

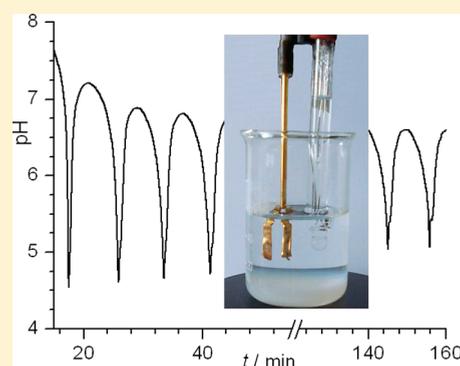
# Generation of pH-Oscillations in Closed Chemical Systems: Method and Applications

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**ABSTRACT:** All pH-oscillators reported to date function only under open (flow reactor) conditions. We describe an approach to generating pH-oscillations in a closed system by starting from an open system pH-oscillator, finding semibatch conditions under which it oscillates with an inflow of a single reactant to an otherwise closed reactor containing the remaining components, and replacing this inflow with a layer of silica gel impregnated with the key reactant. We present data showing the successful application of this technique to the  $\text{BrO}_3^- - \text{Mn}^{2+} - \text{SO}_3^{2-}$ ,  $\text{IO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ , and  $\text{BrO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$  systems. In all three cases, sulfite ion is the species that is replenished via dissolution from the gel layer.



## INTRODUCTION

There are now about 200 variants of chemical oscillators known. On the basis of the similarities in their chemistry, these systems can be grouped into families such as bromate, chlorite, bromite, oxygen, sulfur, Cu(II)-catalyzed, manganese-based, and pH oscillators.<sup>1</sup> Along with the earlier discovered bromate and chlorite oscillators, the pH-oscillators represent the group that has been most frequently employed to study nonlinear chemical dynamics, and it is this group that offers the greatest promise for practical applications. Periodic changes in pH obviously occur in all chemical oscillators that operate in unbuffered aqueous solutions, even in those that require strongly acidic media like the Bray–Liebhafsky or Belousov–Zhabotinsky reactions. We define pH-oscillators<sup>2</sup> as systems in which  $\text{H}^+$  plays the most important kinetic role in bringing about the oscillatory behavior. In such systems, the variation in pH, which can be as large as 4 pH-units, is neither a consequence nor an indicator, but rather the driving force of the oscillations. Two major composite reactions are switched on and off in every pH-oscillator: one that produces  $\text{H}^+$  in an autocatalytic fashion, and another that consumes  $\text{H}^+$  in a slow process with an appropriate time lag.<sup>2</sup>

To date, about 20 pH-oscillators have been reported. All of them function only under flow conditions, that is, in a continuously fed stirred tank reactor (CSTR) or in a semibatch arrangement, in which some of the reactants are fed in, and no example is known in which pH-oscillations occur in a batch (closed) reactor. There is considerable interest in developing batch pH-oscillators, because in several proposed applications a batch pH-oscillator would be more convenient to use than the equivalent CSTR variant or because the application is simply not feasible if

continuous flows are required. One potential application of pH-oscillators was proposed in 1995 and patented in 2000 by Giannos et al.,<sup>3,4</sup> who suggested their use in a pulsating drug delivery device. In experiments designed to test this idea,<sup>5</sup> pulses of the active drug-species to be transported through a membrane were produced in a CSTR. Unless the CSTR can be replaced with a batch-like system, however, such a device has little or no chance to be useful in a living organism. In several other recent applications of pH-oscillators, long-lasting batch systems, if they had been available, would have made these experiments considerably easier and/or more practical. These investigations include the study by Liedl and Simmer,<sup>6</sup> who induced periodic switches in the conformation of a DNA molecule between its folded and unfolded forms in the iodate–sulfite–thiosulfate flow system, and the work of Lagzi et al.,<sup>7</sup> who used the formaldehyde–sulfite–gluconolactone CSTR oscillator to control the dissociation of acidic head-groups on the surface of metal nanoparticles. Ryan et al.<sup>8</sup> designed a molecular motor that was actuated by the bromate–manganese(II)–sulfite CSTR pH-oscillator. In this last case, the periodic changes in the pH forced a pH-responsive hydrogel to undergo repetitive shrinking and swelling, enabling the chemical energy to be transformed to mechanical work. For continuous operation of such a “motor” and in some other cases, for example, in producing stationary patterns, such as self-replicating spots<sup>9</sup> and Turing structures,<sup>10</sup> or in generating sustained oscillations in the concentration of nonredox ions,<sup>11</sup> CSTR pH-oscillators may be equally or more appropriate, but long-lasting

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batch oscillators are likely to be of considerable utility in a variety of applications, particularly those involving biochemical systems where expensive materials, such as enzymes, DNA, etc., are used.

