OSCILLATING CHEMICAL REACTIONS

HISTORY

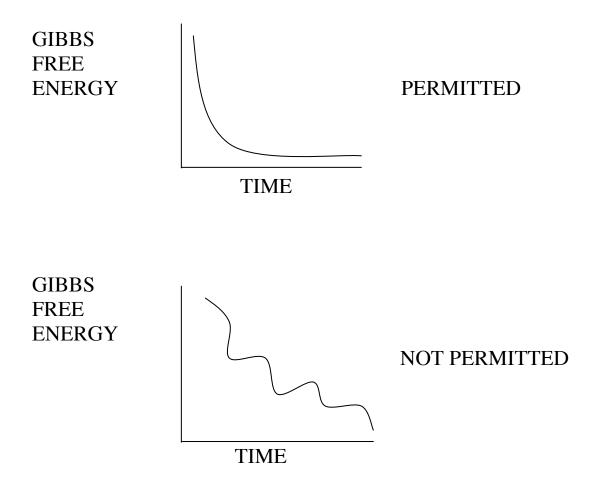
Every living system is believed to contain hundreds of chemical oscillators. In 1828, A.T. Fechner was the first scientist to publish a report of oscillations in a chemical system. He described an electrochemical cell that produced an oscillating current. In 1899, another scientist by the name of W. Ostwald observed that the rate of chromium dissolution in acid periodically increased and decreased. Both of these systems were heterogeneous and it was believed then, and through much of the last century, that homogeneous oscillating systems were nonexistent. While theoretical discussions date back to around 1910, the systematic study of oscillating chemical reactions and of the broader field of non-linear chemical dynamics did not become well established until the mid 1970's.

The types of reactions make for some of the most fascinating chemical demonstrations. To many they are examples of "chemical magic." To those having some familiarity with chemistry, they pose both mystery and challenge. One reason that these reactions are so fascinating is that they appear to contradict known chemical behavior. Experience tells us that under a given set of constant conditions, a chemical reaction goes in only one direction. It rarely appears to reverse its direction, let alone repeatedly.

When considering a chemical oscillator, one can first draw an analogy to a physical oscillator such as a pendulum. A pendulum oscillates from side to side through an equilibrium position. A chemical oscillator is quite different. It does not oscillate through its equilibrium position and, in actuality, is far from equilibrium. If such reactions oscillated through their equilibrium positions they would defy the Second Law of Thermodynamics. This Law asserts that once a chemical system reaches equilibrium it cannot deviate from that condition spontaneously.

The oscillations in an oscillating chemical reaction are driven by a decrease in free energy of the system. A decrease in free energy is what drives all chemical reactions but not all reactions oscillate. So why do they oscillate? There must be unique pathways, or reaction mechanisms, that these reactions take as they approach equilibrium.

In a closed system, the free energy must decrease monotonically.



The concentration of reactants must continually decrease while the concentration of products increase; however, the concentration of the intermediates can oscillate as the system relaxes towards equilibrium.

In an oscillating system the energy-releasing reaction can follow at least two different pathways, and the reaction periodically switches from one pathway to another. One of these pathways produces a specific intermediate, while another pathway consumes it. The concentration of this intermediate triggers the switching of pathways. When the concentration of the intermediate is low, the reaction follows the producing pathway, leading then to a relatively high concentration of intermediate. When the concentration of the intermediate is high, the reaction switches to the consuming pathway. Eventually the reaction reverts to the producing pathway and the cycle continues. The reaction reaches equilibrium when the energy-releasing reaction that drives the oscillations reaches completion.

REACTION MECHANISMS

In order to better understand why and how these reactions occur, we must first examine the minimum conditions that must be met in order for an oscillation to occur. To see how a reaction pathway affects the concentration of components of a reaction mixture B. Z. Shakashiri, the author of <u>Chemical Demonstrations: A</u> <u>Handbook for Teachers</u>, examined several hypothetical reaction mechanisms and the pattern of concentration changes that are produced.

