Modelling and Mathematical Methods in Process and Chemical Engineering

Belousov-Zhabotinskii reaction

The Belousov-Zhabotinskii reaction is actually a system of many coupled reactions. In a simplified description, the following reactions are considered:

$$BrO_3^- + Br^- \xrightarrow{r_1} HBrO_2 + HBrO$$

$$HBrO_2 + Br^- \xrightarrow{r_2} 2HBrO$$

$$BrO_3^- + HBrO_2 \xrightarrow{r_3} 2HBrO_2 + 2Ce^{4+}$$

$$2HBrO_2 \xrightarrow{r_4} BrO_3^- + HBrO$$

$$CH_2(COOH)_2 + Ce^{4+} \xrightarrow{r_5} hBr^- + \text{products}$$

with the corresponding rates:

$$r_1 = k_1[H^+]^2[BrO_3^-][Br^-] = k_1 H^2 A Y \tag{1a}$$

$$r_2 = k_2[H^+][HBrO_2][Br^-] = k_2 H X Y \tag{1b}$$

$$r_3 = k_3[H^+][BrO_3^-][HBrO_2] = k_3 H A X \tag{1c}$$

$$r_4 = k_4[HBrO_2]^2 = k_4 X^2 \tag{1d}$$

$$r_5 = k_5[CH_2(COOH)_2][Ce^{4+}] = k_5 B Z \tag{1e}$$

where $A = [BrO_3^-]$, $B = [CH_2(COOH)_2]$, $H = [H^+]$, $X = [HBrO_2]$, $Y = [Br^-]$, $Z = [Ce^{4+}]$ and h is a stoichiometric coefficient which represents the ratio between the average number of Br^- ions produced and the number of Ce^{4+} ions consumed during the malonic oxidation step of the oscillation.

Based on this simplified kinetic scheme and using the law of mass action one obtains the following set of kinetic equations* in the unknowns X, Y, Z. This model is known as the Oregonator.

$$\begin{cases} \dfrac{dX}{dt} = k_1 H^2 A Y - k_2 H X Y + k_3 H A X - 2k_4 X^2 \\ \dfrac{dY}{dt} = -k_1 H^2 A Y - k_2 H X Y + h k_5 B Z \\ \dfrac{dZ}{dt} = 2k_3 H A X - k_5 B Z \end{cases} \tag{2}$$

*Mazzotti M., G. Serravalle, and M. Morbidelli, *Chem. Eng. Sci.* **49** (1994) 681–688

In order to simplify the analysis of this system, we want to make it dimensionless (this will reduce the number of parameters). We begin by introducing the dimensionless variables

$$x = X/X_0, \qquad y = Y/Y_0, \qquad z = Z/Z_0, \qquad \tau = t/t_0, \qquad a = A/A_0, \qquad b = B/B_0 \tag{3}$$

System (2) becomes

$$\begin{cases} \dfrac{dx}{dt} = \dfrac{k_1 H^2 A_0 Y_0 t_0}{X_0} ay - k_2 H Y_0 t_0 xy + k_3 H A_0 t_0 ax - 2k_4 X_0 t_0 x^2 \\ \dfrac{dy}{dt} = -k_1 H^2 A_0 t_0 ay - k_2 H X_0 t_0 xy + \dfrac{h k_5 B_0 Z_0 t_0}{Y_0} bz \\ \dfrac{dz}{dt} = \dfrac{2k_3 H A_0 X_0 t_0}{Z_0} ax - k_5 B_0 t_0 bz \end{cases} \tag{4}$$

Due to the third equation of system (4) we choose

$$t_0 = \frac{1}{k_5 B_0} \tag{5}$$

as reference time and system (4) becomes

$$\begin{cases} \dfrac{dx}{dt} = \dfrac{k_1 H^2 A_0 Y_0}{k_5 B_0 X_0} ay - \dfrac{k_2 H Y_0}{k_5 B_0} xy + \dfrac{k_3 H A_0}{k_5 B_0} ax - \dfrac{2k_4 X_0}{k_5 B_0} x^2 \\ \dfrac{dy}{dt} = -\dfrac{k_1 H^2 A_0}{k_5 B_0} ay - \dfrac{k_2 H X_0}{k_5 B_0} xy + \dfrac{h Z_0}{Y_0} bz \\ \dfrac{dz}{dt} = \dfrac{2k_3 H A_0 X_0}{k_5 B_0 Z_0} ax - bz \end{cases} \tag{6}$$

in order to eliminate the fraction that multiplies the third term of the first equation of (6), we multiply that equation by

