Nonlinear Dynamics Lab

April 25, 2016

Report due May 6, 2016

Tasks

You can choose between item 2 and item 3 from the list below. Your work should be written up as a very brief report. Note that Table 2 lists two different sets of reaction rate data from the literature. Choose the one which fits the experiments best and discuss possible discrepancies.

1. Choose one of the data series given in Table 3–4 below. Derive a table with the correct approximately constant values for the concentrations A, B, and H and for the initial values of the time dependent concentrations X, Y, and Z for each of the experiments.

2. Solve the system of differential equations (9) for each of the experiments and measure the period of oscillations. (This can be done manually from a time series plot as high accuracy is not required.) Compare to the the measured values.

3. *Alternative task:* Perform a relaxation oscillation analysis and determine an analytic approximation to the period of oscillation as explicitly as you can. Compare with the measured values.

Modeling the Belousov–Zhabotinskii reaction

The mathematical modeling of the Belousov–Zhabotinskii reaction was pioneered by Field, Körös and Noyes [2] who proposed what is now known as the FNK mechanism. We use the adaptation to the ferroin catalyzed variant of the reaction proposed by Rovinsky and Zhabotinskii [5] with simplification and in the notation of [1], which leads to the following system of rate equations:

$$\dot{X} = -k_1\, HXY + k_2\, H^2AY - 2\, k_3\, X^2 - k_4\, HAX + 2\, k_{-4}\, U^2 + k_5\, HU(C-Z)\,, \tag{1}$$

$$\dot{Y} = -k_2\, HXY - k_2\, H^2AY + q\, k_7\, B^* \tag{2}$$

$$\dot{Z} = -k_6\, BZ + k_{-6}\,(C-Z)\, HB^* + k_5\, HU\,(C-Z) \tag{3}$$

$$\dot{U} = 2\, k_4\, HAX - 2\, k_{-4}\, U^2 - k_5\, HU\,(C-Z) \tag{4}$$

$$\dot{B}^* = k_6\, BZ - k_{-6}\,(C-Z)\, HB^* - k_7\, B^* \tag{5}$$

Name of Compound	**Variable**	**Assumption**
Bromate	$A = [BrO_3{}^-]$	Adiabatic
Organic compounds	$B = [\mathrm{Org}]$	Adiabatic
Oxidized organic compounds	$B^* = [\mathrm{Ox1}]$	Quasi-static
Total iron	$C = [Fe^{2+}] + [Fe^{2+}]$	Constant
Hydrogen ions	$H = [H^+]$	Buffered
Bromine dioxide	$U = [BrO_2]$	Quasi-static
Bromous acid	$X = [HBrO_2]$	
Bromide	$Y = [Br^-]$	
Iron(III)	$Z = [Fe^{3+}]$	

Table 1: List of chemical compounds

The reaction constants k_6, k_{-6}, and k_7 are not individually known, but it is known that the B^*-equation is rapid, hence we may assume that it is in a quasi-steady state where

$$k_6\, BZ - k_{-6}\, (C - Z)\, HB^* = k_7\, B^* \tag{6}$$

and therefore

$$B^* = \frac{k_6\, BZ}{k_{-6}\, (C - Z)H + k_7} \approx \frac{k_6\, BZ}{k_{-6}\, (C - Z)H}\,. \tag{7}$$

Similarly, it is known that the U-equation is rapid and that the term $k_{-4}\, U^2$ is small compared to the others. Hence, neglecting this term and assuming quasi-stationarity gives

$$k_5\, HU\, (C - Z) = 2\, k_4\, HAX\,. \tag{8}$$

Altogether,

$$\dot{X} = -k_1\, HXY + k_2\, H^2 AY - 2\, k_3\, X^2 + k_4\, HAX \tag{9a}$$

$$\dot{Y} = -k_1\, HXY - k_2\, H^2 AY + q\, \frac{k_J\, B}{H}\, \frac{Z}{C - Z} \tag{9b}$$

$$\dot{Z} = -\frac{k_J\, B}{H}\, \frac{Z}{C - Z} + 2\, k_4\, HAX \tag{9c}$$

where

$$k_J = \frac{k_6\, k_7}{k_{-6}}\,. \tag{10}$$

Values for all the constants from the literature are listed in Table 2.

This system can be further simplified and analyzed as a relaxation oscillation; see, e.g., [3].

