

Belousov Zhabotinsky(BZ) Reaction - Overview

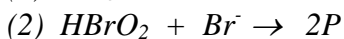
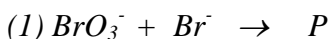
The reaction was originally developed as an inorganic representation of the biochemical Krebs cycle

It involves the acidic oxidation by bromate of an organic substrate in the presence of a metal catalyst

The mechanism BZ reaction can be understood using a 3 variable representation of the chemistry developed in the 70's. This is known as the Oregonator model. It considers the BZ mechanism to be composed of three fundamental processes. All of these processes are occurring simultaneously. However, during different parts of the oscillations different processes can be considered to be dominant

The three important species are HBrO_2 (bromous acid), Br^- (bromide) and the metal catalyst which can be in one of two oxidation states M^{2+} (red) and M^{3+} (blue). The species P indicates 'other products'. MA refers to malonic acid (the organic substrate)

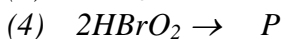
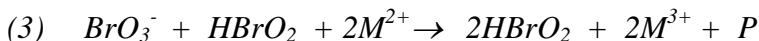
Process A



What is going on during process A?

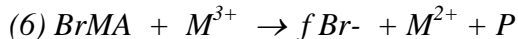
- a. the bromide concentration is high.*
- b. the bromide consumes HBrO_2 in the system*
- c. the bromate reacts to remove the bromide*

Process B



- a. The bromide is eventually consumed by process A*
- b. HBrO_2 is then produced autocatalytically (step 3) and the metal catalyst is converted from a reduced to oxidized state (with a corresponding red to blue colour change)*
- c. This process is braked by the self reaction of HBrO_2 (step 4)*

Process C



Bromide is produced and the metal catalyst is converted back from blue to red

Experimental procedure A – Homogeneous reaction

In this part of the experiment you make up the catalyst-free solution. Then add the catalyst and observe any oscillations.

I. Preparation of reaction

50 ml of catalyst free BZ solution is prepared using

- a. 4 ml of 1 M NaBr
- b. 8 ml of 1 M malonic acid
- c. 13 ml 3 M H₂SO₄
- d. 18 ml of distilled water
- e. 7 ml of 2 M NaBrO₃

a. The reactants should be added in the above sequence. On the addition of the final reactant the solution will turn brown (due to the production of bromine). You can use a measuring cylinder to measure out the reactants. The flask should be covered and left for approximately 3 minutes until the solution clears

b. tip ~1/2 contents of the volumetric flask into a small beaker.

c. now add 0.3 ml of catalyst solution. Gently swirl the contents to ensure good mixing.

d. keep swirling - the solution should(!) oscillate from red to blue.

Interaction of coupled micro-oscillators.

The aim of this work is to identify phase/frequency relationships between spatially coupled oscillators

The experiment utilizes a catalyst free BZ reaction solution and catalyst loaded micrometer beads. An independent bead (i.e. a bead remote from all other beads) will undergo oscillations in the oxidation state of the catalyst on the bead surface. A single bead can be considered to be a micro version of the homogeneous reaction you performed in the beaker in part A.

The catalyst is red in the reduced state and blue in the oxidized state. During this oscillation in the redox state a number of chemicals are generated at the bead surface (mainly HBrO_2 and Br^-) which will diffuse out into the surrounding solution. These chemicals have a short lifetime in the surrounding solution (step 1 and step 2 lead to their consumption in the surrounding solution). However if another bead is close enough, the diffusing chemicals can lead to coupling of the oscillation to that of nearby neighbours.

At large distances the beads are expected to act independently and a collection of beads will show a range of natural frequencies. At high densities of beads, when the beads are basically touching, chemical waves are seen with the waves initiated at high frequency pacemaker sites. At intermediate distances the weak coupling may lead to a number of interesting phenomena such as synchronization, resonance, entrainment and dephasing.

The bead system based system is constructed using the following catalyst-free recipe

- a. 2ml of 1 M NaBr
- b. 4 ml of 1 M malonic acid
- c. 12 ml 3 M H_2SO_4
- d. 11 ml of distilled water
- e. 21 ml of 2 M NaBrO_3

Before mixing the reactants make sure you have tipped the contents of your volumetric flask into the waste vessel and wash this (as well as the measuring cylinder)

The reactants should be added in the above order. On the addition of the final reactant the solution will turn brown (due to the production of bromine). The flask should be covered and left for approximately 3 minutes until the solution clears

Add a few beads to the petri dish and then add the catalyst free solution. (Floating beads are a problem at this point - try to minimize floaters)

Oscillator behavior we are interested in

- a. the natural frequency of a set of beads
- b. two beads which are initially far apart. Move one closer to the other. Measure their frequency as they move together. Plot frequency relationships as a function of separation. Phase relationships as a function of separation
- c. Single group of 10+ close packed beads. Observe their frequency distribution
- d. set of 10+ beads- initially far apart - decrease their average separation. What happens to the frequency and phase relationship of the beads as they are moved closer together.

In order to take measurements:

1. arrange the beads into an appropriate spatial structure
2. run quick_movie2 for 100 frames - make a note of the time you run quick_movie2
3. make changes to the spatial arrangement of beads
4. run quick_movie2 (also make a note of the time).
5. repeat the above as many times as necessary

Movies you create are found in

C:\mark\india\data\%todays date%\movie\qm_%starttime%.m

Data analysis

The important data obtained from each experiment is a time series of bead gray intensity. The beads must first be identified.

Use **setup_beads_wks_shang** to select the experimnt of interest. The file to load is in the directory

C:\mark\india\data\%todays date%\parameter\p%date%_%time%.m