iodide selective electrode, with four standard iodide solutions of appropriate concentrations. Calibration was always done at the same total flow rate, i.e., 30.0 mL/min. Once the calibration curve had been obtained, the three lines were opened and the reactants allowed to flow in at the appropriate flow rates. Once a steady state has been reached, its stability (and reproducibility) was checked through microliter injections of concentrated solutions of NaI and then NaClO<sub>2</sub>. These small excursions above and below the steady states were found to be very important in obtaining reproducible values for the steady states. Once reproducibility was obtained within  $\pm 0.05$  mV, the system was perturbed with a 10–25- $\mu$ L injection of a concentrated NaI solution. The decay was then monitored and the run stopped when the iodide concentration has come back to its initial steady state. As one gets closer to the marginal stability point, the search for the "true" steady states becomes more difficult. It is then typically a long (and sometimes frustrating!) process that can take hours. The experimental difficulty is here twofold. First, as one gets closer to the marginal stability point, the distance between the stable and the unstable branches become smaller and smaller. As a result, the amount of NaClO<sub>2</sub> that one can inject to test the stability of a given steady state becomes increasingly small. The second aspect of the difficulty is related to those long-living unstable states which are known to exist beyond the hysteresis limit, i.e., for  $[\text{I}^-]_0 < [\text{I}^-]_c$ .<sup>14</sup> As shown previously,<sup>5</sup> the lifetime of such metastable states increases dramatically as one gets close enough to the marginal stability point. (We have often observed metastable states with lifetimes of 30–45 min.) As a result, metastable states can easily be mistaken for true steady states if one does not wait long enough to ascertain their stability. The experimental limitations described above unfortunately prevent us from reaching the "true" hysteresis limit, thereby introducing an unavoidable uncertainty in the determination of the marginal stability point. Our best estimate is  $[\text{I}^-]_c = (1.94 \pm 0.02) \times 10^{-4}$  M.

## Results and Discussion

**Experiment.** In a CSTR, the chlorite-iodide reaction can assume either one of two stable steady states, depending on the constraints and the history of the system. The lower branch of steady states corresponds to the "thermodynamic branch", and the iodide concentrations there are very small. In this paper, we focus our attention on the upper branch of steady states, the "flow branch", where the steady-state iodide concentrations are close to the iodide feed concentration. The relaxation kinetics were studied for each of the steady states shown in Figure 1. No

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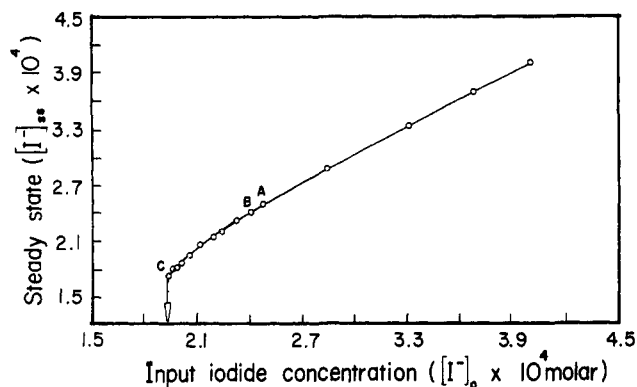
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(11) The present work was undertaken before the paper by Kramer and Ross, ref 7, was published, at the end of 1985.

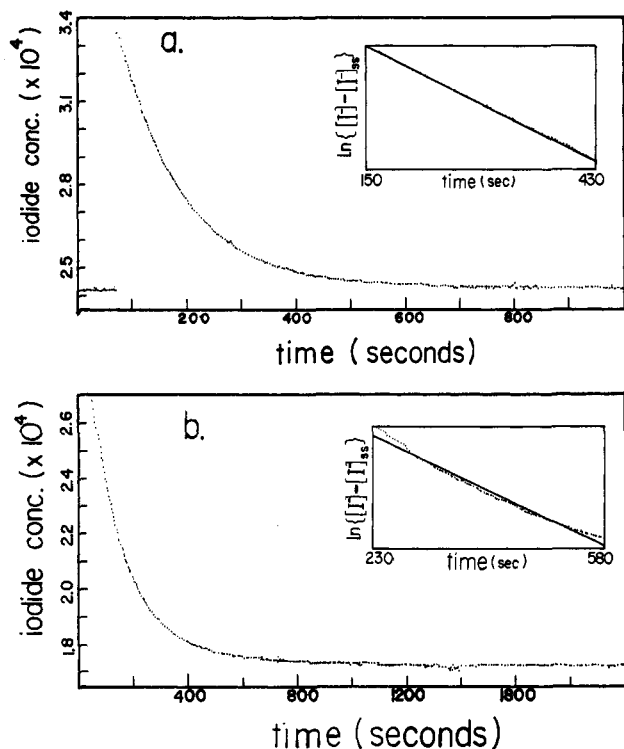
(12) Dateo, C. E.; Orban, M.; DeKepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 504–9.

