

Using Demonstrations Involving Combustion and Acid–Base Chemistry To Show Hydration of Carbon Dioxide, Sulfur Dioxide, and Magnesium Oxide and Their Relevance for Environmental Climate Science

C. Frank Shaw, III,[†] James W. Webb,* and Otis Rothenberger

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, United States

ABSTRACT: The nature of acidic and basic (alkaline) oxides can be easily illustrated via a series of three straightforward classroom demonstrations for high school and general chemistry courses. Properties of carbon dioxide, sulfur dioxide, and magnesium oxide are revealed inexpensively and safely. Additionally, the very different kinetics of hydration of SO₂ (rapid) and CO₂ (slow) are evident. The pH changes observed by use of universal indicator provide striking visual evidence that makes the concepts of acidic and basic oxides less abstract and more concrete than verbal or written descriptions alone. By using the MgO solution for the SO₂ hydration reaction, one can mimic environmental interactions that lead to the neutralization of alkaline and acidic species. Interestingly, the SO₂ and CO₂ demonstrations can easily be adapted to environmental chemistry courses and especially the very relevant realm of climate change science. The difference in hydration rates explains why CO₂ is a greenhouse gas, but SO₂ is not listed as one. Variations of the CO₂ hydration demonstration reveal the sensitivity of oceans to acidification by dissolved CO₂ and the relationship of fossil fuel combustion to ocean acidification.

KEYWORDS: High School, Introductory Chemistry, First-Year Undergraduate, General, Demonstrations, Environmental Chemistry, Analogies, Transfer, Acids, Bases

INTRODUCTION

Because of its biological importance, carbon dioxide has long been a focus of attention in introductory chemistry courses. More recently, the role of carbon dioxide in climate and other environmental changes has necessitated broadening the scope of this topic in introductory courses. Liquefaction, hydrate formation, radiation absorbance, and hydration are among the carbon dioxide properties that are discussed in general readership science journalism articles related to anthropogenic climate change and the possible sequestration of anthropogenic carbon dioxide. The hydration of carbon dioxide is of interest for several reasons. First, this process is of biological importance. Second, the kinetics of the process are slow compared to other hydration reactions, a fact that allows biological systems to control this important process with the enzyme carbonic anhydrase. Finally, the process can produce a secondary ecological change that is concomitant with carbon dioxide's greenhouse gas effect-specifically, lowering the pH of natural waters. Sulfur dioxide, in contrast, is not a significant greenhouse gas, nor is it a substantial contributor to ocean acidification due to the rapidity of its dissolution into atmospheric water. Magnesium oxide hydration is also slow and leads to a basic oxide that hydrates to form an alkaline solution, in contrast to CO_2 and SO_2 .

The hydration of carbon dioxide has been reviewed in this journal previously.¹ A clock experiment that makes use of the relatively slow rate of carbon dioxide hydration has also been described.² Additionally, this journal has reported a laboratory experiment that investigates the catalytic action of carbonic anhydrase.³ We report here a very simple classroom demonstration of the slow rate of carbon dioxide hydration

as part of a more general demonstration of acid/base anhydrides and the role of combustion in producing acids and bases. Applications to environmental chemistry and climate change are presented.

CHEMISTRY OF THE DEMONSTRATIONS

The general purpose of these three demonstrations is to follow the chemical fate of several elements from combustion through hydration. The elements carbon, sulfur, and magnesium are investigated in the demonstrations and involve the following series of reactions.

