A pH-Regulated Chemical Oscillator: The Homogeneous System of Hydrogen Peroxide−Sulfite−Carbonate−Sulfuric Acid in a CSTR[1]

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Periodic oscillations in both pH and the potential of a platinum electrode have been observed in the H_2O_2−Na_2SO_3−Na_2CO_3−H_2SO_4 system using a continuous-flow stirred tank reactor. This homogeneous system was studied at 25 °C over a wide range of concentrations and flow rates. Phase diagrams delineating the behavior of the system under various conditions have been obtained. The main features of the experimental results have been duplicated by a computer simulation based on a proposed model. Positive feedback in H^+ is provided mainly by the autocatalytic oxidation of HSO_3^- by H_2O_2. The main process for negative feedback in H^+ is the dehydration of H_2CO_3 to CO_2. Simulations predict a period-doubling route to chaos, which is also suggested by experimental results. The effects of carbonate and acid impurities in the Na_2SO_3 source and of atmospheric CO_2 are both simulated and discussed.

Introduction

The first pH-regulated chemical oscillator, involving the reaction of hydrogen peroxide with sulfide ion in a continuous-flow stirred tank reactor (CSTR), was discovered over 10 years ago.[2] Since that time, the number of pH oscillators has grown rapidly. The two main characteristics of pH oscillators are (1) a large-amplitude change in pH is observed and (2) the pH change is an important kinetic driving force, rather than being just a result of the oscillation.

Recently, some promising ideas for practical applications of pH oscillators have been proposed. One of these potential applications involves development of temporally controlled drug delivery systems.[3,4] These systems are based on the changing ratio of the charged to uncharged forms of the drug as the pH of the donor solution undergoes oscillation. Since only the uncharged form of the drug can permeate lipophilic membranes, a periodic delivery profile is obtained. Another proposed application is in simulating the periodic motion of muscular tissue. A pH oscillator can be used to control the rhythmically pulsatile mechanical motion of polymer hydrogel systems.[5]

While the discovery of the first pH oscillators may have been somewhat fortuitous, Epstein et al. subsequently have developed a model for the family of pH oscillators, which allows for their systematic design.[6,7] Two types of reactions involving H^+ are required in designing a pH oscillator: (1) an autocatalytic H^+-producing reaction (positive feedback); (2) an H^+-consuming reaction (negative feedback).

Mixed Landolt type systems, involving oxidation of sulfur(IV) species by IO_3^-, BrO_3^-, or H_2O_2, often have been used as the autocatalytic reactions. Reductants such as ferrocyanide, thiosulfate, or thiourea typically have been used along with the above-mentioned oxidants to provide the H^+-consuming reactions. Recently, the enzyme horseradish peroxidase (HRP) has been used to vary the strength of the negative feedback in a pH oscillator.[8]

While studying one of the sulfur-based oscillators in a CSTR, we were surprised to observe that sustained regular oscillations, both in pH and in potential of a platinum electrode, could be obtained with only the reagents H_2O_2 and Na_2SO_3 being introduced into the reactor. Although the reaction between hydrogen peroxide and sulfite ion is thought to be a significant (if not rate-determining) step in models for several sulfur-based oscillators, it was not at first clear what reaction(s) provided the negative feedback in H^+.

Further studies led to the inevitable conclusion that impurities in the Na_2SO_3 played a significant role in the pH oscillator. Different sulfite sources gave very different results, even to the extreme of one source giving oscillations under certain conditions, while the other gave only steady state. Addition of the proper amount of acid or base (depending on the sulfite source) was found to give oscillations where only steady state was observed previously. This observation is consistent with the known presence of acid-producing impurities, such as thiosulfate, in sulfite samples.[9]

Carbonate also is known to be a significant impurity in Na_2SO_3. Addition of small amounts of Na_2CO_3 to the system enhanced oscillations, thus demonstrating the importance of carbonate in this oscillator.

Since sulfite is sensitive to oxidation by O_2 in air, Na_2SO_3 solutions were prepared fresh daily. In addition, it was found that bubbling both the water used for solution preparation and the solutions themselves (before entering the reactor) with N_2 gave different results than without bubbling. This strongly suggested that the CO_2 in air had a significant effect on the system. Further, it suggested that the CO_2 generated by reaction of carbonate with acid might play a vital role in the oscillator.

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Thus, the pH oscillator reported here involves the $H_2O_2-Na_2SO_3-Na_2CO_3-H_2SO_4$ system in a CSTR. This system was studied over a range of concentrations and flow rates at 25 °C. Although the results of this study will receive the main emphasis in this paper, the earlier results for the $H_2O_2-Na_2SO_3$ system will also be presented for comparative purposes and to emphasize the important role that impurities can play in an oscillating system.

While we were in the midst of preparing this manuscript, Rabai reported the results of a study done on a similar system using a rather different method.[10] In the discussion below, we will point out the main differences between the two studies and the significance of this present work.

Experimental Section

Materials. Reagent grade H_2O_2, Na_2SO_3, Na_2CO_3, and H_2SO_4 were used without further purification. With one exception, all reagents used were distributed by Fisher (certified A.C.S.). In the study of the effect of impurities in sodium sulfite, both Fisher and Fluka Na_2SO_3 sources were used.

For the earlier experiments with only H_2O_2 and Na_2SO_3 in the CSTR, the sulfite source was Fisher [98.9%; free alkali (as Na_2CO_3), 0.05%; unknown S_2O_3]. The study of the effect of sulfite impurities involved both Fluka [>99.5%; titratable free base, unknown; <0.02% as S_2O_3] and Fisher [99.8%; titratable base, 0.02 meq/g; unknown S_2O_3]. In the studies done on the $H_2O_2-Na_2SO_3-Na_2CO_3-H_2SO_4$ system, only the latter source of sodium sulfite was used.

All solutions were made using triply distilled water. The water used in preparing solutions for the multicomponent oscillator was first purged with N_2. For reasons mentioned in the Introduction, sulfite solutions were prepared fresh daily. Stock solutions of Na_2CO_3 and H_2SO_4 were prepared, the latter being standardized by titration with standardized NaOH using phenolphthalein as an indicator. The concentration of H_2O_2 was determined iodometrically using standardized $Na_2S_2O_3$.