In this Article, we propose a method that makes it possible to convert known CSTR pH-oscillators to a form in which oscillations can occur in a closed configuration. We apply this technique to construct three batch-like pH-oscillators.

## THE GENERAL APPROACH

Our approach is based on the hypothesis that it is possible to transform at least some CSTR pH-oscillator first to a semibatch oscillator, then to a batch-like system using the method described below.

A CSTR pH-oscillator consists of an oxidant (designated as "A") and one or two substrates (designated as "B" or "B" and "C"). "A" is always present in stoichiometric excess to "B", and "B" is in excess to "C" when that species is present. To maintain sustained oscillations in the CSTR, components "A", "B", and "C" must be replenished by input flows. In the one-substrate variants, component "B", and in the two-substrate systems, component "C" is completely consumed during each oscillatory cycle. To make a CSTR pH-oscillator oscillate in a semibatch arrangement, in which some reactants are initially in the reactor and others are continuously fed in, the oxidant and all other components (the second substrate if present, any auxiliary reagents such as a catalyst, or acid) are premixed in a beaker, and the component that is consumed during a CSTR oscillation is introduced by the input flow. If we succeed in producing a semibatch oscillator, to convert it to a batch-like system, we must ensure the continuous supply of the consumed component without feeding it from outside. We generate this reagent inside the reactor by slow dissolution from a gel layer that resides in the reaction vessel and contains a high concentration of the component in question. This concept should be applicable to both single- and double-substrate pH-oscillators.

To test our approach in the laboratory, we selected the  $\text{BrO}_3^- - \text{Mn}^{2+} - \text{SO}_3^{2-}$ ,<sup>12</sup> the  $\text{IO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ ,<sup>13</sup> and the  $\text{BrO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ <sup>14</sup> two-substrate CSTR pH-oscillators (abbreviated as BMS, IFS, and BFS, respectively). These systems show large amplitude, easily reproducible pH-oscillations, and their mechanisms are among the best understood of all pH-oscillators. The species to be supplied at a constant rate in seeking oscillations under semibatch and closed conditions is  $\text{SO}_3^{2-}$  in each of these systems.

## EXPERIMENTAL SECTION

**Chemicals.** Reagent grade chemicals,  $\text{NaBrO}_3$ ,  $\text{KIO}_3$ ,  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Reanal), anhydrous  $\text{Na}_2\text{SO}_3$  (Sigma), and sodium silicate solution (Sigma–Aldrich, ~27%  $\text{SiO}_2$ , 14%  $\text{NaOH}$ ), were used without further purification. The  $\text{Na}_2\text{SO}_3$  and  $\text{Mn}^{2+}$  content of the salts were determined by titration with  $\text{I}_2$  and EDTA standard solutions. Bromate (0.6 M), iodate (0.3 M), manganese(II) (0.01 M), and ferrocyanide (0.08 M) stock solutions were prepared with distilled water passed previously through a Millipore purification system. The  $\text{K}_4\text{Fe}(\text{CN})_6$  stock solution was allowed to stand for a day before use and was stored in an amber glass bottle.

**Apparatus.** All information related to the behavior of the BMS, IFS, and BFS systems in a CSTR was taken from the literature.<sup>12–15</sup> The experiments described here were carried out under semibatch and batch conditions. In both configurations, the changes in pH were followed in time using a combined glass electrode (Radelkis OP-823P) connected to

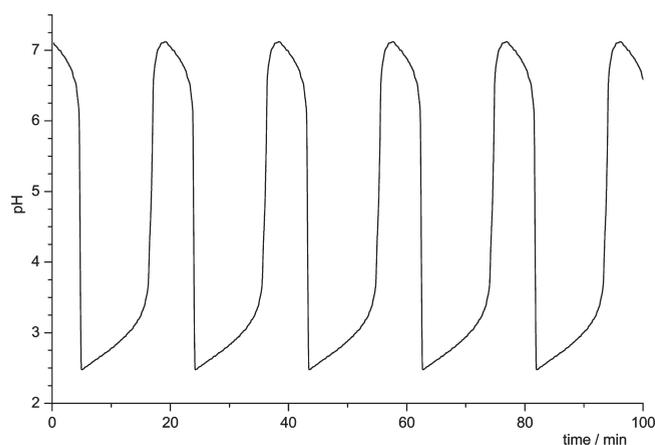
a pH-meter (Hanna pH-209). The pH versus time curves were recorded either on a Kipp & Zonen flatbed recorder or with a personal computer through a pH-meter and a 16 bit A/D converter (NI-6010-PCI) with a sampling rate of 2 Hz. The reaction mixtures were thermostatted to 45 °C (recommended in refs 12–15) and in some cases to 25 °C.

