

OSCILLATING CHEMICAL REACTION

PHYS3301 Scientific Computing

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On

BELOUSOV-ZHABOTINSKY REACTION



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ABSTRACT

This project primarily aims to investigate the Belousov-Zhabotinsky reaction and how this reaction oscillates to produce spiral patterns. Furthermore, aims to use the Oregonator, which consists of three coupled differential equations to simulate the oscillation found in this reaction. (*Belmonte, Quyang and Flesselles, 1997*) Deciding which program will be best suited was the first method that was taken in order to achieve the described aims. Firstly, **C++** was used since it is a familiar language but it was soon realized that it would be difficult to code the numerical derivation for the necessary equations. Secondly, **Mathematica** was used to solve these equations via the *NDSolve* function. However, due to lack of experiences in the use of **Mathematica** we were unable to get a suitable solution. This is turn led to the use of **Matlab** was used because of its extensive graphing functions and ease of coding. In addition, Paul demonstrated a bit of experience in the use of **Matlab** to be able to meet the above-mentioned aims of this project.

INTRODUCTION

Certain chemical reactions are able to oscillate in time and in space. The oscillating chemical reaction exists throughout nature. For example, the rhythm of the cicada influenced by nature of chemical oscillators. This is evident in the rate of chirping as it increases or decreases when the temperature rises or falls. These reactions are also responsible for the sleep cycle, breathing and the heartbeat. (*A. Winfree, 1980*) This project will investigate the most famous oscillating chemical reaction Belousov-Zhabotinsky reaction. This chemical reaction, which was discovered in 1951, oscillates with a clock-like precision as it approaches equilibrium. From the rates of the reaction, the non-linear differential equations can be concluded, hence a numerical analysis can be derived from the reaction, which is the major aim of this project.

HISTORY OF B-Z REACTION

The Belousov-Zhabotinsky reaction is defined to be a chemically active medium, which maintains self-oscillations and propagating waves. (*S. Scott, 1991*) In easier terms, it is basically a chemical reaction that is unstable and oscillates with clock-like

precision, which displays chaos under certain conditions. Boris Belousov founded it in 1951, which had been accidentally discovered whilst Belousov had been attempting to model the Krebs's cycle. Belousov wrote a paper with his findings but his paper was rejected. His theory seemed impossible because he discovered a reaction, which could not make up its mind and that refused to settle down to a stable state. This reaction conflicts with the Second Law of Thermodynamics, which states that mass is conserved and cannot be created or destroyed. However, during the sixties and seventies, Anatol Zhabotinsky researched Belousov's reaction in greater detail and was able to prove that this reaction was true.