The first reaction mechanism is considered to be one of the simplest ones. The overall reaction is the conversion of A to P, involving one intermediate X as shown below:

Mechanism (1)	$A \rightarrow X$	Step 1
	$X \rightarrow P$	Step 2

In the reaction above, the relative rates of each step may vary. In one case, step 1 can occur at a much faster rate than step 2. As a result, A is converted to X quickly. X will then be slowly converted to P. In a second case, step 1 can occur at the same rate as step 2, resulting in [A] decreasing at about the same rate as [P] increases. In a third case, step 1 can occur at a much slower rate than step 2, resulting in X being converted to P almost as quickly as it is formed. In such a case its concentration will never become significant.

In case 2 described above, [X] rises and falls in a nearly symmetrical curve. Although this presents one cycle of an oscillation, it is too simple a mechanism to produce repeated fluctuations in the concentrations of any of the reaction components; thus, sustained oscillations cannot be achieved.

In order to move towards achieving a system with sustained oscillations Mechanism (1) must first be altered. This alteration assures that [X] can repeatedly rise and fall. The rate of the second step increases as [X] increases. This step eventually becomes faster than step 1. [X] then decreases and [P] increases. Initial conditions must be restored in order for [X] to rise again and both [X] and [P] must be low.

In order to lower the [P] another step is added to the mechanism. This additional step consumes P and changes the overall reaction to $A \rightarrow Q$. P now becomes an intermediate and can be renamed Y.

Mechanism (2)	$A \rightarrow X$	Step 1
	X→ Y	Step 2
	$Y \rightarrow Q$	Step 3

The third, $Y \rightarrow Q$, causes [Y] to decrease after it has risen but it has not yet caused [X] to rise again, after its initial decline. This mechanism was modified to ensure that [X] will rise whenever it is low. If the rate of the step that consumes X is slow when [Y] is low, the increase will occur.

Mechanism (3)	А→Х	Step 1
	$X + Y \rightarrow 2Y$	Step 2
	Y→Q	Step 3

In the above mechanism Y is a reactant created in step 2, which will be consumed in step 3. The rate of this step is proportional to both [X] and [Y]. As a result, X is consumed slowly only when [Y] is low and [X] can increase as it is produced in the first step.

This mechanism was first described by Alfred Lotka. He was able to show that a set of consecutive reactions can give rise to weakened oscillations that quickly disappear as the reaction approaches equilibrium. He analyzed the changes in concentrations of intermediates, X and Y, and found that under certain conditions this mechanism did lead to periodic oscillations in their concentrations.

A key feature of this system, and of most chemical systems that exhibit oscillations, is autocatalysis. In autocatalysis the rate of growth of a chemical species increases with the concentration of that species. In 1920, Lotka presented a second mechanism, which lead to sustained oscillations.

Mechanism (4)	$A + X \rightarrow 2X$	Step 1
	$X + Y \rightarrow 2Y$	Step 2
	Y→Q	Step 3

The overall reaction above is $A \rightarrow Q$, with X and Y as the intermediates formed. Both step 1 and step 2 are autocatalytic; however, neither of Lotka's two proposed mechanisms applied to real chemical systems.

The first homogeneous isothermal chemical oscillator was the reaction of iodate, iodine and hydrogen peroxide studied by William C. Bray at the University of California, Berkeley, in 1921 and later by one of his students, Herman Liebhafsky. Bray was investigating the effect of iodate on the decomposition of hydrogen peroxide. He serendipitously discovered oscillations in the concentrations of iodine and in the evolution of oxygen in a mixture of hydrogen peroxide and potassium iodate in dilute sulfuric acid.

There was much skepticism by chemists, for the next 50 years, to accept the Bray reaction as a representation of a genuine chemical oscillator. These chemists believed that the reaction was not truly homogeneous and that the oscillations were an artifact of dust or gas bubbles. During the 1970's their work was revived and carefully studied by Noyes and his co-workers. Through careful experimentation and mathematical modeling, they built on the theoretical groundwork that had been laid by the studies of non-equilibrium thermodynamics, and were able to successfully convince the scientific community of the validity of the Bray reaction as a chemical oscillator.

