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COMMENTS

Comment on "The Effect of Rapidness of Flow Rate Changes on the Bistable Experiments: The Chlorite/Iodide Reaction" †

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The dynamics of nonlinear oscillatory chemical systems in continuously fed stirred tank reactors (CSTR) depend a lot on the flow rate[1] of the feed chemicals. For quantitative determination of bistability and oscillations[2] in a CSTR, it is desirable that the product chemicals as recorded by the monitors have sustained concentrations inside the reactor. The conventional technique of bistability experiments in CSTR does not help to get stable concentrations of the products inside the reactor at a particular flow rate because one has to change the flow rate of the feed chemicals in both ways at short time intervals, set fixed by the experimenter himself. To analyze it in mathematical terms, let us first consider that there is a CSTR initially filled with a chemical of concentration C_o. We intend to replace the chemical by feeding water into it with an inflow rate k_o for unit reactor volume (or inverse residence time). This replacement is an exponential process and should obey the relationship

$$C_t = C_o \exp(-k_o t) \tag{1}$$

where C_t (C_o) is the concentration of the chemical at time t(0); $C_t < C_o$. The residence time (τ) of such a system for unit reactor volume is given by

$$\tau = 1/k_o \tag{2}$$

Therefore eq 1 takes the form

$$C_t = C_o \exp(-t/\tau) \tag{3}$$

Suppose, we wish to calculate the concentration of the chemical inside the reactor immediately after nth residence time has passed i.e., $t = n\tau$. Then from eq 3 we have

$$C_t = C_o \exp(-n) \tag{4}$$

Equation 4 suggests that, after inflow of water for five residence time, 0.6% of the initial concentration of the chemical is still present in the reactor. From eq 1 we have

$$\lim_{(t\to\infty)} C_t = C_o \lim_{(t\to\infty)} \exp(-k_o t) = 0 \tag{5}$$

Therefore, 100% replacement of the chemical by water is not possible by inflow of water for finite time. Obviously, small residence time (small reactor volume and high flow rate) favors quick replacement of the chemical by water in this flow experiment.

To apply the above ideas in the case of a bistable experiment, we confine our attention to the concentrations of the product chemicals as recorded by the monitors at two successive flow rates. For example, if we maintain the time interval of five residence time between two successive flow rate changes, eq 4 suggests that 0.6% of the product concentration produced in the previous flow rate is still present in the reactor even after five residence time has passed fran the start of the next flow rate. If we maintain a much shorter time interval of only one residence time between two successive flow rate changes and monitor the concentrations of the products, the latter flow rate should show the concentrations which include 36.8% of the product concentrations generated in the previous flow rate in addition to the concentrations actually generated in the latter flow rate. Our calculations have ignored the contribution of the product concentrations in the previous flow rates other than the two considered here, because as flow rate is changed, residence time also changes. However, stepwise application of eq 4 may resolve these cases satisfactorily.

The above discussion indicates that higher speed of the flow rate changes induces the bistable system more susceptible to the memory effect of the former flow rates and thereby enhances the domain of stability of the thermodynamic or the flow branch as the case may be. This we have experienced in the past during the bistability experiments of the minimal bromate oscillator, but we never mentioned it in the text.[3,4] The width of bistability hysteresis, particularly the down transition from the thermodynamic to flow branch, depends very much on the rapidness of the flow rate changes with which it is accomplished; rapid flow rate changes shifts the down transition to a higher flow rate. It is worthy to note that some workers[5] in the past have used time intervals of as low as three residence time between two successive flow rate changes in the bistability experiments of the minimal bromate oscillator; obviously, their experiment produced down and up transitions at relatively higher and lower flow rates, which we can interpret from our understanding of the CSTR experiments as reported here.

For the bistability experiments of the chlorite/iodide reaction, we used a reactor according to the design described elsewhere.[6] The measurements were obtained using a macroelectrode (dimension, 0.5 × 15 mm) against a reference electrode (Ag/AgCl/Na_2SO_4) placed into the feedstream of the iodide solution before entering into the reactor. In the bistability experiments of this system[6−9] in nonpremixed mode, one obtains a thermodynamic branch which is unstable[7] in the region between close to zero upto a moderately high flow rate. As the flow rate is slightly increased from zero, the thermodynamic branch slowly transits to an intermediate branch. We label it the middle iodide (MI) branch because its electrode potential lies between those of other two branches, but much closer to that of the flow branch characterized by relatively high concentration of both iodide and iodine, The theory that rapid increase of flow rates should stabilize the thermodynamic branch may well be applied to construct the apparently unstable thermodynamic branch in the

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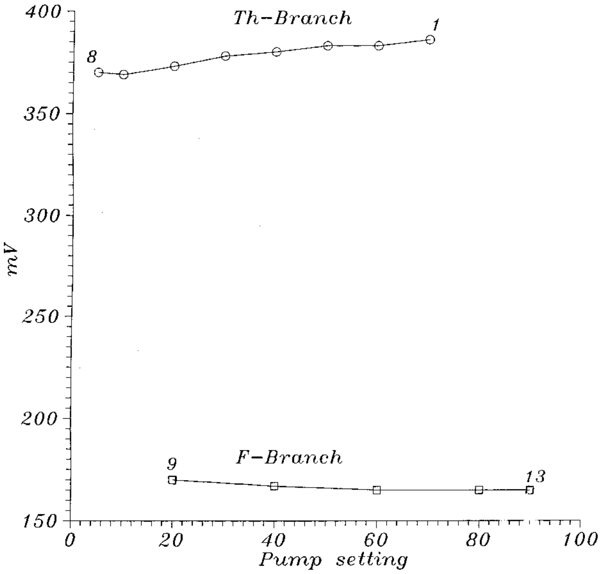

