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Peter E. Strizhak
National Academy of Sciences of Ukraine

John A. Pojman
University of Southern Mississippi

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Infinite period and Hopf bifurcations for the *p*H-regulated oscillations in a semibatch reactor ($\text{H}_2\text{O}_2\text{-Cu}^{2+}\text{-S}_2\text{O}_3^{2-}\text{-NaOH}$ system)

Peter E. Strizhak

L. V. Pisarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prospect Nauki 31, Kiev 252028, Ukraine

John A. Pojman

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043

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Dynamic behavior of the *p*H-regulated oscillations has been studied for the hydrogen peroxide oxidation of thiosulfate ions in the presence of trace amounts of copper(II) ions in a semibatch reactor. A solution of 0.08 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.112 M NaOH was flowed at 0.160 mL/min into 300 mL of solution containing the H_2O_2 and Cu^{2+} in a vessel. There exists a critical value of the H_2O_2 or Cu^{2+} concentrations below which the system does not oscillate. The oscillations appear due to an infinite period bifurcation at low initial concentrations of the H_2O_2 . The initial concentration of Cu^{2+} may be considered as a bifurcation parameter in this case. Increase of the initial hydrogen peroxide concentration causes the *p*H-regulated oscillations through a nondegenerate supercritical Hopf bifurcation. The classification of bifurcations is based on the analysis of the behavior of oscillation amplitude and period at different initial concentrations of the H_2O_2 and Cu^{2+} . Our results show a possibility to distinguish different scenarios for the appearance of transient oscillations in semibatch experiments. © 1996 American Institute of Physics. [S1054-1500(96)00203-0]

We have studied *p*H-regulated oscillations in the hydrogen peroxide oxidation of thiosulfate ions in the presence of trace amounts of copper(II) in a semibatch reactor. There exists a critical value of the H_2O_2 or Cu^{2+} concentration below which the system does not oscillate. At low initial concentrations of H_2O_2 , the oscillations arise via an infinite period bifurcation with the initial concentration of Cu^{2+} as the bifurcation parameter. At fixed $[\text{Cu}^{2+}]$, increasing the initial hydrogen peroxide concentration leads to oscillations through a nondegenerate supercritical Hopf bifurcation. Our classification of bifurcations is based on an analysis of the amplitude of oscillation and the period as functions of $[\text{H}_2\text{O}_2]$ and $[\text{Cu}^{2+}]$. Our results demonstrate that it is possible to distinguish different bifurcations that lead to the birth of oscillations in semibatch experiments, in which the system naturally moves through the parametric space as time increases, and all phenomena are transient.

I. INTRODUCTION

Semibatch experiments are a modern tool to investigate nonlinear phenomena in chemical reactions.¹⁻³ This technique possesses a middle place between CSTR (continuous flow stirred tank reactor) and batch (closed reactor) experiments. In a semibatch experiment reactants are flowed into a vessel containing other reagents. The oscillatory behavior has been found for different chemical systems under semibatch conditions. Periodic pulsating phenomena were observed during the reaction of certain molten polymers with oxygen.⁴ The catalyzed oxidation of benzaldehyde by oxygen,⁵ the oxidation of NADH by O_2 ,⁶ the reduction of bromate by H_2 ,⁷ and the gas-phase reaction between H_2 and

Cl_2 show oscillations in semibatch experiments.² Recently, nonlinear phenomena have been studied for oscillating reactions in homogeneous solutions in a semibatch reactor, specifically, *p*H-regulated oscillations.^{1,8}

The experiments performed in a semibatch reactor show that this technique should be considered as a tool to investigate nonlinear phenomena in chemical systems. The semibatch experiments can be easier to perform than CSTR experiments. However, there is a question about the lack of the well-controlled conditions for the semibatch experiments. The oscillations appear after a pseudoinduction period and disappear owing to the dilution of the solution. Of course, there is no true induction period because its length depends not only on the chemistry but also on the applied physical conditions. Usually the flow rate is sufficiently low in a semibatch experiment that oscillations exist during a long time interval. During this time interval the dynamic behavior is very similar to that in a CSTR. This idea shows that semibatch experiments can be useful to find new systems that oscillate in a CSTR at low flow rate. The similarity between semibatch and CSTR experiments leads to the question whether it is possible to check the origin of oscillations in a semibatch experiment using bifurcation theory.