In the semibatch experiments, the components  $\text{BrO}_3^-$  and  $\text{Mn}^{2+}$  or  $\text{IO}_3^-$  and  $\text{Fe}(\text{CN})_6^{4-}$  were mixed in a glass beaker ( $V = 110 \text{ cm}^3$ , height 10.0 cm, i.d. 3.5 cm), the mixture was stirred with a magnetic stirrer (rotation rate 300 rpm), and the solution of  $\text{Na}_2\text{SO}_3$  (with 0.025 M  $\text{H}_2\text{SO}_4$  added to decrease its pH to facilitate initiation of the auto-catalytic reactions between  $\text{BrO}_3^-/\text{IO}_3^-$  and  $\text{SO}_3^{2-}$ ) was introduced into the reactor by a peristaltic pump (Gilson Minipuls) through a single thin tube at a very low flow rate (25–50  $\mu\text{mol}/\text{min}$ ).

In the experiments performed in the closed (batch-like) configuration, the reaction vessel was a beaker containing a silica gel layer, which served as a reservoir of the reagent  $\text{Na}_2\text{SO}_3$ . Before the experiments were started, the gel layer was rinsed twice with 25  $\text{cm}^3$  distilled water to remove any base remaining on the gel surface. The other components of the system ( $\text{BrO}_3^-$  and  $\text{Mn}^{2+}$ , or  $\text{IO}_3^-$  and  $\text{Fe}(\text{CN})_6^{4-}$ , or  $\text{BrO}_3^-$  and  $\text{Fe}(\text{CN})_6^{4-}$ ) were previously prethermostatted, mixed, and poured into the reactor. Experiments were performed at different concentrations of the reagents in the reaction mixture and in the gel. The total volume of the reaction mixture was 40–60  $\text{cm}^3$ . The initial pH of the solution was usually 8–9, which slowly decreased due to the reaction between  $\text{BrO}_3^-$  or  $\text{IO}_3^-$  and  $\text{SO}_3^{2-}$ . When the pH reached about 7 and the concentrations of all reagents were in the proper range, oscillations in pH appeared. The preoscillatory induction time was usually 10–30 min, but it can be nearly eliminated by decreasing the initial pH to 6–7 by adding 1–2 drops of 1.0 M  $\text{H}_2\text{SO}_4$  to the reaction mixture. Care must be taken with the mode and the intensity of stirring. Using a magnetic stirrer or stirring very rapidly may damage or even destroy the gel layer, resulting in an erratic release of  $\text{Na}_2\text{SO}_3$  from the gel. To avoid this problem, we employed a stirrer that rotates at a relatively slow rate (100–250 rpm) on a propeller suspended from the top of the vessel.

**Preparation of Silica Gel Layer Loaded with Reagent  $\text{Na}_2\text{SO}_3$ .** The silica gel was prepared from sodium silicate solution. 30.0 g of sodium silicate solution was diluted with distilled water to about 70  $\text{cm}^3$  in a beaker, 25.2 g of anhydrous  $\text{Na}_2\text{SO}_3$  was dissolved in this solution (gentle heating speeds up the dissolution), and the mixture was washed into a volumetric flask and made up to 100.0  $\text{cm}^3$  with distilled water. This stock solution contained 2 M  $\text{Na}_2\text{SO}_3$  and is referred to as the "gel base" below. Gelation was initiated by adding  $\text{H}_2\text{SO}_4$  to the gel base. On mixing 2.65  $\text{cm}^3$  gel base with 1.00  $\text{cm}^3$  1.0 M  $\text{H}_2\text{SO}_4$ , gelation is complete within 1–2 min. The gel layer was prepared in beakers of different sizes ( $V = 80 \text{ cm}^3$ , i.d. 3.80 cm and  $V = 100 \text{ cm}^3$ , i.d. 4.90 cm), which served as the reaction vessels for the closed system experiments. Using different volume reaction vessels but maintaining the above ratio of gel base to acid, we prepared gel layers of different thicknesses and surface areas. Generally, 5.30 or 7.95  $\text{cm}^3$  of gel base and 2.00 or 3.00  $\text{cm}^3$  of 1 M  $\text{H}_2\text{SO}_4$  were mixed, which resulted in gel layers that were about 5 or 7 mm thick, and had about 12 or 19  $\text{cm}^2$  surface area, respectively, with an  $\text{Na}_2\text{SO}_3$  concentration of 1.45 M (the  $\text{SiO}_2$  content ~5.9%). We shall refer to the gel layer prepared by mixing 5.30  $\text{cm}^3$  gel base and 2.00  $\text{cm}^3$  1 M  $\text{H}_2\text{SO}_4$  in a  $V = 80 \text{ cm}^3$  beaker as "gel-layer A" and that made from 7.95  $\text{cm}^3$  gel base and 3.00  $\text{cm}^3$  (in a few cases 3.25  $\text{cm}^3$ ) 1.0 M  $\text{H}_2\text{SO}_4$  in a 100  $\text{cm}^3$  beaker as "gel layer B". The gel layers can be used immediately in the experiments, or they can be stored for 4–5 days before use if the beaker is sealed with Parafilm.

