OSCILLATING REACTIONS – BELOUSOV-ZHABOTINSKY REACTION

INTRODUCTION

The chemical reaction should occur if any reaction products are characterized by a lower free enthalpy (ΔG) than the reactants. The system will, therefore, seek to balance, or moves towards a state with lower energy resource. It is also an important entropic factor. The system will tend to a state with the lowest energy state, which is an increase of entropy. The resultant of these two factors, energy, and entropy, is described by the free energy (ΔF) (for V = const.) or free enthalpy ΔG (for p = const.). The above reasoning provides only the possibility of the reaction final state. Equilibrium thermodynamics does not determine the time after which the system reaches a new equilibrium state. Steady-state velocity can be described by chemical kinetics. For the most part, dependence of the products or substrates concentration is described as a function monotonically decreasing or increasing in time.

However, there are reactions that take place between two stationary states. These oscillatory responses are due to the concentration of reactants oscillating around a certain level. An example of concentration changes of the one of the reactants in time (oscillating Belousov-Zhabotinsky reaction) is shown in Figure 1. Such processes are widespread in living organisms.

A case in point is the stimulation of the heart rate, or the periodic potential variations resulting from changes in the concentrations of K^+ ions on the membrane of nerve cells. Oscillating reactions occur in systems that are far from equilibrium and are stimulated by irreversible processes. The oscillatory reaction mechanism is complex. Generally, the total velocity of this type is described by several constituent reactions.

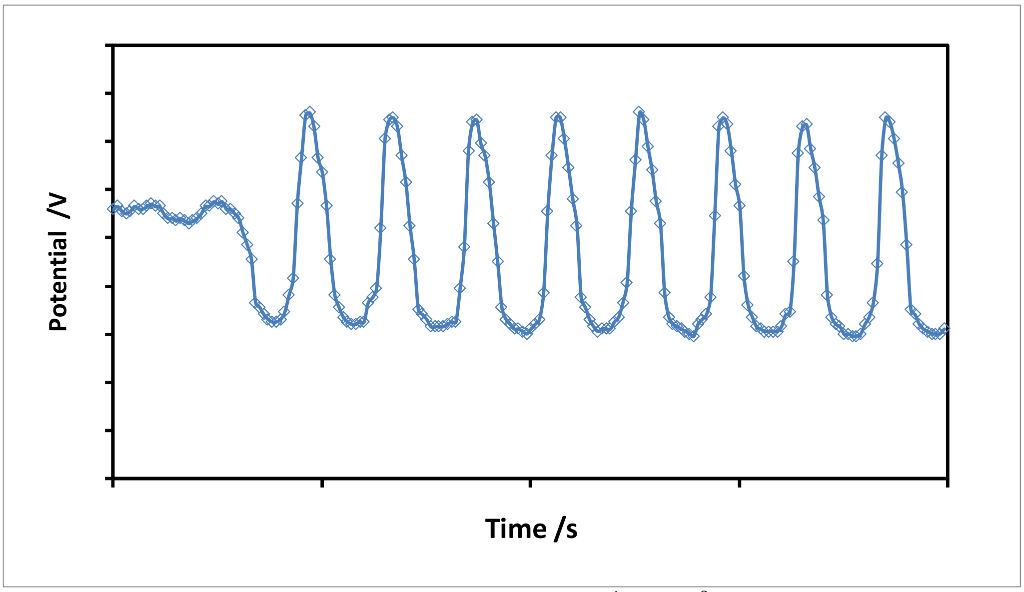

Figure 1. Profile of the ion concentration ratio changes of Ce^{4+} and Ce^{3+} in the Belousov-Zhabotinsky reaction measured potentiometrically.

