

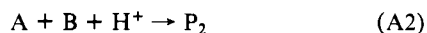
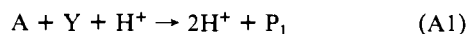
# A Systematically Designed pH Oscillator: The Hydrogen Peroxide-Sulfite-Ferrocyanide Reaction in a Continuous-Flow Stirred Tank Reactor<sup>1</sup>

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**Abstract:** The alternator model has been used to construct an oscillatory reaction in a continuous-flow stirred tank reactor (CSTR). The unbuffered oxidation of hydrogen sulfite ions by hydrogen peroxide, which is autocatalytic in H<sup>+</sup>, is linked to the reaction between hexacyanoferrate(II) and hydrogen peroxide, which consumes H<sup>+</sup> in a linear fashion. The resulting system gives oscillation in pH and in the concentration of hexacyanoferrate(III). A simple model, consisting of the empirical rate laws of the component reactions, is used to simulate the experimental results and gives excellent agreement.

Large-amplitude pH oscillation has recently been observed<sup>3-9</sup> in a number of unbuffered systems in a continuous-flow stirred tank reactor (CSTR). In most of these cases, there are two major component reactions, one of which produces H<sup>+</sup> autocatalytically, while the other consumes H<sup>+</sup>. If the component from which the hydrogen ions form can be regenerated during the reaction, an oscillatory pH change can occur, not only in a CSTR, but also in a closed system as well.<sup>10</sup> A simplified model, dubbed the alternator, has been suggested to describe the pH oscillation in the closed system of iodate, sulfite, and thiosulfate ions.<sup>10</sup> The alternator is closely related to the Lotka model.<sup>11</sup> It consists of an autocatalytic hydrogen ion production (A1), a hydrogen ion consumption step (A2), and a third reaction (A3) that regenerates the reactant Y that serves as the source of the hydrogen ion.



It was shown<sup>12</sup> that process A3 can be replaced by the input flow in a CSTR. For this reason, only two component processes are necessary to construct an oscillatory reaction in a CSTR: a reaction autocatalytic in H<sup>+</sup> and a hydrogen ion consuming reaction. If these two processes take place simultaneously and at comparable rates, the system may show experimentally measurable pH oscillations in a CSTR at appropriate initial concentrations and flow rates.

We report here a study of the unbuffered hydrogen peroxide-hydrogen sulfite-hexacyanoferrate(II) system, which shows oscillation of this type in a CSTR. In this system both reactions A1 and A2 of the alternator model are present. Hydrogen peroxide can oxidize hydrogen sulfite to sulfate in an autocatalytic reaction, while the hexacyanoferrate(II)-hydrogen peroxide re-

action consumes hydrogen ions in acidic solution. The rates of these reactions are similar in magnitude, so the requirements of the alternator scheme are satisfied.

In this paper we utilize the H<sub>2</sub>O<sub>2</sub>-HSO<sub>3</sub><sup>-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> system to demonstrate how the alternator model can be used to construct and to analyze relatively simple oscillatory reactions. We anticipate that this procedure will lead to the design of many new pH oscillators of this type, because many reactions produce or consume hydrogen ions at rates that depend upon [H<sup>+</sup>]. As noted above, such oscillators are excellent candidates to exhibit the rarer phenomenon of oscillation in a closed (batch) system as well as in a CSTR.

## Experimental Section

**Materials.** Analytical-grade reagents were used for all experiments without further purification. Stock solutions of potassium hexacyanoferrate(II), sodium sulfite, hydrogen peroxide, and sulfuric acid were prepared with doubly distilled water. Since the hexacyanoferrate(II) and sulfite solutions are oxygen-sensitive, and the pH measurements in unbuffered solution are disturbed by carbon dioxide, chemically pure argon was bubbled through the water before the reagents were dissolved in it. Stock solutions were kept under argon. The solution of hexacyanoferrate(II) ions was kept from light during storage. Protection against light is necessary to avoid light-catalyzed formation of monoaquopentacyanoferrate(II), which accelerates the side reaction of decomposition of hydrogen peroxide. Stock solutions of hydrogen peroxide were stored in a polyethylene bottle to retard decomposition. All solutions except sulfuric acid were prepared daily.

Sulfuric acid was used to maintain the initial or input hydrogen ion concentration. The concentrations were checked by iodometric (in the case of Na<sub>2</sub>SO<sub>3</sub>), permanganometric (H<sub>2</sub>O<sub>2</sub>), and acid-base (H<sub>2</sub>SO<sub>4</sub>) titrations.

