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The Purple Flask: A Novel Reformulation of the Blue Bottle Reaction

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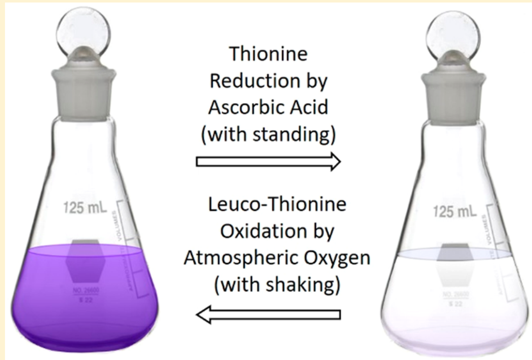
Supporting Information

ABSTRACT: Herein we describe The Purple Flask, a novel color-changing redox reaction that uses ascorbic acid as an electron donor, atmospheric oxygen as an electron acceptor, a copper−iron mixture as a redox catalyst, and the purple phenothiazine dye thionine as redox indicator. This formulation has several advantages over other versions of the classic "blue bottle" reaction for classroom demonstrations: (i) It uses noncaustic chemicals and proceeds at mildly acidic pH 4.2. (ii) The purple color generated by the oxidation reaction is intense, but fades rapidly. (iii) The reduction reaction rate is very temperature sensitive, which enables exploration of the impact of temperature on reaction kinetics. The Purple Flask is a vivid classroom demonstration that quickly captures student attention and can be used to illustrate the principles of redox chemistry in settings ranging from middle school through high school advanced placement chemistry and introductory college chemistry.



KEYWORDS: *Elementary/Middle School Science, High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Laboratory Instruction, Inquiry-Based/Discovery Learning, Aqueous Solution Chemistry, Oxidation/Reduction, Kinetics*

INTRODUCTION

Color-changing redox reactions are popular chemistry demonstrations. Perhaps the most famous and frequently performed is the "Blue Bottle",[1−3] in which the blue phenothiazine dye methylene blue (MB^+) is reduced by glucose at highly alkaline pH (eq 1) to form colorless leuco-methylene blue (MBH) and arabinonate,[4] and then oxidized back to MB^+ by atmospheric oxygen (eq 2) when the bottle is shaken:

$$MB^+_{(oxidized,\ blue)} + glucose(CH{=}O) + 2OH^- \rightarrow MBH_{(reduced,\ colorless)} + arabinonate(COO^-) + H_2O \quad (1)$$

$$MBH_{(reduced,\ colorless)} + \frac{1}{2}O_2(g) \rightarrow MB^+_{(oxidized,\ blue)} + OH^- \quad (2)$$

This classic reaction is easy to perform and reproducible, and it uses only three inexpensive chemicals. Moreover, over the years many variations have been described that use a variety of colorful redox indicators.[5−7] Unfortunately, for the purpose of hands-on classroom laboratory exercises, almost all these formulations have a major drawback: they require 0.5−2.0 M KOH or NaOH, which is highly caustic, requires careful disposal, and is unsuitable for use by younger students. To circumvent this problem, Wellman and Nobel[8] developed a "green" blue bottle reaction in which ascorbic acid serves as the electron donor at pH 2. However, this variation has a much lighter hue and displays slower color change kinetics than the original reaction.

Herein we describe The Purple Flask, a color-changing redox reaction that uses ascorbic acid as an electron donor, atmospheric oxygen as an electron acceptor, a copper−iron mixture as a redox catalyst, and the methylene blue analogue thionine as the redox indicator. This formulation offers several advantages for classroom demonstrations:

(1) It uses noncaustic chemicals and proceeds at mildly acidic pH 4.2.
(2) The purple color generated by the oxidation reaction is intense yet fades very rapidly.
(3) The rate of the reduction of thionine to colorless leuco-thionine is very temperature sensitive, which enables exploration of the impact of temperature on reaction kinetics.

