# The Fascinating World of Oscillations in Chemistry

## Instructions to the demonstration experiments

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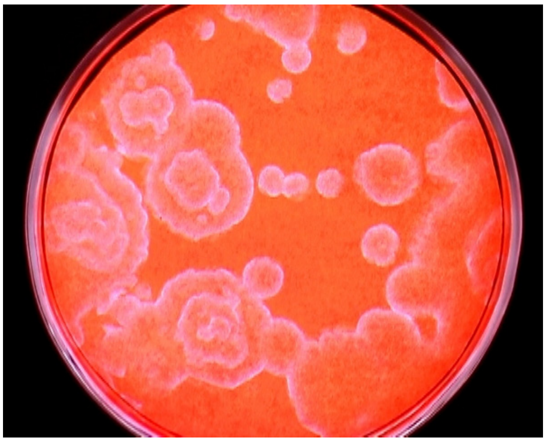
# Chemical Waves



## Equipment:

two beakers (50 mL)
two beakers (100 mL)
graduated cylinder (100 mL)
volumetric pipet (2 mL)
two volumetric pipets (10 mL)
magnetic stirrer with stir bar
spatula
Petri dish (diameter: 10 cm)
overhead projector and black cardboard

## Chemicals:

sodium bromate
concentrated sulfuric acid
malonic acid
sodium bromide
ferroin indicator solution (0.1 wt.%)

## Safety:

sodium bromide ($NaBrO_3$):

H272, H302, H315, H319, H335
P210, P261, P305 + P351 + P338

concentrated sulfuric acid ($H_2SO_4$):

H290, H314
P280, P301 + P330 + P331, P303 + P361 + P353, P305 + P351 + P338, P310

malonic acid ($CH_2(CO_2H)_2$):

H302, H318
P273, P305 + P351 + P338

The chemicals cause very severe skin burns and eye damage. Therefore, it is absolutely necessary to wear a lab coat, safety goggles and protective gloves. Because bromine is produced during the preparation, this step should be performed in a fume hood.

## Procedure:

Preparation: The following solutions have to be prepared:
Solution A: 2 mL of concentrated sulfuric acid are added to 67 mL of deionized water. Subsequently, 5 g of sodium bromate are dissolved in the acidic solution.
Solution B: 1 g of malonic acid is dissolved in 10 mL of deionized water.
Solution C: 1 g of sodium bromide is dissolved in 10 mL of deionized water.
Under a fume hood, a 100 mL beaker is placed on the magnetic stirrer. 12 mL of solution A are poured into the beaker. Subsequently, 2 mL of solution B and 1 mL of solution C are

added while stirring. After the addition of the last solution, one can observe a yellow brown color caused by the production of bromine. After the solution has cleared, 3 mL of the ferroin indicator solution are added.
Procedure: The solution is gently poured into the Petri dish on the overhead projector so that it just covers the bottom (for better visibility of the effect, it is recommended to cover the free projector area by black cardboard).

**Observation:**

After a short while, some light blue spots appear in the solution. These spots grow into a series of expanding more or less concentric rings. The colors disappear if the dish is shaken, and then reappear. Eventually, a noticeable gas evolution begins to take place additionally.

**Explication:**

Oscillating chemical reactions such as the Belousov-Zhabotinsky reaction are reactions that show periodic variations of some of the components in time or space. In cases where one (or more) of the components has a visible color, they are spectacular and suited to stimulate the students´ interest in chemistry. However, the mechanisms of these reactions are very complex. The Belouzov-Zhabotinsky reaction (in short BZ reaction), for example, the reaction between malonic acid and bromate with the overall reaction equation

$$3\ CH_2(CO_2H)_2|w + 4\ BrO_3^-|w \rightarrow 4\ Br^-|w + 9\ CO_2|w + 6\ H_2O|l,$$

is thought to involve around 18 different steps which have been the subject of a number of research papers. But in order to gain a first understanding of this type of reaction, the following strongly simplified reaction scheme can be considered:
The first step should be an autocatalytic process where X is an intermediate:

$$A + X \xrightarrow{k_1} 2\,X\,.$$

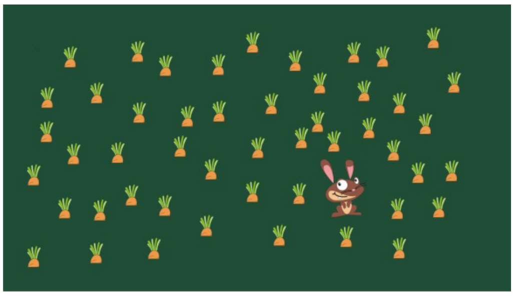
*k* is a rate coefficient (rate constant). In the second step X reacts with another intermediate Y in a second autocatalytic process:

$$X + Y \xrightarrow{k_2} 2\,Y\,.$$

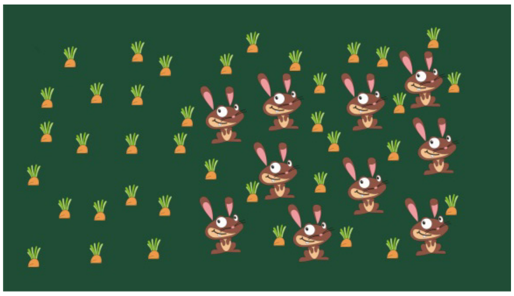
The final step is the conversion of Y to the stable product P:

$$Y \xrightarrow{k_3} P\,.$$

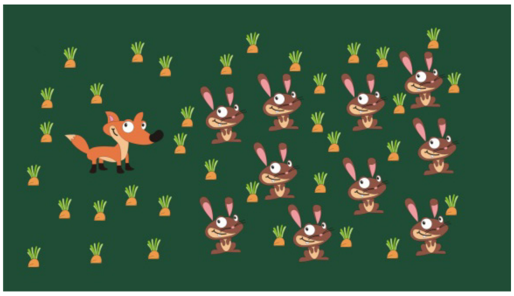
To visualize the situation predator-prey models can be used. Here, A can be carrots, X a population of rabbits, Y a population of foxes and P the foxes that have died.



At the beginning, there is a real abundance of carrots.

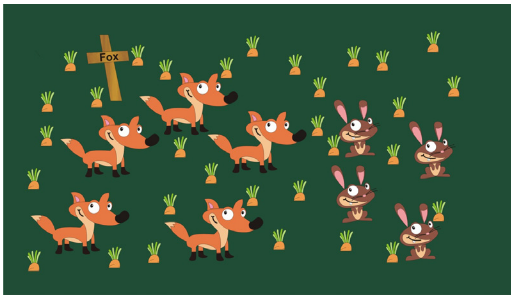


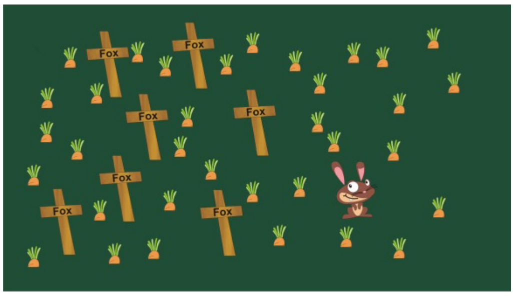
The rabbits live very well on carrots and become plentiful.



This brings the foxes into to arena because they like to eat rabbits.

The number of the foxes starts to grow whereas the rabbit population diminishes.




Eventually, the voracious foxes have eaten nearly all of the rabbits. Famine sets in and the foxes die bringing the system back to the first step.

In the case of the BZ reaction, the reduced (red color) and oxidized states (blue color) of the redox catalyst ferroin are oscillating out of phase such as the rabbit and the fox populations. The cycles repeat as long as the supply of reactant (carrots) holds out.

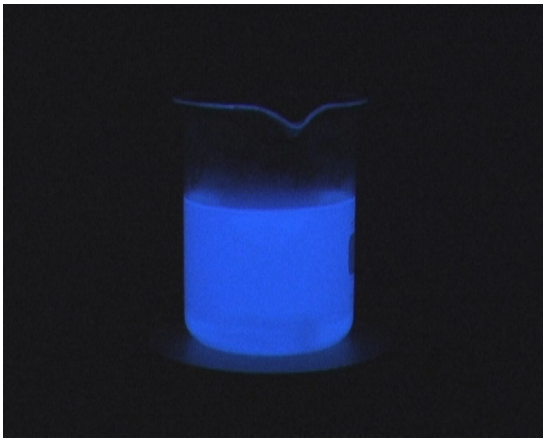
The coupling between an autocatalytic chemical reaction such as the BZ reaction and diffusion by using an unstirred layer of the reaction mixture can create spatial structures. One can observe the propagation of succeeding concentration fronts, a phenomenon called “chemical waves.”