**Apparatus and Methods.** The reaction was followed by continuous measurement of pH and light absorption. The pH was measured with an Aldrich combination calomel pH electrode (type Z 11323-9) and an Orion 501 pH meter. A Varian DMS 200 UV-visible and a Perkin-Elmer UV-vis 552A spectrophotometer were used to determine the concentration of hexacyanoferrate(III), the only light-absorbing species in the visible region. For Fe(CN)<sub>6</sub><sup>3-</sup>, λ<sub>max</sub> = 420 nm (ε = 1040 M<sup>-1</sup> cm<sup>-1</sup>) in this reaction system. In some cases the light absorption was too high to measure at 420 nm because of the long optical path of the CSTR, and measurements were made at 460 nm.

The flow experiments were performed at 25.0 °C in a thermostated plastic reactor of 40 mL volume with quartz windows. The reactor was designed to fit into the sample compartment of the Perkin-Elmer spectrophotometer. In some experiments the reactor was outside the spectrophotometer, and the reaction mixture was protected from light. A magnetic stirrer at the bottom kept the solution homogeneous. No stirring rate effect on the parameters of the oscillation or the steady states was observed between 200 and 700 rpm. The sulfuric acid and sulfite solutions were premixed, and the CSTR was fed by a Sage 375A peristaltic pump at measured rates through three inlet tubes (i.d. 2.5 mm). The effluent was forced out at the same rate through an exit port in the top of the reactor. The flow rate could be varied continuously by changing the pump speed.

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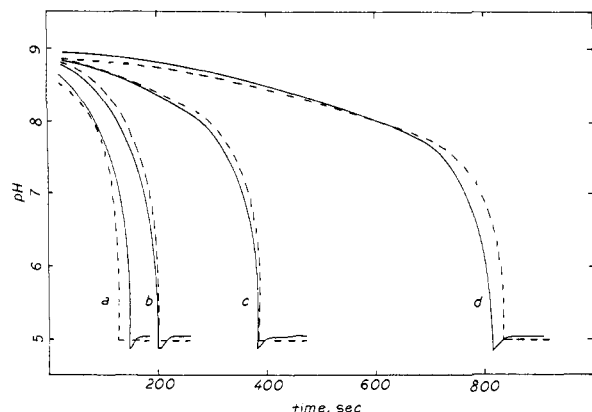
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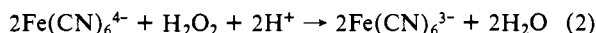
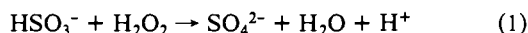
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**Figure 1.** Measured (—) and calculated (---) pH-time curves in the hydrogen sulfite-hydrogen peroxide reaction.  $[H^+]_0 = 1.0 \times 10^{-5}$  M;  $[H_2O_2]_0 = 5.0 \times 10^{-2}$  M (a, b),  $2.5 \times 10^{-2}$  M (c),  $1.25 \times 10^{-2}$  M (d);  $[SO_3^{2-}]_0 = 1.0 \times 10^{-3}$  M (a),  $2.2 \times 10^{-3}$  M (b-d).

## Results

As indicated above, two component reactions were used to construct the oscillatory reaction. These are the oxidation of hydrogen sulfite ions by hydrogen peroxide (1), and the oxidation



of hexacyanoferrate(II) ions by hydrogen peroxide (2). We first studied the component reactions separately under closed conditions and tried to model the experimental pH vs time curves. Then we investigated and analyzed the mixed system in batch. Finally, experiments and simulations were carried out for the mixed system in a CSTR.

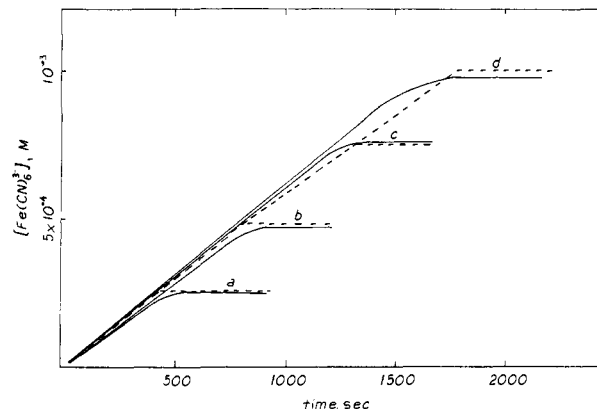
**Reaction 1.** The oxidation of S(IV) by hydrogen peroxide has been widely investigated. Hoffman and Edwards<sup>13</sup> studied this reaction over the pH range 4–8. The reaction rate was found to be first order in both total sulfite and hydrogen peroxide, while the order with respect to hydrogen ion was determined to be between 1 and 2. These results were obtained in the presence of high concentrations of several buffers, and the buffers affect the rate significantly, because of the general-acid catalysis of this redox reaction. For this reason, the rate law and rate constants given by Hoffman and Edwards cannot be used to describe the kinetic curves found in the unbuffered reaction system.