The beginning of nonlinear dynamics can be traced back to the studies of Boris Pavlovich-Belousov (1893-1970) who was looking for an inorganic analog of the Krebs cycle, a key metabolic process in which citric acid is an intermediate. In 1958 he discovered another example of a closed homogeneous oscillating reaction. He studied a solution of potassium bromate, cerium (IV) sulfate, and citric acid in dilute sulfuric acid. He expected to see monotonic conversion of yellow Ce (+4) into colorless Ce (+3). Instead, the color of the solution oscillated. It repeatedly cleared and became yellow again. Belousov found that oscillations stilled occurred when citric acid was replaced by any number of carboxylic acids with the common structural feature:

$$O O$$

$$|| ||$$

$$R - C - CH 2 - C - OH$$

The cerium ions can be replaced by manganese ions, and the oscillation will still occur. Together these reactions form a family of reactions known as the Belousov-Zhabotinsky (BZ) reactions.

In 1961, Anatol Zhabotinsky, a graduate student in biophysics at Moscow State University, began investigating this same system. He replaced citric acid with malonic acid to obtain a better formulation, which did not produce precipitate. In several of his experiments, Belousov used the redox indicator ferroin to intensify the color change during oscillations. Ferroin is red in reduced solution and blue in oxidized form, providing a more easily visible variation than the pale yellow to colorless change of the ceric-cerous system. Zhabotinsky found that ferroin alone could catalyze the BZ reaction without cerium. This advance allowed them to study unstirred solutions in thin layers, in which they discovered propagating chemical waves. A homogeneous system was now shown to exhibit not only temporal but also spatial self-organization.

In 1980, twenty years after Belousov's death, the Lenin Prize was awarded to Belousov, Zhabotinsky, V.I. Krinsky and G.R. Ivantinsky for their work on the BZ reaction.

The Belousov-Zhabotinsky Reaction Mechanism

The reaction mechanism for the Belousov-Zhabotinsky reaction, presented in Shakashiri, was proposed by Field, Kuros, and Noyes in 1972. The BZ reaction consists of an organic substrate, usually malonic acid, a catalyst, bromate ion, and an aqueous medium. The BZ reaction is driven by the acidic bromate oxidation of the substrate.

During the course of the reaction, malonic acid is brominated by molecular bromine. The production of molecular bromine is accomplished through two complete processes. One of these processes involves ions and two electron transfers. The other involves radicals and one electron transfer. These reactions consume bromate ions and oxidize Ce (III) to Ce (IV). The Ce (IV) ions participate in reactions that produce bromide ions. Process A occurs when the bromide ion concentration is above a critical level.

PROCESS (A)

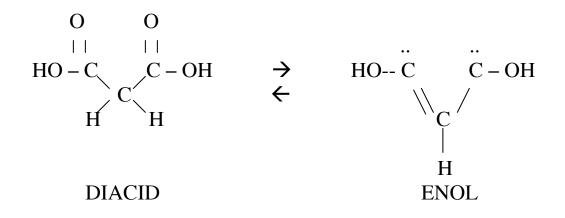
BrO₃ $^{-}$ + Br $^{-}$ + 2 H+ \rightarrow HBrO₂ + HOBr (1) HBrO₂ + Br $^{-}$ + H+ \rightarrow 2 HOBr (2) HOBr + Br $^{-}$ + H+ \rightarrow Br₂ + H₂O (3)

The bromous acid produced by this reaction can react further with bromide ions, forming more hypobromous acid, as shown in equation 2. Hypobromous acid itself reacts with bromide ions to produce elemental bromine, as shown in equation 3. The net transformation occurring in this entire process may be obtained by the stoichiometric addition of equations 1, 2 and 3. The net reaction is as follows:

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BrO _{3} - + 5 Br - + 6 H+ \rightarrow 3 Br 2 + 3 H 2 O (4)
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This reaction is the reduction of bromate ions in a series of oxygen transfers (two electron reductions).

