A Chemical Oscillator: Briggs-Rauscher Reaction

This is a summary of a mathematical model for the *Briggs-Rauscher Reaction*. For more details, consult [1]. You can also take a look at the following video: https://www.youtube.com/watch?v=IggngxY3riU

Here are the reactions

$$2\,H^+ + I^- + IO_3{}^- \xrightarrow{k_1} HOI + HIO_2$$
$$H^+ + HIO_2 + I^- \xrightarrow{k_2} 2\,HOI$$
$$HOI + I^- + H^+ \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} I_2 + H_2O$$
$$HIO_2 + IO_3{}^- + H^+ \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} 2\,IO_2 + H_2O$$
$$2\,HIO_2 \xrightarrow{k_5} HOI + IO_3{}^- + H^+$$
$$IO_2 + Mn^{2+} + H_2O \xrightarrow{k_6} HIO_2 + MnOH^{2+}$$
$$H_2O_2 + MnOH^{2+} \xrightarrow{k_7} HO_2 + Mn^{2+} + H_2O$$
$$2\,HO_2 \xrightarrow{k_8} H_2O_2 + O_2$$
$$I_2 + MA \xrightarrow{k_9} IMA + I^- + H^+$$
$$HOI + H_2O_2 \xrightarrow{k_{10}} I^- + O_2 + H^+ + H_2O$$

where MA and IMA are malonic and iodomalonic acids, respectively. The color of the mixed solutions oscillates between gold, dark blue and transparent. The gold color is a result of high concentration in I_2, whereas the dark blue color is a result of the presence of both I_2 and I^-.

Let x_i for $i = 1, 2, \cdots, 10$ denote the concentrations of the various species, as illustrate in the following table.

Concentration Symbol	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}
Species	$IO_3{}^-$	I^-	I_2	HIO_2	HOI	IO_2	$MnOH^{2+}$	HO_2	MA	H_2O_2

The differential equations can thus be written as

$$\begin{aligned}
\dot{x}_1 &= -k_1h^2x_2x_1 - k_4hx_1x_4 + k_4'x_6^2 + k_5x_4^2 + k_0(X_{10} - x_1)\\
\dot{x}_2 &= -k_1h^2x_2x_1 - k_2hx_4x_2 - k_3hx_5x_2 + k_3'x_3 + k_9x_9x_3/(1 + C_9x_3) + k_{10}x_{10}x_5 + k_0(X_{20} - x_2)\\
\dot{x}_3 &= k_3hx_5x_2 - k_3'x_3 - k_9x_9x_3/(1 + C_9x_3) + k_0(X_{30} - x_3)\\
\dot{x}_4 &= k_1h^2x_2x_1 - k_2hx_4x_2 - k_4hx_1x_4 + k_4'x_6^2 - 2k_5x_4^2 + k_6x_6(A - x_7) + k_0(X_{40} - x_4)\\
\dot{x}_5 &= k_1h^2x_2x_1 + 2k_2hx_4x_2 - k_3hx_5x_2 + k_3'x_3 + k_5x_4^2 - k_{10}x_{10}x_5 + k_0(X_{50} - x_5)\\
\dot{x}_6 &= 2k_4hx_1x_4 - 2k_4'x_6^2 - k_6x_6(A - x_7) + k_0(X_{60} - x_6)\\
\dot{x}_7 &= k_6x_6(A - x_7) - k_7x_7x_{10} + k_0(X_{70} - x_7)\\
\dot{x}_8 &= k_7x_7x_{10} - 2k_8x_8^2 + k_0(X_{80} - x_8)\\
\dot{x}_9 &= -k_9x_9x_3/(1 + C_9x_3) + k_0(X_{90} - x_9)\\
\dot{x}_{10} &= -k_7x_7x_10 + k_8x_8^2 - k_{10}x_{10}x_5 + k_0(X_{100} - x_{10})
\end{aligned}$$

where C_9 is a constant that emerges from a particular quasi-steady state approximation (see [1, **Reaction 9**]). Furthermore, the rate equations derived from the chemical equations were augmented by flow terms $k_0X_{i0} - k_0x_i$ for each species ($i = 1, 2, \cdots, 10$), where k_0 is the flow rate (reciprocal of the residence time) and the input concentration X_{i0} is the concentration that the corresponding species would have if all the chemicals were combined in a single input flow without reaction. Finally, the following concentrations are assumed to be constants:

$$[H^+] = h; \qquad [Mn^{2+}] + [MnOH^{2+}] = A.$$

Here are the numerical values of the various parameters and the Matlab code.