Reactor. A Plexiglas water-jacketed reactor was used for all CSTR experiments. The reactor volume was 44−47 mL, depending on the particular reactor used for a given experiment. Inlet ports were on the lower side of the reactor, and an outlet port was in the reactor cap. A combination glass electrode was used to follow pH; potential was monitored using a platinum electrode with a calomel reference electrode. All electrode probes were inserted through the reactor cap. A magnetic stirrer was used to ensure uniform mixing.

Methods. Reactant solutions were pumped into the reactor through two inlet tubes by means of a Manostat peristaltic pump. For experiments with the multicomponent system, one inlet stream contained H_2O_2 and H_2SO_4 and the other contained Na_2SO_3 and Na_2CO_3. Throughout these experiments, the solutions in their reservoirs were bubbled with N_2 but not the reactor itself.

Maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered down to zero in obtaining the flow (F) branch. Sufficient time was allowed at each flow rate for the system to either oscillate or reach a stationary steady state. The thermodynamic (T) branch then was obtained by increasing the pump speed gradually until the maximum flow rate was reached. Both pH and potential were recorded throughout. All experiments were carried out at 25 °C.

Results

$H_2O_2-Na_2SO_3$ System. The early experiments were done with only hydrogen peroxide and sodium sulfite solutions being fed into the CSTR at 25 °C. As indicated previously, the solutions were not bubbled with N_2. Figure 1 shows the phase diagram in the $[H_2O_2]_0-[SO_3^{2-}]_0$ plane at the critical flow rate (reciprocal residence time) of $k_0 = 7.3 \times 10^{-4}$ s^{-1}. Regular oscillations were observed in the region where $[H_2O_2]_0 = 0.024-0.12$ M and $[SO_3^{2-}]_0 = 0.002-0.014$ M. Outside of this region, either the basic steady state (SSI) or the acidic steady state (SSII) was observed, with the exception that there was a very small region of bistability between SSI and SSII at very low reactant concentrations. The maximum amplitude of the oscillations was about 2 pH units and for potential about 85 mV.

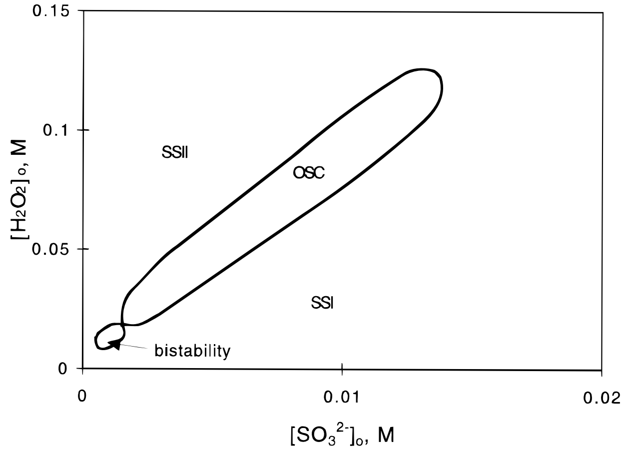

Figure 1. Phase diagram in the $[H_2O_2]_0-[SO_3^{2-}]_0$ plane at $k_0 = 7.3 \times 10^{-4}$ s^{-1} based on 20 experimental points. Regions are defined as follows: SSI, basic steady state; SSII, acidic steady state; OSC, oscillations.

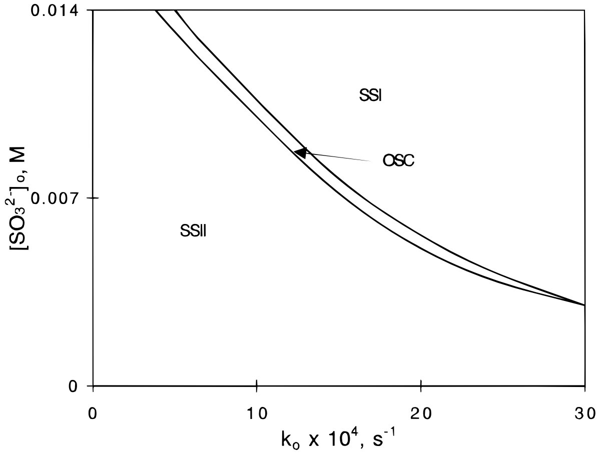

Figure 2. Phase diagram in the $[SO_3^{2-}]_0-k_0$ plane with $[H_2O_2]_0 = 0.12$ M. Regions defined as in Figure 1.

The phase diagram in the $[SO_3^{2-}]_0-k_0$ plane with $[H_2O_2]_0 = 0.12$ M is given in Figure 2. Oscillations occurred in only a very narrow region, where $[SO_3^{2-}]_0 = 0.0035-0.0125$ M and $k_0 = (31-6.2) \times 10^{-4}$ s^{-1}. Outside of this region, either SSI or SSII was observed.

$H_2O_2-Na_2SO_3-Na_2CO_3-H_2SO_4$ System. In addition to the hydrogen peroxide and sodium sulfite reactants being fed into the reactor in the manner indicated above, in most of the experiments sodium carbonate and sulfuric acid were added as well. As mentioned previously, the solutions were bubbled continuously with N_2 prior to entering the reactor. Periodic oscillations were obtained at 25 °C over a wide range of initial reactant concentrations and flow rates. The results are summarized in Figures 3−5 by use of phase diagrams.

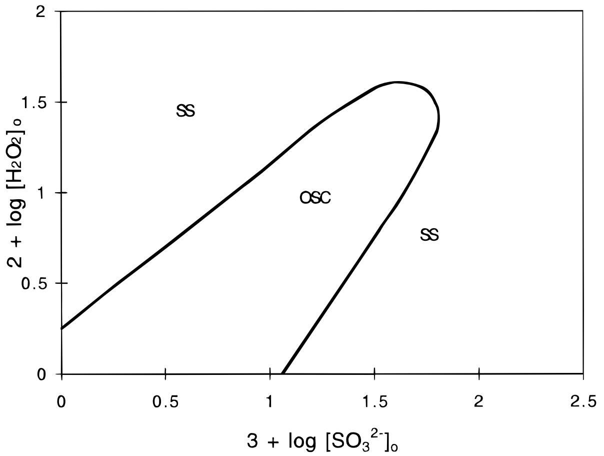

Figure 3. Phase diagram in the log $[H_2O_2]_0$−log $[SO_3^{2-}]_0$ plane. Fixed concentrations: $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M; $[H^+]_0 = 5.21 \times 10^{-4}$ M. Based on 28 experimental points. Regions are defined as follows: OSC, oscillations; SS, steady state.

