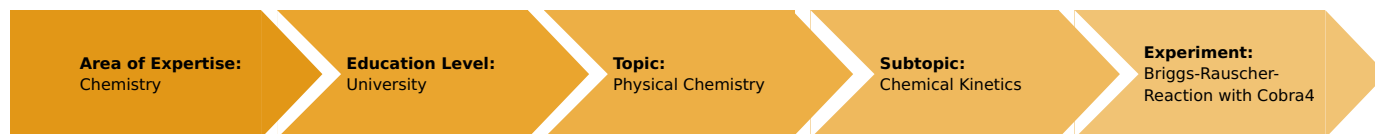


Briggs-Rauscher-Reaction with Cobra4 (Item No.: P3121660)

Curricular Relevance



Difficulty



Intermediate

Preparation Time



1 Hour

Execution Time



1 Hour

Recommended Group Size



2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g
- PC with USB interface, Windows XP or higher

Experiment Variations:

Keywords:

homogenous oscillating reactions, autocatalytic reactions, measurement of potentials in reactions

Overview

Short description

Related Topics

Homogenous oscillating reactions, autocatalytic reactions, measurement of potentials in reactions.

Principle

Under some circumstances, complex reactions can occur whose reaction rate does not monotonously change, but is subject to periodic fluctuations. These fluctuations can be experimentally followed by measuring the potential over a definite time period.



Fig. 1: Experimental set up.

Fig. 1: Experimental set up.

Safety instructions



Sulphuric acid, 95 - 98 %

H314: Causes severe skin burns and eye damage

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P301 + 330 + 331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.

P309 + 310: IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.

P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing

Potassium iodate

H272: May intensify fire; oxidizer

H315: Causes skin irritation

H319: Causes serious eye irritation

H335: May cause respiratory irritation

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P220: Keep/Store away from clothing/.../combustible materials.

P221: Take any precaution to avoid mixing with combustibles.

P261: Avoid breathing dust/fume/gas/mist/vapours/spray

P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing.

Malonic acid

H302: Harmful if swallowed.

H318: Causes serious eye damage.

H319: Causes serious eye irritation.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

P262: Do not get in eyes, on skin, or on clothing.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing.

P310: Immediately call a POISON CENTER or doctor/physician.

Manganese(II) sulphate monohydrate

H373: May cause damage to organs through prolonged or repeated exposure

H411: Toxic to aquatic life with long lasting effects

P273: Avoid release to the environment

P314: Get Medical advice/attention if you feel unwell

Hydrogen peroxide, 30 %

H271: May cause fire or explosion; strong oxidizer.

H332: Harmful if inhaled.

H302: Harmful if swallowed.

H314: Causes severe skin burns and eye damage.

H318: Causes serious eye damage.

P220: Keep/Store away from clothing/.../combustible materials

P261: Avoid breathing dust/fume/gas/mist/vapours/spray

P280: Wear protective gloves/protective clothing/eye protection/face protection

P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing

P310: Immediately call a POISON CENTER or doctor/physician

Oxygen

H270: May cause or intensify fire; oxidizer.

P220: Keep/Store away from clothing/.../combustible materials.

Iodine

H315: Causes skin irritation.

H372: Causes damage to organs through prolonged or repeated exposure.

H400: Very toxic to aquatic life.

P273: Avoid release to the environment.

Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Wireless/USB-Link incl. USB cable	12601-10	1
2	Cobra4 Sensor-Unit Chemistry	12630-00	1
3	curricuLAB measureLAB	14580-61	1
4	Holder for Cobra4 with support rod	12680-00	1
5	USB charger for Cobra4 Mobile-Link 2 and Wireless/USB-Link	07932-99	1
6	Adapter, BNC-plug/socket 4 mm	07542-26	1
7	Teclu burner, DIN, natural gas	32171-05	1
8	Safety gas tubing, DVGW, sold by metre	39281-10	1
9	Hose clip f.12-20 diameter tube	40995-00	2
10	Lighter f.natural/liquified gases	38874-00	1
11	Tripod, ring-d=100 mm, h=180 mm	33299-00	1
12	Wire gauze 120x120mm, ceramic cen.	33287-03	1
13	Reference electrode, AgCl	18475-00	1
14	Platin.electrode in prot.tube,8mm	45206-00	1
15	Connecting cord, 32 A, 500 mm, red	07361-01	1
16	Retort stand, h = 750 mm	37694-00	1
17	Right angle boss-head clamp	37697-00	2
18	Holder for two electrodes	45284-01	1
19	Spring balance holder	03065-20	2
20	Beaker, low, BORO 3.3, 400 ml	46055-00	1
21	Beaker, low, BORO 3.3, 150ml	46060-00	2
22	Beaker, high, BORO 3.3, 50 ml	46025-00	2
23	Beaker, high, BORO 3.3, 600 ml	46029-00	1
24	Glass rod, boro 3.3, l=200mm, d=4mm	40485-02	1
25	Graduated cylinder 100 ml	36629-00	1
26	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
27	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
28	Powder spatula, steel, l=180mm	47561-00	1
29	Wash bottle, plastic, 500 ml	33931-00	1
30	Protecting glasses, clear glass	39316-00	1
31	Gloves, Neoprene, medium	46347-00	1
32	Boiling beads, 200 g	36937-20	1
33	Pasteur pipettes, 3ml, PE, 500pcs	36616-00	1
34	Potassium iodate 100 g	31443-10	1
35	Sulphuric acid, 95-98% 500 ml	30219-50	1
36	Malonic acid 100 g	31551-10	1
37	Manganese-II sulphate 250 g	31559-25	1
38	Starch, soluble 100 g	30227-10	1
39	Hydrogen peroxide, 30%, 250 ml	31710-25	1
40	Water, distilled 5 l	31246-81	1