Parameter	h	A	k_1	k_2	k_3	k_4	k_5	k_6	k_7
Value	0.056	0.004	1.43×10^3	2×10^{10}	3.1×10^{12}	7.3×10^3	6×10^5	10^4	3.2×10^4
Parameter	k_8	k_9	k_{10}	k'_3	k'_4	k_0	X_{10}	X_{20}	X_{30}
Value	7.5×10^5	40	37	2.2	1.7×10^7	1/156	0.035	0	10^{-6}
Parameter	X_{40}	X_{50}	X_{60}	X_{70}	X_{80}	X_{90}	X_{100}		
Value	0	0	0	0	0	0.0015	0.33		

```matlab
%% Clear Workspace
close all;
clc;
clear;
set(groot,'defaulttextinterpreter','latex');
set(groot, 'defaultAxesTickLabelInterpreter','latex');
set(groot, 'defaultLegendInterpreter','latex');

%% Simulation Parameters
tf = 4000;

%% Initial Conditions
IC = [1e-2, 1e-8, 6e-7, 1e-10, 1e-10, 1e-10, 1e-13, 0, 1e-3, 0]';
% IC = [1e-2, 1e-9, 6e-4, 1e-6, 1e-6, 1e-7, 1e-9, 0, 1e-3, 0]';

%% Solving
Options = odeset('AbsTol', 1e-12, 'RelTol', 1e-12);
[t, x] = ode15s(@(t,x) BR_RHS(t, x), [0, tf], IC, Options);

%% Plotting
figure();
plot(t, log10(x), 'LineWidth', 2);
grid on;
axis([0 2000 -14 0]);
legend('$x_1$', '$x_2$', '$x_3$', '$x_4$', '$x_5$', '$x_6$', '$x_7$', '$x_8$', '$x_9$', '$x_{10}$');
xlabel('Time'); ylabel('$\log_{10}$(Concentration)');
set(gca, 'FontSize', 30);
figure();
subplot 121
plot(t, log10(x(:,2)), 'LineWidth', 2); hold on
plot(t, log10(x(:,3)), 'LineWidth', 2);
grid on;
axis([0 2000 -14 0]);
legend('[I$^-$]', '[I$_2$]');
xlabel('Time'); ylabel('$\log_{10}$(Concentration)');
set(gca, 'FontSize', 30);
subplot 122
plot(log10(x(:,2)), log10(x(:,3)), 'LineWidth', 2, 'Color', 'black'); hold on
grid on;
xlabel('$\log$[I$^-$]'); ylabel('$\log$[I$_2$]');
set(gca, 'FontSize', 30);
```

```
function dx = BR_RHS(t, x)
    %% Parameters
    %     X10 = 0.04; X30 = 2.5e-6; % Bistability
    X10 = 0.035; X20 = 0; X30 = 1e-6; X40 = 0;
    X50 = 0; X60 = 0; X70 = 0; X80 = 0; X90 = 0.0015; X100 = 0.33;
    h = 0.056; A = 0.004;
    k1 = 1.43e3; k2 = 2e10;
    k3 = 3.1e12; K3 = 2.2;
    k4 = 7.3e3; K4 = 1.7e7;
    k5 = 6e5; k6 = 1e4; k7 = 3.2e4; k8 = 7.5e5; k9 = 40;
    C9 = 1e4; k0 = 1 / 156; k10 = 37;
    %% Computing
    x1 = x(1); x2 = x(2); x3 = x(3); x4 = x(4); x5 = x(5);
    x6 = x(6); x7 = x(7); x8 = x(8); x9 = x(9); x10 = x(10);
    dx1 = -k1*h^2*x2*x1 - k4*h*x1*x4 + K4*x6^2 + k5*x4^2 + k0*(X10 - x1);
 dx2 = -k1*h^2*x2*x1 - k2*h*x4*x2 - k3*h*x5*x2 + K3*x3 + k9*x9*x3/(1 + C9*x3) + k10*x10*x5 + k0*(X20 - x2);
    dx3 = k3*h*x5*x2 - K3*x3 - k9*x9*x3/(1 + C9*x3) + k0*(X30 - x3);
    dx4 = k1*h^2*x2*x1 - k2*h*x4*x2 - k4*h*x1*x4 + K4*x6^2 - 2*k5*x4^2 + k6*x6*(A - x7) + k0*(X40 - x4);
 dx5 = k1*h^2*x2*x1 + 2*k2*h*x4*x2 - k3*h*x5*x2 + K3*x3 + k5*x4^2 - k10*x10*x5 + k0*(X50 - x5);
    dx6 = 2*k4*h*x1*x4 - 2*K4*x6^2 - k6*x6*(A - x7) + k0*(X60 - x6);
    dx7 = k6*x6*(A - x7) - k7*x7*x10 + k0*(X70 - x7);
    dx8 = k7*x7*x10 - 2*k8*x8^2 + k0*(X80 - x8);
    dx9 = -k9*x9*x3/(1 + C9*x3) + k0*(X90 - x9);
    dx10 = -k7*x7*x10 + k8*x8^2 - k10*x10*x5 + k0*(X100 - x10);
    dx = [dx1; dx2; dx3; dx4; dx5; dx6; dx7; dx8; dx9; dx10];
end
```