We also tested agarose, agar–agar, and polyvinyl alcohol gels as potential sources of  $\text{Na}_2\text{SO}_3$ , but only experiments carried out with silica gel were successful. The major problems arose from the lower solubility and the sensitivity of  $\text{Na}_2\text{SO}_3$  to heat and to acid when the gels were prepared from substances other than sodium silicate solution. Agarose and agar–agar undergo gelation only after being heated to a temperature



**Figure 1.** Sustained pH-oscillations measured in the BMS CSTR system. Initial concentrations (if no reaction took place):  $[\text{BrO}_3^-]_0 = 0.15 \text{ M}$ ;  $[\text{Mn}^{2+}]_0 = 2.25 \times 10^{-3} \text{ M}$ ;  $[\text{SO}_3^{2-}]_0 = 0.188 \text{ M}$ ;  $[\text{H}^+]_0 = 1.38 \times 10^{-2} \text{ M}$ ;  $k_0 = 3.7 \times 10^{-3} \text{ s}^{-1}$ ;  $T = 45 \text{ }^\circ\text{C}$ .

at which the sulfite partly oxidizes. Polyvinyl alcohol requires an acid catalyst for gelation, which causes part of the sulfite to be transformed to volatile  $\text{SO}_2$ . In contrast, silica gel can be prepared at room temperature, holds a high concentration of  $\text{Na}_2\text{SO}_3$ , and is practically unchanged after several days under careful storage.

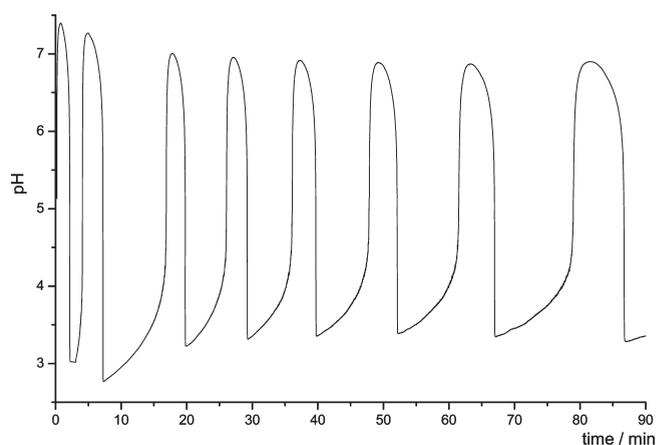
**Dissolution Rate of  $\text{Na}_2\text{SO}_3$  from the Silica Gel.** We measured the rate of release of  $\text{Na}_2\text{SO}_3$  from the silica gel into the solution above the gel under conditions similar to those used in the experiments in closed systems. First, “gel layer A” was prepared, which contained 10.60 mmol of  $\text{Na}_2\text{SO}_3$ . Next, distilled water of the same volume as the reaction mixture ( $40 \text{ cm}^3$ ) was repeatedly poured above the gel layer, and after stirring the solution was decanted from the gel, and its sulfite content was titrated with 0.05 M  $\text{I}_2$  solution. The dissolution rate was followed at  $T = 25 \text{ }^\circ\text{C}$  for about 6 h, during which 25 samples were analyzed. The same procedure was repeated at  $T = 45 \text{ }^\circ\text{C}$  using “gel layer B” ( $\text{Na}_2\text{SO}_3$  content 15.90 mmol). The data, shown as the aggregate sulfite concentration that dissolved into the aliquot water portions versus time, are given below.