MATERIALS

The Purple Flask reaction requires the following solutions:

- An ascorbic acid solution prepared from 12.0 g (68 mM) of ascorbic acid (CAS 50-80-7), 2.0 g (19 mM) of

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J. Chem. Educ. XXXX, XXX, XXX−XXX

anhydrous sodium carbonate (CAS 497-19-8), and 1000 mL of distilled water.

- A thionine stock solution prepared from 0.1 g (38 mM) of thionine chloride (CAS 581-64-6) and 10 mL of distilled water. Thionine acetate (CAS 78338-22-4) can be substituted.
- A copper–iron catalyst solution prepared from 0.12 g (70 mM) of copper(II) chloride dihydrate (CAS 10125-13-0), 2.4 g (0.89 M) of iron(III) chloride hexahydrate (CAS 10025-77-1), 1.0 g (0.57 M) of ascorbic acid (CAS 50-80-7), and 10 mL of distilled water. Anhydrous copper(II) and iron(III) chlorides can be substituted, provided the molar concentrations are maintained. Ascorbic acid is included in the solution as a preservative.

Store all solutions at room temperature. Protect the copper–iron catalyst solution from light.

PROCEDURE

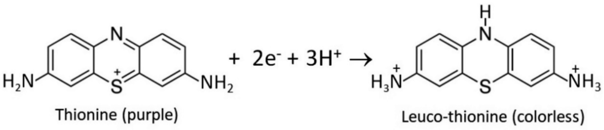
Fill a glass flask fitted with a water-tight stopper with 100 mL of ascorbic acid solution. The flask should be about half full. Add 6 drops of thionine solution (~0.25 mL) and 3 drops of copper–iron catalyst solution (~0.125 mL). Cap the flask and swirl gently. The purple color will fade rapidly. Then shake the flask vigorously. Within seconds the solution will turn a rich purple. However, immediately the color will start to fade; in less than 60 s the solution will be colorless. Shaking the container again will cause the purple color to reappear. This color change cycle can be repeated many times.

HAZARDS

Purple thionine solutions can stain hands, clothing, countertops, and sinks. Allow the reaction to turn colorless before appropriate disposal. Ascorbic acid, if ingested in large amounts, can cause indigestion and diarrhea. Sodium carbonate can cause skin and eye irritation on contact, and nausea and abdominal pain if ingested. Copper and iron salts can stain skin and are toxic if ingested in sufficient quantity, causing nausea, vomiting, and abdominal pain. All these chemicals pose a health hazard if inhaled.

DISCUSSION

Thionine is a purple tricyclic phenothiazine dye that is a structural analogue of methylene blue in which the two $N(CH_3)_2$ groups are replaced by primary amine groups. Thionine is commonly used as a histologic stain[9] and has been extensively studied as a component of electrochemical sensors[10] and dye-sensitized photogalvanic cells,[11] where it is usually paired with ferrous iron as an electron donor.[12] Thionine [$TN^+(NH_2)_2$] readily undergoes reduction by electron donors, such as ascorbic acid, to form colorless leuco-thionine, [$TNH(NH_3^+)_2$]. Below pH 5, this reduction involves uptake of 2 electrons and 3 protons (eq 3):



(3)

Adding sodium carbonate to the ascorbic acid [$Asc(OH)_2$] solution raises its pH to 4.2, which is just above the pK_1 of $Asc(OH)_2$, 4.17.[13] This makes $Asc(OH)_2$ a better electron donor,[14] as its redox potential decreases from 0.39 V at pH 0.0 to 0.15 V at pH 4.2.[15] Similarly, the redox potential of $TN^+(NH_2)_2$ is pH-dependent and decreases from 0.56 V at pH 0.0 to 0.20 V at pH 4.2.[16] The Purple Flask half-reactions and redox potentials are (eqs 4–6):

$$\text{dehydro-Asc}(=O)_2 + 2H^+ + 2e^- \rightleftharpoons Asc(OH)_2 \quad E^0 = 0.15\ \text{V} \tag{4}$$

$$TN^+(NH_2)_2 + 3H^+ + 2e^- \rightleftharpoons TNH(NH_3^+)_2 \quad E^0 = 0.20\ \text{V} \tag{5}$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \quad E^0 = 0.98\ \text{V (at pH 4.2)} \tag{6}$$