Our results show a possibility to distinguish different bifurcations for the birth of oscillations in semibatch experiments, in which the system naturally moves through the parametric space, and all phenomena are transient. We present evidence that it is possible in this case to apply bifurcation analysis, with some special considerations.

In this paper we apply bifurcation theory to the analysis of oscillations obtained from the semibatch experiment. We investigated the influence of the initial concentrations of copper(II) and hydrogen peroxide in a vessel with a solution

containing thiosulfate and hydroxide ions flowed in at a constant rate. This system has been reported by Rabai and Epstein in a semibatch reactor¹ and has been studied previously in a CSTR by Orban and Epstein.⁹ We found that *pH*-regulated oscillations appeared through an infinite period bifurcation or Hopf bifurcation. We present evidence that the initial concentration of copper(II) in a vessel may be considered as a bifurcation parameter. These results are of interest not only from the dynamical point of view but also because they show what bifurcations must be realized in a realistic chemical scheme for the $\text{H}_2\text{O}_2\text{-Cu}^{2+}\text{-S}_2\text{O}_3^{2-}\text{-NaOH}$ oscillating system.

II. EXPERIMENTAL SECTION

The major reagents used without additional purification were $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (Aldrich), $\text{Na}_2\text{S}_2\text{O}_3$ (Fisher, certified), NaOH (Aldrich), and hydrogen peroxide water solution [50%, about 14.6 M, (Aldrich)]. Solutions were prepared using deionized water. The stock concentration of hydrogen peroxide solution was determined by titration with the Ce^{4+} [$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, (Aldrich)] in 0.5 M H_2SO_4 (Aldrich) using ferrion (Fisher, aqueous solution) as an indicator.¹⁰

The semibatch experiments were performed in a 600 mL reactor at constant temperature 26 ± 0.5 °C. The behavior of the system was followed by measuring the *pH* (Corning Ion analyzer 250, combined glass *pH* electrode) and the Pt electrode potential versus $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{K}_2\text{SO}_4$ reference (Radiometer K601). The signals were digitized with a Macintosh IICx. A four-channel peristaltic pump (Rainin Instruments, model Rabbit-Plus) was used to feed the input solution into the reactor. Experiments were performed at a constant flow rate of 0.160 mL/min. The concentrations of reagents in the inflow solution were the same in all experiments: 0.08 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.112 M NaOH . The initial volume of solution containing copper(II) ions and hydrogen peroxide was 300 mL. The dynamical states of the system were determined by measuring the responses of *pH* and Pt electrodes as functions of the initial concentration of the reagents (Cu^{2+} and H_2O_2) in a vessel.

III. RESULTS AND DISCUSSION

Figure 1 shows the time evolution of the *pH* at different initial concentrations of copper(II) and hydrogen peroxide in a vessel. The systems start their evolution at *pH* ~6. The oscillations appear after long times (1–7 h) and exist during 2–10 h in the *pH* range between 5.5 and 9. The oscillations disappear when the *pH* increases over 9 due to dilution of the reaction mixture by the inflow of solution. The amplitude of the *pH*-regulated oscillations and their shape depend in a complex manner on the initial concentrations of the Cu^{2+} and H_2O_2 in the reactor. Our experiments show that there exists a critical value of the initial concentration for both reagents below which the *pH*-regulated oscillations do not exist. Large amplitude *pH*-regulated oscillations exist if the reaction starts at low initial concentrations of hydrogen peroxide. In Fig. 1(a) we show the case when large amplitude