$$\varepsilon = \frac{k_5 B_0}{k_3 H A_0} \tag{7}$$

which yields

$$\begin{cases} \varepsilon \dfrac{dx}{dt} = \dfrac{k_1 H Y_0}{k_3 X_0} ay - \dfrac{k_2 Y_0}{k_3 A_0} xy + ax - \dfrac{2k_4 X_0}{k_3 H A_0} x^2 \\ \dfrac{dy}{dt} = -\dfrac{k_1 H^2 A_0}{k_5 B_0} ay - \dfrac{k_2 H X_0}{k_5 B_0} xy + \dfrac{h Z_0}{Y_0} bz \\ \dfrac{dz}{dt} = \dfrac{2k_3 H A_0 X_0}{k_5 B_0 Z_0} ax - bz \end{cases} \tag{8}$$

the second term of the first equation of (8) implies that the reference concentration Y_0 should be chosen as

$$Y_0 = \frac{k_3 A_0}{k_2} \tag{9}$$

which gives

$$\begin{cases} \varepsilon\dfrac{dx}{dt} = \dfrac{k_1 H A_0}{k_2 X_0} ay - xy + ax - \dfrac{2k_4 X_0}{k_3 H A_0} x^2 \\ \dfrac{dy}{dt} = -\dfrac{k_1 H^2 A_0}{k_5 B_0} ay - \dfrac{k_2 H X_0}{k_5 B_0} xy + \dfrac{h k_2 Z_0}{k_3 A_0} bz \\ \dfrac{dz}{dt} = \dfrac{2k_3 H A_0 X_0}{k_5 B_0 Z_0} ax - bz \end{cases} \tag{10}$$

In the next step we eliminate the fraction that multiplies the last term of the first equation of (10) be defining

$$X_0 = \frac{k_3 H A_0}{2k_4} \tag{11}$$

and we end up with

$$\begin{cases} \varepsilon\dfrac{dx}{dt} = \dfrac{2k_1 k_4}{k_2 k_3} ay - xy + ax - x^2 \\ \dfrac{dy}{dt} = -\dfrac{k_1 H^2 A_0}{k_5 B_0} ay - \dfrac{k_2 k_3 H^2 A_0}{2k_4 k_5 B_0} xy + \dfrac{h k_2 Z_0}{k_3 A_0} bz \\ \dfrac{dz}{dt} = \dfrac{k_3^2 H^2 A_0^2}{k_4 k_5 B_0 Z_0} ax - bz \end{cases} \tag{12}$$

Finally we have to define a reference concentration Z_0 and the third equation of (12) implies the choice

$$Z_0 = \frac{(k_3 H A_0)^2}{k_4 k_5 B_0} \tag{13}$$

which yields

$$\begin{cases} \varepsilon\dfrac{dx}{dt} = \dfrac{2k_1 k_4}{k_2 k_3} ay - xy + ax - x^2 \\ \dfrac{dy}{dt} = -\dfrac{k_1 H^2 A_0}{k_5 B_0} ay - \dfrac{k_2 k_3 H^2 A_0}{2k_4 k_5 B_0} xy + \dfrac{h k_2 k_3 H^2 A_0}{k_4 k_5 B_0} bz \\ \dfrac{dz}{dt} = ax - bz \end{cases} \tag{14}$$

multiplying the second equation of (14) by

$$\delta = \frac{2k_4 k_5 B_0}{k_2 k_3 H^2 A_0} \tag{15}$$

gives

$$\begin{cases} \varepsilon\dfrac{dx}{dt} = \dfrac{2k_1 k_4}{k_2 k_3} ay - xy + ax - x^2 \\ \delta\dfrac{dy}{dt} = -\dfrac{2k_1 k_4}{k_2 k_3} ay - xy + 2hbz \\ \dfrac{dz}{dt} = ax - bz \end{cases} \tag{16}$$

and introducing

$$q = \frac{2k_1k_4}{k_2k_3}, \qquad f = 2h \tag{17}$$

we eventually obtain the dimensionless form of (2) given on the problem sheet, that reads:

$$\begin{cases} \varepsilon \dfrac{dx}{d\tau} = qay - xy + ax - x^2 \\ \delta \dfrac{dy}{d\tau} = -qay - xy + fbz \\ \dfrac{dz}{d\tau} = ax - bz \end{cases} \tag{18}$$

Note that the transformation into dimensionless form has reduced the number of parameters form six (k_j, h where $j = 1, 2, 3, 4, 5$) to four and typical values are

$$\varepsilon = 0.12, \qquad \delta = 0.0006, \qquad q = 0.0008, \qquad f = \mathcal{O}(1) \tag{19}$$