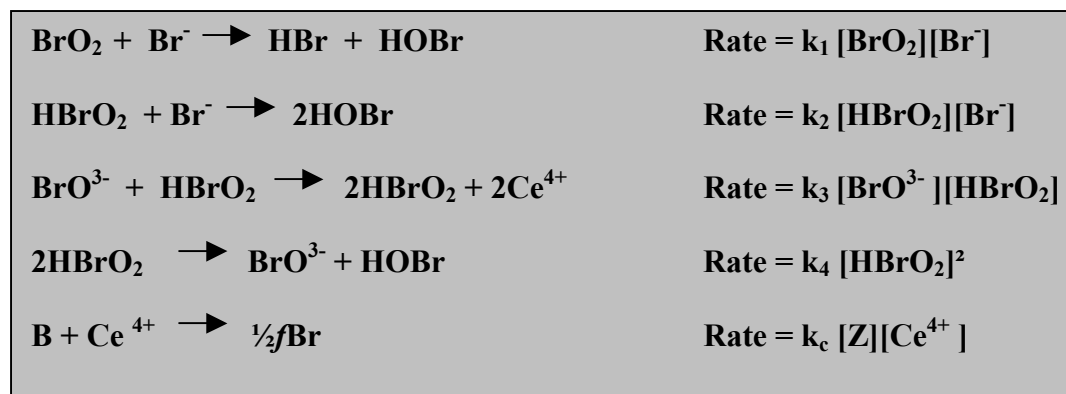


Belousov's basic reaction was investigated by Field, Kovos and Noyes (1972) and then simplified in 1974. Their investigation resulted in the FKN model, which is a model that demonstrates the underlying mechanism of the Belousov-Zhabotinsky reaction. Using this model, kinetic equations can be derived. A simplified version is given by three coupled differential equations, which is known by the *Oregonator*. (Belmonte, Quyang and Flesselles, 1997)

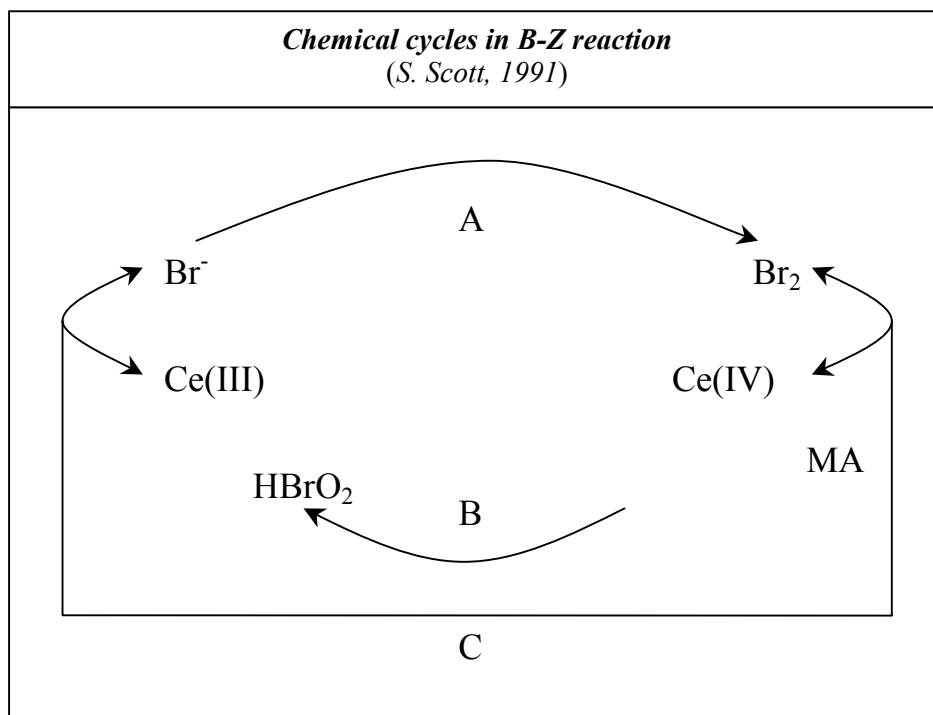
THE BELOUSOV-ZHABOTINSKY REACTION

The original Belousov reaction is made up of the oxidation of malonic acid by bromate ions (Potassium Bromate) in a medium of sulphuric acid. This reaction requires a catalyst (which is a substance that speeds up the rate of the reaction) so Cerium was used. The oxidized cerium ion Ce^{4+} is pale yellow in color and the reduced state Ce^{3+} is clear. The oscillations within this reaction can be clearly observed for it results a rapid change from yellow to clear and back to the yellow.

The reactions of Belousov's original reaction are as follows, which are stated by Peterson (1998).



The rates of this reaction are worked out from the reaction and it is usually dependent on the concentration of the reacting molecules or sometimes on the concentration of the molecules that are formed from this reaction.



To create a system of differential equations the following symbols are used to represent the following:

X	HBrO₂
Y	Br⁻
Z	Ce⁴⁺ (the catalyst)
A	BrO³⁻
B	All oxidizable organic species

A and B are concentrations so therefore they are treated constant. Therefore, the rate equations for x , y and z are

—
$\frac{dZ}{dt} = 2k_3AX - k_cBZ$

The B represents all oxidizable organic species present and f is the stoichiometric factor, which is a factor relating quantitatively between the reactants and the products. The stoichiometric factor requires a partial knowledge of the chemistry that is involved.