(13) Kumpinsky, E.; Epstein, I. R. *J. Chem. Phys.* **1985**, *82*, 53–7.

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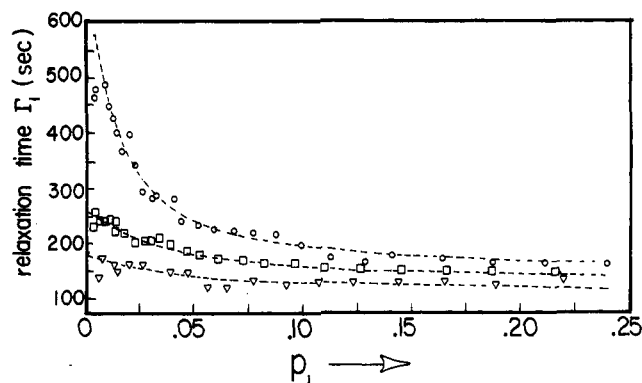
**Figure 1.** Experimental values of the steady-state iodide concentrations,  $[I^-]_{ss}$ , for the upper branch (flow branch) of the chlorite-iodide reaction in our CSTR. The reactor parameters are given in the text. The steady states are shown as a function of the feed iodide concentration,  $[NaIO_3]$ . The marginal stability point is estimated to be at  $[I^-]_0^c = 1.94 \times 10^{-4}$  M.



**Figure 2.** Experimental relaxation curves for (a)  $[I^-]_0 = 2.03 \times 10^{-4}$  M and (b)  $[I^-]_0 = 1.95 \times 10^{-4}$  M. Insets: corresponding plots of  $\ln\{[I^-] - [I^-]_{ss}\}$  vs. time, on which are superimposed the linear regression fits.

slowing down could be detected for all these points to the right of, and including, point A. For those points, the decay was found to obey first-order kinetics, with relaxation times equal, within experimental error, to the residence time, i.e.,  $112.0 \pm 0.5$  s. As one gets closer to the hysteresis limit, point B was approximately the first for which a slight critical slowing down could be detected. This point corresponds to a composition at which the upper branch begins to deviate significantly from the feed iodide concentration. Point C is the last point for which a stable steady state could be reached ( $[I^-]_0 = 1.95 \times 10^{-4}$  M).

Figure 2 illustrates typical relaxation curves for two "limit" cases, i.e., point A and point C. Even though both relaxations are exponential-like, a quantitative analysis of the corresponding data clearly shows that only the decay corresponding to point A can be described by a single exponential. The insert in Figure 2a shows the good agreement between the linear regression fit and the function  $\ln\{[I^-] - [I^-]_{ss}\}$  vs. time. This is to be compared with the relaxation curve corresponding to point C, where the deviation from a single-exponential character is clearly seen. This deviation was found to become more pronounced as one gets closer to the marginal stability point. These deviations initially met with



**Figure 3.** Relaxation times as a function for the magnitude of the perturbation  $p_1$  for  $[I^-]_0 = 2.40 \times 10^{-4}$  M ( $\nabla$ ),  $[I^-]_0 = 2.07 \times 10^{-4}$  M ( $\square$ ), and  $[I^-]_0 = 1.95 \times 10^{-4}$  M ( $\circ$ ).  $p_1$  is defined as  $\{[I^-]_i - [I^-]_{ss}\}/[I^-]_{ss}$ . Graphical extrapolations to zero perturbation are also shown as dotted lines.

our skepticism however, since the relaxation in the arsenous acid-iodide system was initially reported to apparently obey first-order kinetics.<sup>1</sup> Nevertheless, systematic and careful electrode calibrations before and after some of our runs confirmed our initial findings.