Jaeschke and Herrmann<sup>14</sup> studied the oxidation of S(IV) by  $H_2O_2$  in an unbuffered solution, varying the initial pH by addition of HCl. They found that the second-order rate constant for reaction 1 was strongly pH dependent ( $k_1 = 1.48 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup> at pH 2.0 and  $1.3 \times 10^2$  M<sup>-1</sup> s<sup>-1</sup> at pH 5.5, respectively). In this pH region, the main S(IV) species is  $HSO_3^-$ , and this pH dependence suggests that reaction 1 is autocatalytic in hydrogen ion.

We made a few kinetic runs in an unbuffered reaction mixture of sulfite and hydrogen peroxide and followed the pH change during the reaction under closed conditions. The results are illustrated in Figure 1. The kinetic curves and the above-mentioned published results suggest a rate law of the form 1' for reaction 1. The value of  $k_1'$  can be derived from Jaeschke and

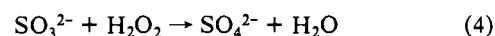
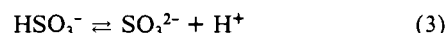
$$v_1 = (k_1 + k_1'[H^+])[HSO_3^-][H_2O_2] \quad (1')$$

Herrmann's data. At pH 2, the  $[H^+]$ -containing term is predominant, and the third-order rate constant can be obtained by dividing the published (pseudo-second-order) value by the hydrogen ion concentration. We obtain  $k_1' = 1.48 \times 10^7$  M<sup>-2</sup> s<sup>-1</sup>. Rate equation 1' is not, of course, sufficient to describe the experimental pH-time curves. The deprotonation equilibrium 3 and



**Figure 2.** Concentration of hexacyanoferrate(III) as a function of time in the unbuffered hexacyanoferrate(II)-hydrogen peroxide reaction.  $[Fe(CN)_6^{4-}]_0 = 2.0 \times 10^{-3}$  M;  $[H_2O_2]_0 = 2.0 \times 10^{-3}$  M.  $[H^+]_0 = 2.5 \times 10^{-4}$  M (a),  $5.0 \times 10^{-4}$  M (b),  $7.5 \times 10^{-4}$  M (c),  $1.0 \times 10^{-3}$  M (d). Solid lines, measured; dashed lines, calculated.

the reaction 4 between unprotonated sulfite and hydrogen peroxide must also be taken into consideration.

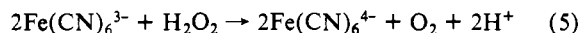


As in an earlier study,<sup>10</sup> the forward and reverse rate constants for reaction 3 were chosen, consistent with the equilibrium constant, as  $k_3 = 3 \times 10^3$  s<sup>-1</sup> and  $k_{-3} = 5 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>. Mader<sup>15</sup> investigated reaction 4 in alkaline medium and found a simple rate law (4') in the absence of buffer, with  $k_4 = 0.2$  M<sup>-1</sup> s<sup>-1</sup>.

$$v_4 = k_4[SO_3^{2-}][H_2O_2] \quad (4')$$

The pH-time curves obtained in the sulfite-hydrogen peroxide reaction were simulated by using the above rate equations and rate constants. Thus, all rate constants except  $k_1$  were taken from the literature. The value of  $k_1$ ,  $7$  M<sup>-1</sup> s<sup>-1</sup>, was obtained by fitting our data. All numerical simulations were carried out with the GEAR method.<sup>16</sup> The calculated kinetic curves are indicated with dashed lines on Figure 1. The agreement between the calculated and measured curves is quite good. The calculation does not reflect the small pH peak at the end of the reaction, but this feature seems to be unimportant in the oscillating system. This small peak does not appear if  $[H^+]_0 > 1 \times 10^{-4}$  M.