There are three main processes, which are based on the FKN model. They are bromide consumption (A), the autocatalytic stage (B), and regeneration stage (C). The Bromide transforms into different oxidized forms, which is process A. The role of this process is to remove the Br^- . This ion is the *inhibitor* for process B, the autocatalytic stage. Process B only starts when the bromide ion reaches a lower critical value, whilst the HBrO_2 (*activator*). The oxidation of the catalyst transforms Ce^{3+} into Ce^{4+} . (*Belmonte, Quyang and Flesselles, 1997*)

From the previous differential equations and the FKN model, a set of coupled differential equations can be formulated for the three processes of the three intermediate products. The variables are converted to dimensionless variables from the previous differential equations above, hence, the formulation of the following equations known as the **Oregonator**:

$$\frac{dx}{dt} = x - x^2 - y(x - q)$$

$$\frac{dy}{dt} = qy - xy + fz$$

$$\frac{dz}{dt} = x - z$$

The concentration variables, the time τ and the parameters ε_1 , ε_2 , and q are all normalized by average chemical concentrations and rate constants. The f has been explained above.

The constant rates values for the Oregonator from Tyson's "Lo" (*Belmonte, Quyang and Flesselles, 1997*) are:

$$\begin{aligned} k_1 &= 1 \text{ M}^{-1} \text{ s}^{-1} \\ k_2 &= 10^6 \text{ M}^{-2} \text{ s}^{-1} \\ k_3 &= 2 \text{ M}^{-3} \text{ s}^{-1} \\ k_4 &= 2 \times 10^3 \text{ M}^{-3} \text{ s}^{-1} \\ k_5 &= 10 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

These parameters are: $\varepsilon_1 \sim 4 \times 10^{-2}$, $\varepsilon_2 \sim 2 \times 10^{-4}$ and $q \sim 8 \times 10^{-4}$. Since time scales are well separated and the y variable can be considered at its equilibrium value, then the equations become the two-variable Oregonator:

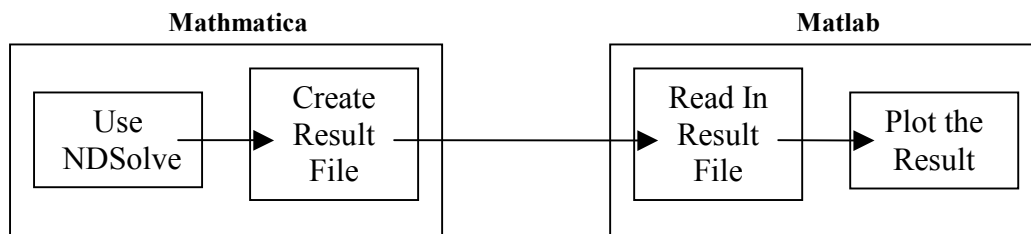
$$\varepsilon \frac{dx}{dt} = x - x^2 - fz \frac{x - q}{x + q}$$

$$\frac{dz}{dt} = x - z$$

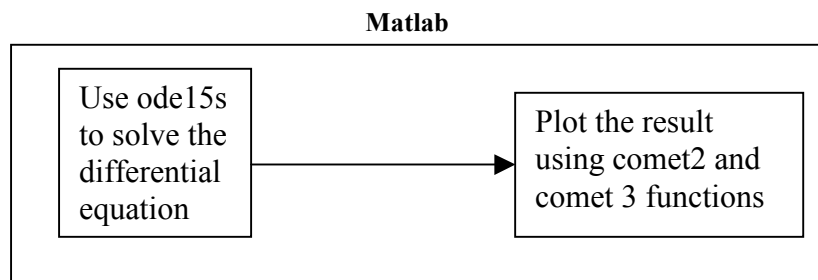
From the above equation, a numerical solution can be derived. Using the initial conditions described, we are able to plot Belousov-Zhabotinsky's oscillatory behavior.

