Waldemar Nowicki

EXPERIMENT 2

The Belousov-Żabotyński reaction

Basic notion: oscillating reaction

Introduction

Oscillating reactions are those in which the concentrations of reagents undergo periodical changes in time. An example of oscillating reactions is the Belousov-Żabotyński reaction (BŻ),whose approximate chemical equation is

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \xrightarrow{Ce(III)/Ce(IV)} 3BrCH(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (1)$$

The redox system Ce(IV)/Ce(III) is the catalyst of the reaction. The apparent simplicity of equation (1) hides a complex and not fully explained yet mechanism.
The aim of the experiment is to check the effect of the initial concentrations of reagents on the oscillations of BŻ reaction.

Theory

A simplified kinetic model of the Belousov-Żabotyński reaction has been give n by Field, Kö rös and Noyes (FKN model) [1-3]. This model assumes the occurrence of 6 reactions of which the first five are as follows:

$$Br^- + BrO_3^- + 2H^+ \xrightarrow{k_1} HBrO_2 + HOBr \quad (2)$$

$$Br^- + HBrO_2 + H^+ \xrightarrow{k_2} 2HOBr \quad (3)$$

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{k_3} 2\,BrO_2^\bullet + 2H_2O \quad (4)$$

$$Ce^{3+} + BrO_2^\bullet + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Ce^{4+} + HBrO_2 \quad (5)$$

$$2\,HBrO_2 \xrightarrow{k_5} HOBr + BrO_3^- + H^+ \quad (6)$$

The sixth reaction is a sum of a few stages including the reduction of Ce(IV) and oxidation of malonic acid

$$2Ce^{4+} + HOBr + 2BrO_3^- + 2CH_2(COOH)_2 \xrightarrow{k_6} Ce^{3+} + 3H^+ + 3\,Br^- + 6CO_2 + 4H_2O \quad (7)$$

The rate constants of the first five reactions were determined experimentally in independent measurements. According to the FKN model, the rate constant of the sixth reaction is a function of concentrations of some reagents.

$$k_6 = a[Ce^{4+}] + b[BrO_3^-] + c[CH_2(COOH)_2] + d[H^+] + e \quad (8)$$

where *a*, *b*, *c*, *d*, *e* – are constants.

The simplified FKN model expressed by equations (2-8) can be even more simplified to the so-called OREGONATOR model (the name comes from Oregon university at which Field and Noyes worked). This model, after a slight modification caused by the fact that OREGONATOR fails in calculations of concentrations of some reagents (like e.g. cerium ions) is shown below [1]. Substituting $X \equiv HBrO_2$, $Y \equiv Br^-$, $Z \equiv Ce^{4+}$, $W \equiv BrO_2^{\bullet}$, $C \equiv Ce^{3+}$, $A \equiv BrO_3^-$ and $P \equiv HOBr$, we get a set of equations without the reagents whose concentrations changes during the reaction are inessential, e.g. sulphuric acid present in large excess.

$$A + Y \xrightarrow{k_1} X + P \quad (9)$$

$$X + Y \xrightarrow{k_2} 2\,P \quad (10)$$

$$A + X \xrightarrow{k_3} 2\,W \quad (11)$$

$$C + W \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X + Z \quad (12)$$

$$2\,X \xrightarrow{k_5} A + P \quad (13)$$

$$Z \xrightarrow{k_6} g\,Y + C \quad (14)$$

The stoichiometric coefficient *g* in the simplified equation (14) takes the value of 0.5.

The reactions of modified OREGONATOR (9-14) lead to the following kinetic equations:

$$\frac{d[X]}{dt} = k_1[A][Y] - k_2[X][Y] - k_3[A][X] + k_4[W][C] - k_{-4}[Z][X] - 2k_5[X]^2 \quad (15)$$

$$\frac{d[Y]}{dt} = -k_1[A][Y] - k_2[X][Y] + gk_6[Z] \quad (16)$$

$$\frac{\mathrm{d[Z]}}{\mathrm{d}t} = k_4[\mathrm{W}][\mathrm{C}] - k_{-4}[\mathrm{X}][\mathrm{Z}] - k_6[\mathrm{Z}] \tag{17}$$

$$\frac{\mathrm{d[W]}}{\mathrm{d}t} = 2k_3[\mathrm{A}][\mathrm{X}] - k_4[\mathrm{W}][\mathrm{C}] + k_{-4}[\mathrm{Z}][\mathrm{X}] \tag{18}$$

$$\frac{\mathrm{d[C]}}{\mathrm{d}t} = -k_4[\mathrm{W}][\mathrm{C}] + k_{-4}[\mathrm{X}][\mathrm{Z}] + k_6[\mathrm{Z}] \tag{19}$$

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_1[\mathrm{Y}][\mathrm{A}] - k_3[\mathrm{A}][\mathrm{X}] + k_5[\mathrm{X}]^2 \tag{20}$$

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_1[\mathrm{Y}][\mathrm{A}] + 2k_2[\mathrm{X}][\mathrm{Y}] + k_5[\mathrm{X}]^2 \tag{21}$$

The set of differential equations (15-21) can be solved by numerical methods.