**<u>Disposal:</u>**

After the reaction has been completed, the solution is neutralized with sodium hydroxide. The precipitate is separated by sedimentation and decantation and subsequently disposed of as inorganic hazardous waste. The liquid is flushed down the drain with copious amounts of water.

Reference:
http://mysite.science.uottawa.ca/mroger2/BZreaction.html

# Chemical Light Buoy



## Equipment:

three volumetric flasks (1000 mL)
two beakers (250 mL)
beaker (500 mL)
beaker (1000 mL)
graduated cylinder (50 mL)
two graduated cylinders (200 mL)
graduated cylinder (300 mL)
hotplate stirrer with stir bar
spatula

## Chemicals:

hydrogen peroxide solution (30 % w/w)
potassium thiocyanate
copper sulfate pentahydrate
sodium hydroxide
luminol

## Safety:

hydrogen peroxide solution ($H_2O_2$):

H302, H315, H318, H335
P280, P302 + P352, P305 + P351 + P338, P310

potassium thiocyanate (KSCN):

H302 + H312 + H332, H412
P261, P280, P302 + P352

copper sulfate pentahydrate ($CuSO_4 \cdot 5\,H_2O$):

H302, H318, H410
P273, P280, P301 + P312, P305 + P351 + P338, P330

sodium hydroxide (NaOH):

H290, H314
P280, P301 + P330 + P331, P305 + P351 + P338, P310

luminol ($C_8O_7N_3O_2$):

H302, H315, H319, H335
P280, P302 + P352, P304 + P340, P305 + P351 + P338

The chemicals cause very severe skin burns and eye damage. Therefore, it is absolutely necessary to wear a lab coat, safety goggles and protective gloves.

**Procedure:**

Preparation: The following solutions have to be prepared:
Solution A: 0.15 M KSCN: 14.55 g of potassium thiocyanate are dissolved in deionized water. Subsequently, the volume is made up to 1000 mL with deionized water.
Solution B: $6 \times 10^{-4}$ M $CuSO_4 \cdot 5\,H_2O$: 0.15 g of copper sulfate pentahydrate are dissolved in deionized water. Afterwards, the volume is made up to 1000 mL with deionized water.
Solution C: 0.1M NaOH and $3.7 \times 10^{-3}$ M luminol: 4 g of natrium hydroxide are dissolved in 100 mL of deionized water and then 0.55 g of luminol are added while stirring. This solution is subsequently filled up to 1000 mL with deionized water.
Procedure: The 1000 mL beaker is placed on the hotplate stirrer. 150 mL of solution A are poured into the beaker. Subsequently, 300 mL of solution B and 150 mL of solution C are added while stirring. Then, the solution is heated to a temperature of about 45 °C. When the desired temperature is reached, 30 mL of the hydrogen peroxide solution are added. Then, the lights have to be switched off.

**Observation:**

After a short while, the solution produces an iridescent sky blue glow for about one second. The light pulses appear nine or ten times with intervals of about thirty seconds in between before the reaction stops. When the lights are turned on, one can observe an evolution of gas.

**Explication:**

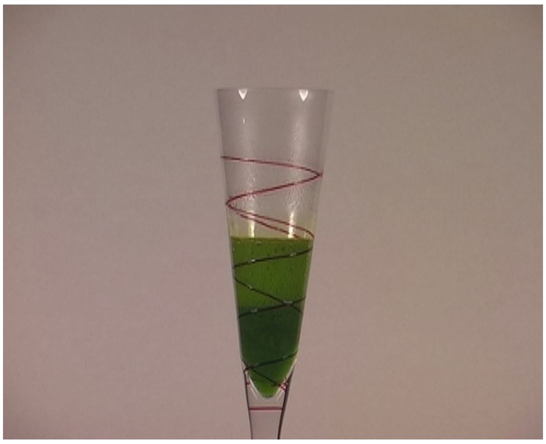
In the present experiment, a chemiluminescent substance (luminol) interacts with a oscillating system (Cu(II)-catalyzed reaction between $H_2O_2$ and KSCN). Because of the light emission, such chemiluminescent oscillating reactions are especially fascinating.
Whereas the heating of the solution to a temperature of about 45 °C enhances the effect during the demonstration by decreasing the oscillation periods compared to room temperature, a temperature above 55 °C should be avoided because the oscillations would last for only a short time. The light emission would be even quenched at a temperature of 65-70 °C.