The term of Belousov-Zhabotinsky reaction (BZ) should be regarded as a group of reactions consisting of oxidation of the organic compound by the bromate anion in the presence of a catalyst. The catalyst is usually a metal cation at two oxidation states: M^{+n} and $Mn^{+(n+1)}$. The next reaction is the oxidation of the cation M^{+n} by bromate to form $M^{+(n+1)}$, which in turn oxidizes the organic compound into primary form by reducing the M^{+n}. The reaction occurs in an acidic environment. There are several mechanisms of the BZ reaction, which are based on 20 to 50 reactions. All of these mechanisms are based on two general steps: catalyst oxidation by bromate (1) and the reduction of the organic substance (2).

$$M^{+n} \xrightarrow{BrO_3^-} M^{+(n+1)} \quad (1)$$

$$M^{+(n+1)} \xrightarrow{organic\ compounds} M^{+n} \quad (2)$$

Organic compounds oxidized are as follows:
- dicarboxylic acids: malic, malonic, oxaloacetic, 2 3-dihydroxy succinic or oxalic,
- unsaturated dicarboxylic acids: maleic, fumaric,
- ketones: butanone, acetylacetone, acetylcyclohexanone, cyclopentanone.

The catalysts are usually Ce^{+3} and Mn^{+2} ions. However, other cations complexes can also be used.

The acidity of the environment is created by the presence of H_2SO_4 but other acids can be used as well.

EXERCISE PURPOSE

The purpose of the exercise is the observation of the Belousov- Zhabotinsky reaction with cerium ions as a catalyst. Oscillating changes of cerium ions are determined by the measurements of the potential of platinum electrode vs the saturated calomel electrode.

APPARATUS

- PC Computer.
- Universal multimeter METEX.
- Magnetic stirrers and magnetic dipole.
- Calomel and platinum electrodes.
- Connecting wires.
- Lab stand.

LAB GLASS

- Beaker - 50 ml
- Beaker - 100ml.
- Pipette - 5 ml - 4 pcs.
- Wash bottle.

CHEMICALS

- Saturated solution of $KBrO_3$.
- Solution of $Ce(SO_4)_2$ - 0.002 mol·dm^{-3}.
- Solution of H_2SO_4 - 4 mol·dm^{-3}.

- Citric acid solution - 1.2 mol·dm^{-3}.

EXPERIMENT PROCEDURES

W a r n i n g !
In order to obtain accurate results, maintain the high purity of the lab glass used, in particular pipettes. After each use, the pipette should be rinsed thoroughly with distilled water.

1. Turn on the computer.
2. Place the calomel and platinum electrodes in the holder and connect to the METEX millimetre.
3. Start the METEX SCOPEVIEW application on the desktop and multimeter METEX.
4. METEX SCOPEVIEW setup:
   - Click the POWER to check communication transfer with METEX multimeter (measured values should be displayed
   - Click SCOPE to run the control setup
   - Set the range of the vertical axis (follow the instructor’s recommendations)
   - Check REPETITIVE option
   - Click RECORD button to enter a new file name to collect new data
   - Click the SCOPE to run the recording Panel
   - Recording starts after clicking RUN button, ending after STOP button
   - Additional information concerning the SCOPE VIEW program can be found in the service instructions present nearby the exercise.
5. Place the magnetic dipole in the reaction beaker.
6. Run the magnetic stirrer
7. Add the 5 ml solution of:
   - Calcium bromide
   - Citric acid
   - Cerium sulphate
8. Run recording by clicking RUN
9. Add 5 ml sulfuric acid solution after recording c.a. 20 seconds
10. Stop recording after 20 minute of reaction.
11. Repeat reactions with different values of sulfuric acid (4 and 3 ml.)

CALCULATION

Using the data obtained, draw the dependence of the potential of the platinum electrode on reaction time. Determine induction time and the amplitude of the reactions for different concentration of sulphuric acid.

Template of the table and draft of the study

……………………………... *Faculty* ……………………………….. *Field of study* *Full-time/ part-time studies*	……………………………………………… *Name and surname*	……………………………….... *Date:*
Group no.: ………………… *Team no.:* …………………	……...…………… *Exercise no.:*	………………………………….. *Instructor:*

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Nr grupy: …………………... *Nr zespołu:* …………………..	……...…………… *Nr ćwiczenia:*	………………………………….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: