C H E M I S T R Y   1 8 9

Foundations of Chemistry II - Honors

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THE IODINE CLOCK AND REACTIONS THAT OSCILLATE
PART 2

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF KANSAS

The Iodine Clock and Reactions that Oscillate – Part 2

Introduction

Oscillating reactions are an exciting class of chemical processes. The repeated fluctuation in color has captured the fascination of many, and challenged chemists to understand the mechanism behind the observed color change.

The first oscillating reaction was reported in print in 1828, with the report of an electrochemical cell that produced oscillating current. This oscillating current process and the Liesegang reaction (exhibiting the phenomenon of periodic precipitation) were for many decades the only known examples of chemical oscillators. In the early 1900's, Lotka presented theoretical support for homogenous oscillating chemical processes. This work was rapidly supported by the work by Bray, who observed the reaction between hydrogen peroxide and potassium iodate in dilute sulfuric acid. The reaction produced an oscillation in concentration of free iodine, resulting in a fluctuating color change.

Belousov presented another class of homogenous oscillating reactions in 1958. By combining potassium bromate, ceric sulfate, and citric acid in dilute sulfuric acid, oscillations in the concentration of ceric and cerous ions could be observed visually. Zhabotinsky extensively studied the reaction process, substituting various carboxylic acids in place of the citric acid. Similarly, substitution of cerium by manganese also exhibited the oscillation in color.

This week, your group will pick one of the two oscillating reactions described in the accompanying handouts and study it in detail. These reactions all involve redox reactions that you should be familiar with. From the experiments described in the handouts you should be able to determine the reaction order for each of the reagents involved in the oscillating reaction as well as a rate constant. In addition, you should focus on the processes that give rise to an oscillating behavior. Suggested mechanisms for these reactions have been provided. What are the colored species that are responsible for the reaction? Why does the reaction not just change colors in one direction and stop?

Oscillating chemical reactions seem to violate many of the laws of thermodynamics that we have come to understand in chemistry. We have discussed thermodynamics extensively in this course and you should have learned that the free energy change for a reaction will allow us to predict that a reaction will proceed spontaneously in only one direction for a given set of conditions. The capability for a reaction to seemingly reverse its process has led many to question our general understanding of equilibrium and reaction processes. Although the idea that the reaction is passing through an equilibrium state and back out is a reasonable one, and allows us to relate the oscillating reaction to a pendulum of a clock, the actual dynamics of the reaction are quite more complex. In fact, the chemical reaction does not pass back and forth through an equilibrium state. The actual oscillating reaction is made up of a series of reactions. Each reaction has a different sequence and required reactants. When the concentration of a particular intermediate reaches a certain level, the dominant chemical process changes, and that reactant may be used up. The concentration of particular reagents may pass repeatedly through the same values (giving rise to the same colors) but the overall energetics of the reaction is such that the free energy for the system is always decreasing. In order to observe oscillations, the system must be at conditions that are quite far from equilibrium. Otherwise, equilibrium would be reached quickly and the oscillations would not be observed (the concentrations would reach a steady state).

Not all reactions oscillate. In order for reactions to oscillate, certain features must be included in the mechanism for the reaction. This mechanism (or pathway) determines how the concentrations of the different species change with time. We have derived the kinetic equations that describe concentration versus time for several simple examples in class. These mechanisms are much more complex that those examples. Three common features are observed in all known oscillating reactions. First, the system is far from equilibrium (as discussed above). Second, there are multiple pathways involved in the reaction and the reaction must switch back and forth between the two pathways (usually triggered by changes in concentration of some reagent). Third, an intermediate produced in one of the pathways has to be consumed in another pathway. This allows for the switching from one pathway to another during the course of the reaction, as the concentration of that intermediate changes.

Your textbook shows the concentration as a function of time for a two step reaction in which the reactant forms an intermediate, which goes on to form products (A → I → P). As the first step happens, the concentration of A decreases and the concentration of I increases. The intermediate I then reacts to form P. Depending on the relative rates of the first and second step, the concentration of I may build up initially, and then begin to decay, but once it starts to decay, it continues to decay until equilibrium is reached. In this mechanism, the concentration of the intermediate can rise and then fall, but it will not repeat. A more complicated mechanism is required for repeated oscillations. A reaction scheme such as the one presented below has been shown to allow for oscillations to occur:

$$A \rightarrow X$$
$$X + Y \rightarrow 2Y$$
$$Y \rightarrow Q$$

In this case, the concentration of X can build up if the concentration of Y is low, but as the concentration of Y increases, the concentration of X decreases. This is the case if step 2 in this reaction is slow. This sort of reaction does indeed lead to short lived oscillations, but these oscillations are quickly damped. The mechanisms for the reactions you will study are more complex than this, but this at least provides some idea what is required. In reality, one possibility for sustained oscillations would be to make steps 1 and 2 both increase in rate as the products from the reaction are formed (this is the case in step 2 above, but not in step 1).