The elemental bromine in aqueous solution is consumed in a reaction with malonic acid, producing bromomalonic acid and hydrobromic acid. Malonic acid exists in solution mainly in the diacid form and is converted relatively slowly to the reactive enol form as shown below:



Bromine does not react with the diacid form of malonic acid, but it reacts readily and quickly with the enol form, brominating it at the central carbon atom and releasing bromide ions as shown below:

Br 2 + H—C = C(OH) 2
$$\rightarrow$$
 Br – C = C(OH) 2 + Br[–] + H+ (5)
CO 2 H CO 2 H

As bromine reacts with the enol, the diacid slowly forms more enol; therefore, the rate at which bromine is consumed is determined by the rate of enolization of the reaction.

The net effect of Process (A) combined with the reaction of bromine with malonic acid is a reduction in the concentration of bromide ions in the solution. Process (B) dominates when the bromide concentration is low. When the bromide concentration becomes low, the HBrO is consumed through equation 2 slowly. At this point Process (B) takes over.

PROCESS (B)

BrO 3⁻ + HBrO 2 + H+ \rightarrow 2 BrO 2 • + H 2 O (6) BrO 2 • + Ce (3+) + H+ \rightarrow HBrO + Ce (4+) (7) 2 HBrO 2 \rightarrow HOBr + BrO 3⁻ + H+ (8) 2HOBr \rightarrow HBrO 2 + Br⁻ + H+ (9) HOBr + Br⁻ + H+ \rightarrow Br 2 + H 2 O (10)

The HBrO produced in equation 1 reacts with BrO^- , producing $BrO_2 \bullet$ radical, as shown in equation 6. This radical reacts with Ce (III) as shown is equation 7. The overall reaction is as follows:

 $2 \text{ Ce}(3+) + \text{BrO}_3 + \text{HBrO}_2 + 3 \text{H} \rightarrow 2 \text{ Ce}(4+) + \text{H}_2 \text{O} + 2 \text{HBrO}_2$ (11)

This overall reaction indicates a sequence that generates HBrO 2 autocatalytically. This autocatalytic sequence provides the minimal conditions essential to chemical oscillations.

The autocatalysis does not continue until the reactants are depleted, because there is a second-order destruction of the autocatalytic species. The reaction is the disproportionation of bromous acid, represented by equation 8. Equations 9 and 10 represent the disproportionation of hypobromous acid to bromous acid and elemental bromine. The net reaction is as follows:

 $3 \text{ HOBr} \rightarrow \text{HBrO } 2 + \text{Br} 2 + \text{H} 2 \text{ O}$ (12)

The net transformation that takes place in Process (B) may be obtained by the stoichiometric addition of 5 (equation 6) + 10 (equation 7) + 3 (equation 9) + (equation 10). The net reaction is as follows:

 $2 \operatorname{BrO} \overline{3} + 12 \operatorname{H} + 10 \operatorname{Ce} (3+) \rightarrow \operatorname{Br} 2 + 6 \operatorname{H} 2 \operatorname{O} + 10 \operatorname{Ce} (4+)$ (13)

The Ce (4+) from the above reaction is reduced by an organic species. One of the reducing agents is the bromomalonic acid that was produced.

The organic radical intermediates of the process above also reduce HOBr to bromide ions, so that it can react via equation 3. When enough HOBr and Ce (4+) have been produced, bromide ions are produced so rapidly that the rate of equation 2 surpasses that of equation 5, and the reaction follows Process (A) again.

Process (A) and Process (B) result in a competition between bromide ions and bromate ions to react with bromous acid. When the bromide ion concentration is high, nearly all of the bromous acid reacts with it, following Process (A). During the process the concentration of bromine decreases, and the bromide ions become less and less successful at competing for the bromous acid. Eventually, Process (B) takes over. The concentration of bromide ions eventually becomes high enough to cause a shift back to Process (A). The switching back and forth between both processes is the origin of the oscillations observed in this reaction. This reaction is extremely temperamental. Even small amounts of chloride ions present can interfere with the mechanism of the BZ reaction, inhibiting the oscillations. Chloride ions present in the reaction can be oxidized to chlorous acid (HClO) which can then reduce the Ce (IV) back to Ce (III) suppressing the oscillations. Oscillations may return when the chlorous acid is completely oxidized to ClO⁻.