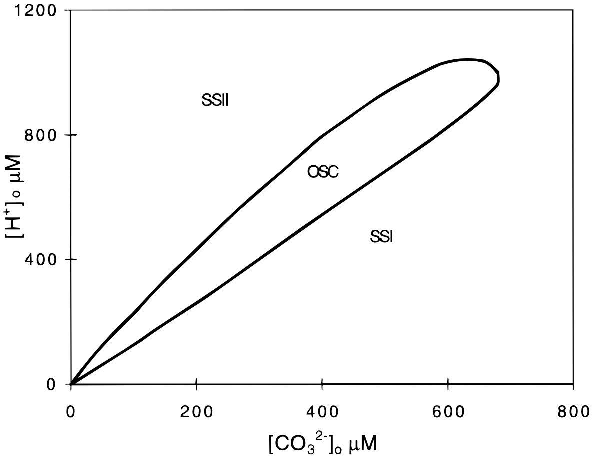

Figure 4. Phase diagram in the $[H^+]_0$−$[CO_3^{2-}]_0$ plane. Fixed concentrations: $[H_2O_2]_0 = 5.85 \times 10^{-2}$ M; $[SO_3^{2-}]_0 = 6.00 \times 10^{-3}$ M. Based on 30 experimental points. Regions defined as in Figure 1.

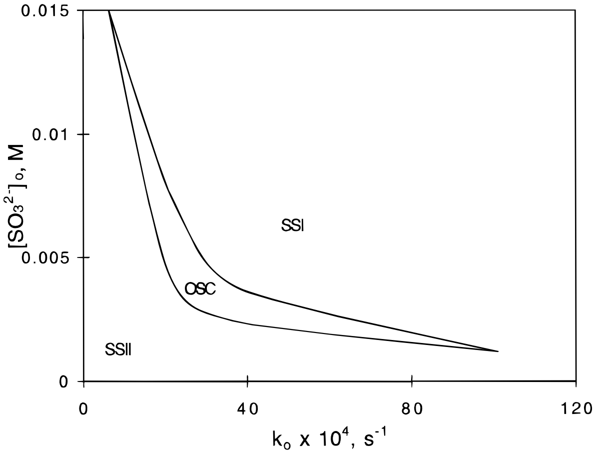

Figure 5. Phase diagram in the $[SO_3^{2-}]_0$−k_0 plane. Fixed concentrations: $[H_2O_2]_0 = 3.0 \times 10^{-2}$ M; $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M; $[H^+]_0 = 5.21 \times 10^{-4}$ M. Regions defined as in Figure 1.

TABLE 1: Reaction Mechanism for the Hydrogen Peroxide−Sulfite−Carbonate pH Oscillator

no.	reaction
(1)	$H_2O_2 + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O$
(2)	$SO_3^{2-} + H^+ \rightarrow HSO_3^-$
(3)	$HSO_3^- \rightarrow SO_3^{2-} + H^+$
(4)	$H_2O_2 + HSO_3^- \rightarrow SO_4^{2-} + H^+ + H_2O$
(5)	$H_2O_2 + HSO_3^- + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O$
(6)	$CO_3^{2-} + H^+ \rightarrow HCO_3^-$
(7)	$HCO_3^- \rightarrow CO_3^{2-} + H^+$
(8)	$HCO_3^- + H^+ \rightarrow H_2CO_3$
(9)	$H_2CO_3 \rightarrow HCO_3^- + H^+$
(10)	$H_2CO_3 \rightarrow CO_2$ (aq) $+ H_2O$
(11)	CO_2 (aq) $+ H_2O \rightarrow H_2CO_3$

Figure 3 shows the phase diagram in the $[H_2O_2]_0$−$[SO_3^{2-}]_0$ plane for fixed concentrations of Na_2CO_3 and H_2SO_4. The wide range of peroxide−sulfite concentrations where oscillations are observed is emphasized by the fact that this is a log−log plot. For $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M and $[H^+]_0 = 5.21 \times 10^{-4}$ M, regular oscillations were observed up to about 0.35 M H_2O_2 and 0.03 M Na_2SO_3. Specific flow rates where oscillations occurred were dependent on the initial concentrations of hydrogen peroxide and sodium sulfite.

The phase diagram in the $[H^+]_0$−$[CO_3^{2-}]_0$ plane is given in Figure 4. Oscillations were obtained only for rather specific $[H^+]_0/[CO_3^{2-}]_0$ ratios at fixed concentrations of H_2O_2 and Na_2SO_3. For $[H_2O_2]_0 = 5.85 \times 10^{-2}$ M and $[Na_2SO_3]_0 = 6.00 \times 10^{-3}$ M, regular oscillations were observed up to slightly over 1×10^{-3} M H^+ and about 6.6×10^{-4} M CO_3^{2-}. Specific flow rates where oscillations occurred were dependent on the initial concentrations of acid and carbonate. It is clear from the diagram that the region of oscillations narrows greatly at low concentrations of H^+ and CO_3^{2-}. On the other hand, at sufficiently high acid and carbonate concentrations, only steady state is observed.

Finally, the $[SO_3^{2-}]_0$−k_0 phase diagram is shown in Figure 5. Oscillations were found over a rather narrow range of $[SO_3^{2-}]_0$ and k_0 at fixed concentrations of hydrogen peroxide, carbonate, and acid. For $[H_2O_2]_0 = 3.0 \times 10^{-2}$ M, $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M, and $[H^+]_0 = 5.21 \times 10^{-4}$ M, regular oscillations were observed only in the region where $[SO_3^{2-}]_0 = (2.00−15.0) \times 10^{-3}$ M and $k_0 = (89.0−6.03) \times 10^{-4}$ s^{-1}. The limited oscillatory region found in Figure 5 is similar to that shown in Figure 2, where in the latter case neither carbonate nor acid was added and solutions were not bubbled with N_2.

Mechanism

The H_2O_2−SO_3^{2-}−CO_3^{2-}−H^+ oscillator can be thought of as being derived from the H_2O_2−SO_3^{2-}−$Fe(CN)_6^{4-}$−H^+ oscillating system,[11] with CO_3^{2-} substituted for $Fe(CN)_6^{4-}$. It would be expected that the H^+-producing reactions in the present oscillator would be the same as those in the ferrocyanide system. Also, it would be reasonable to assume that the dehydration of carbonic acid might replace the oxidation of ferrocyanide as the H^+-consuming process.