**Disposal:**

After the experiment, the solution is concentrated in a water bath and the residue is collected in the container for heavy metal waste.

Reference:
H. W. Roesky: „Glanzlichter chemischer Experimentierkunst“, Wiley-VCH (2006), p. 131-132 (in German)

# Dancing Absinthe



## Equipment:

champagne flute or glass
beaker (100 mL)
graduated cylinder (50 mL)
3 graduated cylinders (10 mL)
spatula

## Chemicals:

hydrogen peroxide solution  (30 % w/w)
copper(II) chloride dihydrate
concentrated hydrochloric acid (37 % w/w)
deionized water
concentrated sodium hydroxide solution (32 % w/w) or acetone

## Safety:

hydrogen peroxide solution ($H_2O_2$):

H302, H315, H318, H335
P280, P302 + P352, P305 + P351 + P338, P310

copper(II) chloride dihydrate ($CuCl_2 \cdot 2\,H_2O$):

H290, H302 + H312,H315, H318, H410
P273, P280, P301 + P330 + P331, P302 + P352, P305 + P351 + P338, P312

concentrated hydrochloric acid (HCl):

H290, H314, H335
P280, P303 + P361 + P353, P304 + P340, P305 + P351 + P338, P310

concentrated sodium hydroxide solution (NaOH):

H290, H314
P280, P303 + P361 + P 353, P305 + P351 + P338, P310

The chemicals cause very severe skin burns and eye damage and the vapors may also cause respiratory irritation. Therefore, it is absolutely necessary to wear a lab coat, safety goggles and protective gloves and to work in a fume hood.

## Procedure:

Preparation: The champagne flute is filled with concentrated sodium hydroxide solution and allowed to stand for approx. 12 hours. Subsequently, the flute is carefully rinsed with deionized water. Alernatively, the flute can be rinsed with some acetone. Afterwards, the remaining acetone is allowed to evaporate.
Procedure: 10 g of copper(II) chloride dihydrate are dissolved in a mixture of 50 mL of concentrated hydrochloric acid and 10 mL of deionized water in the beaker. 10 mL of the strongly acidified copper(II) chloride solution are poured in the champagne flute and 10 mL

of hydrogen peroxide solution are added. Afterwards, the flute should not be touched anymore.

**Observation:**

After a few minutes, an evolution of gas starts which becomes more and more intense whereby a foam head is formed. In the following, the strength of gas evolution and foam formation changes in rhythmical intervals for several minutes. During the course of the reaction, the frequency of the oscillations increases until only a strong evolution of gas can be observed. Thereby, hydrochloric acid vapors escape and finally the reaction comes to a standstill after the consumption of the hydrogen peroxide.

**Explication:**

The present oscillating reaction is based on the decomposition of hydrogen peroxide. This decomposition is homogeneously catalyzed by many heavy metal ions such as $Fe^{3+}$ but also by a hydrochloric copper(II) chloride solution. There are indications that not only the copper(II) ions and the copper chloro complexes are catalytically active but also the chloride ions. In the case of the copper(II) ions one assumes a reaction chain analogous to the HABER-WEISS mechanism.
First, the produced oxygen remains physically dissolved in the solution. Only when the solution is supersaturated with $O_2$, larger amounts of gas can be released and the solution foams up. Thereby, more $O_2$ is released as can be reproduced by the catalytic reaction. As a consequence, the concentration of oxygen in the solution falls below the saturation limit and the gas evolution decreases remarkably. Only if the solution is again supersaturated, the next strong gas evolution can take place.

**Disposal:**

After the experiment, the solution is neutralized and poured into the container for heavy metal waste.

Reference:
H. Kunz, F. Johannsmeyer, M. Oetken: „Das pulsierende Sektglas“, *ChemKon*, Vol. 7 (2000), p. 30–31 (in German)