Task

1. Measure the change in potential during a Briggs-Rauscher.reaction.

Set-up and procedure



Prepare the solutions required for the experiment as follows:

- Solution 1: Dissolve 7.1 g of potassium iodate and 2.4 g of sulphuric acid in 300 ml of water in a 400 ml beaker.
- Solution 2: Dissolve 2.6 g of malonic acid and 0.5 g of manganese(II) sulphate monohydrate in 120 ml of water in a 150 ml beaker.
- Solution 3: Add 1.0 g of starch to 100 ml of water in a 150 ml beaker and use the Teclu burner to help dissolve it. Subsequently transfer 45 ml of the solution to a 50 ml beaker.
- Solution 4: Measure out 40 ml of the 30 % hydrogen peroxide solution and transfer it to a 50 ml beaker.
- Plug the Cobra4 Sensor-Unit Chemistry on the Cobra4 Wireless-Link and fix the combination to the stand.
- Start the PC and Windows®.
- Connect the PC with the Cobra4 Wireless/USB Link via USB cable or wireless connection.
- Switch on the Cobra4 Wireless-Link. The sensor is now automatically recognized and is allocated to an ID number, which is displayed in the Cobra4 Wireless-Link via the Data LED.
- Set up the experiment as shown in Fig. 1.
- Use stand accessories to fix the electrode holder to the stand.
- Fix the spring balance holder to the electrode holder.
- Fix the silver chloride reference electrode and platinum electrode with the spring balance holder to the stand.
- Plug the BNC-socket/4 mm sockets adapter to the pH-input of the Cobra4 Sensor-Unit Chemistry.
- Connect the silver chloride reference electrode to the black socket of the adapter.
- Use connecting cords to connect the platinum electrode to the red socket of the adapter.
- Slip the magnetic stirring bar in the 600 ml beaker, pour solution 1 in and place the beaker on the magnetic stirrer.
- Switch the magnetic stirrer on and adjust it to a medium stirring rate.
- Start the software "measureLAB" .

Load the "Briggs-Rauscher reaction" experiment. (Experiment> Open experiment). All pre-settings that are necessary for measured value recording are now carried out.




- Dip the electrodes in the solution and click on  in the icon strip to start the measurement.
- Successively pour solutions 2, 3 and 4 into the 600 ml beaker.
- Observe the change in colour of the reaction mixture in the beaker and also watch the curve of measurement values displayed by the computer monitor.
- When no further colour changes occur, click on  in the icon strip to stop measurement.
- Save your project by clicking on the button  in the top bar.

Fig. 2 shows the graph of the measurement.

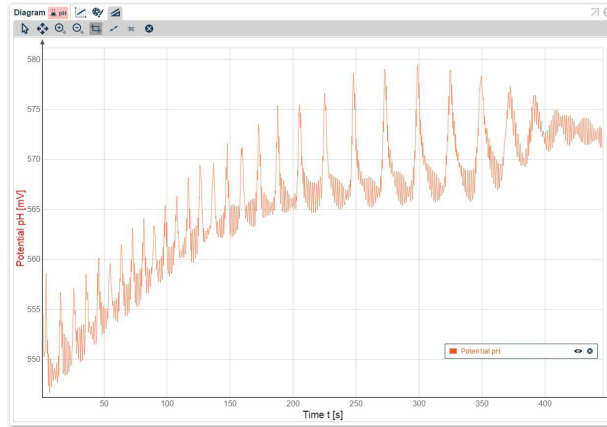


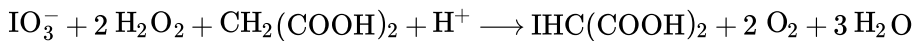
Fig. 2: Graph of measured potential against time.

Theory and evaluation

The Briggs-Rauscher reaction is a so-called homogeneous oscillating reaction, i.e. the reaction rate of the complete process is subject to periodic fluctuations. In general, oscillating reactions can always occur when the following conditions are fulfilled: The reaction must run highly exergonic ($\Delta G \ll 0$). At least one of the reaction steps must contain a positive or negative back-coupling. Such back-coupling processes occur when the result of the individual partial steps of the reaction, such as changes in temperature or concentration, act back on the rate constants of the individual partial steps of the reaction. In this way, the whole reaction becomes non-linear.