## RESULTS AND DISCUSSION

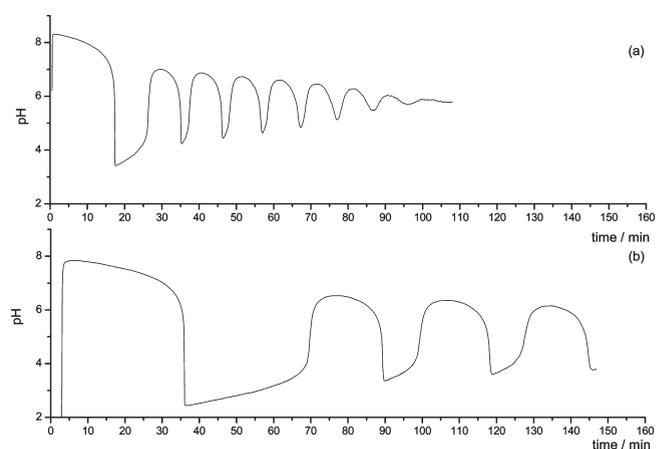
**Oscillations in the BMS System in Semibatch and Closed Conditions.** Oscillations in the BMS flow system were first reported by Okazaki et al.,<sup>12</sup> who observed large amplitude pH-oscillations in a range of input concentrations and flow rates at  $45 \text{ }^\circ\text{C}$ . The oscillations in pH are due to the oxidation of  $\text{HSO}_3^-$  to  $\text{SO}_4^{2-}$  and of  $\text{Mn}^{2+}$  to  $\text{MnO}(\text{OH})^+$  by  $\text{BrO}_3^-$ , both of which produce  $\text{H}^+$ , and the oxidation of  $\text{HSO}_3^-$  to  $\text{HS}_2\text{O}_6^-$  by  $\text{MnO}(\text{OH})^+$ , which consumes  $\text{H}^+$ . The sustained pH-oscillations measured earlier<sup>15</sup> and again in this work in a CSTR are presented in Figure 1.

We were successful in getting the BMS oscillator to work in semibatch mode using the method described in the Experimental Section. The reaction conditions and the oscillatory traces are shown in Figure 2. The amplitude and waveform of the oscillations strongly resemble those measured in the CSTR.

To generate pH-oscillations in the closed BMS system, solutions of  $\text{BrO}_3^-$  and  $\text{Mn}^{2+}$  were poured into the reaction vessel containing “gel layer A”, and the pH was recorded as a function of time. Oscillations were observed at  $[\text{BrO}_3^-] = 0.3\text{--}0.1 \text{ M}$  and  $[\text{Mn}^{2+}] = 2 \times 10^{-3}$  to  $5 \times 10^{-3} \text{ M}$ . In addition to our experiments at  $T = 45 \text{ }^\circ\text{C}$ , we performed runs at room temperature as



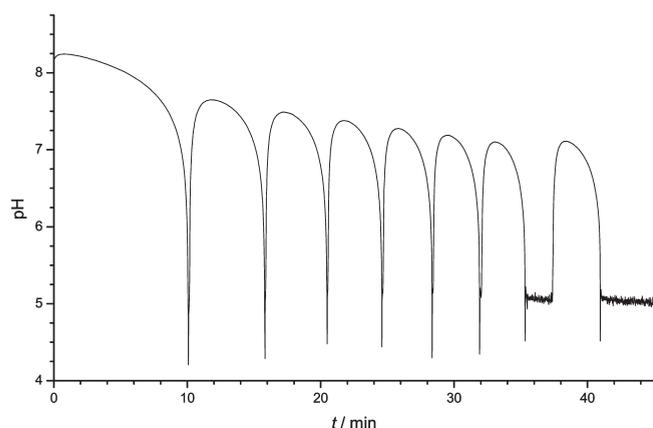
**Figure 2.** pH-oscillations in the semibatch BMS system. Initial mixture in the reactor:  $V = 20.0 \text{ cm}^3$ ;  $[\text{BrO}_3^-]_0 = 0.30 \text{ M}$ ;  $[\text{Mn}^{2+}]_0 = 5 \times 10^{-3} \text{ M}$ . A solution of  $[\text{Na}_2\text{SO}_3]_0 = 0.472 \text{ M}$  and  $[\text{H}^+]_0 = 2.5 \times 10^{-2} \text{ M}$  was pumped into the reactor at input rate  $30 \text{ } \mu\text{mol}/\text{min}$ ,  $T = 45 \text{ }^\circ\text{C}$ .



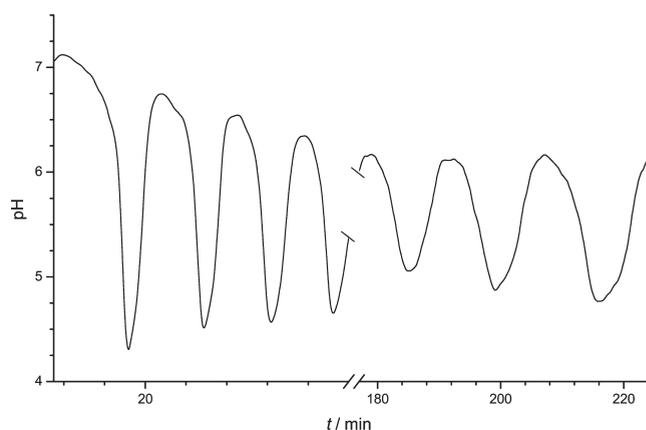
**Figure 3.** pH-oscillations recorded in the closed BMS system at two temperatures. (a) Solution in the reactor:  $V = 40.0 \text{ cm}^3$ ,  $[\text{BrO}_3^-] = 0.15 \text{ M}$ ;  $[\text{Mn}^{2+}] = 2.5 \times 10^{-3} \text{ M}$ , “gel layer A”,  $T = 45 \text{ }^\circ\text{C}$ . (b) Solution in the reactor:  $V = 40.0 \text{ cm}^3$ ,  $[\text{BrO}_3^-] = 0.225 \text{ M}$ ;  $[\text{Mn}^{2+}] = 3.75 \times 10^{-3} \text{ M}$ , “gel layer B”,  $T = 25 \text{ }^\circ\text{C}$ .