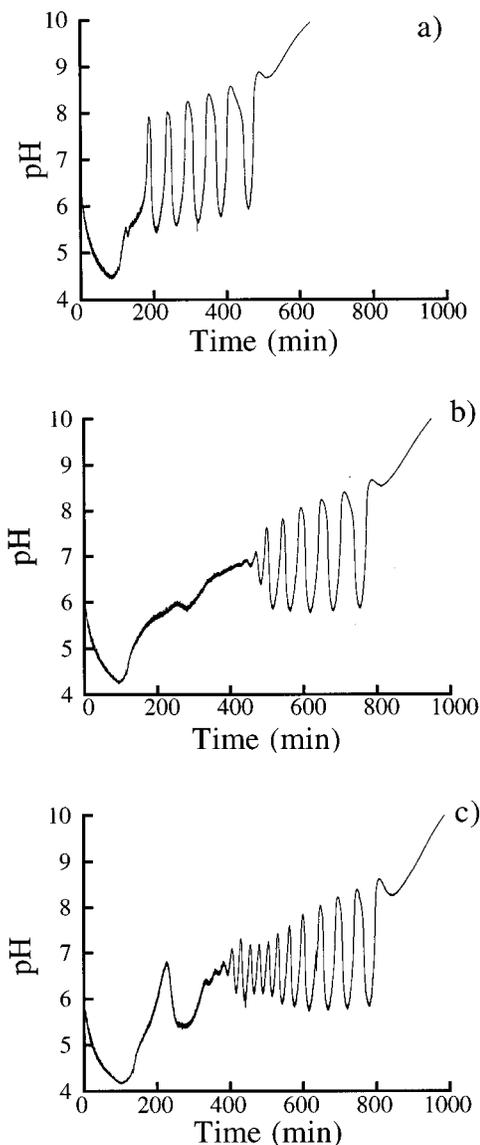


FIG. 1. Semibatch *pH* oscillations observed for different initial concentrations of reagents. A solution of 0.08 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.112 M NaOH is flowed at 0.160 mL/min into 300 mL of solution containing the following initial concentrations of reagents: (a) $[\text{Cu}^{2+}]_0 = 8.83 \times 10^{-6}$ M, $[\text{H}_2\text{O}_2]_0 = 0.056$ M, (b) $[\text{Cu}^{2+}]_0 = 8.83 \times 10^{-6}$ M, $[\text{H}_2\text{O}_2]_0 = 0.131$ M, (c) $[\text{Cu}^{2+}]_0 = 1.47 \times 10^{-5}$ M, $[\text{H}_2\text{O}_2]_0 = 0.131$ M.

pH oscillations appear just after the pseudoinduction period. The amplitudes of these oscillations do not vary significantly.

The increase of the initial concentration of the H_2O_2 leads to the appearance of the *pH* oscillations of another kind that are shown in Figs. 1(b) and 1(c). In this case the *pH* goes through few peaks during the pseudoinduction period before almost regular oscillations appear. Figure 1(c) shows the existence of a broad peak at 250 min. The oscillation period is much smaller when the oscillations appear at 340 min. We propose that the oscillations appear from the pseudosteady state that undergoes complicated changes. After the onset of oscillations, their amplitude grows monotonically.

The different behavior of *pH*-regulated oscillations de-

pending on the initial concentrations of reagents allows us to suggest that transient oscillations in this system may appear through different bifurcations. Our further steps to show that the appearance of oscillations at low initial concentration of H_2O_2 may be associated with an infinite period bifurcation, whereas oscillations appear through a Hopf bifurcation at high initial concentration of H_2O_2 . To understand the origin of oscillations in both cases we will attempt to apply bifurcation theory to the experimental data. Bifurcation theory in its classical presentation describes the qualitative change of the asymptotic dynamics of the system as a control parameter is varied.^{11–13} The asymptotic state of a semibatch reactor is identical to that of the feedstream. Therefore, the application of bifurcation theory to nonlinear phenomena in a semibatch reactor can be performed using some restrictions because the oscillations do not correspond to the asymptotic regime.