Experiment

Method

In the experiment, the potentiometric measurement of oscillations in the Belousov-Żabotyński reaction is combined with the numerical solution of the set of kinetic equations (15-21) describing the modified OREGONATOR model.

Reagents and apparatuses

–Solution of H_2SO_4 of a concentration 0.5 mol/dm^3: 45.09 g H_2SO_4/dm^3 H_2O or 24.37 cm^3 H_2SO_4/dm^3 H_2O
– Solution of KCl of a concentration 0.1 mol/dm^3
– Solution of KNO_3 of a concentration 0.1 mol/dm^3
– $KBrO_3$ (solid)
– Malonic acid (solid)
– $Ce(SO_4)_2$ (solid)
– Combined platinum electrode
– pH-meter
– Y-T recorder.

Procedure

1. Assembly a setup for measurements of electromotive force, made of a milivoltmeter and a galvanic cell with a silver-chloride reference electrode and a platinum indicatory electrode. Both electrodes are placed in one combined sensor. Prior to the experiment, supplement the electrolyte in the reference half-cell. Silver-chloride reference half-cell needs to be filled with a solution od chlorides (KCl in concentration of 0.1 mol/dm^3). As the presence of chlorides disturbs the BŻ reaction, use a salt bridge filled with a solution of KNO_3 (0.1 mol/dm^3). Connect the analogue output of the milivoltmeter with an Y-T recorder. The rate of paper shift should be chosen so that to ensure accurate observation of the cycles of periods from 50s to 200s.

2. Prepare the initial solutions of malonic acid, potassium bromate and cerium sulphate according to the specification given in Table 1. **Caution;** the substances should be dissolved in a 0.5 mol/dm^3 solution of sulphuric acid.

Table 1

Malonic acid 0.60 mol/dm^3	6.2436 g malonic acid /100 cm^3
$KBrO_3$ 0.18 mol/dm^3	3.0062 g KBr O_3/100 cm^3
$Ce(SO_4)_2$ 6.0×10^{-3} mol/dm^3	0.2426 g $Ce(SO_4)_2 \times 4H_2O$/100 cm^3

3. Mix the initial solutions at the ratios given in Table 2 and immerse the electrodes in the mixture. **Caution;** the solutions should be added in the order potassium bromate, malonic acid and cerium sulphate. Switch on the recorder and set the amplification so that the scale of the recorder was not exceeded and its indications were clear.

Table 2

$KBrO_3$ solution	Malonic acid solution	H_2SO_4 solution	$Ce(SO_4)_2$ solution
9 cm^3	3 cm^3	10 cm^3	5 cm^3
9 cm^3	3 cm^3	5 cm^3	10 cm^3
9 cm^3	3 cm^3	0 cm^3	15 cm^3

3. Record the oscillating curves for the solutions from Table 2. Time of measurement should not exceed 0.5 h.

4. Carry out the reaction with the solutions mixed in the way specified in Table 3. Time of measurement should be at least 1.5 h. The rate of paper shift can be lowered.

Table 3

$KBrO_3$ solution	Malonic acid solution	H_2SO_4 solution	$Ce(SO_4)_2$ solution
1,5 cm^3	0,5 cm^3	10 cm^3	15 cm^3
3 cm^3	1 cm^3	8 cm^3	15 cm^3

5. After completion of the experiment, measure the distances between subsequent peaks recorded on the sheet of paper, neglecting the induction period at the beginning of the reaction.

6. Calculate the mean periods of oscillations obtained for particular concentrations of cerium(IV) sulphate (Table 2) and mark the points on the plot showing the dependence of oscillation period on the concentration of the catalyst.

Simulation of Belousov-Żabotyński reaction (OREGONATOR program)

Start the program "oscillating reactions" contained in the file "oregonat.exe". This program simulates the course of BŻ reactions on the basis of the modified model OREGONATOR, by solving the set of differential equations (15-19) by the Runge-Kutta or Fehlberg method [4,5]. Accept the concentrations of reagents proposed by the program. These concentrations are close to those used in the experiment. Observe on the screen the plots illustrating oscillations of the reagents concentrations, preceded by a period of latency (as in the experiment). Follow the phase shift of regent concentrations. After completion of the program, it should be

restarted but for the changed initial concentrations of selected substrates. It is particularly recommended that the reaction course should be followed carefully at different concentrations of cerium ions and hydrogen ions. After introduction of a new set of initial concentrations, the new values of rate constants of reactions 9-12 are calculated and printed on the screen (notice, that in modified OREGONATOR model, rate constants depend on hydrogen ion concentration).