**Reaction 2.** Since the oxidizing properties of hydrogen peroxide depend strongly upon pH, reaction 2 can take place only in nearly neutral or acidic solution. In alkaline medium, hexacyanoferrate(III) is able to oxidize hydrogen peroxide:



According to Bockris and Oldfield,<sup>17</sup> the redox potential of hydrogen peroxide as a function of pH is given by

$$E(V) = 0.84 - 0.0509pH$$

This variation suffices to change the direction of hydrogen peroxide's reactions with hexacyanoferrate(II)/(III) (standard oxidation potential 0.36 V) over the range pH 7–9. These reactions are essentially stoichiometric, and no significant catalytic decomposition of hydrogen peroxide occurs in the presence of hexacyanoiron complexes in darkness. Catalysis by ferro- and ferricyanide in light arises not directly from these ions, but rather from the hydrolysis products  $(Fe(CN)_5H_2O)^{2-/3-}$ .<sup>18</sup>

Figure 2 shows typical kinetic curves of the formation of  $Fe(CN)_6^{3-}$  in the unbuffered hexacyanoferrate(II)-hydrogen peroxide reaction at several initial hydrogen ion concentrations. In these experiments, hydrogen peroxide and ferrocyanide were in stoichiometric

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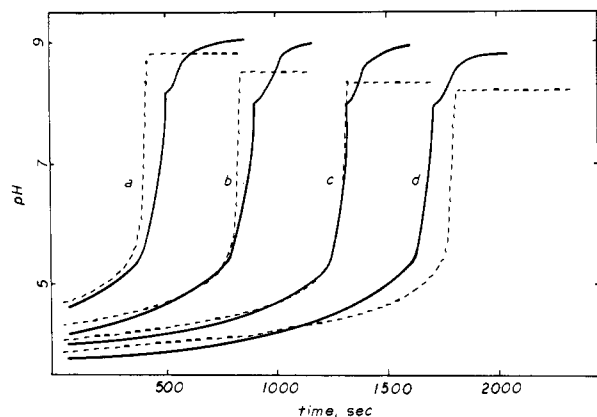
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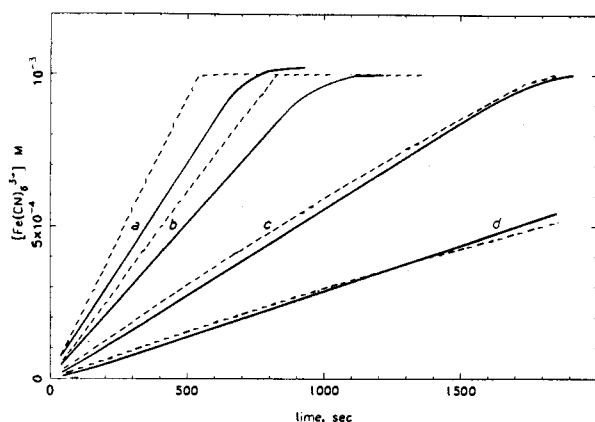
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**Figure 3.** Measured (solid lines) and calculated (dashed lines) pH-time curves in the hexacyanoferrate(II)-hydrogen peroxide reaction. Initial concentrations as in Figure 2.



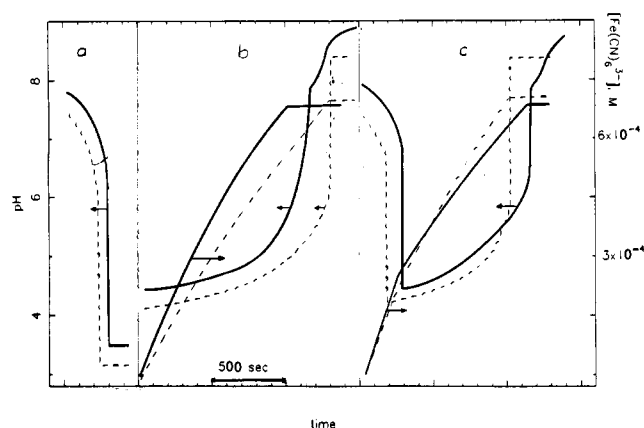
**Figure 4.** Kinetic curves for the hexacyanoferrate(II)-hydrogen peroxide reaction in unbuffered solution.  $[\text{Fe}(\text{CN})_6^{4-}]_0 = 1.0 \times 10^{-3} \text{ M}$ ;  $[\text{H}^+]_0 = 1.0 \times 10^{-3} \text{ M}$ ;  $[\text{H}_2\text{O}_2]_0 = 6.0 \times 10^{-3} \text{ M}$  (a),  $4.0 \times 10^{-3} \text{ M}$  (b),  $2.0 \times 10^{-3} \text{ M}$  (c),  $1.0 \times 10^{-3} \text{ M}$  (d). Solid lines, measured; dashed lines, calculated.