THE SIMULATION OF BELOUSOV-ZHABOTINSKY REACTION

For the simulation part, our original plan was to solve the differential equation in *Mathematica*, writes the result to a file, pass it to *Matlab* for plotting the output:

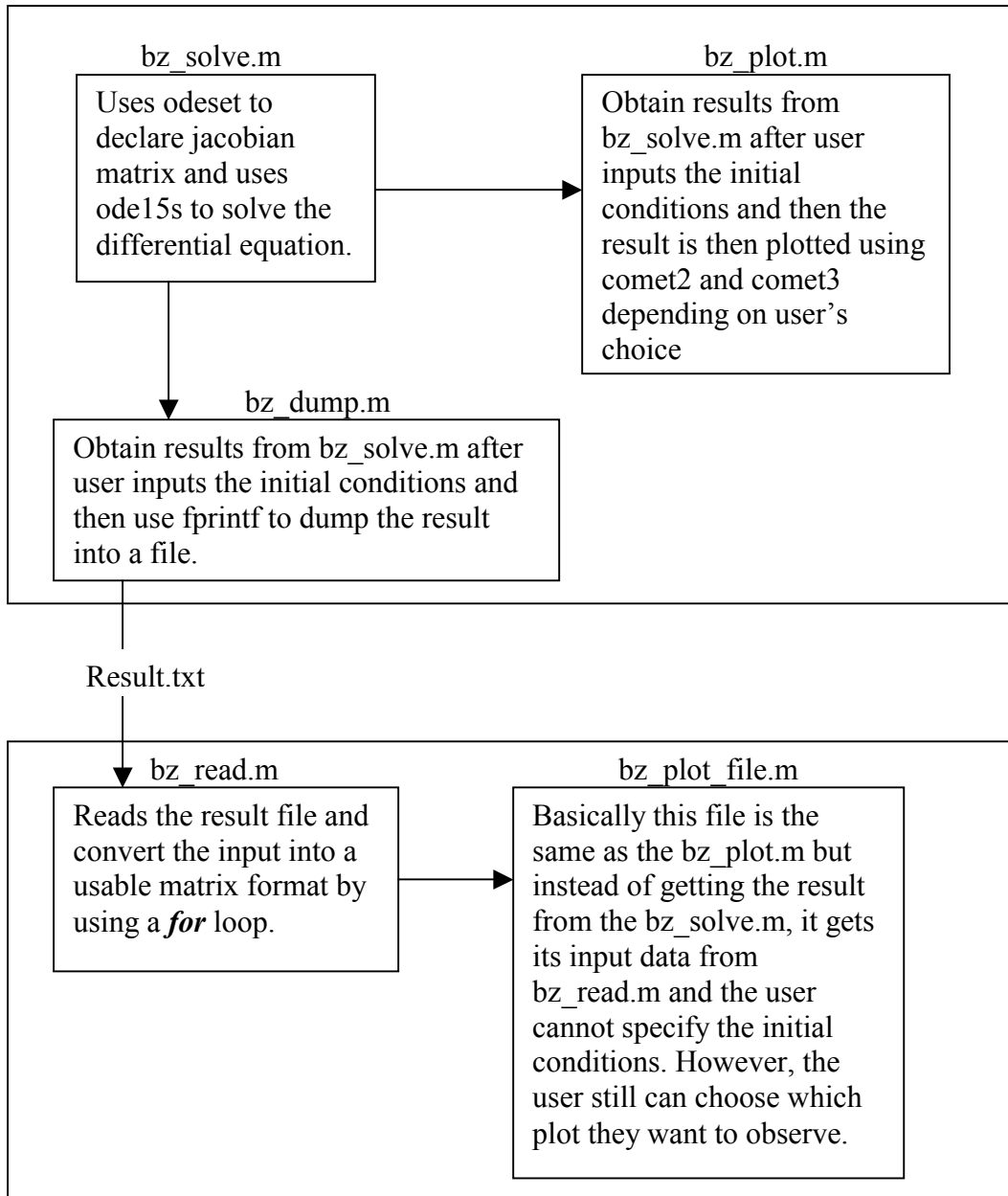


However, we were unable to find a way in which *Mathematica* can save the result into a file. So we turned into the second option:



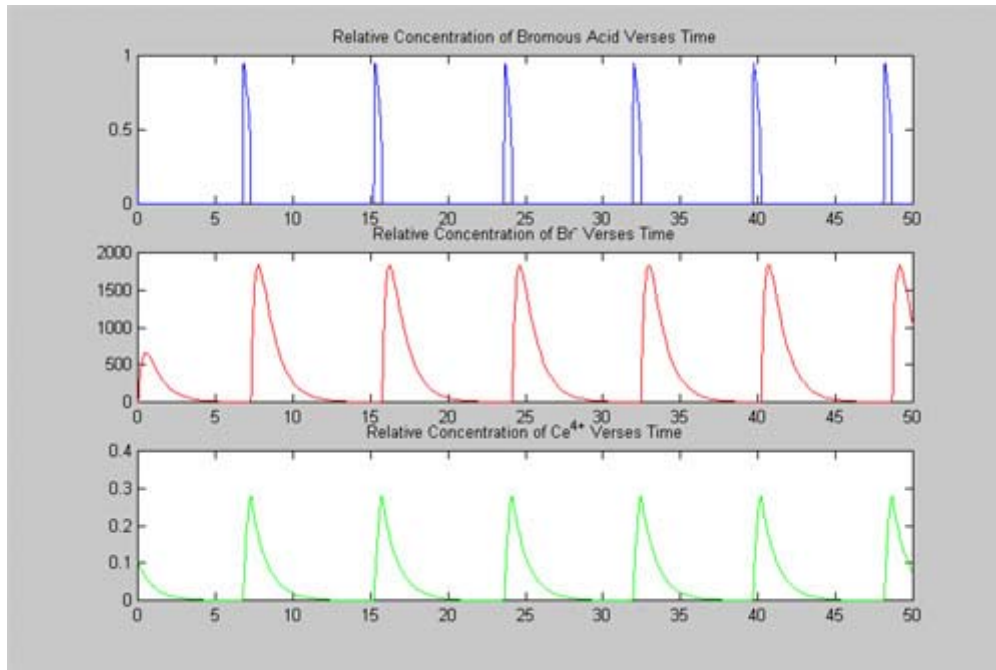
This works fine on *Matlab R12 - ver6.0* but in the vislab, there is only *Matlab 5.3* available, so after some futile attempts on converting the m-files from version 6.0 into version 5.3, we decided to use version 6.0 to solve the differential equation, output the result onto a file, which is then read by *Matlab 5.3* in the vislab and results are plotted successfully. The following diagram is the flow chart of the final simulation part of the project:

Final Simulation Project Flow Chart



RESULT:

Our results are mainly graphs plotted by *Matlab*, which gives us the general idea of how Belousov-Zhabotinsky Reaction is like. The following are the results obtained, which can also be generated by executing the m-file “bz_plot_file.m” under *Matlab* 5.3 environment:



While running the simulation, it is advised to start with the following initial values: $c_1 = 0.04$, $c_2 = 0.0002$, $q = 0.0008$, $f = 1$ or $1/2$ or $1/4$, $t_{\text{Max}} = 25 \sim 100$, $x_i = 1$, $y_i = 1$ and $z_i = 1$. Feel free to change the initial values around, but be prepared to see some buzzard result.

If for any reason, it is impossible to find a *Matlab 6* environment to run the demo with, please use the pre-produced result files inside the txx folders.

