

Oregonator model of the Belousov-Zhabotinsky reaction

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Boris Belousov in the 1950's discovered that a mixture of malonic acid, potassium bromate, and cerium sulfate in an acidic aqueous mixture in a batch reactor did not react directly to equilibrium. Instead, the composition and color of the solution oscillated for a significant period. His reports of this work were rejected by peer-reviewed journals because reviewers felt that an oscillating chemical reaction violates thermodynamic equilibrium and, thus, was not possible. His work did appear in a conference proceeding. Anatol Zhabotinsky discovered Belousov's conference paper in the 1960's, repeated and expanded the work, and was able to publish his research. Since then, there have been many papers on this complex chemical system and related systems. From the Epstein (2008) obituary of Zhabotinsky:

The discovery of oscillating reactions revolutionized the way that scientists thought about chemical dynamics. Indeed, Ilya Prigogine — who received the 1977 Nobel Prize in Chemistry, in part for demonstrating that chemical systems far from equilibrium can exhibit periodic oscillations — regarded the BZ reaction as the most important scientific discovery of the twentieth century, surpassing quantum theory and relativity. Whether or not one accepts this assessment, it is clear that the discovery of a 'simple' chemical reaction that displays periodic temporal and spatial behaviour had far-reaching consequences, even leading to a greater understanding of the processes that underlie life itself, such as biological clocks and morphogenesis.

Note the words "spatial" and "morphogenesis." We will discuss those in subsequent notes. Now we will focus on "temporal" and "clocks."

In addition to color changes, selective electrodes can be used to measure ion concentrations. This figure is from Field, et al. (1972). Note the "induction period" before the oscillations start, due partially to bromination of malonic acid. The oscillations eventually die out as the system approaches equilibrium.

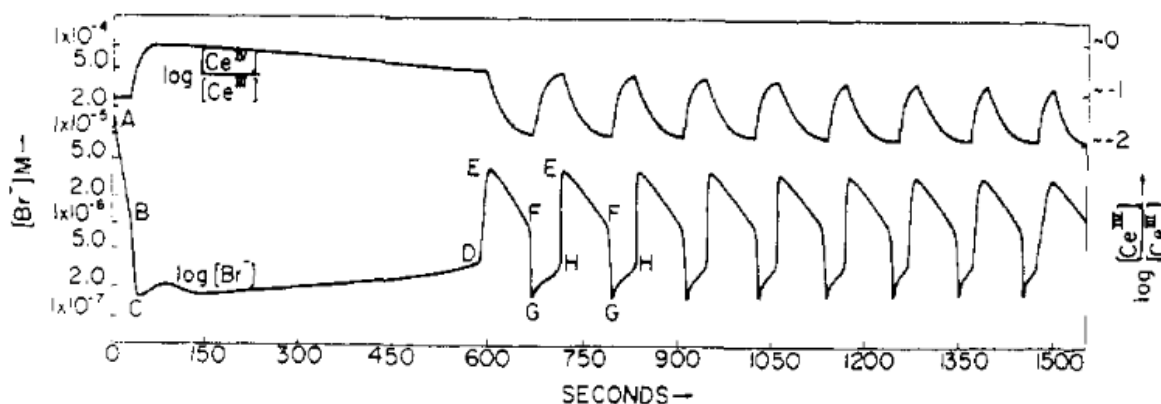
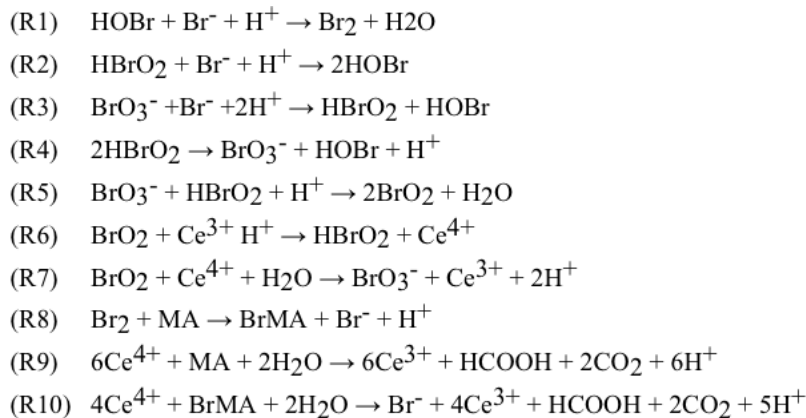
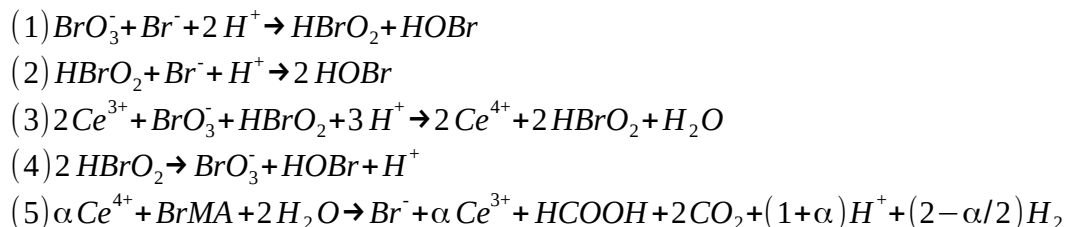