chiometric excess over the initial  $[\text{H}^+]$ . The ferricyanide concentration grows linearly with a slope independent of  $[\text{H}^+]$  until it suddenly levels off as the reaction reaches completion. Simultaneous pH measurements (Figure 3) reveal that the pH of the reaction mixture rises slightly during the early part of the reaction, then increases suddenly at the moment that  $[\text{Fe}(\text{CN})_6^{3-}]$  levels off in Figure 2. The final hexacyanoferrate(III) concentration is equal to the initial hydrogen ion concentration within the experimental error in each experiment. These curves imply that the concentration of  $\text{H}^+$  does not affect the rate over a wide range of pH. However, the reaction stops when nearly all the hydrogen ion is consumed (when the pH increases to 9). When only  $\text{H}_2\text{O}_2$  is in excess, we again observe nearly zero-order concentration-time curves (Figure 4) at several hydrogen peroxide concentrations, indicating that the reaction is also zero order with respect to hexacyanoferrate(II) ion over a wide range of concentrations.

Over the narrow range studied, the reaction is first order in hydrogen peroxide. We note that preliminary experiments at higher  $[\text{H}_2\text{O}_2]_0$  showed an order with respect to  $\text{H}_2\text{O}_2$  less than 1. Since the extended concentration range is not relevant for describing the oscillatory phenomena, we did not pursue the details of the reaction under these circumstances. The results of our kinetics experiments lead to the simple rate law

$$v_2 = -d[\text{H}_2\text{O}_2]/dt = k_2[\text{H}_2\text{O}_2] \quad (2')$$

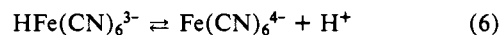
We find  $k_2 = 1.6 \times 10^{-4} \text{ s}^{-1}$ . This simple rate law is not valid at very low  $[\text{Fe}(\text{CN})_6^{4-}]$  or at low pH, but it holds in the range of concentrations that occur during the oscillation. Sobkowski<sup>19</sup>



**Figure 5.** pH and hexacyanoferrate(III) concentration as functions of time in the subsystems (a, b) and in the mixed system (c).  $[\text{H}^+]_0 = 7.0 \times 10^{-4} \text{ M}$  (a-c);  $[\text{SO}_3^{2-}]_0 = 4.0 \times 10^{-3} \text{ M}$  (a, c);  $[\text{Fe}(\text{CN})_6^{4-}]_0 = 2.0 \times 10^{-3} \text{ M}$  (b, c);  $[\text{H}_2\text{O}_2]_0 = 4.2 \times 10^{-3} \text{ M}$  (a),  $2.0 \times 10^{-3} \text{ M}$  (b),  $6.2 \times 10^{-3} \text{ M}$  (c). Solid lines, measured; dashed lines, calculated. Horizontal arrows indicate axis to which curve refers.

studied the oxidation of hexacyanoferrate(II) ions by hydrogen peroxide in more acidic solutions. He found that the reaction is first and 0.5 order with respect to  $\text{H}_2\text{O}_2$  and  $\text{Fe}(\text{CN})_6^{4-}$ , respectively. The conditions of Sobkowski's experiment differ significantly from those of our work, so we are not surprised that his rate law differs from ours.

In order to describe the behavior of pH and  $[\text{Fe}(\text{CN})_6^{3-}]$  in the closed system, we must take into consideration the protonation-deprotonation equilibrium of hexacyanoferrate(II), which is very important in unbuffered solution, and affects the pH of the solution.

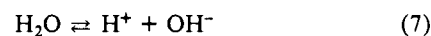


The equilibrium constant,  $K_6$ , which is strongly dependent on ionic strength, has been given by Jordan and Ewing.<sup>20</sup> At the ionic strength used in our experiments ( $I \approx 0.02 \text{ M}$ ),  $K_6 = 1.8 \times 10^{-4} \text{ M}$ . No protonation of the ferri complex takes place.