Figure 1. Transition from high potential thermodynamic branch to low potential flow branch by decreasing flow rate in the chlorite/iodide system; thirteen changes of flow rates have been made to accomplish the experiment, which starts from flow rate number one on the thermodynamic branch: $[\mathrm{KI}]_o$, 3×10^{-5} M; $[\mathrm{ClO_2^-}]_o$, 0.96×10^{-5} M; $[\mathrm{OH^-}]_o$, 0.55×10^{-4} M; $[\mathrm{Na_2SO_4}]_o$, 0.052 M; $[\mathrm{H_2SO_4}]_o$, 0.0052 M; stirring rate, 1500 rpm; reactor volume, 31.4 mL; temperature, 20 ± 0.3 °C (nonpremixed mode of mixing was used).

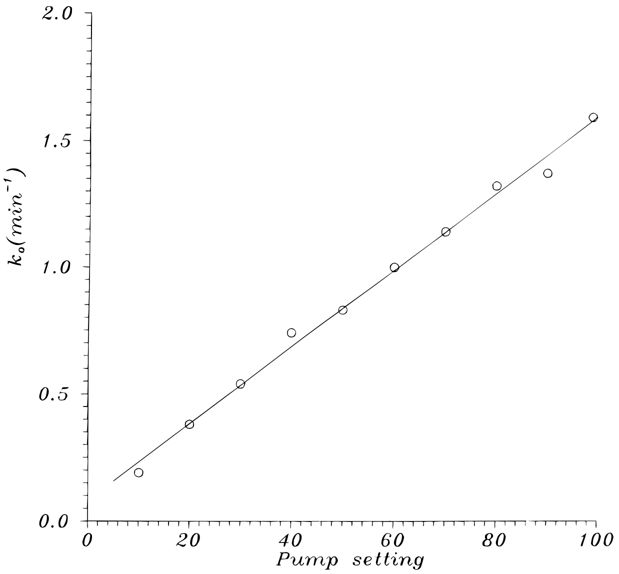

Figure 2. Flow rate per unit reactor volume vereus pump setting calibration for the experiment reported in Figure 1.

bistability experiments of this system. To get it, one has to increase at high stirring the flow rate at a high speed, starting from zero until the corresponding flow rate crosses over the unstable region of the thermodynamic branch. Beyond that, the thermodynamic branch is stable showing normal behavior until it transits to the flow branch at a still higher flow rate. We applied this technique in the past (vide Figure 3 of ref 9) to construct the unstable thermodynamic branch in this system, but we did not mention it explicitly in the text.[9,10] Alternatively, one can cross over the low flow rate hole to reach the other side of the thermodynamic branch by one large step increase of the flow rate from zero (thermodynamic equilibrium state) to an appropriate higher flow rate, at which the thermodynamic branch is stable. It is curious to note that the authors of a previous paper[6] on the bistability experiments in this system have not even mentioned how they have drawn the unstable thermodynamic branch in this system. The following section describes those experiments showing the dramatic effect of rapidness of flow rate changes on the bistable dynamics of this system.

The decrease of flow rates in steps from the stable region of the thermodynamic branch results in a transition from the thermodynamic to the intermediate (MI) state. After the system has transitioned to the MI state, we start to increase the flow rate in steps. The system continues to remain on the MI state initially, but transitions gradually to the flow branch at a higher flow rate preceeded by a rather cumbersome state due to very slow relaxation of the system in this low flow rate phase. By controlling the rapidness of the flow rate changes, one can all together eliminate this MI state to obtain an apparently direct transition from the thermodynamic branch to the flow branch by stepwise decrease of flow rates. Figure 1 demonstrates the result of such a controlled experiment, which was obtained by decreasing flow rates in small steps, while maintaining a time interval of five residence time frames between two successive flow rate changes. At pump setting 5 (viz. the eighth flow rate as indicated in Figure 1), the thermodynamic branch transits to the MI state. But we did not allow the state MI to gain stability by the continuation of flow at the same rate for 10 residence time frames (about 11 hours) until the system attains stability on the flow branch. After a new pump setting 20 (viz. the nineth flow rate as indicated in Figure 1) on the flow branch had been established, we restored the time interval of five residence time between two successive flow rate changes, to complete the construction of the rest of higher flow rate region of the flow branch. It indicated that rapid changes of flow rates may generate new nonlinear features in this system, whereas very delayed changes of flow rates in an appropriate time frame may, however, help to eliminate altogether some of these additional nonlinear features, to make the proceedings of the experiment more simple, though sometimes very very time consuming. Figure 2 is the flow rate per unit reactor volume versus pump setting calibration, which provides semiquantitative information about the experiment reported in Figure 1. The experiment reported in Figure 1 could be reproduced more than 85% on repetition.

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(10) Under slow stirring ($S = 880$ rpm) in the nonpremixed mode, the concentration difference between the tip of the stirrer blade and the axis of the reactor should reach 380% instead of 800%, which was a mistake in our calculation in ref 9.