In situations such as the one encountered with point C (and others), one is confronted with the problem of determining a common reference point for unbiased estimates of the critical slowing down. This problem was recently encountered as well by Ganapathisubramanian and Showalter in their investigation of the iodate-arsenous acid reaction.<sup>6</sup> These authors chose to base their approach on a comparison of dynamical exponents obtained for a given initial perturbation and/or "extent of relaxation". Our approach is slightly different and based on the following considerations: (1) In a typical relaxation experiment, the initial time is usually chosen as to coincide with the time at which the perturbation is made. The magnitude of the perturbation (say  $p_0$ ) is then determined by the amount injected as the perturbation. This choice of initial time is however arbitrary as, in principle, any point along the relaxation curve can be defined as  $t = 0$ . Each point of a relaxation curve can therefore be seen as the initial perturbation, and the decay thereafter, as the relaxation that would have taken place, had the corresponding perturbation been injected. As a consequence, a single relaxation curve contains the same information that would be obtained from a collection of consecutive experiments in which various initial perturbations (from 0 to  $p_0$ ) would be injected. (2) Even though the overall relaxation curve (for a finite perturbation) may not be represented by a single exponential, previous model calculations have clearly shown that this limit should be reached for small enough perturbations.<sup>5</sup> The linear dynamical exponent that characterizes the approach to the marginal stability point should then follow naturally from the first-order "final" part of the relaxation. In order to apply these ideas to our experimental data, each relaxation curve was divided into  $N$  segments, each of them containing an equal number of data points (typically 20–30). Assuming single-exponential decay within each segment, corresponding first-order relaxation times, here labeled  $\tau_i$ , were calculated from plots of  $\ln\{[I^-] - [I^-]_{ss}\}$  vs. time. At each of these relaxation times was then associated the iodide concentration at the beginning of the corresponding segment,  $[I^-]_i$ . The dependency of the relaxation times ( $\tau_i$ ) on the magnitude of the perturbation ( $p_i$ ) is illustrated in Figure 3, where  $p_i = ([I^-]_i - [I^-]_{ss})/[I^-]_{ss}$ . It should be pointed out that only the first half of the full decay curve was usually considered in this treatment. As pointed out by Showalter,<sup>6</sup> the relaxation times are very sensitive to the value of the steady states. As the extent of the relaxation increases, so as the uncertainty in the relaxation times. The results shown in Figure 3 illustrate two important points: (1) As mentioned earlier, the deviation from a first-order single-exponential relaxation becomes more important as one gets closer to the hysteresis limit. The increasing nonlinear dependency of  $\tau_i$  on  $p_i$  as one gets closer to the marginal stability point,  $[I^-]_0^c$ , clearly illustrates this point. (2) The "intensity" of the critical

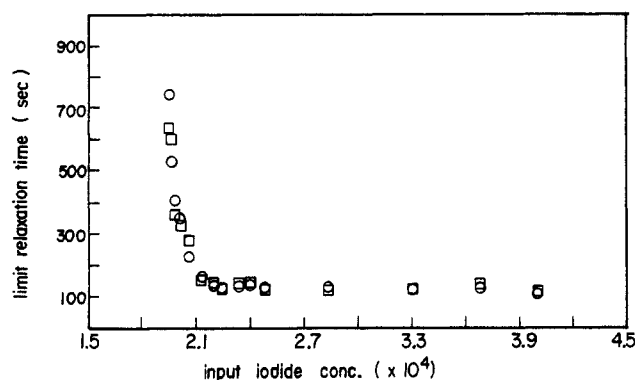


Figure 4. Limit relaxation times  $\tau_0$  as a function of the feed iodide concentration,  $[I^-]_0$ . The average results from two different sets of experiments are shown ( $\square$  and  $\circ$ ).

