# Fantastic Four Color Oscillator

Oxidation States

## Introduction

You won't believe your eyes as you watch this amazing oscillating reaction! The color of the oscillating redox reaction changes from green to blue to purple to red in a seesaw battle between Ce(IV)/Ce(III) and Fe(II)/Fe(III) ions. And that's not all—this four-color cycle will repeat itself for almost an hour!

## Concepts

- Oscillating reactions
- Oxidation–reduction reactions
- Kinetics and catalysis
- Oxidation states

## Materials

Cerium(IV) ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$ , 2.7 g
Ferroin solution, 0.5%, 15 mL
Malonic acid, $CH_2(CO_2H)_2$, 8 g
Potassium bromate, $KBrO_3$, 9.5 g
Potassium bromide, KBr, 1.8 g
Sulfuric acid solution, $H_2SO_4$, 3 M, 225 mL
Beaker, 1-L
Graduated cylinder, 250-mL
Graduated cylinder, 25-mL
Magnetic stir bar
Magnetic stirrer

## *Safety Precautions*

*A small amount of bromine is generated in this demonstration; perform this demonstration in a hood or well-ventilated lab only. Potassium bromate is a strong oxidizing agent and poses a fire risk in contact with organic material; it is a strong irritant and moderately toxic. Malonic acid is a strong irritant, slightly toxic, and corrosive to eyes, skin, and respiratory tract. Potassium bromide is slightly toxic by ingestion and a severe body tissue irritant. Cerium(IV) ammonium nitrate is a strong oxidizer and a skin irritant. Ferrous sulfate is slightly toxic by ingestion and 1,10-phenanthroline is highly toxic by ingestion. Sulfuric acid solution is corrosive to eyes, skin, mucous membrane, and other body tissue. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the laboratory. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.*

## Preparation

Solution A (0.23 M $KBrO_3$) — In a 250-mL Erlenmeyer flask, dissolve 9.5 g of potassium bromate in 250 mL of distilled or deionized water. Label this Solution A.

Solution B (0.31 M $CH_2(CO_2H)_2$ and 0.059 M KBr) — In a second 250-mL Erlenmeyer flask, dissolve 8 grams of malonic acid and 1.8 g of potassium bromide in 250 mL of distilled or deionized water. Label this Solution B.

Solution C (0.019 M $Ce(NH_4)_2(NO_3)_6$ and 2.7 M $H_2SO_4$) — In a third 250-mL Erlenmeyer flask, dissolve 2.7 g of cerium(IV) ammonium nitrate in 25 mL of distilled or deionized water and add 225 mL of 3 M sulfuric acid. Label this Solution C.

## Procedure

1. Place a 1-L beaker on the magnetic stirring plate and place the magnetic stir bar in the beaker.
2. Pour 250 mL of Solution A and 250 mL of Solution B into the 1-L beaker.
3. Adjust the stirrer speed to produce a vortex in the solution. The solution may become amber, and will turn colorless after about one minute.
4. Once the solution is colorless, add 250 mL of Solution C and 15 mL of ferroin solution.


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5. Keep stirring the green cloudy mixture and it will become a green solution. Over a period of about a minute, the color of the solution will change from green to blue, then to violet, and finally to red-brown.
6. The color of the solution will suddenly return to green, and the cycle will repeat itself more than 20 times, lasting over an hour.

## Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. The reaction mixture should be neutralized with sodium carbonate and flushed down the drain with excess water according to Flinn Suggested Disposal Method #24a.

## Tips

- The solution composition for the fantastic four-color oscillator is 0.077 M $BrO_3^-$, 0.10 M malonic acid, 0.020 M $Br^-$, 0.0063 M $Ce^{4+}$, 0.90 M $H_2SO_4$, and 0.17 mM ferroin.
- Although the mechanism of this oscillating reaction is quite detailed, the demonstration can tailored to the concepts being taught. The oscillating chemical reaction produces vivid colors corresponding to the changes in the oxidation states of cerium and iron ions.
- This reaction is very sensitive to the chloride ion concentration. Do not use or rinse glassware with tap water.

## Discussion

This oscillating reaction demonstrates the classic Belousov-Zhabotinsky (BZ) reaction, which is a cerium-catalyzed bromate–malonic acid reaction.

The overall reaction occurring in this demonstration is the cerium-catalyzed oxidation of malonic acid by bromate ions in dilute sulfuric acid. The bromate ions are reduced to bromide ions, while the malonic acid is oxidized to carbon dioxide and water. The overall reaction can be represented by Equation 1:

$$3CH_2(CO_2H)_2 + 4BrO_3^- \rightarrow 4Br^- + 9CO_2 + 6H_2O \qquad \textit{Equation 1}$$

In order to gain some understanding and appreciation for how this overall reaction can produce the amazing, repetitive color changes observed in the demonstration, it is necessary to look at the reaction mechanism or, in other words, how the reactants are transformed into products.