CONCLUSION:

From doing this project, we realized that the Belousov-Zhabotinsky Reaction is quite a fascinating scientific phenomenon such that its cyclical nature can be seen as analogues to: the heartbeat, circadian rhythms, the menstrual cycle, variations in hormone levels, and many others. We also acquired a solid skill in the using of computer program tools to solve scientific problems, such as solving differential equations and displaying results in graphs that can help us to understand the concept more firmly and stimulate interests in the topic. So here concludes our project.

ACKNOWLEDGEMENTS

This project based on the Belousov-Zhabotinsky reaction would not have been possible without the consistent guidance of Professor Bernard Palithorpe and our tutors. Professor Palithorpe helped us get started and led us in the right direction. Thanks to Elisapesi Latu in her assistance to this project.

REFERENCES

1. **Title:** Mathematical Models In The Applied Science
Author: A. C. Fowler, University of Oxford
Publisher: Cambridge University Press
Publication Date: 1997
2. **Title:** The Inner Alarm Clock
Author: Arthur T. Winfree
Journal: Nature, vol 287, 1980, p. 875-876
Publication Date: 30 October 1980
3. **Title:** Rotating Chemical Reactions
Author: Arthur T. Winfree, Biol. Sci. Purdue University
Journal: Sci. Am. 230, 82
Publication Date: June, 1974
4. **Title:** Reconstruction of a Set of Differential Equations Modelling an Experimental Homoclinic Chaos in the Belousov-Zhabotinskii Reaction
Author: C. Letellier, J. Maquet, L. Le Sceller and G. Gouesbet
Journal: AIP Conference Proceedings 1997 vol 411 – “Applied Non Linear Dynamics And Stochastic Systems Near the Millenium”, p. 125-130
Editors of Journal: Kadtke, Bulsara
Publication Date: 1997
5. **Title:** When Time Breaks Down – Three-dimensional Dynamics of Electrochemical Waves and Cardiac Arrhythmias
Author: Arthur T. Winfree
Publisher: Princeton University Press
Publication Date: 1987
6. **Title:** Exploring Chaos
Chapter Title: Clocks and Chaos in Chemistry, p. 108-121
Author of chapter: Stephen Scott
Taken from “Chemical Chaos”, S. Scott, 1991.
7. **Website:** <http://www.sci.wsu.edu/idea/OscilChem/>
Title: History of Oscillating Chemical Reactions
Author: Ron Poshusta
Date last viewed: 10/5/2001
8. **Website:** <http://online.redwoods.cc.ca.us/instruct/darnold/DEProj/Index.htm>
Title: Belousov-Zhabotinsky Reaction
Author: Gabriel Peterson, Spring 1998
Date last viewed: 1/5/2001
9. **Website:** www.math.psu.edu/belmonte/papers/gros.pdf
Title: Experimental Survey of Spiral Dynamics in the Belousov-Zhabotinsky Reaction
Author: Andrew L. Belmonte, Qi Quyang, Jean-Marc Flesselles
Date last viewed: 28/5/01
10. **Website:** www-chem.st.usm.edu/japgroup/nlcd/intro.html
Title: Introduction – A Bit of History
Author: unknown
Date last viewed: 28/5/2001
11. **Website:** www.keele.ac.uk/depts/ch/resources/chaos/pres1.html

Title: Cruising a Strange Attractor – A Spreadsheet Simulation of Chemical Chaos
Author: unknown
Date last viewed: 10/5/2001

12. **Website:** www.musc.edu/~aliev
Title: Rubin's Home Page
Author: Rubin R. Aliev
Date last viewed: 28/5/01

