7. Well-Stirred Reactors IV

The Belousov-Zhabotinsky Reaction: Models and Experiments


\[
\begin{align*}
Q + W & \rightarrow U + P & (R1) \\
U + W & \rightarrow 2P & (R2) \\
Q + U & \rightarrow 2U + 2V & (R3) \\
2U & \rightarrow Q + P & (R4) \\
B + V & \rightarrow vW & (R5)
\end{align*}
\]
\[ Q = \text{BrO}_3^- \]
\[ B = \text{BrMA} \text{ (bromomalonic acid)} \]
\[ P = \text{HOBr} \]
\[ U = \text{HBrO}_2 \]
\[ V \text{ is the oxidized form of the catalyst, typically Ce}^{4+}, \text{ Fe}^{3+}, \text{ or Ru(bpy)}_3^{3+} \]
\[ W = \text{Br}^- \]
\[ \nu \text{ is an adjustable stoichiometric parameter} \]
B, Q, and P are pool chemicals

dimensionless rate equations – *three-variable Oregonator model*:

\[
\epsilon \frac{du}{dt} = qw - uw + u - u^2 \quad (1a)
\]
\[
\frac{dv}{dt} = u - \nu \quad (1b)
\]
\[
\epsilon' \frac{dw}{dt} = -qw - uw + hv \quad (1c)
\]
\[ h = 2\nu \]
\[ \epsilon' \ll \epsilon \ll 1, \quad q \ll 1, \quad h \approx 1 \]

\[ \Rightarrow w \text{ evolves on the fastest time scale; eliminate by} \]
quasi-steady state approximation

\[ \frac{dw}{dt} = 0 \]
\[ w = \frac{hv}{u + q} \]

two-variable Oregonator model:

\[ \frac{du}{dt} = \frac{1}{\epsilon} \left( u - u^2 - hv \frac{u - q}{u + q} \right) \quad (2a) \]
\[ \frac{dv}{dt} = u - v \quad (2b) \]

non-trivial steady state:

\[ \bar{u} = \frac{1 - h - q + \sqrt{1 - 2h + h^2 + 2q + 6hq + q^2}}{2} \]
\[ \bar{v} = \bar{u} \]
Jacobian

$$J = \begin{pmatrix}
\frac{1}{\epsilon} \left[ 1 - 2\bar{u} - \frac{2hq\bar{u}}{\bar{u} + q} \right] & -\frac{h\bar{u} - q}{\epsilon \bar{u} + q} \\
1 & -1
\end{pmatrix}$$

the two-variable Oregonator is a pure activator-inhibitor system; $U(H\text{BrO}_2) = \text{activator}$, $V$ (the oxidized form of the catalyst) = inhibitor

Hopf condition

$$T = \text{tr} J = 0$$

$$\epsilon_H = 1 - 2\bar{u} - \frac{2hq\bar{u}}{(\bar{u} + q)^2}$$

evaluate the Hopf condition for a specific value of $q$, $q = 8 \times 10^{-4}$
simulations $q = 8 \times 10^{-4}, \epsilon = 0.179064$: $h_{H;1} = 0.5930000024, h_{H;u} = 2.105686789$

$h = 0.58, (u(0), v(0)) = (1.2\bar{u}, 0.8\bar{v})$

relaxation oscillations

the low-$h$ Hopf bifurcation is subcritical
oscillations for $h = 2/3$

the high-$h$ Hopf bifurcation is supercritical, $h = 2.106$: 
$$(u(0), v(0)) = (1.2\bar{u}, 0.8\bar{v}) \rightarrow \text{steady state } (\bar{u}, \bar{v}) = (0.002240495, 0.002240495)$$

$h = 2.105$: 
$$(u(0), v(0)) = (1.2\bar{u}, 0.8\bar{v}) \rightarrow \text{small-amplitude limit cycle}$$

the two-variable Oregonator cannot display chaos; the three-variable Oregonator does not display chaos

\[
\begin{align*}
\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ & \xrightleftharpoons[k_1]{k_{-1}} \text{HBrO}_2 + \text{HOBr} \quad (R6) \\
\text{HBrO}_2 + \text{Br}^- + \text{H}^+ & \xrightleftharpoons[k_2]{k_{-2}} 2\text{HOBr} \quad (R7) \\
\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ & \xrightleftharpoons[k_3]{k_{-3}} 2\text{BrO}_2 \quad (R8) \\
\text{Ce}^{3+} + \text{BrO}_2 + \text{H}^+ & \xrightleftharpoons[k_4]{k_{-4}} \text{HBrO}_2 + \text{Ce}^{4+} \quad (R9) \\
2\text{HBrO}_2 & \xrightleftharpoons[k_5]{k_{-5}} \text{BrO}_3^- + \text{HOBr} + \text{H}^+ \quad (R10)
\end{align*}
\]
\[ \text{Ce}^{4+} \xrightarrow{k_6} \text{gBr}^- + \text{Ce}^{3+} \quad (R11) \]