The oscillations exist during a finite time interval after their onset. They can appear through the birth of a limit cycle or be caused by a damped oscillating decay to a pseudosteady state, which is not the case presented in Fig. 1 because the oscillation amplitude does not decay during the reaction. From this point of view the appearance of oscillations may be considered as a result of the birth of a limit cycle whose properties depend on time. Before the onset of oscillations the pseudosteady state varies slowly in time and loses its stability at a moment of time that corresponds to the appearance of oscillations. One may introduce a bifurcation parameter whose value is time dependent. Its value depends on the initial concentration of reagents in a vessel, concentration of reagents in inflow, and flow rate. We performed experiments at constant flow rate and concentration of reagents in the feedstream. Therefore, the value of the time-dependent bifurcation parameter depends also on the initial concentration of reagents in a vessel:

$$\mu = \mu(t, [\text{H}_2\text{O}_2]_0, [\text{Cu}^{2+}]_0). \quad (1)$$

Investigation of the dependencies of oscillation period (T) and amplitude (A) on the control parameter near the bifurcation point (μ^*) is a useful tool to describe the nature of bifurcation.^{11,13} Such analysis can answer the question whether the control parameter is a real bifurcation parameter. The oscillation period and amplitude depend in a different manner on the value of $\Delta\mu = \mu - \mu^*$ for different bifurcations. In the simplest case these dependencies correspond to those obtained from theoretical consideration. Theory provides that for a nondegenerate supercritical Hopf bifurcation, the oscillation amplitude has a square root dependence on μ , and the oscillation frequency is linearly proportional to this value near the bifurcation point.¹² In another case, the oscillation period decreases from infinity as the system moves away from the bifurcation point; the oscillation period satisfies the following scaling law near the bifurcation point.^{14–16}

$$T \propto |\Delta\mu|^{-\gamma}. \quad (2)$$

The value of γ is positive indicating the possibility of infinite period bifurcation. Some theoretical predictions of this value have been discussed in the literature for period lengthening

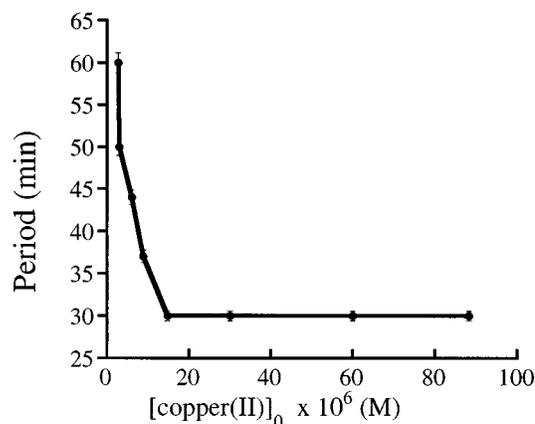


FIG. 2. The dependence of oscillation period on the initial copper(II) concentration at constant initial hydrogen peroxide concentration (0.0523 M). A solution of 0.08 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.112 M NaOH is flowed at 0.160 mL/min into a vessel. The value of the oscillation period is determined as the average over all oscillations.

near the critical value of the control parameter.¹⁴ Notice that in the general case there is no theory that predicts the scaling law for oscillation amplitude. In many cases its value is constant and does not depend on μ .

These results are valid for the true bifurcations if the system reaches an asymptotic regime. One should expect that it is possible to apply these results in the case if the bifurcation parameter changes sufficiently slowly in time, and the system moves through the bifurcation point. Bifurcations of pseudostationary states in closed systems have been treated by Gray and Scott.¹⁷ To apply this concept to the bifurcation analysis of the pH-regulated oscillations in a semibatch, we consider two cases that correspond to low and high initial concentration of hydrogen peroxide in a vessel.

Low initial concentration of hydrogen peroxide. In this case the oscillation amplitude and period do not change significantly during the time interval when oscillations exist. The oscillations appear suddenly after the pseudoinduction period. The pseudoinduction period does not depend on the copper(II) concentration but is determined solely by the initial hydrogen peroxide concentration. Therefore the value of the bifurcation parameter, at the moment of time that corresponds to the appearance of oscillations, depends on the initial concentration of copper(II) only if the initial concentration of hydrogen peroxide is constant:

$$\mu = \mu(t_i, [\text{H}_2\text{O}_2]_0, [\text{Cu}^{2+}]_0) = \mu([\text{Cu}^{2+}]_0), \quad (3)$$

where t_i is the value of the pseudoinduction period.