The amount of oxygen introduced into the system will have an effect on the oscillations present. When oxygen is entrained into the system the oscillation cease. This occurs because the oxygen molecules can react with malonyl radicals present in the reaction via an autocatalytic process that increases the radical concentration. The malonyl radicals react with bromomalonic acid, liberating bromide ions. The net effect of oxygen is the increase of bromide ion concentration beyond the range allowable for oscillations.

The ferroin concentration introduced into the system will also have an effect on the mechanism of the BZ reaction. It does not merely act as an indicator. Ferroin alone can also catalyze the BZ reaction.

The Briggs-Rauscher Reaction

The Briggs-Rauscher (BR) reaction was developed by Thomas S. Briggs and Warren C. Rauscher. It is a hybrid of two other oscillating systems, the Bray-Liebfafsky (BL) reaction and the Belousov-Zhabotinsky (BZ) reaction. Bray was investigating the dual role of hydrogen peroxide as an oxidizing agent and a reducing agent when he discovered oscillations in the evolution of oxygen gas from the reaction mixture. He mixed hydrogen peroxide, potassium iodate, and sulfuric acid. In this mixture, the hydrogen peroxide reduced the iodate to iodine and was oxidized to oxygen gas in the process.

This discovery of oscillations prompted Liebfafsky to study this reaction prior to 1933 and after 1969, when he retired as an industrial chemist. Few others paid much attention to this reaction until after the discovery of the BZ reaction. Belousov reported oscillations during the reaction of citric acid with acidic bromate ions and cerium (IV) ions. Zhabotinsky discovered that these oscillations still

occurred if specific organic compounds, such as malonic acid, were substituted for citric acid, and if other one-electron transfer agents, such as Mn (II) ions, were substituted for cerium ions.

Briggs and Rauscher combined the hydrogen peroxide and the iodate of the BL reaction with malonic acid and manganese ions of the BZ reaction, and discovered the oscillating reaction that bears their name. In the BR reaction, the evolution of oxygen and carbon dioxide gases and the concentrations of iodine and iodine ions oscillate. It is one of the most visually impressive chemical oscillators. A stirred solution goes through 15 or more cycles of colorless, to amber, to blue-black, before ending in a blue-black mixture with the odor of iodine in starch.

The sulfuric acid keeps the medium acidic. The manganese sulfate monohydrate provides the Mn (2+), which participates in some of the steps of the reaction. The starch indicates the presence of iodine and iodide ions.

The details of the reaction are quite involved, but in outline this is what is thought to be happening. Initially, iodate and hydrogen peroxide reaction to form hypoiodous acid, HOI.

 $IO_{3} + 2H_{2}O_{2} + H + \rightarrow HOI + 2O_{2} + 2H_{2}O \quad (colorless) \quad (1)$

This reaction can occur by two alternative sets if intermediate mechanisms. One of these pathways is slow and the other is fast. The slow mechanism requires iodide ions as intermediates. These ions are consumed and then regenerated. Since no iodide ions are present initially, reaction (1) proceeds by the rapid mechanism at first.

The HOI produced in reaction (1) is consumed by a reaction with hydrogen peroxide.

 $HOI + H 2 O 2 \rightarrow I^{-} + O 2 + H + H 2 O \qquad (colorless) (2)$

The iodide produced in this reaction is consumed in two competing pathways. First, the iodide causes reaction (1) to shift to its slow mechanism pathway. This slows the production of HOI. Second, the iodide reacts with the HOI to produce iodine and an amber color.

$$I + HOI + H + \rightarrow I_2 + H_2O \qquad (amber) (3)$$

When this reaction first occurs, there is a large amount of HOI present but only a small amount of iodide ions. As a result, the iodide ions are quickly consumed to form elemental iodine. As reaction (2) proceeds, the amount of HOI decreases and the concentration of iodide ions increases. When sufficient iodide ions have formed, they form a deep blue color in conjunction with the elemental iodine and starch present.