Combustion of butane and hydration of CO₂:

$$C_4H_{10}(g) + 6\frac{1}{2}O_2(g) \to 4CO_2(g) + 5H_2O(g)$$
 (1)

$$CO_2(g) \to CO_2(aq)$$
 (2)

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$$
 (3)

$$H_2CO_3(aq) \rightleftharpoons HCO_3^{-}(aq) + H^+(aq)$$
(4)

Nonmetal oxide:

$$SO_2S(s) + O_2(g) \rightarrow SO_2(g)$$
 (5)

$$SO_2(g) + H_2O(l) \rightarrow SO_2(aq)$$
 (6)

$$SO_2(aq) + H_2O(l) \rightarrow H_2SO_3(aq)$$
 (7)

Received: April 27, 2016

Revised: October 12, 2016

ACS Publications

 $H_2SO_3(aq) \rightleftharpoons HSO_3^{-}(aq) + H^+(aq)$ (8)

Metal oxide:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
⁽⁹⁾

$$MgO(s) + H_2O(l) \rightarrow Mg^{2+}(aq) + 2OH^{-}(aq)$$
 (10)

Acid/base neutralization:

$$Mg(OH)_{2}(aq) + H_{2}SO_{3}(aq)$$

$$\rightarrow Mg^{2+}(aq) + SO_{3}^{2-}(aq) + 2H_{2}O(l)$$
(11)

The demonstrations also illustrate the relative rates of hydration reactions 3 and 7 for carbon dioxide and sulfur dioxide, respectively. They are the rate-determining steps because the respective dissociation reactions 4 and 8 are very rapid. SO_2 is a bent, polar molecule, whereas CO_2 is a linear, nonpolar molecule. The structural differences and dipole moments are important factors in the difference of the rate-determining steps. The larger size of sulfur compared to that of carbon also plays a role.

DEMONSTRATION APPARATUS

A demonstration apparatus that accommodates a "single pot" observation of both combustion and hydration can be constructed from an 800 mL cylindrical Fleaker flask and a cap that has a hole 14 mm in diameter to accommodate a butane charcoal lighter and a #1 stopper (Figure 1). Alternatively, a 1000 mL Erlenmeyer flask and #9 stopper with a 14 mm hole or a Florence flask can be used, but the visual effect is best in the cylindrical flask.⁴



Figure 1. Apparatus for formation of CO_2 or SO_2 by combustion. The cylindrical flask should be held tightly, canted about 20°, and gently rotated to prevent overheating the glass above the flame. If the tip of the lighter is splashed and fails to light after three tries, a back-up lighter should be immediately substituted, lest butane is accumulated and ignited. The canted angle best accommodates the lighter and fluid (250–400 mL).

Demonstration Procedures

In each of the following nonmetal oxide demonstrations, the cylindrical flask is charged with 400 mL of DI water, 1 drop of 2 M potassium hydroxide solution, and sufficient indicator solution to give the solution a visually appealing color. Either phenolphthalein or universal indicator may be used. For pedagogic and visual reasons, specific recommendations are made in each of the following procedures.

CO₂ Formation and Hydration. Carbon dioxide is generated by the combustion of butane. In the carbon dioxide demonstration, one vigorous shake does not dispel the red phenolphthalein color. Vigorous shaking over several seconds is required, thus providing a simple demonstration of the relatively slow hydration of carbon dioxide. The above reactions (eqs 1 and 5) produce a stoichiometric excess of products (CO₂ and SO₂, respectively) compared to the quantity of KOH used, as observed by the indicator color changes.

Use of universal indicator is appropriate for this demonstration. Alternative carbon dioxide demonstrations using universal indicator are described in the carbon dioxide clock demonstration and two climate science demonstration procedures below.

The Carbon Dioxide Clock Revisited. With some minor modifications, the previous carbon dioxide procedure can be run as a visually appealing carbon dioxide hydration clock. To an approximation, universal indicator runs through the colors of the spectrum (ROYGBIV) in the pH sequence 2, 4, 6, 7, 8, 10, and 12.^{5,6} Thus, the relatively slow hydration of carbon dioxide can be monitored by using universal indicator. In this variation of the carbon dioxide hydration experiment, 4 drops of 2 M potassium hydroxide solution are used to prolong the clock effect. In addition, the cylindrical flask is continuously shaken for about 4 s after replacing the butane lighter with the solid rubber stopper.