The mechanism involves two different competing processes—Process A involves ions and two-electron transfers; Process B involves radicals and one-electron transfers. The dominant process at any particular time depends on the bromide ion concentration. Process A (see *Equation 2a*) occurs when the bromide ion concentration rises above a certain critical level, while Process B (see *Equation 3a*) is dominant when the bromide ion concentration falls below a certain critical level. Oscillations occur because Process A consumes bromide ions, leading to conditions which favor Process B. Process B (indirectly) produces bromide ions, leading to conditions that favor Process A.

### Process A

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad \textit{Equation 2a}$$

Bromate ions are reduced by bromide ions through a series of oxygen transfers (two-electron reductions) as shown in *Equation 2a*. This reaction occurs when Solutions A and B are mixed. The amber color which may develop is caused by the production of elemental bromine. This color soon disappears as the bromine reacts with malonic acid as shown in *Equation 2b*.

$$Br_2 + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + Br^- + H^+ \qquad \textit{Equation 2b}$$

Process A results in an overall decline in the bromide ion concentration and, once the necessary intermediates are generated and most of the bromide ions are consumed, the rate becomes negligible and Process B takes over.

## Process B

$$2BrO_3^- + 12H^+ + 10Ce^{3+} \rightarrow Br_2 + 10Ce^{4+} + 6H_2O \qquad \textit{Equation 3a}$$

Bromate ions are reduced by cerium(III) ions to produce bromine through a simple redox reaction as shown in *Equation 3a*. Process B produces Ce(IV) ions and $Br_2$. Both of these species react at least in part to oxidize the malonic acid (see *Equation 2b*) and the bromomalonic acid (see *Equation 3b*) to form additional bromide ions. As the concentration of bromide ions increases, the rate of *Equation 2a* increases until eventually Process A once again dominates.

$$BrCH(CO_2H)_2 + 4Ce^{4+} + 2H_2O \rightarrow Br^- + 4Ce^{3+} + HCO_2H + 2CO_2 + 5H^+ \qquad \textit{Equation 3b}$$

As the reaction oscillates between Process A and Process B, triggered by changes in the bromide ion concentration, concentrations of other species in solution oscillate as well—these concentration changes will explain the color changes observed. While Process A occurs, the cerium ions are in their reduced state, Ce(III). During Process B, some cerium ions are oxidized to Ce(IV) and thus the ratio of Ce(III) to Ce(IV) oscillates as well.

The indicator used in this demonstration is ferroin, which is tris(1,10-phenanthroline) iron(II) sulfate. As the concentration of Ce(IV) increases, the Ce(IV) oxidizes the iron in ferroin from Fe(II) to Fe(III). The Fe(II) complex is red while the Fe(III) complex is blue; thus the color of the solution changes as the iron is oxidized. As the concentration of Ce(III) increases, the Fe(III) is reduced back to Fe(II) and the color of the solution changes accordingly.

The color changes in this demonstration, however, are more complex than simple red-blue oscillations from the ferroin. There are also changes in color due to the cerium ions in solution—Ce(III) is colorless while Ce(IV) is yellow. A simplified equation to help explain the color changes is shown below in *Equation 4:*

$$\underset{\textit{yellow}}{\mathrm{Ce(IV)}} + \underset{\textit{red}}{\mathrm{Fe(II)}} \rightleftarrows \underset{\textit{blue}}{\mathrm{Fe(III)}} + \underset{\textit{colorless}}{\mathrm{Ce(III)}} \qquad \textit{Equation 4}$$

A possible explanation for the appearance of the oscillating colors in solution is provided below; however, a more complete understanding of the color changes might be gained by reviewing the original references.

Green = The yellow Ce(IV) is oxidizing Fe(II) to blue Fe(III); a small amount of Fe(II) has been oxidized to the blue Fe(III) complex; thus, the mixture of yellow and blue forms a green solution.

Blue = All Ce(IV) is reduced to colorless Ce(III); all Fe(II) is oxidized to the blue Fe(III) complex; thus, the solution is blue.

Violet = The colorless Ce(III) is reducing the blue Fe(III) complex to the red Fe(II); the mixture of blue and red appears violet.

Red = All of the blue Fe(III) is reduced to the red Fe(II) complex; colorless Ce(III) is present; the solution appears red.

## Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

***Unifying Concepts and Processes: Grades K–12***
Evidence, models, and explanation
***Content Standards: Grades 9–12***
Content Standard B: Physical Science, structure and properties of matter, chemical reactions

## Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Fantastic Four Color Oscillator* activity, presented by Irene Cesa, is available in *Oxidation States*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

## Materials for *Fantastic Four Color Oscillator* are available from Flinn Scientific, Inc.

Materials required to perform this activity are available in the *Fantastic Four-Color Oscillator—Chemical Demonstration Kit* available from Flinn Scientific. Materials may also be purchased separately.

| Catalog No. | Description |
|---|---|
| AP4833 | Fantastic Four Color Oscillator—Student Laboratory Kit |
| P0205 | Potassium Bromate, Reagent, 25 g |
| M0091 | Malonic Acid, 25 g |
| P0137 | Potassium Bromide, Reagent, 100 g |
| C0287 | Cerium(IV) Ammonium Nitrate, Reagent, 25 g |
| F0073 | Ferroin, 0.5% Solution, 10 mL |
| AP7235 | Magnetic Stirrer, Flinn, 7" × 7" |

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.