slowing down increases with a decrease in the size of the perturbation. This effect becomes more pronounced as one gets closer to  $[I^-]_0^c$ . This increase in  $\tau_i$  as the extent of the relaxation increases was first thought to be due to a more or less systematic underestimate of the experimental steady states, which would tend to artificially increase the relaxation times. Increasing the experimental values used for the steady states (within experimental error) was indeed found to reduce the observed dependency but not to suppress it. In order to suppress it, unrealistically high values had to be used for the steady states. As the size of the perturbation decreases, one can graphically have access to

$$\tau_0 = \lim_{p \rightarrow 0} \{\tau_i\} \quad (1)$$

Those experimental "limit relaxation times",  $\tau_0$ , correspond to the theoretical limit of infinitesimally small perturbations. As seen in Figure 4, these limit relaxation times clearly diverge as one gets closer to the hysteresis limit. This "critical slowing down" is of the same nature as the one that is observed in the iodate-arsenous acid<sup>1</sup> and the OCP<sup>7</sup> systems. Using the zero perturbation limit as a common reference point, one can estimate the dynamical exponent from the slope of the log-log plot of  $\tau_0$  vs.  $\epsilon = \{[I^-]_0 - [I^-]_0^c\}$ . From relaxation data obtained between points A and C, a value of  $0.45 \pm 0.10$  is found, i.e.,  $\tau_0 \propto \epsilon^{-z}$ , where  $z = 0.45$ . The large uncertainty is here mainly due to the graphical extrapolation procedure used in this work. The value of 0.45 however compares fairly well with theoretical predictions<sup>5</sup> as well as with experimental values obtained in the iodate-arsenous acid reaction.<sup>6</sup>

**Modeling.** In order to give an interpretation to the results presented above, let us consider the following model. The hysteresis limits of a bistable system correspond to saddle-node bifurcation points. We now make use of one of the fundamental results of a bifurcation theory, namely, that in the vicinity of such bifurcation points, the dynamical behavior of any system can ultimately be reduced to the following one-dimensional generic equation (normal form)<sup>15</sup>

$$dx(t)/dt = \alpha\epsilon - \beta x^2 \quad (2)$$

where  $x(t)$  is here proportional to the iodide concentration and

$$\epsilon = [I^-]_0 - [I^-]_0^c \quad (3)$$

$\alpha$  and  $\beta$  are constants that are model-dependent. The flow branch then corresponds to the steady state of eq 2, i.e.

$$[I^-]_{ss} = [I^-]_{ss}^c + \left\{ \frac{\alpha\epsilon}{\beta} \right\}^{1/2} \equiv [I^-]_{ss}^c + X_s \quad (4)$$

Defining

$$x(t) = X_s + \mu(t) \quad (5)$$

and substituting (5) into (2), one finds

$$d\mu(t)/dt = -\beta\mu[2X_s + \mu] \quad (6)$$

In the region  $\epsilon > 0$ , the analytical expression for the relaxation of a perturbation  $\mu(t)$  can therefore be obtained from a straightforward integration of (6), yielding

$$\mu(t) = \frac{\mu(0) e^{-2X_s\beta t}}{1 + \frac{\mu(0)}{2X_s} [1 - e^{-2X_s\beta t}]} \quad (7)$$

Equation 7 is the general expression for the relaxation curve near a saddle-node bifurcation point and should therefore be relevant to our results, near the upper hysteresis limit. Let us first note that in the limit of very small perturbations, i.e.,  $\mu(0)/2X_s \ll 1$ , the decay (7) becomes first-order, with a relaxation time

$$\tau = \frac{1}{2\beta X_s} \equiv \frac{1}{2(\alpha\beta\epsilon)^{1/2}} \quad (8)$$

As expected, a value of  $1/2$  is then obtained for the dynamical exponent ( $z$ , in  $\tau \propto \epsilon^{-z}$ ) which characterizes the approach to the marginal stability point  $[I^-]_0^c$ .<sup>4,5</sup> As the hysteresis limit is approached, the approximation  $\mu(0)/2X_s \ll 1$  becomes less and less valid. Deviations from a single-exponential decays are therefore expected to become more important as one gets closer to the hysteresis limit. As seen previously, this is indeed what is observed experimentally (Figure 3). We will now examine the experimental partitioning procedure from the point of view of the theoretical model presented above. The characteristic relaxation time  $T$  associated with an exponential decay that reaches point  $\mu_1$  at time  $t_1$  and point  $\mu_2$  at time  $t_2 = t_1 + \Delta$  is given by