In order for the mechanism to reflect that the rapid rise in pH coincides with the cessation of reaction, reaction 5 must be taken into consideration. No complete kinetics study of this reaction has yet been published, but according to Eaton and Pankratz,<sup>21</sup> reaction 5 is first order in  $\text{Fe}(\text{CN})_6^{3-}$ , but less than first order in  $\text{H}_2\text{O}_2$ , if the latter is in large excess. The rate increases with pH. In our experiments  $\text{H}_2\text{O}_2$  is not present in large excess, so our results can best be described by the simplified rate law (5') with

$$v_5 = -d[\text{H}_2\text{O}_2]/dt = k_5[\text{H}_2\text{O}_2][\text{Fe}(\text{CN})_6^{3-}][\text{OH}^-] \quad (5')$$

$k_5 = 1 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ . Reaction 5 is required only to characterize the conclusion of the batch reaction; it can be neglected in simulations of the oscillation in a CSTR. Finally, we take into account the water dissociation equilibrium, which controls the  $[\text{H}^+]/[\text{OH}^-]$  ratio.



The rate constants for (7) are known:<sup>22</sup>  $k_7[\text{H}_2\text{O}] = 1 \times 10^{-3} \text{ M s}^{-1}$  and  $k_{-7} = 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ .

By use of the above rate equations and rate constants, the experimental pH-time curves can be simulated in the batch reaction between hexacyanoferrate(II) and hydrogen peroxide. The small shoulder on the sharply increasing part of the experimental curves cannot be calculated by this model. It is probably due to the deprotonation of hydrogen cyanide formed from the hexacyano complexes in the aqueous solution.

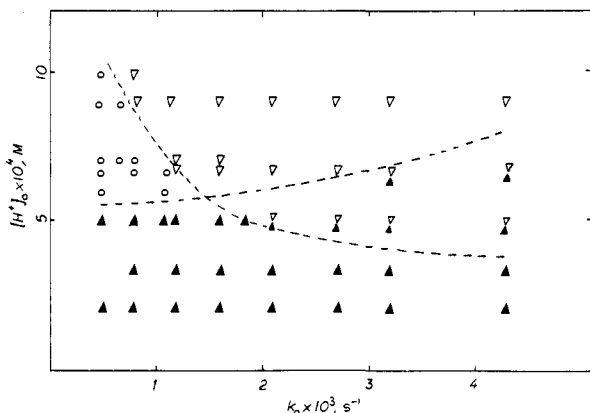


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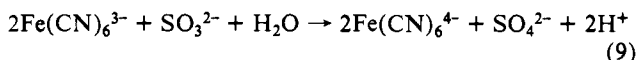
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**Figure 6.** Phase diagram for the mixed system in the  $k_0$ - $[H^+]_0$  plane. Fixed concentrations:  $[SO_3^{2-}]_0 = 4.0 \times 10^{-3}$  M;  $[H_2O_2]_0 = 6.2 \times 10^{-3}$  M;  $[Fe(CN)_6^{4-}]_0 = 2.0 \times 10^{-3}$  M. Symbols: ▲, high pH (7–8) steady state; ▼, low pH (4–5) steady state; ▽, bistability; ○, oscillation.

**Mixed System—Batch.** When all three reactants are present, reactions 1 and 2 take place together. As Figure 5 shows, the experimental pH–time curves of the mixed system (Figure 5c) can be viewed as an almost exact superposition of the curves of the component subsystems (Figure 5a,b). Hydrogen sulfite reacts autocatalytically with hydrogen peroxide to produce  $H^+$  at an increasing rate. Once the hydrogen sulfite has been consumed, the rapid production of  $H^+$  stops, and owing to the hexacyanoferrate(II)–hydrogen peroxide reaction (2), its concentration begins to decrease. Do the kinetic equations of the subsystems suffice to describe the experimental curves of the composite system in Figure 5? The additivity of the experimental pH–time curves suggests that no significant interactions occur between the hydrogen sulfite–hydrogen peroxide and hexacyanoferrate(II)–hydrogen peroxide subsystems. Only one additional reaction, process 9, needs to be taken into consideration for the mixed system. In



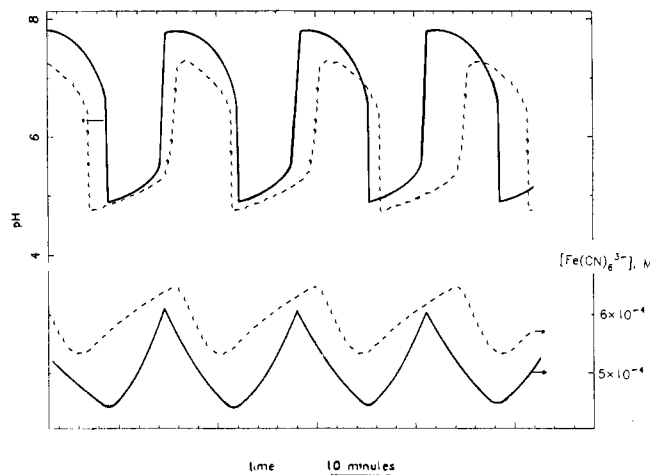
reaction 9, hydrogen ions are produced, while hexacyanoferrate(III) oxidizes sulfite in the alkaline medium.