\[ \text{A} + \text{Y} \xrightarrow{\kappa_1} \text{X} + \text{P} \quad (R12) \]

\[ \text{X} + \text{Y} \xrightarrow{\kappa_2} 2\text{P} \quad (R13) \]

\[ \text{A} + \text{X} \xrightarrow{\kappa_3} 2\text{W} \quad (R14) \]

\[ \text{C} + \text{W} \xrightarrow{\kappa_4} \text{X} + \text{Z} \quad (R15) \]

\[ 2\text{X} \xrightarrow{\kappa_5} \text{A} + \text{P} \quad (R16) \]

\[ \text{Z} \xrightarrow{\kappa_6} \text{gY} + \text{C} \quad (R17) \]

with

\[ \text{A} = \text{BrO}_3^- \]
\[ \text{P} = \text{HOBr} \]
\[ \text{W} = \text{BrO}_2 \]
\[ \text{X} = \text{HBrO}_2 \]
\[ Y = \text{Br}^- \]
\[ Z = \text{Ce}^{4+} \]
\[ C = \text{Ce}^{3+} \]
\[ \kappa_i = h_i ([\text{H}^+]) k_i \]
\[ h_1 = [\text{H}^+]^2 \]
\[ h_2 = h_3 = h_4 = h_{-5} = [\text{H}^+] \]
\[ h_{-1} = h_{-2} = h_{-3} = h_{-4} = h_5 = h_6 = 1 \]
\[ v_1 = \kappa_1 [A][Y] - \kappa_{-1} [X][P] \]
\[ v_2 = \kappa_2 [X][Y] - \kappa_{-2} [P]^2 \]
\[ v_3 = \kappa_3 [A][X] - \kappa_{-3} [W]^2 \]
\[ v_4 = \kappa_4 [C][W] - \kappa_{-4} [X][Z] \]
\[ v_5 = \kappa_5 [X]^2 - \kappa_{-5} [A][P] \]
\[ v_6 = \kappa_6 [Z] \]

rate equations for CSTR

\[
\frac{d[A]}{dt} = -v_1 - v_3 + v_5 + \alpha ([A]_0 - [A])
\]
\[ \frac{d[P]}{dt} = \nu_1 + 2\nu_2 + \nu_5 - \alpha[P] \]
\[ \frac{d[W]}{dt} = 2\nu_3 - \nu_4 - \alpha[W] \]
\[ \frac{d[X]}{dt} = \nu_1 - \nu_2 - \nu_3 + \nu_4 - 2\nu_5 - \alpha[X] \]
\[ \frac{d[Y]}{dt} = -\nu_1 - \nu_2 + g\nu_6 + \alpha([Y]_0 - [Y]) \]
\[ \frac{d[Z]}{dt} = \nu_4 - \nu_6 - \alpha[Z] \]
\[ \frac{d[C]}{dt} = -\nu_4 + \nu_6 + \alpha([C]_0 - [C]) \]

the model describes mixed-mode oscillations and chaotic behavior

Barkley et al, Figure 1, varying \([Y]_0\): steady state – Hopf bifurcation – limit cycle – secondary Hopf bifurcation – torus (quasiperiodic behavior); bistability between torus and stable steady state created by a saddle-node bifurcation; torus is destroyed by colliding with an unstable torus; unstable limit cycle undergoes a period-doubling bifurcation, before terminat-
ing in a saddle-loop bifurcation (homoclinic orbit) of
the unstable steady state of the middle branch of the
steady state curve

review of experimental and numerical evidence for
chaos in the BZ reaction: Argoul, F.; Arneodo, A.;
Richetti, P.; Roux, J. C. & Swinney, H. L.: “Chemical
chaos: from hints to confirmation,” Acc. Chem. Res., 20,

periodic–chaotic sequences are common in experi-
ments on the BZ reaction

a simple model of chaotic behavior in the BZ reac-
tion: Gyorgyi, L. & Field, R. J.: “A three-variable mod-
el of deterministic chaos in the Belousov–Zhabotinsky
doi.org/10.1038/355808a0

read Chapter 8 in: Epstein, I. R. & Pojman, J. A., An
Introduction to Nonlinear Chemical Dynamics (Oxford
University Press, 1998)
The Chlorite–Iodide–Malonic Acid Reaction: Models and Experiments

chlorite–iodide–malonic acid (CIMA) reaction belongs to the group of systematically designed chemical oscillating reactions pioneered by the Brandeis group among the very few reactions that can display transient oscillations in batch reactors.