$$T^{-1} = \frac{1}{\Delta} \ln \left\{ \frac{\mu_1}{\mu_2} \right\} \quad (9)$$

By substituting into eq 9 the expression for  $\mu_2(t)$  obtained from eq 7 (with  $\mu(0) \equiv \mu_1$ ), one obtains the following relationship between the effective relaxation time  $T$  and the magnitude of the perturbation  $\mu(0)$ :

$$T^{-1} = \frac{1}{\Delta} \ln \left\{ \frac{1 + \frac{\mu(0)}{2X_s} [1 - e^{-2\beta X_s \Delta}]}{e^{-2\beta X_s \Delta}} \right\} \quad (10)$$

In terms of the experimental variables

$$p_i \equiv \{[I^-]_i - [I^-]_{ss}\} / [I^-]_{ss}$$

one can write

$$\mu(0) \equiv [I^-]_i - [I^-]_{ss} = p_i [I^-]_{ss} = c p_i \quad (11)$$

where  $c = [I^-]_{ss}^c$ . Substituting (11) in (10), one gets

$$T^{-1} \simeq \frac{1}{\Delta} \ln \left\{ \frac{1 + \frac{cp}{2X_s} [1 - e^{-2\Delta(\alpha\beta\epsilon)^{1/2}}]}{e^{-2\Delta(\alpha\beta\epsilon)^{1/2}}} \right\} \quad (12)$$

These effective relaxation times are formally equivalent to the  $\tau_i$ 's previously obtained from the partitioning of our experimental decay curves. As shown in Figure 5, a plot of  $T$  as a function of the magnitude of the perturbation,  $p$ , presents the same characteristics as the corresponding experimental relaxation curves (Figure 3). Because of a fairly reduced set of experimental data points, no serious attempt was made to fit these curves to our experimental results. (This would indeed require accurate values of both constants  $\alpha$  and  $\beta$ .) Further quantitative work is therefore required in that direction. On the other hand, it can be shown that the experimental "partitioning" procedure used in this work should provide a reasonable fit to our model, provided the time increment,  $\Delta$ , is not too large (see Appendix). Let us note as well that the experimental procedure by which the limit relaxation times,  $\tau_0$ , are obtained corresponds to the weak perturbation limit,

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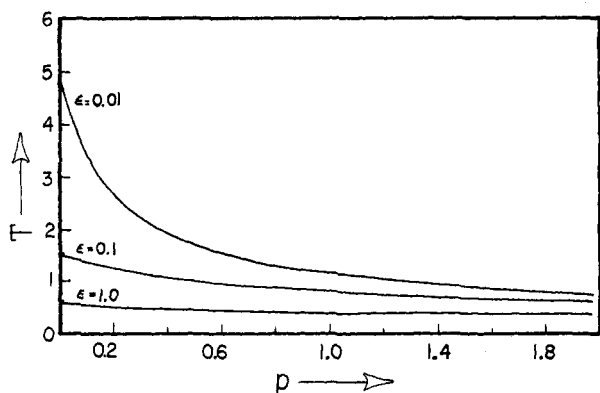


Figure 5. Effective relaxation times  $T$  as a function of the magnitude of the perturbation  $p$ , as per eq 12. For all curves,  $c = 1$ ,  $\alpha = \beta = 1$ .

i.e.,  $p \rightarrow 0$ . In the framework of our model, this corresponds to  $\mu(0)/2X_s \ll 1$  or

$$\lim_{p \rightarrow 0} T = 1/2(\alpha\beta\epsilon)^{1/2}$$

which is the correct limit (eq 8). As a final note, let us emphasize that as long as the marginal stability point is not reached, i.e. as long as  $X_s \neq 0$ , the "limit" procedure outlined above provides with a natural and unbiased access to the dynamical exponent. This treatment is however valid only as long as  $X_s \neq 0$ . At the marginal stability point,  $X_s = 0$ , and one can show that