The proposed reaction mechanism for the hydrogen peroxide−sulfite−carbonate pH oscillator is given in Table 1. The corresponding rate equations and rate constant values are shown in Table 2.

Reactions 1, 4, and 5 all involve oxidation by hydrogen peroxide and are significant H^+-producing steps at some point in the oscillations. By far, the most important of these is reaction 5. The positive feedback in H^+ is mainly provided by the autocatalytic oxidation of HSO_3^- by H_2O_2. The main process for negative feedback in H^+ is reaction 10, the relatively slow dehydration of H_2CO_3 to aqueous CO_2. The dehydration reaction indirectly results in the rapid consumption of H^+ by HCO_3^- according to reaction 8.

It is important to note that the mechanism proposed in Table 1 involves only homogeneous reactions. Unlike the model used by Rabai[10] in which it was required that aqueous CO_2 be

TABLE 2: Rate Equations and Rate Constant Values

rate equations	rate constants at 25 °C
$R_1 = k_1[H_2O_2][SO_3^{2-}]$	$k_1 = 0.2\ M^{-1}\ s^{-1}$
$R_2 = k_2[H^+][SO_3^{2-}]$	$k_2 = 5.0 \times 10^{10}\ M^{-1}\ s^{-1}$
$R_3 = k_3[HSO_3^-]$	$k_3 = 3.0 \times 10^3\ s^{-1}$
$R_4 = k_4[H_2O_2][HSO_3^-]$	$k_4 = 3.5\ M^{-1}\ s^{-1}$
$R_5 = k_5[H_2O_2][HSO_3^-][H^+]$	$k_5 = 1.5 \times 10^7\ M^{-2}\ s^{-1}$
$R_6 = k_6[H^+][CO_3^{2-}]$	$k_6 = 1 \times 10^{11}\ M^{-1}\ s^{-1}$
$R_7 = k_7[HCO_3^-]$	$k_7 = 4.8\ s^{-1}$
$R_8 = k_8[H^+][HCO_3^-]$	$k_8 = 5 \times 10^{10}\ M^{-1}\ s^{-1}$
$R_9 = k_9[H_2CO_3]$	$k_9 = 8.6 \times 10^6\ s^{-1}$
$R_{10} = k_{10}[H_2CO_3]$	$k_{10} = 16.5\ s^{-1}$
$R_{11} = k_{11}[CO_2\ (aq)]$	$k_{11} = 4.3 \times 10^{-2}\ s^{-1}$

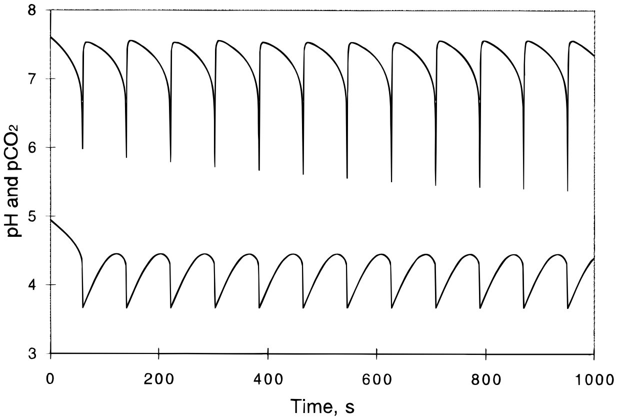

Figure 6. Calculated oscillations in pH (upper) and pCO_2 (lower) at $k_0 = 2.30 \times 10^{-3}\ s^{-1}$. Input concentrations: $[H_2O_2]_0 = 5.97 \times 10^{-2}$ M; $[SO_3^{2-}]_0 = 1.50 \times 10^{-2}$ M; $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M; $[H^+]_0 = 5.22 \times 10^{-4}$ M.

converted to gaseous CO_2 and continuously removed from the system, our mechanism does not require such a heterogeneous process. It also should be noted that the rate constants given in Table 2 are at 25 °C, not at 4 °C as used by Rabai.

Computer Simulations

The rate equations given in Table 2 were integrated numerically with SIMULATE.[12] This program simulates chemical systems following mass-action kinetics and uses a numerical integrator capable of solving stiff systems of differential equations.

$H_2O_2-Na_2SO_3-Na_2CO_3-H_2SO_4$ System. As a test of the mechanism given in Table 1, we attempted to simulate a typical experimental system that gave regular oscillations at 25 °C. This system had reactor concentrations of $[H_2O_2]_0 = 5.97 \times 10^{-2}$ M, $[SO_3^{2-}]_0 = 1.50 \times 10^{-2}$ M, $[CO_3^{2-}]_0 = 3.00 \times 10^{-4}$ M, and $[H^+]_0 = 5.22 \times 10^{-4}$ M. Calculated pH and pCO_2 curves are shown in Figure 6 for a flow rate (reciprocal residence time) of $k_0 = 2.30 \times 10^{-3}\ s^{-1}$. This simultaneous plot clearly shows how $[H^+]$ and $[CO_2]$ parallel one another. It also helps in understanding the chemical processes responsible for the oscillations. After an oscillation occurs, the dehydration of H_2CO_3, along with further input of SO_3^{2-}, serves to bring the system back to the basic steady state (SSI). Eventually, the autocatalytic production of H^+ predominates, causing another oscillation to occur, again converting HCO_3^- to H_2CO_3, which then undergoes dehydration to CO_2.

For the above reactant concentrations, regular oscillations were also obtained at as high a flow rate as $k_0 = 2.64 \times 10^{-3}\ s^{-1}$. The calculated pH curve at this flow rate is shown in Figure 7. Oscillations in this case are of lower frequency and greater amplitude than those in Figure 6.