Figure 1. Potentiometric traces of $\log [Br^-]$ and $\log [Ce(IV)]/[Ce(III)]$ for a representative reaction exhibiting all six periods. Initial concentrations were $[CH_2(COOH)_2]_0 = 0.032 M$, $[KBrO_3]_0 = 0.063 M$, $[KBr]_0 = 1.5 \times 10^{-5} M$, $[Ce(NH_4)_2(NO_3)_6]_0 = 0.001 M$, $[H_2SO_4]_0 = 0.8 M$.

Field, Koros and Noyes at the University of Oregon in the 1970's developed kinetic models of the reaction that were able to explain much of the experimental behavior. Their original model was the FKN model (Leigh, 2015).



This kinetic model was "reduced" (simplified while retaining major behavior) to the Oregonator model:



BrO_3^- is bromate ion (Br at center bonded separately to three O), Br^- is bromide ion, HBrO_2 is bromous acid ($\text{O}=\text{Br}-\text{OH}$), HOBr is hypobromous acid ($\text{Br}-\text{OH}$), BrMA is brominated malonic acid ($\text{BrCH}(\text{COOH})_2$), HCOOH is formic acid, and α is an adjustable stoichiometric coefficient (often 2).

The overall reaction is oxidation of malonic acid ($\text{CH}_2(\text{COOH})_2$) by bromate through a cerium 3+/4+ redox couple.

The mechanism for the Oregonator model was obtained as a result of "reducing" the 10-step Field-Koros-Noyes (FKN) mechanism to a 5-step mechanism. The number of rate coefficients is reduced, and the number of differential equations for batch and other unsteady state reactors is reduced. This reduction was done by methods of chemical kinetics:

- Steady state approximation: molar rate of change of intermediate components present in small concentrations are much smaller than rates of change of other components, so time derivatives for these intermediate components can be set to zero. Eliminates a differential equation for batch reactors and other unsteady-state reactors and converts it into an algebraic equation used to express one component's concentration in terms of other concentrations and, thus, eliminate that component from the rate equations.
- Partial equilibrium approximation: a step with relatively fast forward and reverse rates is in close approach to equilibrium during transient conditions. Forward and reverse rates for this step set equal. Equilibrium relationship used to express one component's concentration in terms

of other concentrations and, thus, eliminate that component from the rate equations.

Step 3 is called "autocatalytic." It is autocatalytic (speeds itself up) in the sense that net HBrO_2 is produced by the reaction (one mole on reactant side and two on product side). As the reaction step proceeds, the increasing HBrO_2 concentration increases the rate of the reaction step and the rate of production of more HBrO_2 .

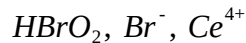
Step 3 also produces Ce(IV) . Ce(IV) reacts in step 5 to produce bromide ion. Bromide ion reacts in step 2 to consume HBrO_2 .

HBrO_2 is called the "activator" component because it speeds up the autocatalytic step 3. Bromide ion is called the "inhibitor" component because it consumes the activator component, HBrO_2 . Step 3 > step 5 > step 2 is called a "negative feedback loop."