SO₂ Formation and Hydration. The preparation and execution of this demonstration is similar to that of the carbon dioxide demonstration, except that in the preparation, two wooden kitchen matches are taped to the end of the butane grill lighter so that the lighter flame will ignite the heads of the matches. The demonstration apparatus is charged with phenolphthalein as described above. With the cylindrical flask tilted slightly to allow the flame to angle away from the stem of the lighter (Figure 1), the trigger on the grill lighter is activated. The resulting flame will cause the match heads to flare, producing sulfur dioxide from the combustion of elemental sulfur and antimony(III) sulfide.⁷ The flame in the cylindrical flask is allowed to self-extinguish. Trying not to agitate the solution in the cylindrical flask, the grill lighter is withdrawn from the cylindrical flask without disturbing the solution, and the hole is stoppered with a #1 or #2 stopper, as appropriate. Finally, the cylindrical flask is given one vigorous shake. The effect with phenolphthalein is dramatic. The solution quickly changes from red to colorless, which can be observed in the chemagic "acidic-oxide" video.8

Use of universal indicator in this case is also instructive. Because two of the procedures below require universal indicator, the demonstration of the universal indicator changing from violet to red during the sulfur dioxide demonstration is useful.

In the case of the sulfur dioxide hydration, the change to the acidic color of universal indicator seems almost instantaneous. For the carbon dioxide demonstration, the change is slow enough to see the various color changes of universal indicator as the solution moves toward a lower pH.

MgO Formation and Hydration. A cylindrical flask is charged with 400 mL of DI water and enough universal indicator to produce a yellow color (pH \sim 6). If necessary, vigorously shake the closed cylindrical flask until ambient carbon dioxide produces a yellow color. Using a pair of tongs, burn a 1 in. strip of magnesium while holding the burning metal over the water within the open cylindrical flask. When the magnesium stops burning, drop the residual magnesium into the solution in the Fleaker and shake the closed cylindrical flask vigorously. Set it aside while the indicator in the solution turns color through blue to violet.

The details above are important because magnesium oxide produced by the combustion of magnesium ribbon presents several demonstration challenges. First, magnesium oxide is not very soluble in water. Second, the rate of solution of the ceramic form of magnesium oxide produced by combustion is very slow. Finally, the water solution of magnesium hydroxide produced using a reasonable length of magnesium ribbon is about pH 9, which is not sufficient to change the phenolphthalein color. The basic anhydride characteristics of magnesium oxide are, however, visually and effectively demonstrated with this variation of the approach for the nonmetal oxides when using universal indicator.⁹

To avoid the bright light of burning Mg and/or the extremely unlikely explosion of H₂ generated by burning Mg as it contacts the water, two alternatives to burning Mg are available: (A) place a length (about 5 cm) of Mg ribbon into the flask with water and heat until a color change is noted. Allow the solution to cool and observe the color change after cooling. (B) Add some Milk of Magnesia, which contains $Mg(OH)_{22}$ to water.

Chemistry Planet Earth. The above demonstration procedures can be combined to illustrate the complete cycle of one of the fundamental reaction sequences of planet earth: combustion, acid/base anhydride formation, and acid/base neutralization. This can be achieved by using the solution produced by MgO formation as the starting contents of a second Fleaker and simply performing the SO₂ formation demonstration (without use of potassium hydroxide). The final shake after the match combustion will change the blue-violet color to red.⁸

HAZARDS

There is a slight possibility that the flame from the combustion reactions could crack the borosilicate glass of the cylindrical flask. Care in tilting and gently rotating the cylindrical flask during combustion minimizes this already small risk. Any substitute reaction vessel should also be borosilicate glass. With the exception of the magnesium combustion, the products of combustion are formed in a contained system. From sad experience, the authors can ensure the reader that any uncontained combustion of magnesium may produce enough smoke to set off a classroom smoke detector, thus causing the needless evacuation of an entire building! The burning of magnesium is a component of the demonstration that should be done within a Fleaker or Erlenmeyer flask or in a fume hood. It should be performed by an experienced demonstrator. Mg burns quickly, and care needs to be taken so that the burning Mg does not touch the glass. Further, some water may "spit" back when the burning Mg contacts the surface. The quantity of Mg used in the demonstration is relatively small (2.5 cm Mg ribbon, ≈ 0.05 g), especially when compared to the ill-fated thermite reaction when molten iron was dropped into water.¹⁸ Alternatives to Mg burning are given above.

