

Chemiluminescent Oscillating Demonstrations: The Chemical Buoy, the Lighting Wave, and the Ghostly Cylinder

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Oscillating reactions have been extensively used in chemical demonstrations (1, 2). They involve several chemical concepts about kinetics, catalysts, and thermodynamics. The spontaneous cyclic color change of a solution is an attraction at any educational-level course and the audience always demands a comprehensible explanation. Different theories and models for oscillating system have been published in this *Journal* (3–6) that attempt to explain students' inquiries.

Oscillating systems do not only occur in homogenous solution phase. Other attractive systems are the mercury beating heart (7), the salt–water oscillator (8, 9), the gas evolution oscillator (10), and the explosion oscillator (11). Chemiluminescent reactions are also among the most fascinating demonstrations and have been successfully used as a pedagogical tool to introduce topics that are difficult to understand. Many of these demonstrations can be found using the *JCE* Online index.

A chemical reaction involving a light-emitting oscillator is a valuable educational and pedagogical tool to improve students' interest and attention about several chemistry concepts. Demas and Diemente (12) reported a luminescent oscillating chemical reaction but it requires an expensive fluorescent complex of ruthenium and an UV-lamp to enhance the effect. In this article, three different demonstrations of a chemiluminescent oscillating reaction in which a chemiluminescent substance (luminol) interacts with a known chemical oscillator producing oscillating chemiluminescence, are presented. These demonstrations have been successfully performed in basic chemistry courses to arouse interest and curiosity in students. Demonstrations fascinate audiences and in courses for science majors they are an excellent way to introduce complex concepts as far-from-equilibrium conditions, nonlinear dynamics and bifurcation, and chaos theories.

Procedure

All drugs are analytical grade. As indicated, all concentrations are critical to obtain reproducible results. It is recommended to use freshly prepared solutions for the

demonstration. Solutions stored for two months produce a longer oscillation period (lower frequency) and oscillate for a shorter time.

Solution A (1.00 M H_2O_2): Dissolve 115 mL of 30% hydrogen peroxide solution in 885 mL of distilled water. It is important to use fresh 30% hydrogen peroxide solution. Old solutions must be titrated with $KMnO_4$ to ascertain the actual hydrogen peroxide concentration. Fresh 3% hydrogen peroxide solutions, available in drugstore, can be used but a change in period of oscillation will be observed as its molar concentration is about 0.88 M.

Solution B (0.15 M KSCN): Dissolve 14.55 g of potassium thiocyanate in one liter of distilled water.

Solution C (6×10^{-4} M $CuSO_4$): Dissolve 0.15 g of copper(II) sulfate pentahydrate in one liter of distilled water.

Solution D (0.10 M NaOH and 3.7×10^{-3} M luminol): Dissolve 4.00 g of sodium hydroxide in 100 mL of distilled water. Then, add 0.55 g of luminol to the solution with constant stirring. Dilute to one liter with distilled water.

Note that the KSCN and NaOH cannot be replaced by NH_4SCN and NH_4OH , respectively, as NH_4^+ ion inhibits oscillations (13).

Hazards

An apron, rubber gloves, and goggles should be worn during preparation and performance of demonstration. Hydrogen peroxide solution, 30%, is a strong oxidant. Potassium thiocyanate may cause skin eruptions. Sodium hydroxide is caustic and corrosive. In all cases, avoid contact with eye and skin.

Demonstrations

The Chemical Buoy

Put a 2-L Erlenmeyer flask on a magnetic stirrer. Then pour 300 mL of solution A, 300 mL of solution B, 600 mL of solution C, and 300 mL of solution D into the flask. The speed of the magnetic stirrer must be fast enough to ensure homogeneity. The room lights should be off. After an induc-

tion time, low emission intensity light is observed and light pulses of four seconds appear with intervals of about two minutes and continues for about half an hour as if it were a buoy in the sea. The addition of a dye as an electronic-energy acceptor will change the color of the light emitted. Thiazol yellow and Fluorescein generate yellow and blue-green light emissions, respectively.

Oscillation periods can be decreased to 30 seconds, enhancing the effect during the demonstration, by heating all solutions to 50–60 °C before mixing to obtain a temperature of the mixture of about 40 °C. Do not allow the temperature to rise to 55 °C as oscillations last for only a short time and are quenched at temperatures of 65–70 °C. At a temperature of 40 °C oscillations last for about 20 minutes.