The next step is to write the balance equations for components in a batch reactor. Assume these reactant components are "present in excess" and their concentrations do not change significantly over the course of a few cycles:



Components whose concentration change significantly:



Rate equations for each step, where these k 's include the concentrations of components in rate equations that remain essentially constant.

$$\begin{aligned} (1) r_{\text{HBrO}_2,1} &= k_1 [\text{BrO}_3^-] [\text{Br}^-] \\ (2) r_{\text{HBrO}_2,2} &= -k_2 [\text{HBrO}_2] [\text{Br}^-] \\ (3) r_{\text{HBrO}_2,3} &= k_3 [\text{BrO}_3^-] [\text{HBrO}_2] \\ (4) r_{\text{HBrO}_2,4} &= -2k_4 [\text{HBrO}_2]^2 \\ (5) r_{\text{Ce}^{4+},5} &= -k_5 [\text{Ce}^{4+}] \end{aligned}$$

Remember this:

$$\frac{r_{1,k}}{\nu_{1,k}} = \frac{r_{2,k}}{\nu_{2,k}} = \text{constant for step } k, \text{ where } \nu \text{ are formal stoichiometric coefficients}$$

and be careful about the formal stoichiometric coefficient of HBrO_2 in step 3 (it is +1).

Thus, the rates of other components that change concentration significantly in each step are given by:

$$\begin{aligned}
 (1) r_{HBrO_2,1} &= -r_{BrO_3^-,1} = -r_{Br^-,1} \\
 (2) r_{HBrO_2,2} &= r_{Br^-,2} \\
 (3) r_{HBrO_2,3} &= 0.5 r_{Ce^{4+},3} \\
 (4) r_{HBrO_2,4} & \text{ (no other component changes conc. significantly in 4)} \\
 (5) r_{Ce^{4+},5} &= -\alpha r_{Br^-,5}
 \end{aligned}$$

Next write balances for components that change concentration significantly in a batch reactor:

$$\frac{dN_j}{dt} = \frac{d(VC_j)}{dt} = \sum_k r_{j,k} V$$

For a constant volume batch reactor $\frac{dC_j}{dt} = \sum_k r_{j,k}$

$$\frac{d[HBrO_2]}{dt} = r_{HBrO_2,1} + r_{HBrO_2,2} + r_{HBrO_2,3} + r_{HBrO_2,4}$$

$$\frac{d[Br^-]}{dt} = r_{Br^-,1} + r_{Br^-,2} + r_{Br^-,5}$$

$$\frac{d[Ce^{4+}]}{dt} = r_{Ce^{4+},3} + r_{Ce^{4+},5}$$

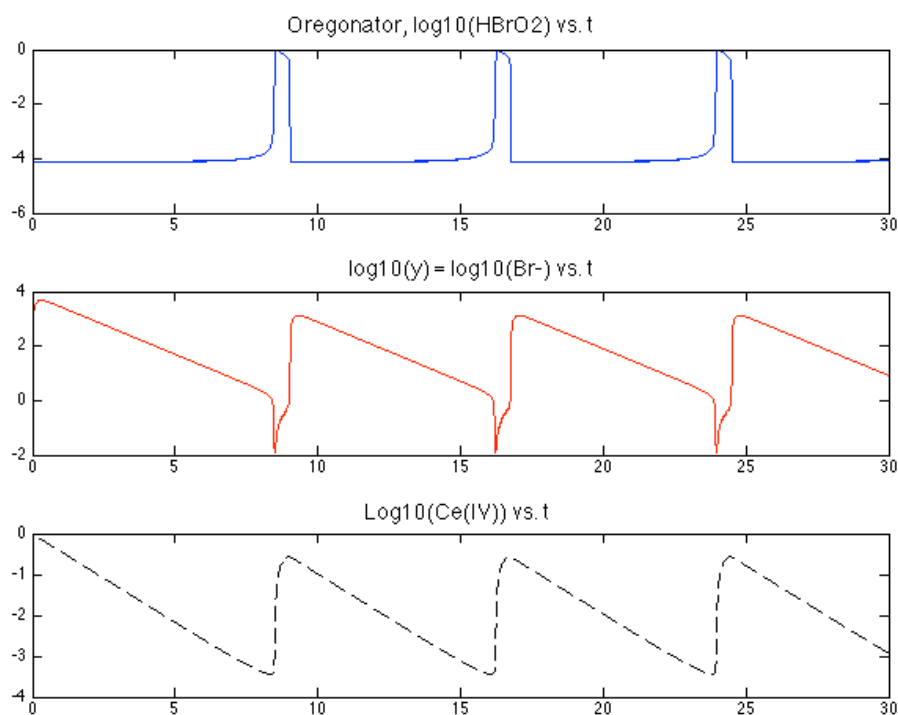
Substituting the rate equations:

$$\frac{d[HBrO_2]}{dt} = k_1[BrO_3^-][Br^-] - k_2[HBrO_2][Br^-] + k_3[BrO_3^-][HBrO_2] - 2k_4[HBrO_2]^2$$

$$\frac{d[Br^-]}{dt} = -k_1[BrO_3^-][Br^-] - k_2[HBrO_2][Br^-] + \frac{1}{\alpha} k_5[Ce^{4+}]$$

$$\frac{d[Ce^{4+}]}{dt} = 2k_3[BrO_3^-][HBrO_2] - k_5[Ce^{4+}]$$

These three ODEs can be integrated from specified initial conditions. Below are results obtained using Matlab to integrate the scaled equation set in Field (2007). The variables shown in the plot are scaled concentrations and time.



References

Epstein, I.R., 2008. Obituary: Anatol Zhabotinsky (1938–2008). *Nature* 455, 1053–1053. doi:10.1038/4551053a

Field, R., 2007. Oregonator. *Scholarpedia* 2, 1386. doi:10.4249/scholarpedia.1386 (accessed April 6, 2015).

Field, R.J., Koros, E., Noyes, R.M., 1972. Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system. *J. Am. Chem. Soc.* 94, 8649–8664. doi:10.1021/ja00780a001

Leigh, E., 2005. Belousov-Zhabotinsky Reaction. <http://home2.fvcc.edu/~dhicketh/DiffEqns/spring05projects/ErikLeigh/BZ.htm> (accessed April 6, 2015).

Listing of main Matlab file

```
% oregonator model
% http://www.scholarpedia.org/article/Oregonator
```

```

% use scaled equations from this link

% scaled concentrations
% A = BrO3(-1)
% B = malonic acid
% x = HBrO2
% y = Br(-)
% z = Ce(IV)

clear all
close all

x0 = 1;
y0 = 1;
z0 = 1;
tf = 1; % start with small tf, solution of this problem is slow

tspan = [0 tf]; % this is a scaled time, not seconds
v0 = [x0,y0,z0];

[t,v] = ode45('oregonatorFunc',tspan,v0);

x = v(:,1); % x = HBrO2
y = v(:,2); % y = Br(-)
z = v(:,3); % z = Ce(IV)

subplot(3,1,1),plot(t,log10(x),'b'),
    title('proportional to log10(HBrO2) vs. t')
subplot(3,1,2), plot(t,log10(y),'r'),
    title('proportional to log10(Br-) vs. t')
subplot(3,1,3), plot(t,log10(z),'k--'),
    title('proportional to log10(Ce(IV)) vs. t')

```

Listing of function file oregonatorFunc.m

```

function ddt = oregonatorFunc(t,v)
% function for oregonator model
% http://www.scholarpedia.org/article/Oregonator
% use scaled equations from this link

% see oregonatorParams.m for params
inve = 1.01010101010101e+02;
invcp = 5.05050505050505e+04;
qp = 7.69696969696970e-03;
qpp = 3.84848484848485e+00;
fp = 5.05050505050505e+04;

x = v(1);
y = v(2);
z = v(3);

dxdt = qp*y - inve*x*y + inve*x*(1 - x);
dydt = -qpp*y - invcp*x*y + fp*z;
dzdt = x - z;

ddt = [dxdt; dydt; dzdt]; % return as column vector

```

end

Listing of file oregonatorParams.m to compute parameter values

```
% params for oregonator model
% http://www.scholarpedia.org/article/Oregonator
% use scaled equations from this link
% calculate params here to save time in ode45 repeat

A = 0.06;
B = 0.02;
q = 7.62e-5;
e = 9.90e-3;
ep = 1.98e-5;
f = 1;

format long e

inve = 1/e
invep = 1/ep
qp = inve*q
qpp = invep*q
fp = invep*f

% results copied to oregonatorFunc.m
%     inve = 1.01010101010101e+02;
%     invep = 5.05050505050505e+04;
%     qp = 7.69696969696970e-03;
%     qpp = 3.84848484848485e+00;
%     fp = 5.05050505050505e+04;
```