 I^{-} + I_2 + starch (indicator) (deep blue) (4)

The iodine formed is eventually consumed by a reaction with malonic acid.

$$I_2 + CH_2(COOH)_2 \rightarrow ICH(COOH)_2 + H_+ + I$$
(5)

When sufficient iodine is consumed the color fades from deep blue to clear. The iodide ions formed shift reaction (1) to its slow pathway. The slow mechanism consists of three steps. The first two steps are as follows:

$$IO_{3}^{-} + I^{-} + 2H + \rightarrow HIO_{2} + HOI$$
(6)

 $HOI + I^{-} + H^{+} \rightarrow 2 HOI$ (7)

The third step is reaction (2). The combination of equation (6) + equation (7) + 2 * equation (2) results in reaction (1). Steps (6) and (7) are slow compared to equation (3); therefore, the iodine is consumed faster than it can be regenerated by equation (2). As a result the iodide ions are consumed, reaction (1) shifts to its fast pathway, and the cycle begins again.

The net result is the cycling of the reaction mixture repeatedly from colorless, to amber, to blue-black, and back to colorless. Eventually the cycling slows down because of the consumption of hydrogen peroxide and malonic acid.

SEE AN OSCILLATING CHEMICAL REACTION (Requires Quicktime)

<u>Part 1</u> (4mb) <u>Part 2</u> (4mb)

Some Practical Applications and Current Research of Oscillating Systems

Oscillating systems are all around us. These systems can be biological or chemical. We can find such oscillating chemical reactions in nature. For example, through close observation of the malachite rock we can observe fractal patterns. This "chaotic" system actually exhibits organizational behavior through these patterns.

Research into oscillating chemical reactions, spatial pattern formation, dynamical systems and neurobiology continues today. Irving R. Epstein, Ph D. heads a research group studying such systems. This group studies oscillating chemical systems both experimentally and theoretically. This group has achieved the first successful design of a new chemical oscillator. It has used their first systematic design algorithm to expand the family of chemical oscillators from two serendipitously discovered reactions to some over two dozen deliberatively constructed systems. While the group continues its search for new types of oscillators, it probes by a variety of techniques, including spectrophotometry, potentiometry, rapid mixing and computer simulation.

This research group is interested in the phenomena that can occur when two or more oscillators are coupled together, either physically, i.e. by diffusion or an electrical connection, or chemically, by having the two oscillators share a common chemical species. Such systems can give rise to surprising phenomena, such as "oscillator death," the cessation of oscillation in two coupled oscillating systems, or the converse, "rythmogenesis," in which coupling the systems at a steady state causes them to start oscillating.

Coupled chemical oscillators provide simple models for networks of oscillating neurons. This group has begun to apply some of the insights gained in its studies to the modeling of small neural networks in conjunction with the Marder laboratory, to develop chemical analogs of neural oscillators and to couple chemical and neural oscillators.

THE OSCILLATING COLOR REACTION

Reactions that produce color changes are popular now. It gives a magic touch to chemical demonstrations to arouse interest in science to students or public audience of all ages. There are various examples which are relatively easy to demonstrate and perfectly safe to handle. Here, we present a modified classical oscillatory Belousov Zhabotinsky reaction, now popularly known as the *Briggs-Rauscher Reaction*.

When three colorless solutions are mixed and stirred together, the resulting solution shortly becomes amber, and then quite turns to blue. The colorless, amber, and blue sequence of colors is repeated for some minutes in a cycle of several seconds. As the reaction proceeds, the time between color changes increases. Eventually the color oscillations will no longer be observed.