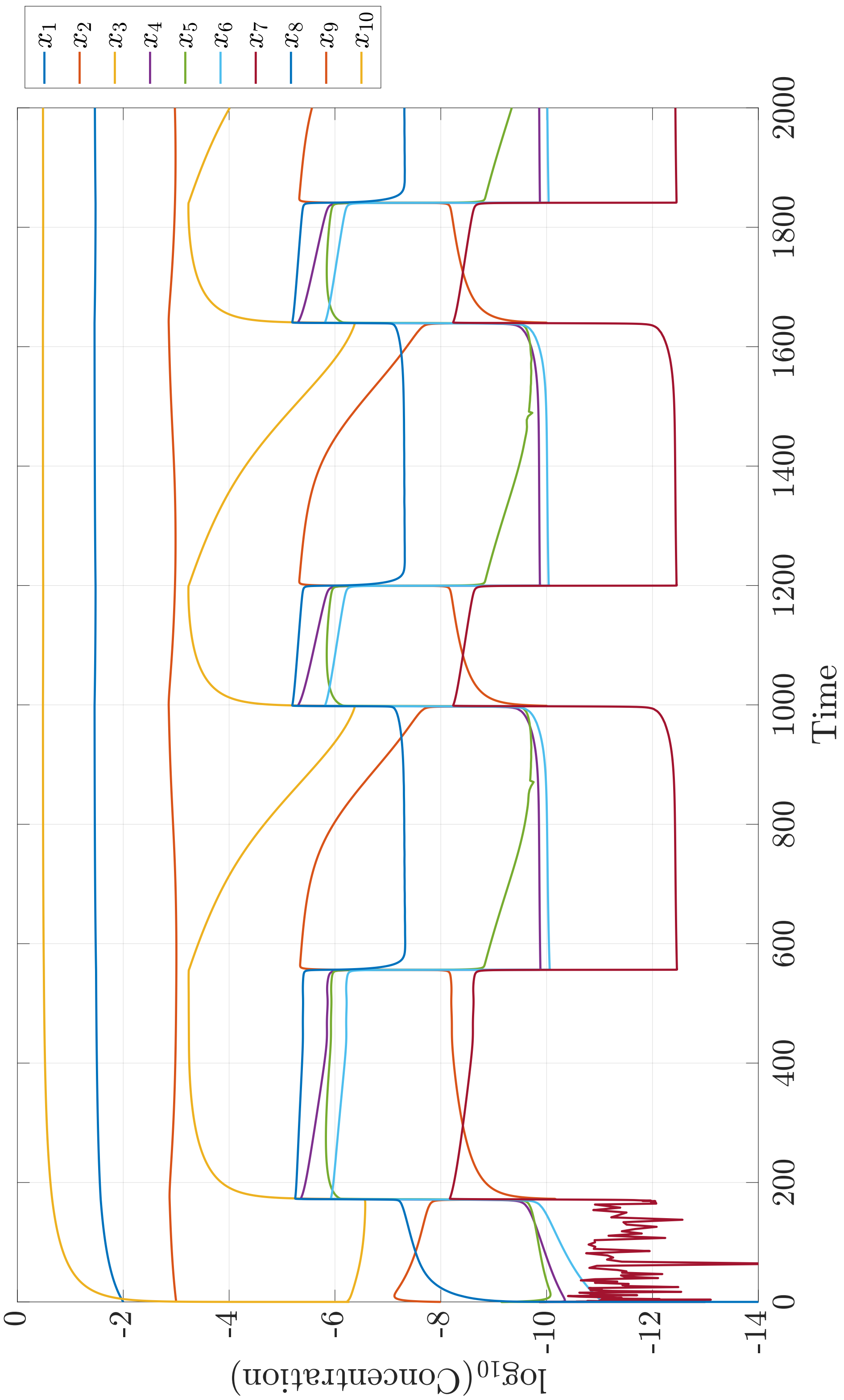
The following code gives you an animation in the relevant phase space.

```
 %% Clear Workspace
close all;
clear;
clc;
set(groot,'defaulttextinterpreter','latex');
set(groot, 'defaultAxesTickLabelInterpreter','latex');
set(groot, 'defaultLegendInterpreter','latex');

%% Simulation Parameters
tf = 4000;
dt = 0.1;
t = 0 : dt : tf;

%% Initial Conditions
IC = [1e-2, 1e-8, 6e-7, 1e-10, 1e-10, 1e-10, 1e-13, 0, 1e-3, 0]';
% IC = [1e-2, 1e-9, 6e-4, 1e-6, 1e-6, 1e-7, 1e-9, 0, 1e-3, 0]';

%% Solving
Options = odeset('AbsTol', 1e-12, 'RelTol', 1e-12);
[¬, x] = ode15s(@(t,x) BR_RHS(t, x), t, IC, Options);
I2 = x(:,3);
I_ = x(:,2);

%% Animation
N_D = 60;
x_Down = downsample(log10(I_), N_D); y_Down = downsample(log10(I2), N_D);
t_Down = downsample(t, N_D);
figure();
```

```
axes1_h = subplot(1,2,1);
% Axis Properties
    hold(axes1_h, 'on');
    axes1_h.XLim = [0, tf];
    axes1_h.YLim = [-11, -2];
    axes1_h.FontSize = 24;
    grid(axes1_h, 'on');
        % Axis Title Properties
        axes1_h.Title.String = 'Trajectories in Time';
        axes1_h.Title.FontSize = 30;
        % Axis Labels Properties
        axes1_h.XLabel.String = '$t$';
        axes1_h.YLabel.String = '$\log$(Concentration)';
axes2_h = subplot(1,2,2);
% Axis Properties
    hold(axes2_h, 'on');
    axes2_h.XLim = [-11, -5];
    axes2_h.YLim = [-7, -3];
    axes2_h.FontSize = 24;
    grid(axes2_h, 'on');
        % Axis Title Properties