well. The results are presented in Figure 3a and b. As in the semibatch reactor, we were able to obtain 5–10 oscillations, whose amplitude gradually decreased. Oscillations with about the same amplitude were also observed at  $T = 25 \text{ }^\circ\text{C}$ , but the period increased significantly. The duration of the oscillatory state was about 100 min at  $T = 45 \text{ }^\circ\text{C}$  and was estimated to be about 2.5 times longer at  $T = 25 \text{ }^\circ\text{C}$ .

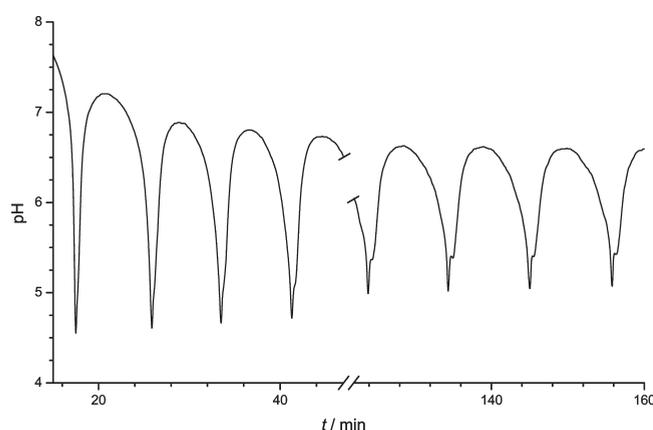
**Long-Lasting pH-Oscillations in the IFS and BFS Systems in a Batch-like Reactor.** Sustained pH-oscillations in the IFS and BFS CSTR systems were first observed by Edblom et al.<sup>13,14</sup> In these systems, as in the BMS reaction, the  $\text{H}^+$ -producing step is the autocatalytic oxidation of sulfite to sulfuric acid by iodate or bromate, which is followed by a slow reaction between iodate or bromate and ferrocyanide, consuming  $\text{H}^+$ . The oscillations can occur at room temperature, but they appear more readily at  $40\text{--}45 \text{ }^\circ\text{C}$ . We therefore performed our semibatch and batch experiments at elevated temperature ( $45 \text{ }^\circ\text{C}$ ). The IFS and BFS systems were shown to exhibit long-lived pH-oscillations under semibatch conditions. Rábai et al.<sup>16</sup> recorded pH-oscillations for



**Figure 4.** pH-oscillations in the IFS system under semibatch conditions. A solution containing 2.0 M  $\text{Na}_2\text{SO}_3$  and 0.04 M  $\text{H}_2\text{SO}_4$  was introduced into a mixture of 14.0  $\text{cm}^3$  0.3 M  $\text{KIO}_3$  and 7.0  $\text{cm}^3$  0.08 M  $\text{K}_4\text{Fe}(\text{CN})_6$  at a rate of 0.072  $\text{cm}^3/\text{min}$ ,  $T = 45^\circ\text{C}$ .