We investigated this situation at $[\text{H}_2\text{O}_2]_0 = 0.056$ M. We found that there exists a critical value of the initial copper(II) concentration ($C^* = 2.55 \times 10^{-6}$ M) below which oscillations do not appear. Figure 2 shows the dependence of the average period on the initial copper(II) concentration in a vessel. The oscillation period decreases monotonically if the initial concentration of copper(II) is increased in a narrow range above its critical value. Further increase of the Cu^{2+} concentration does not change the oscillation period. These

observations allow us to suggest that oscillations appear because of an infinite period bifurcation at low initial concentration of hydrogen peroxide if the initial concentration of copper(II) may be associated with the value of the bifurcation parameter. To show the direct correspondence between these two values one should linearize the dependence (3) in a narrow region where oscillation period depends strongly on the initial concentration of copper(II):

$$\mu = \mu([\text{Cu}^{2+}]_0) = \mu(C_{\text{Cu}}^*) + \alpha(C_{\text{Cu}} - C_{\text{Cu}}^*), \quad (4)$$

where C_{Cu}^* is a critical value of the initial copper(II) concentration. It follows from this equation that

$$\Delta\mu = \mu([\text{Cu}^{2+}]_0) - \mu(C_{\text{Cu}}^*) \approx \Delta C_{\text{Cu}}^* = C_{\text{Cu}} - C_{\text{Cu}}^*. \quad (5)$$

Equations (2) and (5) give us a possibility to expect the existence of a scaling between the oscillation period and the initial concentration of copper(II):

$$T \approx |\Delta C_{\text{Cu}}|^{-\gamma}. \quad (6)$$

We used the experimental data shown in Fig. 2 to find the scaling parameter from the log–log plot of period versus the distance from the critical point in units of the Cu^{2+} concentration. The scaling law is valid in a sufficiently wide interval of initial concentrations of copper $(2.55\text{--}14.7) \times 10^{-6}$ M. The correlation coefficient equals 0.957, which indicates a good approximation of oscillation period dependencies by scaling law (6). The scaling parameter equals $\gamma = 0.14 \pm 0.02$. This value of scaling parameter does not give a direct possibility to classify the infinite period bifurcation in this case as saddle-loop ($\gamma = 1$) or saddle-node ($\gamma = 0.5$).

Analysis of the dynamical behavior of pH-regulated oscillations at low concentration of hydrogen peroxide shows that the increase of copper(II) concentration near its critical value leads to the appearance of oscillations through the infinite period bifurcation. Moreover we showed that it is the case when the initial concentration of copper(II) may be considered as a bifurcation parameter.

The type of bifurcation depends on the hydrogen peroxide concentration. The other bifurcation is realized at high initial concentration of hydrogen peroxide.

High initial concentration of hydrogen peroxide. Our experiments show that the amplitude and period of oscillations vary significantly during a reaction started at high initial concentration of hydrogen peroxide. The pseudoinduction period varies if either of the initial concentrations of reagents in a vessel are changed, as can be seen from data presented in Figs. 1(b) and 1(c). Therefore, it is not evident how to obtain a simple relationship between the time-dependent bifurcation parameter and the initial concentrations of reagents in this case. Moreover, it is crucial in this case that the oscillation amplitude depends on time. It means that transient oscillations are characterized by a departure of the system from a bifurcation point. The monotonic growth of the oscillation amplitude in time is clearly visible from data shown in Figs. 1(b) and 1(c). This suggests that oscillations appear due to the supercritical Hopf bifurcation when the bifurcation parameter varies slowly in time.