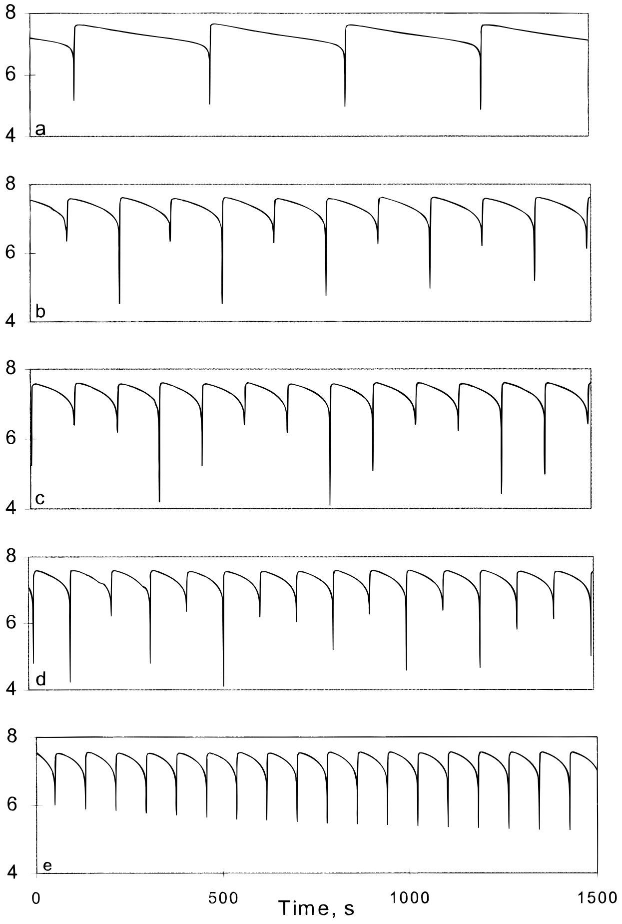

Figure 7. Calculated pH−time responses at different values of $k_0 \times 10^3\ s^{-1}$: (a) 2.64 (low frequency); (b) 2.50 (period 2); (c) 2.44 (period 4); (d) 2.38 (chaos); (e) 2.30 (high frequency). Input concentrations as in Figure 6.

Very interesting results were found as the value of k_0 was reduced from $2.64 \times 10^{-3}\ s^{-1}$ down to $2.30 \times 10^{-3}\ s^{-1}$. Calculated pH curves over this range of flow rates are shown in Figure 7. Period doubling leading to chaos was found. Period 2 oscillations were observed at $k_0 = 2.50 \times 10^{-3}\ s^{-1}$, period 4 oscillations were found at $k_0 = 2.44 \times 10^{-3}\ s^{-1}$, and chaotic behavior occurred at $k_0 = 2.38 \times 10^{-3}\ s^{-1}$. Strong evidence for the existence of chaos is the fact that period 3 oscillations were observed (at $k_0 = 2.32 \times 10^{-3}\ s^{-1}$). Finally, at $k_0 = 2.30 \times 10^{-3}\ s^{-1}$, regular oscillations of higher frequency and smaller amplitude were obtained, as previously shown also in Figure 6.

Generally, it was possible to simulate our experimental results quite well. It should be noted, however, that the specific experimental values of flow rates required to obtain regular oscillations were somewhat lower than those needed in the computer simulation, even though the flow rate ranges were similar. Also, as will be discussed further below, better agreement between experimental and simulated curves was obtained by using a value for k_4 of 3.5 $M^{-1}\ s^{-1}$, rather than that of 7 $M^{-1}\ s^{-1}$ used by Rabai et al.[11]

$H_2O_2-Na_2SO_3$ System. As a further test of the mechanism in Table 1, we attempted to simulate some of the earliest CSTR studies done with only hydrogen peroxide and sodium sulfite solutions being fed into the reactor at 25 °C. As mentioned above, these studies were done without bubbling N_2 through the reservoir solutions. Figure 8 shows the simulated results for an experiment involving reactor concentrations of $[H_2O_2]_0$

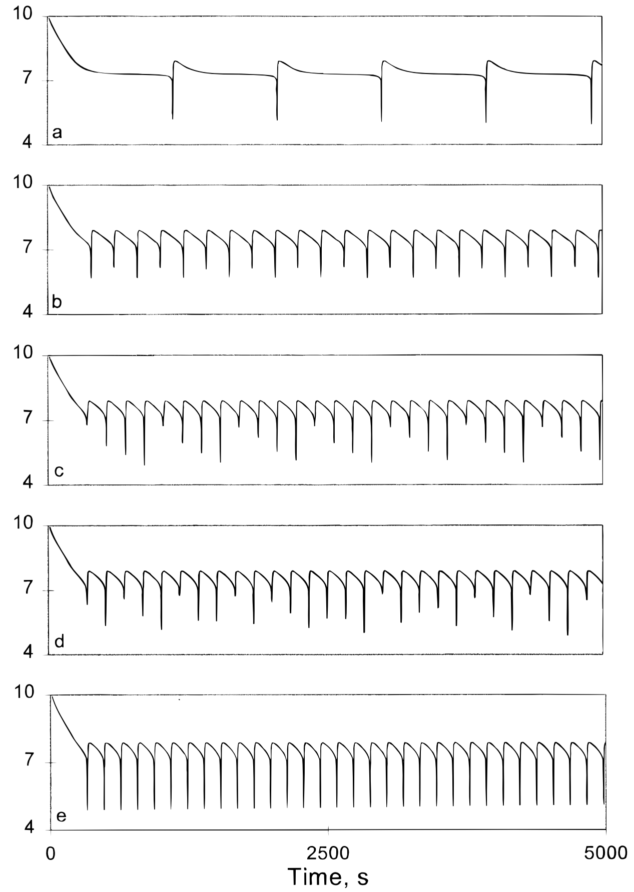

Figure 8. Calculated pH−time responses at different values of $k_0 \times 10^4$ s^{-1}: (a) 6.978 (low frequency); (b) 6.850 (period 2); (c) 6.760 (period 4); (d) 6.745 (chaos); (e) 6.674 (high frequency). Input concentrations: $[H_2O_2]_0 = 0.117$ M; $[SO_3{}^{2-}]_0 = 1.25 \times 10^{-2}$ M; $[CO_3{}^{2-}]_0 = 7.4 \times 10^{-6}$ M; $[H^+]_0 = 1.25 \times 10^{-5}$ M; $[CO_2]_0 = 1.6 \times 10^{-5}$ M.