Universal indicator is an ethanol solution of several standard indicators. There is a fire hazard with the undiluted indicator, but the 1-2% ethanol in the diluted solution does not present a fire hazard in the magnesium or grill lighter combustion demonstrations.

The solutions produced by these demonstrations can be disposed of by flushing them down a drain with water. Standard demonstration safety is assumed: safety glasses, hand washing, and basic knowledge of the familiar chemicals involved. The ACS guidelines for chemical safety in demonstrations suggest a protective shield between the audience and the demonstrations. $^{19}\,$

DEMONSTRATIONS THAT APPLY TO CLIMATE SCIENCE

The carbon dioxide and sulfur dioxide experiments can be adapted to illustrate climate science properties of the two gases.

Ocean Acidification by Exhalation into Ocean Water or Aquarium Sea Water

Ocean water is mildly alkaline; historically, the pH was about 8.25. Increasing levels of CO_2 dissolving in the ocean partially neutralize its alkalinity, which increases the hydrogen ion concentration, $[H^+]$, effectively making the ocean slightly less alkaline and hence slightly more acidic. The acidification of oceans by dissolution of carbon dioxide can be demonstrated by several variations of the experiment described in the formation and hydration of CO₂. The simplest demonstration, which can involve every class member, requires straws; clear plastic cups (9 oz. or larger); aquarium seawater (commercial reef water, pH 8.2-8.3, buffered), ocean water, or seawater prepared in the lab;¹⁰ and universal indicator. Exhaling through a straw into the seawater (six to eight breaths for college students) will cause the blue-green color consistent with pH 8.2 to change after a short time to green and then to yellow (pH \sim 6). The bubbling agitates the buffered solution and facilitates dissolution. Two important climate-science lessons are (a) that carbon dioxide dissolves in the oceans, and (b) as it dissolves, CO2 reduces alkalinity and hence increases acidity of the oceans. Due to the small volume of seawater in this exercise, the effect is greater than a 100-fold increase in acidity. The present (2015) acidity of the oceans is about a 33% increase due to a 0.1 pH unit drop from pH 8.25 to 8.15. However, even this small perturbation is contributing to the loss of coral reefs.^{11–13} Likewise, the failure of Pacific Northwest Coast oyster larvae to attach to adult oysters and rocks is due to the CO₂-rich and therefore more acidic cold-water currents coming south from the Arctic Ocean.^{14,15}

Acidification of the Ocean by Fossil Fuel Emissions

The role of fossil fuels on climate change and the consequences for the ocean can be shown by using the charcoal lighter and aquarium (or authentic) seawater with universal indicator but omitting potassium hydroxide and otherwise following the procedure involving formation and hydration of CO₂. The cylindrical flask is an ideal vessel, but a 1-L Erlenmeyer or Florence flask can be substituted. The blue-green color of the universal indicator indicates $pH \approx 8$, consistent with the value of pH 8.15-8.25 for the oceans. After the combustion reaction has stopped, vigorous shaking brings about color change. A control cylindrical flask with universal indicator and a solid cover (no hole) serves to eliminate the possibility (sometimes suggested by deniers or skeptics) that the shaking alone causes the color change. By calling attention to the relationship of butane (a 4-carbon molecule) to the average gasoline molecule (8-carbon average of heptane, octane, and nonane) used in the family car, a meaningful connection to anthropogenic CO₂ formation, global warming, and ocean acidification (reduced alkalinity, increased acidity) is established.

SO₂ Is Not Listed as a Green House Gas: Why not?

