



Department of Mathematics

IDEA: Internet Differential Equations Activities

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Oscillating Chemical Reactions

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Background Information

History of Oscillating Chemical Reactions

Modern chemists are aware that certain chemical reactions can oscillate in time or space. Prior to about 1920 most chemists believed that homogeneous systems were impossible. The earliest scientific evidence that such reactions can oscillate was met with extreme skepticism in the early history and the heated debate surrounding oscillating reactions in several [references](#).

The most famous oscillating chemical reaction is the Belousov-Zhabotinsky (BZ) reaction. This is also the first chemical reaction to exhibit temporal oscillations. You can demonstrate and carry out experiments on this reaction by following [recipes](#) to be found in standard laboratory manuals.

Theoretical models of oscillating reactions have been studied by chemists, physicists, and mathematicians. The simplest one is the Brusselator. Some other models are the [Brusselator](#) and the [Oregonator](#). The latter was designed to simulate the famous Belousov-Zhabotinsky reaction.

Recipe for the Belousov-Zhabotinsky (BZ) oscillating reaction

source: B.Z. Shakhshiri, "Chemical Demonstrations: A Handbook for Teachers" (University of Wisconsin, Wisconsin, 1985), and in "Time and Space", J. Chem. Ed. **49**, 308 (1972). Also see J.A. Pojman, R. Craven, D.C. Leard, J. Chem. Ed. **71**, 84 (1994) Chemistry Lab experiment.

Prepare a solution with the following concentrations of reactants. The volume should be large enough for the intended audience. The solution should be stirred constantly with a magnetic stirring bar. These concentrations will give a system that oscillates with a period of about 10 minutes and will continue for 50 minutes or more. The reactants can be mixed in any order.

Reactant	Concentration, M
Ce(NH ₄) ₂ (NO ₃) ₆ (catalyst)	0.002
CH ₂ (COOH) ₂	0.275
KBrO ₃	0.0625
H ₂ SO ₄	1.5
Ferriin (indicator)	0.0006

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Chemical Kinetics (under construction)
 Differential Equations (under construction)

Models of Oscillating Chemical Reactions

Why Construct Theoretical Models of Oscillating Chemical Reactions

A model for a chemical reaction consists of the following parts:

- [A mechanism](#). This is a set of elementary chemical reactions to describe how reactants form intermediates, intermediates

reactants, and ultimately products are produced.

- **A set of Rate equations.** These are differential equations corresponding to the reaction mechanism and giving the rates of intermediates, and products.
- **A set of Integrated rate equations.** These show the concentrations as functions of time for reactants, intermediates, and products by integrating the rate (differential) equations.

The criterion for an acceptable theoretical model is that it agree with experimental observations of varying concentrations. When a theoretical chemist finds an acceptable model he says reaction.

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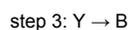
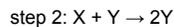
The Lotka-Volterra Model of Oscillating Chemical Reactions

This is the earliest proposed explanation for why a reaction may oscillate.

In 1920 [Lotka](#) proposed the following reaction mechanism (with corresponding rate equations). Each reaction step refers to the reaction in which the reactant molecules combine to produce intermediates or products. For example, in step 1 a molecule of species A combines with a molecule of species X to yield two molecules of species X. This step depletes molecules A (and adds molecules X) at a rate proportional to the product of the concentrations of A and X.

reaction step	molecular reaction	step contributions to differential rate laws
1	$A + X \rightarrow 2X$	$\frac{d[A]}{dt} = -k_1[A][X]$ $\frac{d[X]}{dt} = k_1[A][X]$
2	$X + Y \rightarrow 2Y$	$\frac{d[X]}{dt} = -k_2[X][Y]$ $\frac{d[Y]}{dt} = k_2[X][Y]$
3	$Y \rightarrow B$	$\frac{d[Y]}{dt} = -k_3[Y]$ $\frac{d[B]}{dt} = k_3[Y]$

The overall chemical reaction is merely $A \rightarrow B$ with two transient intermediate compounds X and Y:



The effective rate laws for the reactant A, the product B, and the intermediates X and Y are found by summing the contributions from each step:

$$\frac{d[A]}{dt} = -k_1[A][X]$$

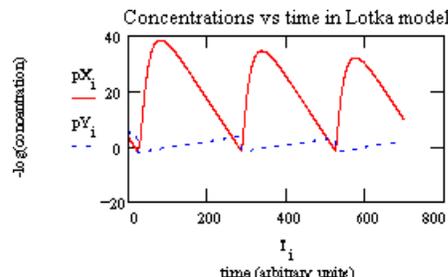
$$\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y]$$

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y]$$

$$\frac{d[B]}{dt} = k_3[Y]$$

Step 1 is called autocatalytic because X accelerates its own production. Likewise step 2 is autocatalytic. **Problem:** Given the mechanism [A], [X], [Y], and [B] as functions of time. Lotka obtained oscillating concentrations for both intermediates X and Y when the reactant (as, for example, A is continuously replaced from an external source as it is consumed in the reaction). An interactive solution is provided in a file ([lotka.mcd](#)) (you need mathcad to view this file). You can also read a summary of the [solution](#) (view with your browser re-interpreted as a model for oscillating populations of predators and preys as was done by Volterra. In this, A represents the prey and Y live. Step 1 represents pre-procreation: prey population doubles at rate $k_1[A]$ (typical exponential growth). Then Y is introduced and consumes the prey in order to sustain (and expand) their population. Step 2 represents this inclination of predators to reproduce in order to consume the prey. Finally (step 3), predators die at a certain natural rate (also exponential) so that they are removed from the ecosystem.