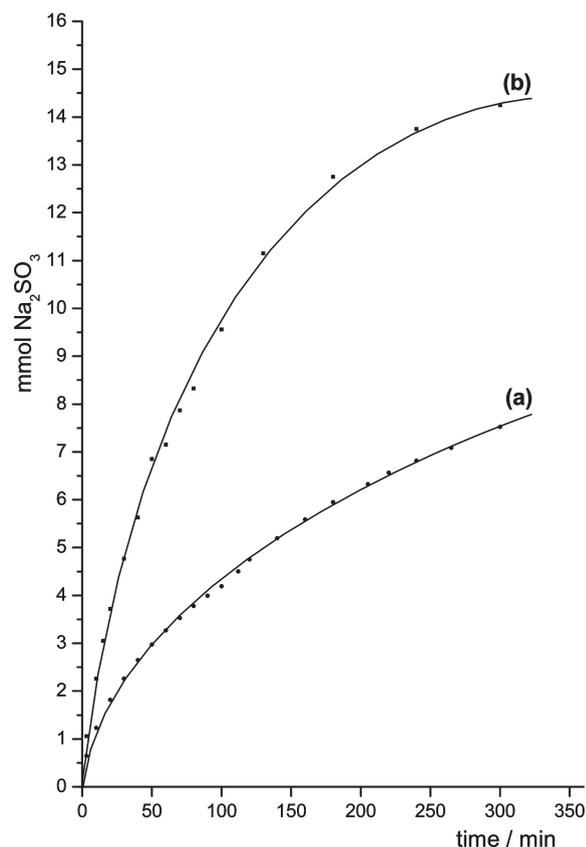
**Figure 6.** Long-lasting pH-oscillations recorded in the BFS closed system. Solution in the reactor:  $V = 40.0 \text{ cm}^3$ ,  $[\text{BrO}_3^-] = 0.09 \text{ M}$ ;  $[\text{K}_4\text{Fe}(\text{CN})_6] = 0.015 \text{ M}$ , “gel layer B”,  $T = 45^\circ\text{C}$ , stirring rate 200 rpm.



**Figure 5.** Long-lasting pH-oscillations recorded in the IFS closed system. Solution in the reactor:  $V = 60.0 \text{ cm}^3$ ,  $[\text{IO}_3^-] = 0.15 \text{ M}$ ;  $[\text{K}_4\text{Fe}(\text{CN})_6] = 0.02 \text{ M}$ , “gel layer B”,  $T = 45^\circ\text{C}$ , stirring rate 200 rpm.

400 min at  $T = 40^\circ\text{C}$  when a slightly acidic  $\text{Na}_2\text{SO}_3$  solution was flowed into a 200  $\text{cm}^3$  mixture of  $\text{IO}_3^- - \text{Fe}(\text{CN})_6^{4-}$  and  $\text{BrO}_3^- - \text{Fe}(\text{CN})_6^{4-}$ . To reduce the volume of the applied reagents to fit the gel-containing beaker, in our semibatch runs the initial concentrations were deduced from the domain of the phase diagram where oscillations occur in the CSTR (see Figure 6 of ref 13). Figure 4 presents the results when a mixture of  $\text{Na}_2\text{SO}_3$  with a small amount of  $\text{H}_2\text{SO}_4$  was introduced into a mixture of  $\text{KIO}_3$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  solutions at a slow pump rate. The oscillatory traces measured in a CSTR (see Figure 5 of ref 13) and under semibatch conditions are similar in shape and size. The amplitude is only slightly damped, but the number of oscillations is obviously limited due mainly to the dilution of the reaction mixture during the semibatch run.

Oscillations were obtained at several compositions of the IFS system in the closed arrangement. Figure 5 shows long-lasting pH-oscillations recorded when a mixture of  $\text{IO}_3^-$  and  $\text{Fe}(\text{CN})_6^{4-}$  was poured over “gel layer B” in a beaker. The oscillations were maintained for more than 4 h, during which 28 cycles appeared with barely decreasing amplitude ( $\Delta\text{pH} = 2.8$  at the start, 1.7 at the end) and slightly increased period ( $\tau = 8$  min at the start, 11 min at the end). This experiment was repeated with a



**Figure 7.** Dissolution of  $\text{Na}_2\text{SO}_3$  (in mmol) from silica gel layers into distilled water versus time. Curve (a): “gel layer A” (initial  $\text{Na}_2\text{SO}_3$ : 10.60 mmol) was used at  $T = 25^\circ\text{C}$ . Curve (b): “gel layer B” (initial  $\text{Na}_2\text{SO}_3$ : 15.90 mmol) was used at  $T = 45^\circ\text{C}$ .

“gel layer B” that had been stored for 100 h before use, and the same results were obtained. In the IFS system, the pH-oscillations can be followed visually as well by using appropriate acid–base indicators. On addition of an indicator mixture of bromothymol-blue (transition range of pH: 6.2 (yellow)–7.6 (blue)) and bromocresol-purple (transition range of pH: 5.2 (yellow)–6.8 (purple)) to the system shown in Figure 5, color