$= 0.117$ M and $[SO_3{}^{2-}]_0 = 1.25 \times 10^{-2}$ M. Since the sulfite source used (Fisher) had 0.05% Na_2CO_3 present as an impurity, a value of 7.4×10^{-6} M was used for $[CO_3{}^2]_0$. On the basis of a determination of the approximate effective amount of acid (or acid-producing) impurity in a similar (Fisher) sulfite source, a value of $[H^+]_0 = 1.25 \times 10^{-5}$ M was used in the simulation. Finally, to account for the effect of atmospheric carbon dioxide, a value of $[CO_2]_0 = 1.6 \times 10^{-5}$ M was estimated. This value corresponds to an observed pH of 6.0 for triply distilled water containing an equilibrium amount of CO_2.[13]

The simulations shown in Figure 8 are perhaps surprisingly similar to those obtained experimentally. The flow rate where oscillations first start in the F-branch (6.978×10^{-4} s^{-1}) is virtually identical to that found experimentally (6.98×10^{-4} s^{-1}). Although this may be somewhat fortuitous, it does tend to support the idea that the mechanism in Table 1 holds here as well. The peaks even show the same type of asymmetry as those observed experimentally (i.e., the pH drops less rapidly as the peak is forming than the pH rises afterward). Finally, as long as the contributions of sulfite impurities and atmospheric carbon dioxide are taken into account, the same kind of period-doubling with reduced flow rate is predicted as that seen in the H_2O_2−Na_2SO_3−Na_2CO_3−H_2SO_4 system. The existence of chaos is indicated by the fact that period 3 oscillations were found (at $k_0 = 6.705 \times 10^{-4}$ s^{-1}).

H_2O_2−Na_2SO_3 Batch System. The pH−time curves obtained by Rabai et al.[11] for the batch reaction of hydrogen peroxide and sodium sulfite in sulfuric acid at 25 °C showed an interesting feature. In each case, as the pH dropped rapidly at the end of the reaction, a small peak or overshoot (typically about 0.2−0.3 pH units) occurred before a constant final pH was reached. This feature only appeared if $[H^+]_0 < 1 \times 10^{-4}$ M and was thought to be unimportant in the oscillating system. Numerical simulations could not account for this phenomenon.

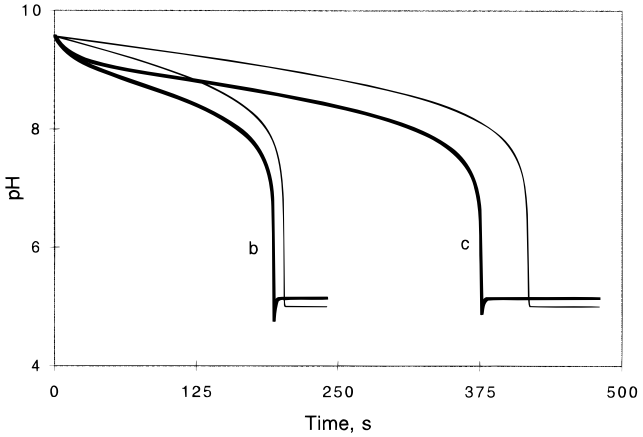

Figure 9. Calculated pH−time curves in the hydrogen peroxide−sulfite batch reaction: $[H_2O_2]_0 = 5.0 \times 10^{-2}$ M (b), 2.5×10^{-2} M (c); $[SO_3{}^{-2}]_0 = 2.2 \times 10^{-3}$ M (b, c). Rabai et al. model (regular curve): $[H^+]_0 = 1.0 \times 10^{-5}$ M; $k_4 = 7$ M^{-1} s^{-1}. Frerichs−Thompson model (bold curve): $[CO_3{}^{2-}]_0 = 2.9 \times 10^{-6}$ M; $[H^+]_0 = 1.2 \times 10^{-5}$ M; $[CO_2]_0 = 1.6 \times 10^{-5}$ M; k_4 (M^{-1} s^{-1}) = 3.0 (b), 3.4 (c).

As a final test of our mechanism in Table 1, we attempted to simulate Rabai et al.'s experimental results for the batch reaction. Figure 9 shows simulations at reactant concentrations corresponding to those for curves b and c in Figure 1 of their paper.[11] The model used in their simulation is essentially steps 1−5 of our mechanism, but with $k_4 = 7$ M^{-1} s^{-1}. Note that no pH overshoot results in this case. When the complete mechanism in Table 1 was used, along with the conditions assumed below, we obtained extremely good agreement between the modeled and experimentally observed pH−time profiles, including the required pH overshoot.

To approximate the conditions present in the above-mentioned experiments, estimates were made of the amount of carbonate and acid impurities in the sodium sulfite source and the amount of carbon dioxide present in the reaction system due to atmospheric CO_2. On the basis of our own experiments, a 2.2×10^{-3} M Na_2SO_3 solution would contain impurities in the amount of $[CO_3{}^{2-}]_0 = 2.9 \times 10^{-6}$ M and $[H^+]_0 = 2.0 \times 10^{-6}$ M. Note that the latter value does not include the amount of H^+ added to the system as H_2SO_4. As described above, a value of $[CO_2]_0 = 1.6 \times 10^{-5}$ M was estimated, based on a pH of 6.0 for triply distilled water.

As noted above, the value of k_4 used by Rabai et al. was 7 M^{-1} s^{-1}. They obtained this value by fitting their experimental data for the batch reaction. In our simulations, we found that values of $k_4 = 3.0$ and 3.4 M^{-1} s^{-1} gave the best fit for curves b and c, respectively. Using these values, our simulations reproduced almost exactly the observed time for completion of reaction. The same is true of the final pH after reaction as well as the magnitude of the pH overshoot. Our own batch reaction experiments indicate that a slightly better value for k_4 is 3.5 M^{-1} s^{-1}. This value should be more accurate than those used in fitting curves b and c, considering the approximations used in the latter case.

It now seems clear that it is necessary to include the effects of carbonate impurities and atmospheric carbon dioxide in order to account for the pH overshoot observed in Rabai et al.'s batch experiments. Also, by not including these effects, one obtains a k_4 value that differs from the apparently correct value by a factor of about 2. When we used $k_4 = 7\ M^{-1}\ s^{-1}$ with the mechanism in Table 1, the simulated reaction times were much less than the observed ones. Likewise, when a value of 3.5 $M^{-1}\ s^{-1}$ was used for k_4 with Rabai et al.'s mechanism, simulated reaction times were a great deal longer than the observed ones.