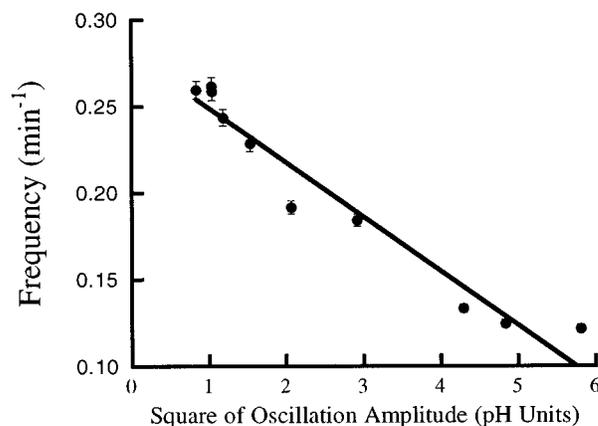


FIG. 3. The dependence of the oscillation frequency on the square of the oscillation amplitude for the experimental data shown in Fig. 1(c).

In this case the equations for the oscillation amplitude and phase can be written in the following form:

$$\begin{aligned} \frac{dA}{dt} &= \mu(t)A - \alpha_1 A^3, \\ \frac{d\theta}{dt} &= \Omega_0 - \alpha_2 A^2, \end{aligned} \quad (7)$$

where $\mu(\tau)$ is a time-dependent bifurcation parameter and values of α_1 , α_2 , Ω_0 are approximately constant.

Here the bifurcation parameter depends on time. This is the difference between these equations and those written for the true supercritical Hopf bifurcation when the bifurcation parameter does not change in time.^{11–13} This difference leads to the absence of the scaling law between oscillation amplitude and the value of the time-dependent bifurcation parameter. Equations (7) illustrate the delay of the Hopf bifurcation in time. The system does not oscillate when the bifurcation parameter corresponds to its critical value for the time-independent case. The system does start to oscillate when the bifurcation parameter exceeds its critical value. Nevertheless it is possible to extract the quantitative relation from these equations in the case of time-dependent bifurcation. The following relation between oscillation frequency and amplitude follows from Eqs. (7):

$$\Omega = 2\pi/T = \Omega_{(0)} - \alpha_2 A^2. \quad (8)$$

This relationship gives a quantitative tool to check the possibility of a time-dependent supercritical Hopf bifurcation. Figure 3 shows the dependence of frequency on the square of the amplitude for the oscillations shown in Fig. 1(c). The oscillation frequency is linearly proportional to the square of the amplitude. (The correlation coefficient of linear dependence is 0.983.) The oscillation frequency grows monotonically if the oscillation amplitude is increased.

The linear dependence presented in Fig. 3 suggests that the pH-regulated oscillations appear due to a nondegenerate supercritical Hopf bifurcation. We found that oscillations appear through a Hopf bifurcation if the initial concentration of

hydrogen peroxide is 0.131 M and the initial concentration of copper(II) is varied. The same situation is realized at the highest values of initial hydrogen peroxide concentrations.

IV. CONCLUSIONS

The analysis of dynamic behavior of *p*H-regulated oscillations performed in this paper shows that the initial concentrations of copper(II) ions and hydrogen peroxide determine the type of bifurcation that is responsible for the appearance of *p*H-regulated oscillations in a semibatch reactor. These observations are in good agreement with experiments in a CSTR.⁹ The *p*H-regulated oscillations may appear due to an infinite period bifurcation or a time-dependent supercritical Hopf bifurcation. These observations should be taken into account in the construction of the realistic kinetic scheme for the *p*H-regulated oscillations in the $\text{H}_2\text{O}_2\text{-Cu}^{2+}\text{-S}_2\text{O}_3^{2-}\text{-NaOH}$ system. We showed that the initial concentration of copper(II) in a vessel may be considered as a real bifurcation parameter if oscillations appear because of an infinite period bifurcation. The time dependence of the control parameter is crucial if oscillations appear owing to a supercritical Hopf bifurcation, and there is no possibility to associate the value of bifurcation parameter with the initial concentrations of reagents.

Our results show an example of where it is possible to apply bifurcation theory to semibatch experiments. These experiments can be used as a tool to investigate the nature of

nonlinear chemical systems only under some restrictions. To check the nature of bifurcation one must consider the time dependence of the control parameter.

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