Triatomic molecules are typically greenhouse gases, and carbon dioxide is a very important greenhouse gas due to the large emissions from the use of fossil fuels. Sulfur dioxide has the

capacity to function as a greenhouse gas. Molecules must undergo dipole moment fluctuations during their vibrational motions to absorb quanta of infrared radiation, which is the first step of the greenhouse gas phenomenon. All molecules of three or more atoms are greenhouse gases of greater or lesser strength. Why, then, is sulfur dioxide not listed in most tables of greenhouse gases? The answer is well-demonstrated in the SO₂ experiment described above, which can be performed without alteration for environmental purposes. The average duration of SO_2 in the atmosphere is one to five days, ^{16,17} compared to one or two decades for methane and centuries for carbon dioxide. The rapid dissolution of SO₂ into atmospheric water droplets leads instead to acid rain, which removes it from the atmosphere, or to formation of sulfate aerosols in the upper atmosphere, which reflect incoming radiation into space, thus having the opposite effect of greenhouse gases. As a result of the fast dissolution of SO_{2} , its atmospheric residence time (one to five days) is many orders of magnitude less than that of CO_2 . Thus, by geological time scales, SO₂ duration is inconsequential. However, this does not ameliorate its damaging property of generating acid rain.

DISCUSSION

Placement in High-School and First-Year Undergraduate Chemical Curricula

Acid/base chemistry: The products of the combustion reactions of Mg, S, and butane clearly delineate the differences between acidic oxides and basic oxides. The pH-dependent visual color changes enhance the perception of the chemical differences between nonmetal and metal oxides.

When buffered aquarium seawater (pH 8.2-8.3) is used with universal indicator, the overall pH change, assuming pH 6 for the final yellow solution, is in excess of two pH units, and the increased acidity can be calculated (>100-fold change). The present much smaller change in acidity due to lowering from pH 8.25 to 8.15 can also be calculated.

Stoichiometry: The mass of butane used to form CO_2 can be obtained by weighing the lighter on an analytical balance before and after combustion so that the moles of CO_2 formed can be compared to the moles of KOH initially added.

Equations: The sequential steps of the combustion reactions can be balanced and summed, leading to an overall equation combining the combustion and hydration.

Chemical equilibrium: The concentration of CO_2 dissolved in an aqueous solution depends on its pH, the temperature, and the CO_2 concentration of the gaseous environment. The CO_2 concentrations in the cylindrical flask after the butane combustion is significantly greater than that of the atmosphere; if left open to the air for an hour or two, the color reverts to a yellow-green or green color, indicating re-equilibration by loss of CO_2 to the atmosphere.

Placement in Environmental Chemistry

Acidification of the oceans: The two climate-science adaptations illustrate three important environmental properties of CO_2 . First, it dissolves readily in the ocean. Second, the dissolution is slow in the absence of agitation, as observed immediately after burning the butane: only with vigorous shaking of the flask or with the agitation induced by bubbling in the exhalation experiment does it rapidly dissolve. Either shaking the cylindrical flask or bubbling via straws increases the surface area, thereby accelerating hydration. Third, the formation of carbonic acid acidifies the ocean. In the

experimental situation, CO_2 must overcome the natural buffering of ocean water, which is observable in the duration of the blue-green shade of pH \approx 8 followed by rapid changes through green, pH 7, to yellow green to yellow, pH \sim 6. In addition to the calculation of the increased acidity upon pH change from 8.2 to 6 (above), students can calculate the actual increase in acidity due to the 0.1 pH unit decrease in the oceans (pH 8.25 to 8.15).

Natural cycles (planet Earth): Combustion generates acidic oxides, principally from nonmetal elements (e.g., sulfur and carbon), and alkaline oxides from oxidation of metals (corrosion) and combustion of natural substances, generating alkaline oxides of the metals present, principally Na, K, Mg, and Ca and leading to alkaline ashes. Using the MgO-containing liquid for the sulfur reaction shows the neutralization of the alkaline solution, leading to an acidic solution.