Oscillating chemical reactions have also interested biologists. The cycles of the oscillating reactions and the repeated cycles are reminiscent of biological rhythms, or circadian rhythms. Circadian rhythms are believed to be involved in the processes of sleep, heartbeat, and breathing. The similarities between oscillating reactions and their mechanisms with those of oscillating biological processes have also been extensively compared. The similarities include the changes in concentration of materials due to stepwise chemical reactions. The ability to make these comparisons to systems outside of the body enables biologists and chemists alike to better understand functions inside the body.

Pre-lab

Safety: Goggles *must* be worn at all times. Most chemicals can be toxic and hazardous if splashed on clothing, exposed skin or in the eyes. If chemicals splash on skin or clothes, remove the affected clothing and flush the affected areas thoroughly with cold water. All solutions generated during this experiment should be collected in a separate container as waste.

Cerium(IV) Ammonium Nitrate and Potassium Bromide are corrosive substances. Begin rinsing *immediately* if skin or eyes are exposed.

Hydrogen Peroxide is a corrosive material that is often used as a bleach. It is capable of bleaching human skin. Rinse *immediately* if skin or eyes are exposed.

Strong Acids such as Sulfuric Acid (H_2SO_4) Nitric Acid (HNO_3) and **Weak Acids** like Acetic Acid ($HC_2H_3O_2$) and Malonic Acid ($HO_2CCH_2CO_2H$) are hazardous if splashed on clothing, exposed skin or in the eyes. Prolonged exposure of the skin to even fairly dilute solutions of acid can cause serious burns. If acids splash on skin or clothes, remove the affected clothing and flush the affected areas thoroughly with cold water.

Potassium Iodide, Potassium Bromide, Manganese Sulfate, Potassium Iodate, Ferroin [systematically named (tris)(1,10-phenanthroline)iron(II) sulfate; $(C_{12}H_8N_2)_3FeSO_4$] and Sodium Thiosulfate may cause skin irritation. As with all chemicals, wash hands thoroughly if skin is exposed.

Disposal of Chemicals: All solutions must be treated to neutralize acid and other reactive species prior to disposal. **Your TA will provide you with detailed information about how you should treat all waste solutions.**

Pre-lab Assignment: Please write out the following in your lab notebook. This assignment must be completed *before* the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and accepted by your TA.

1) *Briefly* describe the objectives of this experiment.
2) Choose one of the two oscillating reactions. Write out the experimental procedure in your lab notebook according to the *"Guidelines for Keeping a Laboratory Notebook"* handout. In consultation with your TA, your group will decide which of the oscillating reactions to study in the lab.

In addition to these pre-lab requirements, *a short quiz will be given at the beginning of lab* based on the material in this lab write-up.

Procedure

See Individual write-ups for the oscillating reactions.

Report

NOTE: Your report for this experiment will include both this experiment and the iodine clock reaction that you will carried out last week. The final report will be due in lab next week.

Your report should include information about the redox reaction involved in your reaction as well as the information you were able to extract about the rate law from the timing of the oscillations. You should also include a detailed discussion about what allows from some reactions to oscillate, while others do not. What is important about the mechanism for these reactions?

Your lab report should be a formal, individual report prepared according to the "Guidelines for Laboratory Reports" you have been given. In addition to the categories discussed in these guidelines you should provide answers to all the questions posed in this laboratory experiment write-up.

References

http://www.chm.davidson.edu/ChemistryApplets/index.html

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Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry, vol. 2*; University of Wisconsin Press: Wisconsin, **1985**.

Weinberg, R.B.; Muyskens, M. *Journal of Chemical Education*. **2007**, *84*, 797-800.

Glossary

integrated rate law

an expression for the time-dependent concentration of reactants and products in a reaction obtained by "solving" the rate law (see below); comparison of concentrations as a function of time with measured concentrations versus time is one way to determine the rate law

rate constant

the constant of proportionality between the reaction rate and the reactant concentrations to their reaction orders; for analogous rate laws (*i.e.,* same reaction orders) the rate constant measures the speed of the reaction; the rate constant depends only on temperature

rate law

a generally empirical relationship between the rate of a reaction (see below) and the concentrations of the reactants, *e.g.,* rate = $v = k[A]^x[B]^y$; a rate law is defined by the reaction order of each reactant, *e.g., x* and *y* above, and the rate constant, *k*

rate of reaction

the speed with which a reaction proceeds expressed in terms of concentration of reactants consumed per unit time or concentration of products produced per unit time; if A is a reactant and C is a product, then the rate can be written as $v = -\Delta[A]/\Delta t = \Delta[C]/\Delta t$, for the limit $\Delta t \rightarrow 0$; the rate generally depends on time, changing as the reaction proceeds