SEE AN OSCILLATING CHEMICAL REACTION (Requires Quicktime) <u>Part 3</u> (4mb) <u>Part 4</u> (4mb)

MATERIALS

Solution A: 410 mL of 30% hydrogen peroxide are diluted to 1.0 liter with distilled water. Solution B: 43 g of potassium iodate are dissolved in about 800 ml of dist. water acidified with 4.3 mL of conc. sulfuric acid and made up to 1000 mL with dist. water Solution C: 16 g of malonic acid and 3.4 g of manganese (II) sulfate monohydrate are dissolved in about 500 mL of dist. water. 0.3 g of soluble starch are dissolved in 50 mL of boiling dist. water. The starch solution is poured into the solution of malonic acid and manganese sulfate. The mixture is diluted with dist. water to 1000

mL.

- *PRESENTATION*: Place the 250 ml beaker to be used for the presentation with the stir bar on the magnetic stirrer. Pour 50 ml of solution A, add an equal volume of solution B, and start the stirrer. Then add an equal volume of solution C. The color oscillations will begin in about half a minute.
- *RESULT*: The initial colorless solution becomes amber almost immediately. Then it suddenly turns blue-black. The blue-black fades to colorless. Thus the color of the solution oscillates between clear, brownish and deep blue.
- **DISCUSSION:** This reaction involves many steps. One of the steps is the generation of iodine, and oxygen gas. When the concentration of iodine gets large enough, triiodide ion is generated and it forms a blue complex with starch. The second step involves the consumption of this iodine, reversing the formation of the blue complex. As the iodine concentration oscillates, the color oscillates from colorless to amber to blue. The basic concept of this reaction is that two reactions can switch back and forth. The product of one is the reactant for the other.

 $5H_2O_2 + 2IO_3 + 2H^+$ $I_2 + 5O_2 + 6H_2O$ $5H_2O_2 + I_2$ $2IO_3 + 2H^+ + 4H_2O$ **<u>HAZARDS</u>**: Iodine is the ultimate product left in the reaction mixture. It may be disposed of by adding sodium thiosulfate to the mixture and stirring. Care should be exercised because the reaction between iodine and thiosulfate is very exothermic. Iodine also stains the skin and dress materials. Con. Sulfuric acid is corrosive and proper eye and hand protection should be taken car

EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF TEMPERATURE AND CHLORIDE ION CONTAMINATION ON THE BRIGGS-RAUSCHER REACTION

OBJECTIVE

In an attempt to prolong the amber color or the solution, one can attempt to prevent the hypoiodous acid from being consumed by reaction with hydrogen peroxide. This is virtually impossible to do, especially since the hydrogen peroxide present in the system is needed to initially produce the hypoiodous acid. A second way that this may be accomplished is by introducing pure hypoiodous acid into the system. This acid, which is not safe enough to handle alone, would need to be kept at a higher concentration than the hydrogen peroxide consuming it. Since neither one of these options are feasible, the temperature of the system may be varied in order to affect the rate of oscillation. In the first part of the following experiment, the temperature of the system will be varied. The length of the color oscillations will be measured. The electric potential of the system oscillate as well and may be observed and measured by a platinum electrode and a double junction reference electrode. With a strip chart recorder the oscillations in electric potential may be printed. Both electrodes and a strip chart recorder may be ordered from a chemical supply company.

Chloride ion contamination in excess of 0.70 M has been reported to suppress oscillations; therefore, the vessels used for the preparation of solutions must be clean. A double junction reference electrode that does not leak chloride ions must be used to measure oscillation in the electric potential of the solution. An ordinary standard calomel electrode or silver-silver chloride electrode are not suitable for this experiment.

In part B of this experiment sodium chloride solutions of different concentrations will be introduced into the chemical system via titration. The electric potentials and color oscillations will be observed and measured.