The Lighting Wave

A 2-m long, 1-cm i.d. glass tube is fixed vertically to a clamp stand. A rubber stopper is used to close the bottom. (A 50-mL burette can be used instead.) Then, 30 mL of solution A, 30 mL of solution B, 60 mL of solution C, and 30 mL of solution D are poured in a 250-mL beaker and heated to 50–60 °C without stirring. Immediately, the solution is poured through a funnel into the glass tube. Lights are off and after a few seconds a pulse of light can be observed shifting several times along the tube. An attractive variation is to use a transparent, flexible, plastic tube to generate different attractive forms such as circles, spirals, or capital letters of institute, and so forth.

Quantities of solutions are mixed according to the internal volume of the tube used. Keep the ratio of volumes at 1:1:2:1 of solutions A, B, C, and D, respectively, in all cases.

The Ghostly Cylinder

Place 400 mL of solutions A, B, C, and D in four different 500-mL beakers and heat the solutions to 50–60 °C. Then, pour the solutions into a 2-L graduated cylinder. The room lights should be off. After a short time, unsteady ghostly clouds of light will be observed in different parts of the cylinder.

Discussion

Orbán (13) has extensively studied oscillations in the Cu(II)-catalyzed reaction between H_2O_2 and KSCN. Schneider and Amrhen (14) introduced a chemiluminescent compound (luminol) in the oscillator system obtaining narrow and slightly asymmetric light pulses. They demonstrated a correlation between oxygen production and chemiluminescence emission frequencies.

As oscillating frequency depends on reagent concentrations and temperature of the system, several combinations of initial concentrations of reagents and temperatures can be tested to observe different behavior of the system and to optimize the oscillator. For instance, a ratio of volume 1:1:1:1 of solutions A, B, C, and D and the addition of 1 volume of distilled water decreased the oscillation period from two minutes to four minutes at a temperature of 20 °C. The effect of this kind of modification can be easily observed by placing two beakers side-by-side.

The light-emitter oscillator arouses curiosity in students and they try to find out a reasonable interpretation of their observations. In this way, several concepts about chemical kinetics, competitive reactions, effect of temperature, far-from-equilibrium conditions, bifurcation and chaos theories, and chemiluminescence applications can be introduced keeping students' attention on these complex chemical topics, while new oscillations are waited for in the dark.

Supplemental Material

CAS numbers of all substances used in these demonstrations are available in this issue of *JCE Online*.

Literature Cited

1. Gilbert, G.; Alyea, H. N.; Dutton, F. B.; Dreisbach, D. *Tested Demonstrations in Chemistry and Selected Demonstrations from the Journal of Chemical Education*; Department of Chemistry, Dennison University: Granville, OH, 1994; Vol. I, pp H65–H66.
2. Lefelhocz, John F. *J. Chem. Educ.* **1972**, *49*, 312–314.
3. Noyes, Richard M. *J. Chem. Educ.* **1989**, *66*, 190–191.
4. Field, R. J.; Schneider, F. W. *J. Chem. Educ.* **1989**, *66*, 195–204.
5. Field, R. J. *J. Chem. Educ.* **1972**, *49*, 308–311.
6. Hans, Degen. *J. Chem. Educ.* **1972**, *49*, 302–307.
7. Avnir, David. *J. Chem. Educ.* **1989**, *66*, 211–212.
8. Yoshikawa, Kenichi; Nakata, Satoshi; Yamanaka, Masahiro; Waki, Takeshi. *J. Chem. Educ.* **1989**, *66*, 205–207.
9. Noyes, Richard M. *J. Chem. Educ.* **1989**, *66*, 207–209.
10. Kaushik, S. M.; Yuan, Zhi; Noyes, Richard M. *J. Chem. Educ.* **1986**, *63*, 76.
11. Weimer, Jeffrey J.; Smith, Wayne L. *J. Chem. Educ.* **1994**, *71*, 325–327.
12. Demas, J. N.; Diemente, D. *J. Chem. Educ.* **1973**, *50*, 357–358.
13. Orbán, Miklós. *J. Am. Chem. Soc.* **1986**, *108*, 6893–6898.
14. Schneider, F. W.; Amrhen, J. *J. Phys. Chem.* **1988**, *92*, 3318–3320.