For the Briggs-Rauscher reaction, as typical example of an oscillating reaction, the following is true:

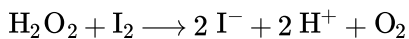
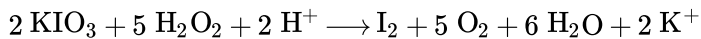
The gross equation is here:



The complete process runs irreversibly in the direction of the reaction arrow during the whole reaction time.

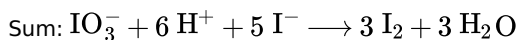
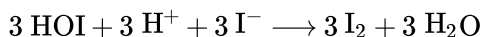
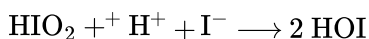
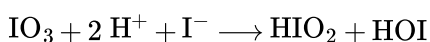
The overall reaction can be divided into the following individual steps:

Starting reaction:

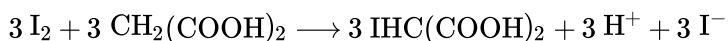


The iodine which is formed is responsible for the amber colouring of the solution. As soon as sufficient iodide has been produced in the third step, I_3^- -ions are formed which infiltrate in the starch macromolecule. The resulting starch- I_3^- -complex has a characteristic deep blue colour. The iodide starts the following process A simultaneously.

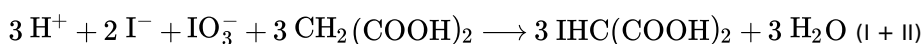
Process A:



The free iodine now reacts with the malonic acid:



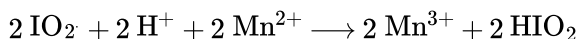
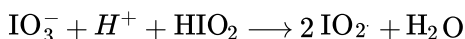
(I) and (II) combined give the overall process A:



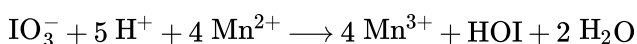
Taken altogether, iodide is consumed and iodomalonic acid is formed in process A. The amount of free iodide is hereby reduced, the starch- I_3^- complex can no longer be formed, the colour changes to colourless and the electrochemical potential drops.

Alongside the process A which has just been described, there is a further process B, which acts against the result of process A. The concentration of the HIO_2 in process A is hereby decisive for the initiation of process B, as, when the iodide concentration has become small enough, HIO_2 will no longer be captured by it and can start a radical reaction itself:

Process B:

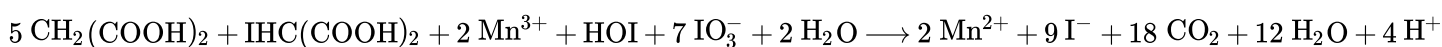


The overall result of process B is therefore:



The autocatalytic formation of HIO_2 is particularly interesting and is decisive for the complete process, i.e. two of the same sort are formed from one molecule. This leads to an exponential increase in the concentrations of the two species Mn^{3+} and HOI . These are so now available for a third partial process C.

Process C:



Mn^{2+} - and, in particular, iodide ions are reformed in this process. As a result, the concentration of free iodine rapidly increases. The starting steps of process A so again gain the upper hand. The starch- I_3^- complex is again formed. There is a colour change to blue and the electrochemical potential increases. Process C so switches between process A and process C and causes the observed oscillations.

The processes break down when there is too great a reduction in the concentrations of the individual reactants. In principle, the reaction could be kept in the oscillating condition for as long as wanted by a steady addition of reactants.

Data and results

As soon as the four solutions have mixed with each other in the beaker, the colour changes from colourless to a very intensive blue. Exactly at this moment, the graph which is displayed shows an increase in the potential (see Fig. 3).

About 25 seconds later there is a sudden change in the colour of the mixture back from blue to colourless. This change is accompanied by an abrupt decrease in the potential measured.

The reaction mixture changes momentary from colourless to amber-coloured and then back to blue. The measured potential increases rapidly again (see Fig. 3). The mixture remains blue for about 15 seconds, after which, the colour again changes suddenly to colourless and amber-coloured. A lowering of the measured potential accompanies this.

The colour change from blue to colourless and amber-coloured and the resulting decrease in the potential takes place a further eight times. The time for which the solution is blue continually increases, however, whereas the phases in which the mixture is colourless or amber-coloured continually become shorter. This is shown in the graph of the measurement not only by the continual increase in the distance between individual peaks, but also by a continually increase in the change of potential from one colour change to the next (see Fig. 3).

The last colour change to colourless and amber takes place after about 335 seconds.

Disposal

The diluted and neutralized (pH 6-8) solutions of sulphuric acid and malonic acid can be disposed by rinsing to the drain.

The remains of hydrogen peroxide and potassium iodate have to be added carefully to an acidic aqueous solution of sodium thiosulphate. When the reaction has finished, dilute the solution with water, neutralize (pH 7-8) this solution and rinse it to the drain.

The manganese(II) sulphate have to be collected in a correspondingly labelled container and passed to safe heavy metal waste disposal.