MATERIALS

Hydrogen Peroxide Solution *
Potassium Iodate Acidified Solution **
Starch Malonic Acid-Manganous Sulfate Solution ***
Sodium Chloride Solutions ****
250 mL Beakers
Magnetic Stirring Bar
Magnetic Stirrer
50-mL graduated cylinders
Platinum Electrode
Double Junction Reference Electrode
Strip Chart Recorder (or computer program)
* 8.6% hydrogen peroxide

*** 0.15 M Malonic Acid 0.020 M Manganese (II) Sulfate Monohydrate 0.30 grams of Soluble Starch

** 0.20 M KIO 3 and 0.77 M sulfuric acid

NOTE: Combined they produce a mixture whose nominal contents are 0.05 M malonic acid, 0.0067 M Mn(2+), 0.067M Iodate ions, 1.3 M hydrogen peroxide, and 0.038 M sulfuric acid.

**** 0.035 M, 0.070 M and 0.10 M Sodium Chloride Solutions

PART A – TEMPERATURE VARIATION

Control Reaction (at Room Temperature)

- Using a 50-mL graduated cylinder, measure out 40-mL of hydrogen peroxide solution and transfer it to a 250-mL beaker. Place this beaker on a magnetic stirrer.
- (2) Using a clean 50-mL graduated cylinder, measure out 40-mL of the potassium iodate acidified solution and transfer it to the beaker in step 1.
- (3) Stir using a stirring rod or magnetic stirrer.
- (4) Place the platinum electrode and double junction reference electrode to the solution. The platinum electrode is connected to the positive terminal of the recorder. The reference electrode is connected to the negative terminal of the recorder.
- (5) Bubbles will appear and shortly thereafter yellow, blue, and colorless oscillations will occur. The oscillations will continue for about 10 minutes.
- (6) Repeat Steps 1-5 with temperature variations. Record observations of color oscillations and electric potential oscillations.

Sample Temperature Variations

- (1) Chill the hydrogen peroxide down to a temperature between 10 and 15 degrees Celcius. The potassium iodate solution and the starch- malonic acid solution are kept at room temperature. This variation may be accomplished by cooling any one of the solutions while keeping the other two at room temperature.
- (2) Chill the hydrogen peroxide and potassium iodate solution to a temperature between 10 and 15 degrees Celcius. The starch-malonic acid solution is kept at room temperature. This variation may be done by cooling any two of the solutions while keeping the third at room temperature.

(3) For temperatures lower below 10 degrees Celcius the solutions may be placed in the freezer.

PART B – CHLORIDE ION CONTAMINATION

Control Reaction (at Room Temperature)

- Using a 50-mL graduated cylinder, measure out 40-mL of hydrogen peroxide solution and transfer it to a 250-mL beaker. Place this beaker on a magnetic stirrer.
- (2) Using a clean 50-mL graduated cylinder, measure out 40-mL of the potassium iodate acidified solution and transfer it to the beaker in step 1.
- (3) Stir using a stirring rod or magnetic stirrer.
- (4) Place the platinum electrode and double junction reference electrode to the solution. The platinum electrode is connected to the positive terminal of the recorder. The reference electrode is connected to the negative terminal of the recorder.
- (5) Bubbles will appear and shortly thereafter yellow, blue, and colorless oscillations will occur. The oscillations will continue for about 10 minutes.
- (6) Repeat Steps 1-5 with chloride ion contamination from 3 different concentrations of sodium chloride solutions. Record observations of color oscillations and electric potential oscillations.

ANALYSIS QUESTIONS

- (1) What is an oscillating chemical reaction?
- (2) What is meant by the term "organized chaos?"
- (3) What is the Briggs-Rauscher reaction?
- (4) How does the Briggs-Rauscher reaction differ from the BL and BZ reactions?

- (5) Why are each of the specific colors in the oscillation observed?
- (6) What is electric potential? How can it be used to monitor the oscillations in this experiment.
- (7) What was observed when the temperature of the system was altered? Explain reasons for these observations.
- (8) What was observed when chloride ions were introduced into the system? Explain reasons for these observations.
- (9) What are some examples of biological oscillators?
- (10) What is a fractal pattern?
- (11) What other variations may be performed on this system and other chemical oscillators?

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