Simulation of oscillating reactions (SciLab[1] package)

Make sure that the *SciLab* package is installed at the computer you use.
By clicking on the LV.sci, oregonator.sci or brusselator.sci file, open the *SciLab* script for simulation of the oscillating reaction of Lotka-Volterra or Belousov-Żabotyński with the use of the OREGONATOR or BRUSSELATOR model. Start the script by choosing execute/load in *SciLab*. The *SciLab* program calculates the concentrations of the reagents on the basis of the kinetic equations of relevant chemical reactions with the use of the *ode* function for numerical solution of differential equations [6] (the form of a differential equation is defined in the block *function ... endfunction*). Results of the calculations, in the form of time dependencies of chosen concentrations and the chosen attractor, are presented in a new window. Check the behaviour of the model for different initial concentrations, different rate constants and different mechanisms of the reaction (obtained by modification of the terms of the kinetic differential equations of chemical reactions). Check the model performance for the rate constants and initial conditions imposed in the experiment. Check the performance of similar kinetic models in the aspect of possible oscillating reactions.

Discussion

On the basis of the experiment and simulations answer the following questions.

1. Which of the reactions presented in the FKN scheme dominate in the upper and which in the lower parts of the plot illustrating the oscillations of the concentrations of the cerium ions? (Take into account the Stockholm convention and $E^0(Ce^{4+}/Ce^{3+})$ = +1.44V, E[Ag/AgCl(0.1M KCl)] = +0.228V)

2. What is the effect of cerium ions concentration on the period of oscillations? Why do the periods of oscillations change?

3. Explain why the rate constants of reactions 9-12 are functions of hydrogen ion concentration?

References

[1] O. Benini, R. Cervelatti, P. Fetto, *J. Chem. Educ.*, 73 (1996) 865.
[2] P. Strizhak, M. Menzinger, *J. Chem. Educ.*, 73 (1996) 868.
[3] A. Okniński, *Catastrophe Theory*, PWN - Polish Sci. Publ., Warszawa, 1992.
[4] G. Dahlquist, A. Bjork, *Metody numeryczne*, PWN, Warszawa, 1983.
[5] M. Marciniak, *Basic numerical functions and procedures in Turbo Pascal*, PWN, Warszawa, 1991.
[6]. http://help.scilab.org/docs/5.4.0/en_US/index.html

Supplementary references

[1] M. Orlik, Reakcje oscylacyjne. Porządek i chaos, WNT, Warszawa, 1996.

[1] Instruction on-line: http://help.scilab.org/docs/5.4.0/en_US/index.html

Related problems

Kinetic equations. Order and molecularity of chemical reaction. Catalyst. Kinetics of complex reactions (reversible, subsequent and chain reactions). Autocatalysis. Basic notions of electrochemistry: half-cell, Nernst equation for half-cell potential, redox electrode, reference electrode.

Related calculations – SciLab scripts

```
//Lotka-Volterra

//concentration
c = 1.0;

//rate constants
k1 = 1.0;
k2 = 0.5;
k3 = 0.8;

function yd = LotkaVolterra(t,y)
yd(1) = y(1)*(k1*c-k2*y(2));
yd(2) = y(2)*(k2*y(1)-k3);
endfunction

t = 0:0.02:20;
y = ode([1.0 2.0]',0,t,LotkaVolterra);

subplot(2,1,1);
plot2d(t',y');

subplot(2,1,2);
plot2d(y(1,:),y(2,:));
```

```
//Oregonator

//concentrations
c=0.04;

//rate constants
k1=0.005;
k2=1.0;
k3=1.0;
k4=1.0;
k5=0.0005;

function yd=oregonator(t,y)
yd(1)=y(1)*(-k2*y(2)+k3*c-2*k4*y(1))+k1*c*y(2)
yd(2)=y(2)*(-k1*c-k2*y(1))+k5*y(3)
yd(3)=2*k3*c*y(1)-k5*y(3)
endfunction

t=0:15:10*10^4;
y=ode([0 0 0.00025]',0,t,oregonator);

subplot(2,1,1)
plot2d(t',y')

subplot(2,1,2)
plot2d(y(1,:),y(3,:))
```

```
//Brusselator

//concentrations
c1=0.04;
c2=0.02;

//rate constants
k1=0.02;
k2=1.0;
k3=1.0;
k4=0.01;

function yd=brusselator(t,y);
yd(1)=y(1)*(-k2*c2+k3*y(1)*y(2)-k4)+k1*c1;
yd(2)=y(1)*(k2*c2-k3*y(1)*y(2));
endfunction

t=0:1:0.5*10^4;
y=ode([0.5 0]',0,t,brusselator);

subplot(2,1,1);
plot2d(t',y');

subplot(2,1,2);
plot2d(y(1,:),y(2,:));
```