Appendix

bz_solve.m:

```
function out = bz_solve(c1,c2,q,f,tMax,xi,yi,zi)
tspan = [0; tMax];
y0 = [0; 0; 0];
y0(1) = xi;
y0(2) = yi;
y0(3) = zi;
options = odeset('Jacobian',@J);
[t,y] = ode15s(@f,tspan,y0,options,c1,c2,q,f);
out(:,1)=t;
out(:,2)=y(:,1);
out(:,3)=y(:,2);
out(:,4)=y(:,3);

%-----
function dydt = f(t,y,c1,c2,q,f)
dydt = [ (y(1)-y(1)^2-y(1)*y(2)+y(2)*q)/c1
        (-q*y(2)-y(1)*y(2)+f*y(3))/c2
        y(1)-y(3)];
%-----
function dfdy = J(t,y,c1,c2,q,f)
dfdy = [ (1-2*y(1)-y(2))/c1 (q-y(1))/c1 0
        -y(2)/c2 -(q+y(1))/c2 f/c2
        1 0 -1];
```

bz_plot.m

```
function bz_plot
disp('Please enter following parametres:');
c1 = input('c1:');
c2 = input('c2:');
q = input('q:');
f = input('f:');
tMax= input('tMax:');
xi = input('xi:');
yi = input('yi:');
zi = input('zi:');

out = bz_solve(c1,c2,q,f,tMax,xi,yi,zi);
opt = 0;
while(opt ~= 8)
    disp('Which graph would you like to print?');
    disp('1. Time vs [HBrO2]');
    disp('2. Time vs [Br-]');
    disp('3. Time vs [Fe3+]');
    disp('4. [HBrO2] vs [Br-]');
    disp('5. [HBrO2] vs [Fe3+]');
    disp('6. [Br-] vs [Fe3+]');
    opt = input('');
end
```

```

disp('7.3D Parametric Plot');
disp('8.Exit');
opt = input('Option:');

switch opt
case 1,
    hold off;
    hold;
    axis([min(out(:,1)) max(out(:,1)) min(out(:,2)) max(out(:,2))]);
    xlabel('Time(sec)');
    ylabel('[HBrO2](M)');
    title('Time vs [HBrO2]');
    comet(out(:,1),out(:,2));
case 2,
    hold off;
    hold;
    axis([min(out(:,1)) max(out(:,1)) min(out(:,3)) max(out(:,3))]);
    xlabel('Time(sec)');
    ylabel('[Br-](M)');
    title('Time vs [Br-]');
    comet(out(:,1),out(:,3));
case 3,
    hold off;
    hold;
    axis([min(out(:,1)) max(out(:,1)) min(out(:,4)) max(out(:,4))]);
    xlabel('Time(sec)');
    ylabel('[Fe3+](M)');
    title('Time vs [Fe3+]');
    comet(out(:,1),out(:,4));
case 4,
    hold off;
    hold;
    axis([min(out(:,2)) max(out(:,2)) min(out(:,3)) max(out(:,3))]);
    xlabel('[HBrO2](M)');
    ylabel('[Br-](M)');
    title('[HBrO2] vs [Br-]');
    comet(out(:,2),out(:,3));
case 5,
    hold off;
    hold;
    axis([min(out(:,2)) max(out(:,2)) min(out(:,4)) max(out(:,4))]);
    xlabel('[HBrO2](M)');
    ylabel('[Fe3+](M)');
    title('[HBrO2] vs [Fe3+]');
    comet(out(:,2),out(:,4));
case 6,
    hold off;
    hold;
    axis([min(out(:,3)) max(out(:,3)) min(out(:,4)) max(out(:,4))]);

```

```

        xlabel('[Br-](M)');
        ylabel('[Fe3+](M)');
        title('[Br-] vs [Fe3+]');
        comet(out(:,3),out(:,4));
    case 7,
        comet3(out(:,2),out(:,3),out(:,4));
        hold;
        xlabel('[HBrO2](M)');
        ylabel('[Br-](M)');
        zlabel('[Fe3+](M)');
        title('3D Parametric Plot');
        hold off;
    case 8,
        disp('Bye!');
    otherwise,
        disp('Invalid option, please try again!');
    end
end
end