Greenhouse gases (CO_2 but not SO_2): Sulfur dioxide has vibrational modes capable of absorbing infrared radiation, as does any 3-atom molecule, even ozone. However, its effect as a greenhouse gas, due to rapid hydration in the atmosphere and return to earth as acid rain, has an insignificant effect compared to that of CO_2 , which is accumulating in the environment.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jwebb@ilstu.edu.

Notes

The authors declare no competing financial interest. $^{^{\dagger}}\mbox{Deceased}.$

REFERENCES

(1) Kern, D. M. The hydration of carbon dioxide. J. Chem. Educ. 1960, 37 (1), 14.

(2) Jones, P.; Haggett, M. L.; Longridge, J. L. The hydration of carbon dioxide: A double clock experiment. *J. Chem. Educ.* **1964**, *41* (11), 610–612.

(3) Spyridis, G. T.; Meany, J. E.; Pocker, Y. Carbonic anhydrase catalysis: An experiment for enzyme catalysis. *J. Chem. Educ.* **1985**, 62 (12), 1124–1125.

(4) Regardless of the flask and lighter used, the diameter of the hole for insertion should allow for some venting to prevent buildup of pressure inside the flask.

(5) Foster, L. S.; Gruntfest, I. J. Demonstration experiments: Using universal indicator. J. Chem. Educ. 1937, 14 (6), 274-276.

(6) Richardson, F. R. Universal indicator for pH 1–13. J. Chem. Educ. **1956**, 33 (10), 517.

(7) In this demonstration, two matches are optimum. The chemistry of match ignition is complex, but the production of sulfur dioxide is the focus of this demonstration.

(8) Rothenberger, O.; Webb, J. W. CheMagic Chemical Demonstration Videos. http://chemagic.org/home/demovideos.html (accessed Sep 2016).

(9) When the hot Mg contacts the water, the actual reaction is probably: Mg + $2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2$. As Mg burns in air, Mg_3N_2 also forms and is hydrolyzed by water to form $Mg(OH)_2$ and NH_3 .

(10) Lyman, J.; Fleming, R. H. Composition of Sea Water. J. Mar. Res. **1940**, *3*, 134–146.

(11) Buth, J. M. Ocean acidification: Investigation and presentation of the effects of elevated carbon dioxide levels on seawater chemistry and calcareous organisms. *J. Chem. Educ.* **2016**, 93 (4), 718–721.

(12) Perera, A. P.; Bopegedera, A. M. R. P. Laboratory experiment Investigating the impact of ocean acidification on calcareous organisms. J. Chem. Educ. 2014, 91 (11), 1951–1953.

(13) Hennige, S. J.; Wicks, L. C.; Kamenos, N. A.; Perna, G.; Findlay, H. S.; Roberts, J. M. Hidden impact of ocean acidification to live and dead coral frame work. *Proc. R. Soc. London, Ser. B* **2015**, *282*, 990–1000.

(14) Feely, R. A.; Sabine, C. L.; Hernandez-Ayon, J. M.; Ianson, D.; Hales, B. Evidence for upwelling of corrosive "acidified" water onto the Continental Shelf. *Science* **2008**, 320 (5882), 1490–1492.

(15) Welch, C.; Ringman, S. *The Seattle Times.* Sea Change: Oysters dying as the NW Pacific Coast is hit hard. http://apps.seattletimes. com/reports/sea-change/2013/sep/11/oysters-hit-hard/ (accessed Sep 2016).

(16) Intergovernmental Panel on Climate Change. Climate Change 2013: The Physical Science Basis, Working Group 1 Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M. M. B., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M., Eds.; IPCC: Bern, Switzerland, 2013; Chapter 6, p 472.

(17) Press, F.; Siever, R. Earth, 4th ed.; W. H. Freeman: New York, NY, 1985; p 342.

(18) Chemical demo goes out of control. Chem. Eng. News, 1990, 68 (10), 23.

(19) American Chemical Society. Safety Guidelines for Chemical Demonstrations. https://www.acs.org/content/dam/acsorg/education/students/highschool/chemistryclubs/chemclub-demo-guidelines.pdf (accessed Sep 2016).