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Brusselator Model of Oscillating Chemical Reactions

The Brusselator model was proposed by I. Prigogine and his collaborators at the Free University of Brussels. The reaction mechanism is:

step	molecular reaction	step contribution to rate laws
1	$A \rightarrow X$	$\frac{d[A]}{dt} = -k_1[A]$ $\frac{d[X]}{dt} = k_1[A]$
2	$2X + Y \rightarrow 3X$	$\frac{d[X]}{dt} = k_2[X]^2[Y]$ $\frac{d[Y]}{dt} = -k_2[X]^2[Y]$
3	$B + X \rightarrow Y + D$	$\frac{d[B]}{dt} = -k_3[B][X]$ $\frac{d[X]}{dt} = -k_3[B][X]$ $\frac{d[Y]}{dt} = k_3[B][X]$ $\frac{d[D]}{dt} = k_3[B][X]$
4	$X \rightarrow E$	$\frac{d[X]}{dt} = -k_4[X]$ $\frac{d[D]}{dt} = k_4[X]$

The net reaction is $A+B \rightarrow C+D$ with transient appearance of intermediates X and Y.

Problem:

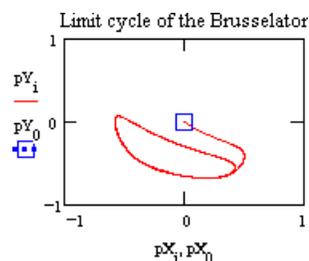
1. Write the system of 2 coupled differential equations for the intermediate concentrations [X] and [Y].

2. (b) Let each of the rate constants $k_i = 1$ and assume the two reactants A and B have constant concentrations, $[A]=1$ and $[B]=1$ (system at the same rate as they are consumed in the reactions). Choose initial concentrations for intermediates ($[X]_0 = 1, [Y]_0 = 1$) and integrate from time 0 to 50 (arbitrary units).
3. (c) Make two plots of the results: $-\log([X])$ and $-\log([Y])$ versus time, and $-\log([Y])$ versus $-\log([X])$.

For a solution of this problem, see the interactive mathcad file [brussels.mcd](#).

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Brusselator Model



Oregonator Model of Oscillating Chemical Reactions

Reference : R.J. Field and R.M. Noyes, J. Chem. Phys. **60**, 1877 (1974).

A simplified form of this model uses the following mechanism.

step	reaction	contributions to the rate equation
1	$A+Y \rightarrow X$	$\frac{d[A]}{dt} = -k_1[A][Y]$ $\frac{dY}{dt} = -k_1[A][Y]$, $\frac{d[X]}{dt} = k_1[A][Y]$
2	$X+Y \rightarrow P$	$\frac{d[X]}{dt} = -k_2[X][Y]$, $\frac{d[Y]}{dt} = -k_2[X][Y]$ $\frac{d[P]}{dt} = k_2[X][Y]$
3	$B+X \rightarrow 2X+Z$	$\frac{d[B]}{dt} = -k_3[B][X]$ $\frac{d[X]}{dt} = k_3[B][X]$, $\frac{d[Z]}{dt} = k_3[B][X]$
4	$2X \rightarrow Q$	$\frac{d[X]}{dt} = -k_4[X]^2$ $\frac{d[Q]}{dt} = k_4[X]^2$
5	$Z \rightarrow Y$	$\frac{d[Z]}{dt} = -k_5[Z]$, $\frac{d[Y]}{dt} = k_5[Z]$

The overall reaction, obtained by adding reactions 1, 2, 4 and twice 3 and 5, is $A + 2B \rightarrow P + Q$.

Problem: Use the following definitions for dimensionless concentration variables (a , h , and r) and rate constant τ for the Oregonator model for the BZ reaction:

$$[\text{HBrO}_2] = 5.025 \times 10^{-11} \text{ a,}$$

$$[\text{Br}] = 3.0 \times 10^{-7} \text{ h,}$$

$$[\text{Ce(IV)}] = 2.412 \times 10^{-8} \text{ r,}$$

$$q = 8.375 \times 10^{-6},$$

$$s = 77.27 .$$

The time variable is also the dimensionless variable $t = t/w$ with $w = 0.1610\text{sec}$. Take the initial concentration $r=1000$.

(a) Set up the differential rate equations for a , h , and r .

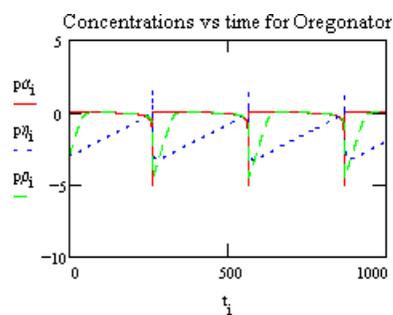
(b) Solve the d.e. from time 0 to $t_1=1000$, and plot concentrations (better to plot the $-\log(\text{conc.})$) versus time.

(c) Also plot the trajectories of a and r versus h in concentration (or $-\log(\text{conc.})$) space. Be careful, this system is "stiff" and requires special treatment.

See an interactive mathcad solution of this problem in the file [oregonat.mcd](#).

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Oregonator model



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Links to other Chemical Kinetics sites

[A chemical kinetics simulator](#)

[A tutorial](#)

[Non-linear chemical kinetics research](#)