```

bz_dump.m

```

function bz_dump
disp('Please enter following parametres:');
c1 = input('c1:');
c2 = input('c2:');
q = input('q:');
f = input('f:');
tMax= input('tMax:');
xi = input('xi:');
yi = input('yi:');
zi = input('zi:');

out = bz_solve(c1,c2,q,f,tMax,xi,yi,zi);
[M N] = size(out);

fid = fopen('result.txt','w');
for i=1:M
    fprintf(fid,'%3.4f %3.4f %3.4f %3.4fn',out(i,1),out(i,2),out(i,3),out(i,4));
end
fclose(fid);

```

bz_read.m

```

function out = bz_read
fid = fopen('result.txt','r');
temp = fscanf(fid,'%f');
fclose(fid);

[M N] = size(temp);

```

```

M = M/4;
for i=1:M
    out(i,1)=temp((i-1)*4+1);
    out(i,2)=temp((i-1)*4+2);
    out(i,3)=temp((i-1)*4+3);
    out(i,4)=temp((i-1)*4+4);
end

```

bz_plot_file.m

```

function bz_plot_file

out = bz_read;
opt = 0;
while(opt ~= 8)
    disp('Which graph would you like to print?');
    disp('1.Time vs [HBrO2]');
    disp('2.Time vs [Br-]');
    disp('3.Time vs [Fe3+]');
    disp('4.[HBrO2] vs [Br-]');
    disp('5.[HBrO2] vs [Fe3+]');
    disp('6.[Br-] vs [Fe3+]');
    disp('7.3D Parametric Plot');
    disp('8.Exit');
    opt = input('Option:');

    switch opt
        case 1,
            hold off;
            hold;
            axis([min(out(:,1)) max(out(:,1)) min(out(:,2)) max(out(:,2))]);
            xlabel('Time(sec)');
            ylabel('[HBrO2](M)');
            title('Time vs [HBrO2]');
            comet(out(:,1),out(:,2));
        case 2,
            hold off;
            hold;
            axis([min(out(:,1)) max(out(:,1)) min(out(:,3)) max(out(:,3))]);
            xlabel('Time(sec)');
            ylabel('[Br-](M)');
            title('Time vs [Br-]');
            comet(out(:,1),out(:,3));
        case 3,
            hold off;
            hold;
            axis([min(out(:,1)) max(out(:,1)) min(out(:,4)) max(out(:,4))]);
            xlabel('Time(sec)');
            ylabel('[Fe3+](M)');

```

```

    title('Time vs [Fe3+]);
    comet(out(:,1),out(:,4));
case 4,
    hold off;
    hold;
    axis([min(out(:,2)) max(out(:,2)) min(out(:,3)) max(out(:,3))]);
    xlabel('[HBrO2](M)');
    ylabel('[Br-](M)');
    title('[HBrO2] vs [Br-]');
    comet(out(:,2),out(:,3));
case 5,
    hold off;
    hold;
    axis([min(out(:,2)) max(out(:,2)) min(out(:,4)) max(out(:,4))]);
    xlabel('[HBrO2](M)');
    ylabel('[Fe3+](M)');
    title('[HBrO2] vs [Fe3+]');
    comet(out(:,2),out(:,4));
case 6,
    hold off;
    hold;
    axis([min(out(:,3)) max(out(:,3)) min(out(:,4)) max(out(:,4))]);
    xlabel('[Br-](M)');
    ylabel('[Fe3+](M)');
    title('[Br-] vs [Fe3+]');
    comet(out(:,3),out(:,4));
case 7,
    comet3(out(:,2),out(:,3),out(:,4));
    hold;
    xlabel('[HBrO2](M)');
    ylabel('[Br-](M)');
    zlabel('[Fe3+](M)');
    title('3D Parametric Plot');
    hold off;
case 8,
    disp('Bye!');
otherwise,
    disp('Invalid option, please try again!');
end
end

```