The overall reduction eq 7 and oxidation eq 8 reactions in the Purple Flask reaction are

$$TN^+(NH_2)_{2(\text{oxidized, purple})} + Asc(OH)_2 + H^+ \rightarrow TNH(NH_3^+)_{2(\text{reduced, colorless})} + \text{dehydro-Asc}(=O)_2 \tag{7}$$

$$TNH(NH_3^+)_{2(\text{reduced, colorless})} + \frac{1}{2}O_2(g) \rightarrow TN^+(NH_2)_{2(\text{oxidized, purple})} + H_2O + H^+ \tag{8}$$

Electron transfers from a redox couple with a lower potential to one with a higher potential are spontaneous; thus, both ascorbate reduction of thionine and leucothionine reduction of dioxygen are spontaneous at pH 4.2. Nonetheless, transition metals can serve as highly effective catalysts for redox reactions.[17] Given the facility with which thionine and iron exchange electrons in photovoltaic applications[11,12] (which is also the basis of the classic thionine photoreduction demonstration[18]), we initially selected iron as a catalyst. However, we thereafter empirically determined that addition of copper at a 1:13 molar ratio to iron yielded superior reaction kinetics than either metal alone. The better catalytic efficacy of the copper–iron mixture might be due to electron exchange between these two metals,[17] although we have no data to support this conjecture. The notable temperature sensitivity of the reduction reaction is likely due, in part, to the increased ability of ascorbic acid to donate electrons at higher temperatures.[15,19] Higher temperatures could also increase the rate at which thionine can accept electrons.

The role of atmospheric oxygen as the oxidant in the Purple Flask reaction can be demonstrated by filling the container to the top with ascorbic acid solution and adding a stirring bar for a mixer, or by sparging the solution with an inert gas such as nitrogen or argon.[1,6] Under these conditions, the solution will not change color. Alternatively, oxygen can be bubbled through the decolorized solution, which will quickly change it to purple. The catalytic role of transition metals in accelerating the oxidation of leuco-thionine can be demonstrated by omitting the copper–iron catalyst solution, in which case the appearance of the purple color upon shaking will be significantly delayed. The impact of temperature on the reduction reaction rate can be demonstrated by warming or cooling the reaction mixture in a water bath immediately before shaking.[3,6] At 30 °C the purple color will fade to colorless in less than 20 s, whereas at 10 °C the decolorization slows dramatically and takes almost 2 min.

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J. Chem. Educ. XXXX, XXX, XXX−XXX

Advanced students can measure the rate at which the purple color disappears as a function of temperature, either by visually estimating the end point or more accurately measuring it with a smartphone colorimeter,[20] and then use this data to determine the reaction order and calculate the reduction reaction activation energy. An example of this application described in the Supporting Information illustrates that the reduction reaction follows first-order kinetics with an activation energy of 52.7 ± 2.6 kJ/mol. Video clips showing the effect of temperature and several other suggested variations are also provided in the Supporting Information.

In summary, the Purple Flask reaction is a novel color-changing redox reaction that provides a vivid classroom demonstration that engages student interest, uses noncaustic chemicals at mildly acidic pH, is suitable and safe for hands-on use, and can be utilized to illustrate and explore the principles of redox chemistry and reaction kinetics in settings ranging from middle school through high school advanced placement chemistry and college chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00627.

Example of how to calculate the activation energy of the reduction of thionine by ascorbic acid by measuring the reaction rate as a function of temperature (PDF, DOCX)

Video showing how to set up the Purple Flask reaction and demonstrating the effect of adding a copper−iron catalyst on the rate of the oxidation reaction (MP4)

Video showing that bubbling oxygen, but not argon, into the colorless Purple Flask reaction causes the same purple color change as shaking the flask (MP4)

Video showing the effect of temperature on the rate of the reduction reaction (color fading) in the Purple Flask reaction (MP4)

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Notes

The author declares no competing financial interest.

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J. Chem. Educ. XXXX, XXX, XXX−XXX