major variant of the CIMA reaction is the simpler chlorine dioxide–iodine–malonic acid (CDIMA) reaction: after an initial induction period, where the chlorite, $\text{ClO}_2^-$, and iodide, $\text{I}^-$, are rapidly consumed to produce chlorine dioxide, $\text{ClO}_2$, and iodine, $\text{I}_2$, the dynamics of the CIMA reaction is given by that of the CDIMA reaction.


\[
\begin{align*}
\text{MA} + \text{I}_2 & \rightarrow \text{IMA} + \text{I}^- + \text{H}^+, \quad (R18) \\
\text{ClO}_2^- + \text{I}^- & \rightarrow \text{ClO}_2^- + \frac{1}{2}\text{I}_2, \quad (R19) \\
\text{ClO}_2^- + 4\text{I}^- + 4\text{H}^+ & \rightarrow \text{Cl}^- + 2\text{I}_2 + 2\text{H}_2\text{O}, \quad (R20) \\
\text{S} + \text{I}_2 + \text{I}^- & \rightarrow \text{SI}_3^-, \quad (R21)
\end{align*}
\]

reaction velocities:

\[
\begin{align*}
v_{18} &= \frac{k_{1a}[\text{MA}][\text{I}_2]}{k_{1b} + [\text{I}_2]}, \\
v_{19} &= k_2[\text{ClO}_2^-][\text{I}^-], \\
v_{20} &= k_{3a}[\text{ClO}_2^-][\text{I}^-][\text{H}^+] + \frac{k_{3b}[\text{ClO}_2^-][\text{I}_2][\text{I}^-]}{\alpha + [\text{I}^-]^2}, \\
v_{21} &= k_4[\text{S}][\text{I}_2][\text{I}^-] - k_4[\text{SI}_3^-].
\end{align*}
\]

\[
\begin{align*}
\text{MA} &= \text{malonic acid, CH}_2(\text{COOH})_2 \\
\text{IMA} &= \text{iodomalonic acid, CHI(COOH)}_2 \\
\text{S} &= \text{starch or another substrate that binds triiodide ion I}_3^- \text{ [starch forms a deep blue complex with I}_3^-;}
\end{align*}
\]
this color corresponds to the reduced state of the system; the oxidized state has a yellow color

\( \alpha \) empirical parameter

independent variables: \([\text{MA}], [\text{I}_2], [\text{ClO}_2], [\text{I}^-], [\text{ClO}_2^-], [\text{S}], \text{and } [\text{SI}_3^-] \)

concentration of \( \text{H}^+ \) considered to be constant, \( \text{Cl}^- \) and IMA are inert products

rate equations of the LER model for the CDIMA reaction in a well-stirred reactor without external feeds:

\[
\begin{align*}
\frac{d[\text{MA}]}{dt} &= -v_{18} \\
\frac{d[\text{I}_2]}{dt} &= -v_{18} + \frac{1}{2}v_{19} + 2v_{20} - v_{21} \\
\frac{d[\text{ClO}_2]}{dt} &= -v_{19} \\
\frac{d[\text{I}^-]}{dt} &= v_{18} - v_{19} - 4v_{20} - v_{21} \\
\frac{d[\text{ClO}_2^-]}{dt} &= v_{19} - v_{20} \\
\frac{d[\text{S}]}{dt} &= -v_{21}
\end{align*}
\]
\[
\frac{d[SI_3^-]}{dt} = v_{21}
\]

experiments \( \implies \) \([I^-]\) and \([\text{ClO}_2^-]\) undergo much larger changes than the concentrations of the input species MA, \(\text{ClO}_2\), and \(\text{I}_2\)


**Lengyel-Epstein (LE) model**

\[
\begin{align*}
A & \rightarrow U \\
U & \rightarrow V \\
4U + V & \rightarrow D \\
S + U & \rightleftarrows W
\end{align*}
\]

(R22) (R23) (R24) (R25)
where $U = I^-$, $V = \text{ClO}_2^-$, and $W = \text{SI}_3^-$

rate equations

\[
\frac{du'}{dt'} = k'_1 - k'_2 u' - 4k'_3 \frac{u'v'}{\alpha + u'^2} - k'_4 u' + k_{-4} w'
\]

\[
\frac{dv'}{dt'} = k'_2 u' - k'_3 \frac{u'v'}{\alpha + u'^2}
\]

\[
\frac{dw'}{dt} = k'_4 u' - k_{-4} w'
\]