Several investigators have studied the kinetics and mechanism of reaction 9. The rate is affected strongly by alkali-metal ions and weakly by added hexacyanoferrate(II), but is independent of pH between 8 and 9. According to Murray,<sup>23</sup> the rate of reaction 9 is given by

$$v_9 = -d[Fe(CN)_6^{3-}]/dt = k_9[Fe(CN)_6^{3-}][SO_3^{2-}] \quad (9')$$

The value of  $k_9$  is between 0.1 and 3  $M^{-1} s^{-1}$ , depending on the identity and concentration of alkali-metal ions and on other conditions. We used  $k_9 = 2.0 M^{-1} s^{-1}$  in our calculations. Reaction 9 is unimportant in the closed system, because sulfite is consumed before hexacyanoferrate(III) reaches a significant concentration, but this process is important in the CSTR, where the concentration of ferricyanide is always high enough to make the reaction with sulfite significant. The dashed lines in Figure 5 show that the calculations successfully predict both the pH- and hexacyanoferrate(III)–time curves found experimentally in the mixed system.

**Mixed System—CSTR.** When the composite system reacts under flow conditions, both bistability and oscillation can occur. An experimentally determined phase diagram is presented in Figure 6. One of the steady states is characterized by a low pH (4–5), while the other has a pH of 7–8. In the region of bistability, either of these two states can occur under the identical set of experimental constraints, and the past history of the flow system decides which of the two possible stable states will be found. In the oscillatory range, both the pH and  $[Fe(CN)_6^{3-}]$  are observed to vary periodically. Typical oscillatory traces are shown in Figure



**Figure 7.** Experimental (—) and calculated (---) oscillations in pH (upper) and in  $[Fe(CN)_6^{3-}]$  (lower) in the mixed system under flow conditions. Input concentrations in the combined feed:  $[SO_3^{2-}]_0 = 4.0 \times 10^{-3}$  M;  $[Fe(CN)_6^{4-}]_0 = 2.0 \times 10^{-3}$  M;  $[H_2O_2]_0 = 6.2 \times 10^{-3}$  M;  $[H^+]_0 = 7.0 \times 10^{-4}$  M;  $k_0 = 8.0 \times 10^{-4} s^{-1}$ . Horizontal arrows indicate axis to which curve refers.

7. The pH varies between 4.8 and 7.9, while the oscillation in hexacyanoferrate(III) concentration occurs between  $4.1 \times 10^{-4}$  and  $5.8 \times 10^{-4}$  M. The flow reactor experiments can be simulated by augmenting the empirical rate law model of the mixed system with flow terms. Figure 7 shows that there is good agreement between the calculated and experimental oscillatory curves.

## Conclusions

In addition to the two fundamental processes of the alternator, our model contains three protonation equilibria (reactions 3, 6, and 7) and three further reactions (4, 5, and 9). These are important to describe the kinetics of this particular system, but they are not essential for a general alternator-type oscillator. It has been shown<sup>12</sup> in the periodate–thiosulfate reaction that this sort of oscillation can be obtained without any protonation equilibria. The alternator is merely a simplified model of a class of chemical oscillators; it does not describe any real oscillatory system in detail. In any given system, the model must be extended and modified by a set of reactions characteristic of the particular species in that system. Preliminary calculations<sup>24</sup> suggest that the first oscillatory pH system, sulfide–hydrogen peroxide,<sup>4</sup> can also be described by an extended alternator model. Another oscillatory system of this type constructed in this laboratory consists of hydrogen peroxide, hydrogen sulfite, and thiosulfate in a CSTR. Detailed study of further systems is in progress.