Discussion

Comparison of Studies. As previously mentioned, another study on a very similar chemical system has been reported by Rabai.[10] However, a number of significant differences in our study relative to the other one are noteworthy. Most of these differences have to do with the way the experiments were carried out. Perhaps the most significant difference is that our study was done on a homogeneous system, whereas the other involved a heterogeneous system. In the latter case, the reactor was continuously bubbled with N_2 to drive off CO_2 at a controlled rate, while in our study only the reagents in their reservoirs were bubbled with N_2. In fact, Rabai stated that oscillations were not sustained if CO_2 was allowed to accumulate in the air space of the reactor. The advantages of using a homogeneous, rather than a heterogeneous, system are obvious. Also, with our procedure it was not necessary to use a second pump to remove excess liquid.

Another advantage of our procedure has to do with the input solutions. Rabai had H_2O_2 in one solution and a mixture of Na_2SO_3, $NaHCO_3$, and H_2SO_4 in the other. This necessitated the experimental compromise of keeping the latter reservoir solution under N_2 to avoid autoxidation of sulfite, but not bubbling, since this would cause loss of the volatile components (SO_2 and, especially, CO_2). In our study, this problem was avoided by putting the acidic components (H_2O_2 and H_2SO_4) in one solution and the basic components (Na_2SO_3 and Na_2CO_3) in the other. This allowed both reservoir solutions to be continuously bubbled with N_2, thus ensuring minimal exposure of reagents to atmospheric O_2 and CO_2. Also, an argument could be made that there is some advantage in using Na_2CO_3, a primary standard, instead of less pure $NaHCO_3$.

In an earlier study involving the twice heterogeneous $H_2O_2-SO_3^{2-}-$marble pH oscillator, Rabai and Hanazaki[14] found that lower temperatures were more favorable for complex dynamical behavior than room temperature. Thus, in the heterogeneous flow system with HCO_3^-, Rabai used a temperature of 4 °C. While it may be more likely that period-doubling and chaos will be observed at lower temperatures, nevertheless our study found such behavior even at 25 °C. It is interesting that in the study with marble as the carbonate source it was observed that 10 °C was the highest temperature at which oscillations could be maintained in a CSTR open to the air but with no N_2 flow passing through the reactor. This finding did not agree with simulations that predicted oscillations should occur even at 25 °C.

The matter of experimental conditions also is relevant in comparing Rabai's hydrogen carbonate study to ours. One important difference is that we used a much wider range of concentrations and flow rates than that indicated by the rather limited experimental results given by Rabai. Again, our data are at 25 °C, a rather more convenient temperature to use than 4 °C. The phase diagrams we have obtained should be especially useful to future investigators of this system.

Finally, the present study emphasizes the effect of sulfite impurities on both the batch and CSTR systems. We already have seen how neglecting both carbonate and acid impurities in sulfite and atmospheric CO_2 can lead to an apparently incorrect value for k_4. Perhaps including these effects might lead to better simulations of experimental oscillations in other CSTR studies involving sulfite. As noted previously, numerous oscillating reactions do involve sulfite as a reductant.

Further Evidence. Some time before we were successful in computer simulations of our experimental results, a number of different types of experiments were done, all of which tended to confirm our proposed mechanism. One such experiment demonstrated that light had no apparent effect on the results. This was consistent with our thinking that free radicals were not an important part of the mechanism.

Several different experiments provided good evidence for the critical role of carbonate (and, hence, also CO_2) in the oscillator. One study involved substituting equivalent amounts of monohydrogen phosphate ion for carbonate, with varying amounts of sulfuric acid. In all cases, bistability was observed but not oscillations. Another study was done in which EDTA (Y^{4-}) was substituted for some of the carbonate. EDTA seems an especially appropriate substitute since its K_{a4} value is nearly identical with the K_{a2} for carbonic acid. When one-fourth of the carbonate was replaced with EDTA, bistability was found; however, by changing the acid concentration, regular oscillations were obtained. Since oscillations occurred at a significantly high concentration of EDTA (4.0×10^{-5} M), this seems to provide additional evidence against the involvement of free radicals and/or metal ions.

In a further attempt to confirm carbonate's role in our pH oscillator, as well as perhaps to construct new oscillators, a significant number of experiments were done with either IO_3^- or BrO_3^- as the oxidizing agent in place of H_2O_2.[1] A parallel is found in the "mixed Landolt" reactions with ferrocyanide.[11,15,16] With iodate, small-amplitude (25−50 mV) oscillations in potential, but not in pH, were observed at 25 °C over a very narrow range of carbonate and acid concentrations. Bistability between the oscillatory state and the acidic steady state was found. It is especially interesting that the flow rate range where bistability was observed is very similar to that predicted (but not observed) by Edblom et al. in their computer simulation of the ferrocyanide reaction at 40 °C.[17]

In the case of bromate with carbonate, we obtained large-amplitude oscillations in both pH and potential at 30 °C comparable to those found with ferrocyanide. However, at least under the conditions we used, only "mono-oscillations" were observed, requiring a slight adjustment of the flow rate to produce the next peak. Because of the extremely long time required to carry out the CSTR experiment, only the F-branch was determined. Thus, it was not possible in this limited study with carbonate to test for the narrow region of bistability between the oscillatory state and the acidic steady state again predicted (but not observed) by computer simulation of the ferrocyanide reaction.[16] Finally, it is interesting to compare our results with bromate to those obtained in a recent study using marble chips as the carbonate source.[18] The amplitudes and range of flow rates where oscillations appear are both very similar to our results.

More direct evidence for the importance of the dehydration of H_2CO_3 in the mechanism was found when a small amount of the enzyme carbonic anhydrase (4210 W-A units per mg protein) was added to the oscillating system. When the anhydrase was added to the $H_2O_2-H_2SO_4$ reservoir, no effect was observed (apparently due to deactivation of the enzyme under strongly acidic conditions). Addition of carbonic anhydrase to the $Na_2SO_3-Na_2CO_3$ reservoir significantly increased the oscillatory rate, lowering the period by a factor of 6−8.

Mechanistic Details. One significant difference between our mechanism and that of Rabai is that we have included the oxidation of SO_3^{2-} by H_2O_2 (reaction 1, Table 1). Since Rabai's work was done at 4 °C, the rate constant for this reaction may have been small enough that the rate of this step could be neglected.[10] However, in the present study at 25 °C, k_1 is not entirely insignificant, especially above pH 7. While including this step is not required in order to obtain oscillations, it does make a significant difference when it comes to computer simulations of experiments. For example, with reaction 1 included in the mechanism, simulation of high-frequency oscillations as in Figures 6 and 7 gives a period of 81 s. If reaction 1 is not included in the mechanism, simulation gives a period of 122 s. Clearly, to obtain the best fit of the data, reaction 1 must be included.