$k'_1 = k_{1a} [\text{MA}]$

$k'_2 = k_2 [\text{ClO}_2]$

$k'_3 = k_{3b} [\text{I}_2]$

$k'_4 = k_4 [\text{S}][\text{I}_2]$

substrate is present in large excess, $[\text{S}]$ can be considered constant

add the first and last rate equation

\[
\frac{d(u' + w')}{dt'} = k'_1 - k'_2 u' - 4k'_3 \frac{u'v'}{\alpha + u'^2}
\]
fast equilibrium assumption for $W$

$$w' = \frac{k'_4}{k_{-4}} u'$$

$$\Rightarrow$$

$$\frac{d}{dt'} \left( u' + \frac{k'_4}{k_{-4}} u' \right) = k'_1 - k'_2 u' - 4k'_3 \frac{u' v'}{\alpha + u'^2}$$

$$\sigma \frac{d u'}{d t'} = k'_1 - k'_2 u' - 4k'_3 \frac{u' v'}{\alpha + u'^2}$$

$$\sigma = 1 + \frac{k'_4}{k_{-4}} = 1 + \frac{k'_4}{k_{-4}} [S][I_2] = 1 + K [S][I_2]$$

experimental range: $1 \leq \sigma < 1000$; no complexing agent: $\sigma = 1$

nondimensionalize the rate equations

$$u' = \sqrt{\alpha} u$$

$$v' = \frac{k'_2 \alpha}{k'_3} v$$
\[ t' = \frac{t}{k'_2} \]

\[ \sigma \frac{du}{dt} = f_u(u, v) = a - u - 4\frac{uv}{1 + u^2} \]

\[ \frac{dv}{dt} = f_v(u, v) = b\left(u - \frac{uv}{1 + u^2}\right) \]

\[ a = \frac{k'_1}{k'_2 \sqrt{\alpha}} \]

\[ b = \frac{k'_3}{k'_2 \sqrt{\alpha}} \]

\[ a \propto \frac{[\text{CH}_2\text{COOH}_2]}{[\text{ClO}_2]} \]

\[ b \propto \frac{[\text{I}_2]}{[\text{ClO}_2]} \]

steady states

\[ a - \bar{u} - 4\frac{\bar{u}\bar{v}}{1 + \bar{u}^2} = 0 \]

\[ \bar{u} - \frac{\bar{u}\bar{v}}{1 + \bar{u}^2} = 0 \]

\[ \frac{\bar{u}\bar{v}}{1 + \bar{u}^2} = \bar{u} \]
\[ a - \bar{u} - 4\bar{u} = 0 \]
\[ \bar{u} = \frac{a}{5} \]
\[ \bar{u}\left(1 - \frac{\bar{v}}{1 + \bar{u}^2}\right) = 0 \]
\[ \bar{v} = 1 + \bar{u}^2 = 1 + \frac{a^2}{25} \]

unique steady state!

stability

\[ J = \begin{pmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{pmatrix} = \begin{pmatrix} A_{11}/\sigma & A_{12}/\sigma \\ A_{21} & A_{22} \end{pmatrix} \]

\[ A_{11} = \left. \frac{\partial f_u}{\partial u} \right|_{(\bar{u}, \bar{v})} = \frac{3a^2 - 125}{25 + a^2} \]
\[ A_{12} = \left. \frac{\partial f_u}{\partial v} \right|_{(\bar{u}, \bar{v})} = -\frac{20a}{25 + a^2} \]
\[ A_{21} = \left. \frac{\partial f_v}{\partial u} \right|_{(\bar{u}, \bar{v})} = b \frac{2a^2}{25 + a^2} \]
\[ A_{22} = \frac{\partial f_v}{\partial v} \bigg|_{(\bar{u}, \bar{v})} = -b \frac{5a}{25 + a^2} \]

\[ \det J = \Delta = \frac{25ba}{\sigma(25 + a^2)} > 0 \]

\[ \Rightarrow (\bar{u}, \bar{v}) \text{ cannot undergo a stationary bifurcation} \]

Hopf condition

\[ T = \text{tr} J = \frac{1}{\sigma} \frac{3a^2 - 125}{25 + a^2} - b \frac{5a}{25 + a^2} = 0 \]

\[ 3a^2 - 125 - 5b\sigma a = 0 \]

\[ b_H = \frac{3a^2 - 125}{5a\sigma} \]

for

\[ a > a^\circ \equiv \sqrt{125/3} \]

the steady is stable, \( T < 0 \), for \( b > b_H \), and unstable, \( T > 0 \), for \( b < b_H \); the LE model has a limit cycle for \( b < b_H \)
The LE system is a pure activator-inhibitor system; iodide ion, $U$, is the activator, $A_{11} > 0$, and chlorite ion, $V$, is the inhibitor, $A_{22} < 0$, and $A_{12} < 0$ and $A_{21} > 0$ consider $a = 50.0$ and $\sigma = 1.0$; then $b_H = 29.5$

$$(\bar{u}, \bar{v}) = (10.0, 101.0)$$

the Hopf bifurcation is subcritical

$$b = b_H = 29.5, (u(0), v(0)) = (1.1 \bar{u}, 0.9 \bar{v})$$

oscillations with finite amplitude