Is there any connection between the design procedure utilized here based on the alternator model and the algorithm<sup>25</sup> based on the cross-shaped phase diagram (CSPD) model<sup>26</sup> used to construct many other oscillators? In a sense, the two approaches are complementary. As Figure 6 shows, the present system indeed possesses a cross-shaped phase diagram, with two steady-state regions and a region of bistability in addition to the oscillatory region. Thus an oscillator can be of both the alternator and CSPD types. The CSPD technique is oriented toward systematic search of the phase space for oscillation, while the alternator approach focuses more on the choice of chemical systems, in this case on autocatalytic pH systems. The CSPD rate equations contain a cubic term, while the alternator may or may not, depending on the details of the kinetics. If no cubic term is present, then oscillations may arise unaccompanied by the other features of the CSPD. Both models involve a relatively complex positive (autocatalytic) feedback process coupled to a simpler negative feedback to generate the oscillations.

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We emphasize that we have not attempted to construct a detailed mechanism of elementary steps, but have considered only component stoichiometric processes and empirical rate laws as building blocks of the reaction system. Much more information will need to be available on the kinetics of the subsystems before a detailed mechanism of elementary steps for the entire system can be developed.

The present system would seem to be closely related to the iodate-ferrocyanide-sulfite<sup>5</sup> (mixed Landolt, EOE) and bromate-ferrocyanide-sulfite<sup>9</sup> oscillators by the replacement of the halate ion with hydrogen peroxide as oxidant. Although those systems have not yet been analyzed in terms of an alternator model, the fact that both show pH oscillations of 3-5 units in amplitude is suggestive that their dynamics must resemble those of the reaction studied here. If so, the mechanistic insights<sup>5,9,27-29</sup>

that have been gained in those systems should be of considerable use in elucidating the mechanism of the hydrogen peroxide-ferrocyanide-sulfite reaction.

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**Registry No.** H<sub>2</sub>O<sub>2</sub>, 7722-84-1; SO<sub>3</sub><sup>2-</sup>, 14265-45-3; Fe(CN)<sub>6</sub><sup>4-</sup>, 13408-63-4.

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## Low-Temperature Investigation of the Ferrimagnetic Chains MnM'(EDTA)·6H<sub>2</sub>O (M' = Co, Ni, and Cu(II)): Thermal and Magnetic Properties

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**Abstract:** We report on the magnetic and thermal properties of the ordered bimetallic chains MnM'(EDTA)·6H<sub>2</sub>O (M' = Co, Ni, and Cu(II)) in the very low-temperature range. Their structure consists of infinite zigzag chains, built up from two alternating (M, M') sites; furthermore, the M-M' distances along the chain are slightly alternating. The magnetic behavior exhibits the characteristic features of 1-d ferrimagnets with a minimum of X<sub>m</sub>T and a divergence upon cooling down. Interchain interactions lead at very low temperature to a long-range antiferromagnetic ordering as outlined by the sharp maximum of X<sub>m</sub>T and the λ-peak in the specific heat data. In the 1-d regime, an analysis of the data from Heisenberg and Ising models is reported. It is emphasized that the degree of J-alternation of these compounds varies in the order [MnNi] < [MnCu] ≪ [MnCo]. A qualitative explanation of this trend is given on basis of the structural features and the electronic ground state of the interacting ions. Finally, the 1-d character of these systems is discussed.

One of the most remarkable advances in low-dimensional magnetism has concerned the recent discovery of a new kind of magnetic systems, namely ferrimagnetic chains or 1-d ferrimagnets.<sup>2</sup> These systems are generally defined as 1-d antiferromagnets made up of two different and alternating spin sublattices, thus giving a net magnetic moment in the ground state. They show a distinctive magnetic behavior (1-d ferrimagnetism) characterized by a minimum at an intermediate temperature, which depends on the strength and anisotropy of the magnetic sublattices, and a divergence at lower temperature. Ordered bimetallic chain compounds provide typical examples of this kind, but actually several homometallic systems also show 1-d ferrimagnetism. That has been emphasized in the case of regular spin chains formed by alternating g-factors on consecutive sites<sup>3,4</sup> and more recently in some exotic networks of interacting ions.<sup>5,6</sup>

In the last few years, several examples of ordered bimetallic chains have been reported.<sup>7-12</sup> We have participated in this effort both in the design of new 1-d ferrimagnets<sup>13,14</sup> and in the development of models required to understand their properties.<sup>3,4,15-20</sup> The bimetallic compounds isolated belong to the isostructural

family MM'(EDTA)·6H<sub>2</sub>O (abbreviated as [MM'], where M = Mn, Co, Ni, and Mg and M' = Co, Ni, Cu, and Zn(II)). The

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