$$t_{1/2} = 1/\beta\mu(0) \quad (13)$$

where  $t_{1/2}$  is the relaxation half-time. One here recognizes the familiar expression for a second-order relaxation. A similar result was obtained by Ganapathisubramanian and Showalter (compare eq 13 with eq 15; ref 6). Therefore, if a limit procedure is not used in the determination of relaxation time (or half-times) (such as in ref 6), one should observe a crossover from first-order-like to second-order-like relaxations as the marginal stability point is approached. As a final comment, let us note that the dynamical exponent  $z = 1/2$  is not to be confused with the exponent  $n = 1$  found by Kramer and Ross in the OCP system.<sup>7</sup> This latter value characterizes the slowing down of the initial velocity near the marginal stability point. The inverse speed, calculated at a value corresponding to the marginal stability point, can be obtained directly from eq 2, i.e.

$$\left. \frac{1}{v} \right|_{ms} \equiv \left. \frac{dt}{dx} \right|_{x=0} \equiv (\alpha\epsilon)^{-1}$$

### Summary and Conclusions

The present study has shown that the bistable chlorite-iodide reaction exhibits the phenomenon of critical slowing down in the vicinity of the upper hysteresis limit. An experimental investigation of the relaxation behavior near this upper marginal stability point also reveals that the deviation from first-order decay kinetics becomes more pronounced as one gets closer to the hysteresis limit. In order to quantify this deviation, a method is suggested in which the relaxation curves are partitioned into smaller segments. This

method leads, through graphical extrapolation, to limit values of the relaxation times. Those values correspond to the relaxation times in the theoretical limit of infinitesimal perturbation. The dynamical exponent that characterizes the linear response in the vicinity of the marginal stability point is found to be equal to  $0.45 \pm 0.10$ . This value seems to agree quite well with both theoretical predictions of  $1/2$ <sup>5</sup> and previous experimental results on the iodate-arsenous acid system.<sup>6</sup> This good agreement must however be viewed with caution since the graphical extrapolation procedure used to obtain values of the limit relaxation times  $\tau_0$  leads to a substantial uncertainty for the dynamical exponent. Our results are compared with a generic model for a saddle-node bifurcation. This model leads to an analytical expression for the relaxation curve. The qualitative agreement between the experimental results and the model is quite good. Quantitative agreement would however require further work.

**Acknowledgment.** This work was supported by CRAD Grant No. 3610-444 F4120 (J.P.L.). G.D. and P.B. gratefully acknowledge the constant support and interest of Professors I. Prigogine and G. Nicolis.

### Appendix

We consider the decay function

$$\mu(t) = \frac{\mu(0)e^{-2\beta X_s t}}{1 + \frac{\mu(0)}{2X_s}[1 - e^{-2\beta X_s t}]} \quad (A1)$$

and its deviation from the single-exponential relaxation

$$U(t) = U(0)e^{-t/\tau} \quad (A2)$$

Let  $t = t_0 + \Delta$ . Since  $t_0 = 0$  can be anywhere along the relaxation curve, one can write (A1) as

$$\mu(\Delta) = \frac{\mu(0)e^{-2\beta X_s \Delta}}{1 + \frac{\mu(0)}{2X_s}[1 - e^{-2\beta X_s \Delta}]} \quad (A3)$$

Provided the time increment  $\Delta$  is small enough, one can approximate (A3) as

$$\mu(\Delta) \simeq \frac{\mu(0)e^{-2\beta X_s \Delta}}{1 + \beta\mu(0)\Delta} \quad (A4)$$

where only the linear terms have been retained. One can also write (A4) as

$$\mu(\Delta) \simeq \mu(0)e^{-2\beta X_s \Delta}[1 - \mu(0)\beta\Delta] \quad (A5)$$

and, again, for small enough  $\Delta$

$$\mu(\Delta) \simeq \mu(0)e^{-\beta\Delta(2X_s + \mu(0))} \quad (A6)$$

which can be seen as a single-exponential decay with an "initial-condition-dependent" relaxation time,  $\tau = 1/[\beta(2X_s + \mu(0))]$  (see eq A2). One would note as well that, in the limit  $\mu(0) \rightarrow 0$ , the correct limit relaxation time  $\tau_0$  is obtained from (A6).

Registry No.  $\text{ClO}_2^-$ , 14998-27-7;  $\text{I}^-$ , 20461-54-5.