As part of a classic series of manometric studies on the equilibrium involving dehydration of H_2CO_3 and hydration of CO_2, Roughton and Booth[19] observed that both reactions were base-catalyzed by certain oxyanions. One of the more effective of these was the sulfite ion, with a catalytic constant of about 900. While this constant, of course, is as much as 3 orders of magnitude less than that for carbonic anhydrase, one still might think that the catalysis of reactions 10 and 11 in Table 1 should be included in our mechanism. However, when this is done, there is no effect on computer simulations. The reason for this is apparent when one realizes just how low the sulfite concentration is at the point where oscillations set in. Whereas the initial concentration of sulfite is much greater than that of carbonate, this is just reversed during an oscillation.

For example, consider an experiment under the same conditions as those noted in Figure 6. As an oscillation is approached, the total concentration of sulfur(IV), $[S(IV)]_T$, decreases until it is approximately equal to the total concentration of carbon(IV), $[C(IV)]_T = [C(IV)]_0$. At this point, the pH of the solution is very close to 7. It is interesting to note that, experimentally, this is the point where the pH begins to drop most rapidly during an oscillation. Just before an oscillation occurs, $[S(IV)]_T$ is about two-thirds of $[C(IV)]_0$. Perhaps the most striking fact is that at the minimum pH the total sulfite concentration has been reduced to about 2% of $[C(IV)]_0$. Following is a typical set of species concentrations (at a minimum pH of 5.69): $[SO_3^{2-}] = 1.80 \times 10^{-7}$ M; $[HSO_3^-] = 5.77 \times 10^{-6}$ M; $[CO_2] = 2.14 \times 10^{-4}$ M; $[HCO_3^-] = 8.57 \times 10^{-5}$ M. Note that at the minimum pH $[SO_3^{2-}]$ is so low that it is less than 10% of $[H^+]$.

Beyond the point of minimum pH, further input of sulfite into the reactor quickly causes $[S(IV)]_T$ to increase until it is once again equal to $[C(IV)]_0$. It is interesting that this condition exists at the point where the maximum pH of 7.53 is reached. As time goes on, $[S(IV)]_T$ continues to increase until it reaches a maximum at pH 7.42. Here, the $[S(IV)]_T/[C(IV)]_0$ ratio is slightly less than 3:2. Apparently, at this point, the rate at which sulfite enters the reactor is equal to the rate at which it is consumed. Then, as $[S(IV)]_T$ gradually decreases due to reaction with H_2O_2 so does the pH. Eventually, the pH is low enough that another oscillation occurs.

Another catalytic reaction that was considered for inclusion in our mechanism involves reaction 1. Mader's kinetic study of the hydrogen peroxide−sulfite reaction in alkaline solution demonstrated a first-order catalytic effect by HCO_3^-.[20] However, the concentrations of carbonate used in our experiments were low enough that this reaction had no effect on the simulations. Mader also observed that the $H_2O_2-SO_3^{2-}$ reaction deviates considerably from second-order behavior when $[H_2O_2][SO_3^{2-}] > 10^{-5}$ M^2. This condition would apply to some of the CSTR experiments in our study during the earlier part of the F-branch and the later part of the T-branch. Because of the low concentration of S(IV) species as described above, this kinetic behavior would not be expected to be significant during oscillations.Thus, no attempt was made to include any higher-order dependence on S(IV) in our mechanism.

Conclusion

The $H_2O_2-SO_3^{2-}-CO_3^{2-}-H^+$ system was studied in a CSTR at 25 °C without bubbling the reactor with N_2 to remove CO_2. This appears to be the first homogeneous pH oscillator involving carbonate and carbon dioxide. In addition to basic and acidic steady states, regular oscillations and period-doubling leading to chaos were observed, depending on conditions. The importance of the effect of atmospheric CO_2 and of carbonate and acid-producing impurities in the sulfite source is emphasized by the fact that oscillations may be obtained in the presence of air but with no added carbonate or sulfuric acid. Successful modeling of the $H_2O_2-SO_3^{2-}$ system, both in batch and CSTR, taking these effects into account provides further evidence of their importance. Perhaps it would be useful to re-evaluate with regard to these effects certain past studies using sulfite and involving carbonate and/or carbon dioxide as a product or reactant.

Unlike many oscillating systems, the present one has the advantage that it involves a relatively small number of elementary reactions having, for the most part, well-known rate constants. Thus, our system may be useful both for understanding and for constructing more complex oscillating systems. One such possibility would be to study the effect of the enzyme peroxidase (HRP) on this pH oscillator, especially relative to negative feedback, and to compare with the effect previously observed in the ferrocyanide system. A second possible application involving an enzyme might be the hydrolysis of urea by urease. Over 70 years ago, Groll observed that this system in a phosphate buffer at 35 °C gave oscillations in the concentration of ammonia.[21] It is interesting that the main products of the hydrolysis reaction are ammonium and hydrogen carbonate ions.

Another application involving an enzyme would be a thorough study of the effect of carbonic anhydrase on our pH oscillator. In the respiratory process, when CO_2 accumulates in the lungs, a signal is transmitted to the brain resulting in a delayed increase in the rate of ventilation.[22] As a result, instabilities and even chaotic behavior associated with cardiac arrhythmia may occur. A recent study has suggested a link between sudden infant death syndrome (SIDS) and a heart rhythm defect referred to as a prolonged QT interval. Chemical waves, such as spiral and scroll waves, have been associated with cardiac arrhythmia. It is tempting to suggest that the hydration of CO_2 and dehydration of H_2CO_3 may be related to the above phenomena.

Finally, in considering the effect of H^+ and CO_2 on the binding of O_2 by hemoglobin, one is led to suggest that one or more pH oscillators are involved in the transport of oxygen and carbon dioxide in the circulatory system. Hemoglobin itself has the ability to either release or consume H^+, depending on whether oxygen is being bound or released, respectively. Perhaps it is more than a coincidence that the usual pH of blood (~7.4) is roughly the same as the pH for an important transition point in our oscillator (see above). It would not be surprising if cardiac arrhythmia is ultimately explained by means of a complex system of pH oscillators.

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