Small-Scale Production of High-Density Dry Ice:

A Variant Combination of Two Classic Demonstrations

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Easily recoverable, thumb-sized pieces of high-density dry ice are conveniently produced by deposition of carbon dioxide within a test tube submerged in liquid nitrogen. A carbon dioxide-filled balloon sealed over the mouth of the test tube serves as a gas reservoir, and further permits a dramatic demonstration of both the gas-to-solid phase transition and Avogadro's law, with complete deflation of a 2-3 L balloon requiring only about 2-3 minutes. The dry ice "cube" that forms within the test tube is readily removed after slightly warming the tube's outer surface, and is of sufficient density to sink in an aqueous indicator solution, permitting its subsequent use for the classic demonstration of carbon dioxide's sublimation and its acidic properties.

KEYWORDS: general public; demonstrations; phase transitions; gases; acids/bases

Solid carbon dioxide ("dry ice") is both a common coolant for numerous commercial and laboratory applications, and a widely used material for classroom demonstration of various scientific principles. One particularly popular demonstration involves the submersion of dry ice in an aqueous indicator solution, resulting in vigorous sublimation of the CO_2, with impressive bubbling and fog production, and subsequent dissolution and acid hydrolysis of the dissolved gas, yielding a dramatic change in solution color *(1)*. For effective presentation of this demonstration, the dry ice must be sufficiently dense to sink in the aqueous indicator solution; otherwise the color change occurs only in the uppermost portion of the solution and is largely obscured by the vigorous bubbling and dense fog. While commercially prepared dry ice is adequately dense, that prepared from cylinders of liquid CO_2 using typical dry ice makers is not. A previous article in this *Journal* reported the use of a tea infuser to submerge such low-density dry ice, citing an advantage in cost relative to available dry ice compactors, and noting the added benefit of being able to control the immersion depth *(2)*.

Liquid nitrogen is also widely employed both for various laboratory applications and as a versatile agent for striking classroom demonstrations, including its use as a coolant to induce thermal contraction, viscous rigidity, and exothermic phase transitions *(3, 4)*. As an example of this latter use of particular relevance to this report, the deposition of carbon dioxide contained in a sealed latex balloon may be achieved by placing the balloon in or on the opening of a container of liquid nitrogen *(5)*, resulting in the formation of powdered dry ice within the balloon. In a slight variation on this procedure, I have used plastic storage bags in lieu of balloons, permitting visual examination of the dry ice produced, and facilitating its easy removal for closer inspection and further "play" if desired. Further extending this approach to include a simplified version of the deposition protocol often used in constructing critical point tubes *(6)*, a classroom demonstration that yields easily recoverable, thumb-sized pieces of high-density dry ice has been developed and is described below.

Materials

Carbon dioxide gas (cylinder or chemical generator)

Liquid nitrogen

Bromothymol blue indicator solution

Dilute aqueous sodium hydroxide

1-L graduated cylinder

150 mm test tubes

Forceps

Small Styrofoam cups and beakers

Latex balloons (12" or larger)

Procedure

Inflate a latex balloon with carbon dioxide to a volume of 2 – 3 L, and seal the balloon by stretching its opening across the mouth of a 150 mm test tube. If the fit is not snug, or if the balloons will not be used immediately, secure the seal with tape or paraffin film to reduce leakage. Though I typically transport to the classroom balloons that were previously inflated using large compressed gas cylinders available in our department's research laboratories, one may instead choose to inflate balloons in front of the audience using either smaller compressed gas cylinders[1] or an appropriate chemical generator.[2]

Place the test tube in a small Styrofoam cup nested within a matched-size beaker, and then fill the cup with liquid nitrogen. The subsequent deposition of carbon dioxide within the cooled test tube typically results in complete deflation of the balloon in about 2 – 3 minutes. To provide contrast, a "control" balloon inflated with nitrogen or air may be treated identically alongside the CO_2 balloon. If air is used, best contrast is achieved when this balloon is filled with a cylinder, pump or compressor, rather than by mouth, since exhaled breath contains significant amounts of condensable water vapor and carbon dioxide. Time-lapsed photographs depicting this process are shown in Figure 1.

Remove the deflated CO_2 balloon from the test tube, warm the outer surface of the tube with a stream of water from a wash bottle, then invert the test tube to eject the dry ice "cube". Use forceps or insulating gloves to transfer the cube to a 1 L graduated cylinder filled with an aqueous solution of bromothymol blue that has been made moderately alkaline with dilute sodium hydroxide. The dry ice sinks to the bottom of the cylinder and yields a striking presentation of the classic sublimation and acidification demonstration, with an abrupt color change occurring within a brief time depending upon the extent to which the solution was initially made alkaline. Time-lapsed photographs depicting this process are shown in Figure 2.