        axes2_h.Title.String = 'Trajectories in Phase Plane';
        axes2_h.Title.FontSize = 30;
        % Axis Labels Properties
        axes2_h.XLabel.String = '$\log$[I$^-$]';
        axes2_h.YLabel.String = '$\log$[I$_2$]';
% Initialize Figure
plot(axes1_h, t_Down(1), x_Down(1), 'b', 'LineWidth', 2);
plot(axes1_h, t_Down(1), y_Down(1), 'r', 'LineWidth', 2);
legend(axes1_h, '$\log$[I$^-$]', '$\log$[I$_2$]', 'AutoUpdate','off');
Box_h1 = fill([-8, -11, -11, -8], [-5, -5, -3, -3], [0.9290, 0.6940, 0.1250]);
Box_h2 = fill([-8, -8, -5, -5], [-5, -3, -3, -5], 'blue');
Box_h1.FaceAlpha = 0.5; Box_h2.FaceAlpha = 0.5;
scatter_h = plot(axes2_h, x_Down(1), y_Down(1), 'ko', 'MarkerFaceColor', 'm', 'MarkerSize', 20);
plot(axes2_h, log10(I_), log10(I2), 'k', 'LineWidth', 2);
pause();
% Animate
for i = 2 : length(t_Down)
    plot(axes1_h, [t_Down(i-1) t_Down(i)], [x_Down(i-1) x_Down(i)], 'b', 'LineWidth', 2);
    plot(axes1_h, [t_Down(i-1) t_Down(i)], [y_Down(i-1) y_Down(i)], 'r', 'LineWidth', 2);
    scatter_h.XData = x_Down(i); scatter_h.YData = y_Down(i);
    drawnow();
end
```

References

[1] Patrick De Kepper and Irving R Epstein. Mechanistic study of oscillations and bistability in the briggs-rauscher reaction. *Journal of the American Chemical Society*, 104(1):49–55, 1982.


log10(Concentration)
Time
0
-2
-4
-6
-8
-10
-12
-14
0
200
400
600
800
1000
1200
1400
1600
1800
2000
x_1
x_2
x_3
x_4
x_5
x_6
x_7
x_8
x_9
x_{10}