Constant	**RZ84** [5]	**MSR91** [4]
k_1	$k_5 = 10^7\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$	$k_5 = 10^7\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$
k_2	$k_7/H, k_7 = 15\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$	$k_7 = 2\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$
k_3	$k_4\,H, k_4 = 1.7 \times 10^4\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$	$k_4 = 2 \times 10^3\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
k_4	$k_1 = 100\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$	$k_1 = 40\,\mathrm{M}^{-2}\,\mathrm{s}^{-1}$
k_{-4}	$k_{-1}/2, k_{-1} = 1.2 \times 10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$k_{-1}/2, k_{-1} = 4 \times 10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
k_5	$k_3/H, k_3 = 1.2 \times 10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$k_3 = 10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
k_J	$K_8 = 2 \times 10^{-5}\,\mathrm{M}\,\mathrm{s}^{-1}$	$K_8 = 3 \times 10^{-6}\,\mathrm{M}\,\mathrm{s}^{-1}$
q	$q = 0.5$	$h = 1.3$

Table 2: Two sets of values for the various constants from Rovinsky and Zhabotinskii [5] and Mori, Schreiber, and Ross [4]. The left hand column refers to our naming of constants. The other columns refer to the names of the constants in the respective papers. Note that sometimes the inclusion of stochiometric factors and of $H = [\mathrm{H}^+]$ is handled differently in the different papers. The values are listed so that the expressions in each row can be identified. RZ84 quote values of H between 2 M and 2.5 M, but it is not clear which value was used when estimating the constants. RZ84 state that they re-estimated their constants $k_{\pm 1}$ to $k_{\pm 5}$ as older values in the literature do not apply to the Ferroin-catalyzed BZ reaction. The values in MSR91 are partially quoted from earlier literature and are therefore not necessarily more reliable than the RZ84 values. Finally, the units for the reaction constants in RZ84 are either wrong (first two table rows) or entirely missing (all the others), they are corrected in this table on the assumption that this was a simple editorial oversight.

Experimental results

To perform the experiment, four solutions are prepared:

Solution 1: 0.5 M sodium bromate with 0.5 M sulfuric acid

Solution 2: 1 M malonic acid

Solution 3: 1 M sodium bromide

Solution 4: 0.025 M ferroin solution

Table 3–5 show three measurement sequences where the period is reported as a response to changing the volume fraction of exactly one of the solutions.

When comparing with simulation data, the concentrations of each of the reactants in Solutions 1–4 must be weighted with the volume fraction of each solution in the final mixture. The concentration $H = [H^+]$ should be taken as the concentration of H_2SO_4, because within the range of concentrations used here, only on of the two hydrogen ion is dissociating from the compound, thus freely available.

References

[1] A. F. Taylor, V. Gaspar, B. R. Johnson, and S. K. Scott, *Analysis of reaction-diffusion waves in the ferroin-catalysed Belousov–Zhabotinsky reaction*, Phys. Chem. Chem. Phys., 1 (1999), pp. 4595–4599.

[2] R. J. Field, E. Körös, and R. M. Noyes, *Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system*, J. Am. Chem. Soc., 94 (1972), pp. 8649–8664.

[3] C. R. Gray, *An analysis of the Belousov–Zhabotinskii reaction*, Rose-Hulman Undergrad. Math J., 3 (2002), pp. 1–15.

[4] E. Mori, I. Schreiber, and J. Ross, *Profiles of chemical waves in the ferroin-catalyzed Belousov–Zhabotinskii reaction*, J. Phys. Chem., 95 (1991), pp. 9359–9366.

[5] A. Rovinsky and A. Zhabotinsky, *Mechanism and mathematical model of the oscillating bromate-ferroin-bromomalonic acid reaction*, J. Phys. Chem., 88 (1984), pp. 6081–6084.

Sol. 1	**Sol. 2**	**Sol. 3**	**Sol. 4**	**Water**	**Period** [s]
800				50	6.6
700				150	21.1
600	100	50	25	250	76.6
500				350	137.1
400				450	182.8

Table 3: Measurement sequence varying the concentration of bromate and sulfuric acid (Solution 1). In the actual lab experiments, the volumes are measured in μl.

Sol. 1	**Sol. 2**	**Sol. 3**	**Sol. 4**	**Water**	**Period** [s]
	150			0	12.9
	125			25	8.8
800	100	50	25	50	8.8
	75			75	6.6
	50			100	31

Table 4: Measurement sequence varying the concentration of malonic acid (Solution 2).

Sol. 1	**Sol. 2**	**Sol. 3**	**Sol. 4**	**Water**	**Period** [s]
		100		0	76.4
		80		20	38.5
800	100	60	25	40	7.9
		40		60	5.8
		20		80	19.8

Table 5: Measurement sequence varying the concentration of bromide (Solution 3).