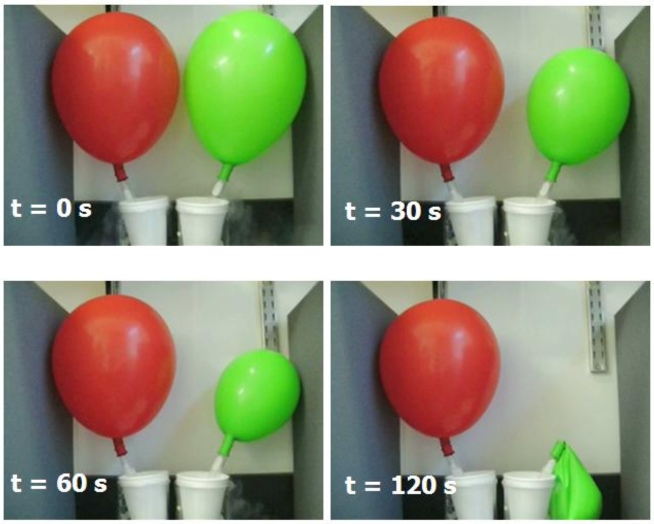

Figure 1. Time-lapse photographs showing the deflation of balloons filled with air (red) and carbon dioxide (green) due to condensation and deposition, respectively; elapsed times as indicated in the photographs.

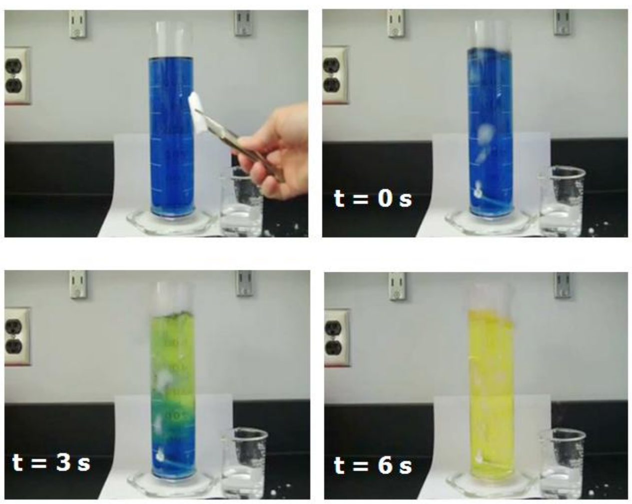

Figure 2. Time-lapse photographs showing submersion and subsequent actions of a dry ice cube produced per Figure 1 in an aqueous bromothymol blue solution; elapsed times as indicated in the photographs.

Hazards

Standard safety precautions should be observed when working with cryogenic materials such as liquid nitrogen (boiling point 77 K) and dry ice (sublimation point 195 K), including the assurance of adequate ventilation and the use of protective eyewear. If an air-filled balloon is used for comparison as described above, prolonged immersion of the test tube in the liquid nitrogen bath may result in the condensation of an appreciable amount of liquid oxygen (boiling point 90 K), which is both a cryogenic material and a powerful oxidant. Any condensed oxygen should be should be handled with care and prevented from contacting organic materials *(7)*.

Bromothymol blue is an eye, skin, digestive and respiratory tract irritant, but is not known to pose any particular toxicity or carcinogenicity risk. Prudent practice would be to store waste solutions for subsequent collection by a waste disposal company, though sink disposal of highly diluted solutions may be considered if allowed by local ordinances.

Discussion

The timeframe of the balloon deflation part of this demonstration allows its presentation as a lecture aid, with the instructor providing a narrative description of the involved processes as they occur. Alternatively, it may serve as the basis for a critical thinking exercise in which the instructor guides students through an assessment of their observations and various tentative explanations. Students often initially suggest a thermal contraction explanation, leading to a citation of Charles' Law ($V=k_CT$), but the near-ambient temperature of the balloon contents (well above the liquid nitrogen coolant) and the drastic difference in the two balloon deflation rates provide contradictory evidence. At this point, the instructor may show students the contents of each balloons' test tube, i.e., a large piece of white solid in one, and little or no liquid in the other. This will lead students to a phase-transition explanation and a citation of Avogadro's law ($V=k_An$) to explain the decrease in balloon volume accompanying its loss of gaseous CO_2 due to deposition within the test tube.

The dry ice cube produced per this deposition approach is easily removed from the test tube, and may be used for various purposes, including the classic demonstration of carbon dioxide's sublimation, dissolution, and acid hydrolysis *(1)*. Given that typical results permit the recovery of cubes weighing between 2 – 3 g, several minutes are typically required for complete sublimation. It is interesting to observe this process through to the end, as near completion the cube becomes more buoyant, presumably due to both the increase in solution density as it is cooled, and the concomitant formation of patches of water ice on the cube surface. Evidence supporting this latter assumption is seen when the sublimation nears completion, as the final seconds of the process usually include a rapid ascent of the cube remnant, which is observed finally as a small piece of water ice floating on the solution's surface.

A video depicting the full course of this demonstration may be viewed at the following URL: http://www.uncp.edu/home/paul/dryice.mov.

Notes

1. In addition to small "lecture bottles" of compressed gas familiar to most educators, even smaller canisters of compressed CO_2 and suitable inflation devices are available from vendors who market these products primarily for bicycle and small vehicle tire inflation (for example, see vendor websites http://www.gas-depot.com or http://www.genuineinnovations.com).

2. Generating CO_2 in the traditional manner (acid dissolution of bicarbonate or carbonate salts) is an alternate approach that would provide the added demonstration of a chemical reaction for the audience. However, the dry ice thus formed will likely be contaminated with significant amounts of water ice and may not be adequately dense unless the evolved gas stream is dried prior to entering the chilled test tube.

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