**Table 1. Variants of pH-Oscillators with  $\text{SO}_3^{2-}$  as Substrate**

oxidant	substrate(1)	substrate(2)	reference
$\text{IO}_3^-$	$\text{HSO}_3^-$	$\text{Fe}(\text{CN})_6^{4-}$	13
$\text{BrO}_3^-$	$\text{HSO}_3^-$	$\text{Fe}(\text{CN})_6^{4-}$	14
$\text{H}_2\text{O}_2$	$\text{HSO}_3^-$	$\text{Fe}(\text{CN})_6^{4-}$	18
$\text{H}_2\text{O}_2$	$\text{HSO}_3^-$	$\text{CaCO}_3$	19
$\text{H}_2\text{O}_2$	$\text{HSO}_3^-$	$\text{HCO}_3^-$	20
$\text{IO}_3^-$	$\text{HSO}_3^-$	$\text{S}_2\text{O}_3^{2-}$	21
$\text{BrO}_3^-$	$\text{HSO}_3^-$	$\text{Mn}^{2+}/\text{MnO}_4^-$	12
$\text{H}_2\text{O}_2$	$\text{HSO}_3^-$	Hemin	22
$\text{ClO}_2^-$	$\text{HSO}_3^-$	$\text{CO}_3^{2-}$	23
$\text{ClO}_2^-$	$\text{HSO}_3^-$		23
$\text{BrO}_3^-$	$\text{HSO}_3^-$		24

oscillations between bluish-purple and yellow could be observed for several hours.

As in the IFS closed system, long-lasting oscillations were observed when the  $\text{IO}_3^-$  was replaced with  $\text{BrO}_3^-$ . An example of such oscillations is shown in Figure 6, where the changes in pH were followed for 220 min and 26 cycles were recorded. In this case, and in other pH-oscillators in which  $\text{BrO}_3^-$  is involved, acid–base indicators cannot be employed to observe color oscillations, because bromate is too strong an oxidant and attacks the indicator.

**Dissolution Rate of  $\text{Na}_2\text{SO}_3$  from the Silica Gel Layer.** The dissolution of the reagent  $\text{Na}_2\text{SO}_3$  embedded in “gel layer A” and in “gel layer B” was followed at  $T = 25$  and  $45$  °C. In Figure 7, we plot the aggregate amounts of  $\text{Na}_2\text{SO}_3$  appearing in the aliquot water samples in contact with the gel layers as a function of time. From Figure 7, it is clear that the dissolution process is long-lasting and surprisingly uniform over a rather wide time interval. The dissolution rate of  $\text{Na}_2\text{SO}_3$  depends mainly on the surface area and the thickness of the gel layer, on the initial amount of  $\text{Na}_2\text{SO}_3$  in the gel, and on the temperature. By varying these parameters, the dissolution rate can be controlled and matched to the flux of  $\text{SO}_3^{2-}$  that gives oscillation under CSTR or semibatch conditions. We estimate the average dissolution rates with “gel layer A” at  $T = 25$  °C and “gel layer B”, respectively, at  $T = 45$  °C as 60 and 120  $\mu\text{mol}/\text{min}$  during the first hour, about 25 and 50  $\mu\text{mol}/\text{min}$  during the next 2 h, and about 10–20  $\mu\text{mol}/\text{min}$  after 3 h. These values fall in the range of sulfite concentrations that give rise to oscillations in the BMS, IFS, and BFS CSTR systems.<sup>12–14</sup> Therefore, the oscillations we find in the BMS, IFS, and BFS closed systems can be regarded as batch-like versions of the original CSTR oscillators.

## CONCLUSIONS

Our experiments show that some chemical oscillators, believed until now to be capable of functioning only under CSTR conditions, can be transformed to batch-like systems. Here, we have demonstrated the feasibility of our approach with three pH-oscillators: the  $\text{BrO}_3^- - \text{Mn}^{2+} - \text{SO}_3^{2-}$ ,  $\text{IO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$ , and  $\text{BrO}_3^- - \text{Fe}(\text{CN})_6^{4-} - \text{SO}_3^{2-}$  flow systems were shown to oscillate in a flow-free arrangement if a continuous supply of the reagent  $\text{SO}_3^{2-}$ , consumed during an oscillatory cycle in flow, is provided by dissolution from a silica gel layer containing a high concentration of  $\text{Na}_2\text{SO}_3$ . Many other pH-oscillators, listed in Table 1, utilize the reagent  $\text{SO}_3^{2-}$ . It is likely that some, perhaps all, of these can be made to oscillate in a closed environment. One

can also envision extending further the number of CSTR oscillators that can operate under semibatch and batch-like conditions by using other families of oscillators, perhaps with other types of gels. For example, promising candidates include the  $\text{H}_2\text{O}_2 - \text{S}_2\text{O}_3^{2-} - \text{Cu}^{2+}$  and the  $\text{H}_2\text{O}_2 - \text{S}^{2-}$  CSTR systems, which have already been reported to oscillate in a semibatch reactor.<sup>17</sup>

The question may be raised whether the oscillations generated by using the method suggested here represent true batch systems. One might alternatively refer to them as “two-compartment oscillators”, “heterogeneous batch pH-oscillators”, or “continuously fed batch systems”. Whatever name is used, the key point is that these are closed systems that may substitute where appropriate for the more cumbersome CSTR oscillators in present and future applications.

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