

## Spring Shock!

### Impact of Spring Snowmelt on Lakes and Streams

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#### Background

Acids from atmospheric pollution may be deposited to the environment through dry deposition (by acidic aerosols or gas-phase acids) or by wet deposition. Wet deposition includes acid rain, acid sleet, acid fog, and acid snow. In poorly buffered watersheds acid precipitation causes acidification. In many areas of the U.S. and Europe, year-round or chronic acidification has eradicated native fish species in lakes and streams (1, 2). Some streams that are not chronically acid may become acidic during the spring spawning season. This acute or episodic acidification (spring shock) can result in a decreased rate of sport fish hatching and reduced viability of the fry that do manage to hatch (3). One reason for the toxicity of acidification is the increased solubility of metals, especially aluminum, at low pH.

Acute acidification during snowmelt or storms is a complex process and may be due to a number of factors. One of these may be early or preferential release of acid impurities during the initial stages of snowmelt. The fact that the first liquid formed is more acidic is related to two-component phase equilibria often studied in introductory chemistry classes and can be demonstrated by a simple experiment using frozen vinegar.

#### Integrating the Activity Into Your Curriculum

When a pure substance is cooled slowly to its freezing point, solid begins to appear (unless there is supercooling). Solid and liquid coexist in equilibrium at the freezing point until all of the liquid is gone, and then the solid's temperature begins to fall. However, if something is dissolved in the liquid, the situation is different. The freezing point of the solution is lower than for pure solvent, and pure solid solvent (not a solid solution) usually freezes out. For example, ice beer is made by lowering the temperature of the beer to  $-4^{\circ}\text{C}$ , at which point pure water freezes out (4). This makes the beer somewhat stronger (higher alcohol concentration). Similarly, when a solution of dye in water freezes, pure water is formed first and the solution becomes more concentrated (5). Eventually the solution reaches a high enough concentration that both components freeze out as a mixture of two solids. When the temperature rises the opposite occurs. The mixture of solids melts first (at the lowest temperature), producing a solution that contains a high concentration of both components. For this activity the components are water and vinegar, and what melts first forms a liquid more concentrated in acetic acid than normal vinegar. As melting continues, the concentration of acetic acid decreases and the pH goes up.

#### About This Activity

This activity involves collecting liquid periodically while frozen vinegar cubes melt. It cannot be done in a single class or laboratory period. To do the activity at school, the instructor could begin at the start of the day, and have each chemistry (or other science) class collect one or two samples and measure the pH. Data could be combined and analyzed the following day. It is also possible to have students freeze and melt vinegar at home, perhaps over a weekend, and bring the samples to school to measure pH. If liquid samples are to be transported they must be stored in leakproof containers and properly labeled. Small plastic bottles with screw caps or plastic zip-lock bags (sandwich size) work fairly well.

The pH change observed is generally 1.3 to 1.4 pH units, within an approximate range of 2.6 to 4.1. The initial pH will be below that of vinegar that has not been frozen, and the pH will rise with time. Indicators or pH paper will not give meaningful results for changes over this pH range. A fairly good pH meter, preferably one that can be read to  $\pm 0.01$  pH unit, is required. Because pH meters vary, directions for use of the pH meter are left to the instructor.

The length of time for melting and the amount of liquid collected at each 30-minute interval will vary. Under typical conditions, 20 to 30 mL of liquid will be collected during each interval. If at least 10 mL of liquid is collected, you can make a measurement using a standard pH electrode. To do this, locate a vial slightly larger in diameter than the electrode. Transfer the liquid to the vial and insert the electrode.

#### Literature Cited

1. Halstead, J. A. *J. Chem. Educ.* 1997, 74, 1456A-B.
2. U. S. Environmental Protection Agency Web site: <http://www.epa.gov/>.
3. Bunce, N. J. *Environmental Chemistry*; Wuerz: Winnipeg, Canada, 1994, p 177.
4. See <http://www.labatt.com/Labatt/tastetastemaxice.html> and <http://www.budice.com/brewice.html>.
5. Moore, J. W.; Stanitski, C. L.; Wood, J. L.; Kotz, J. C.; Joesten, M. D. *The Chemical World: Concepts and Applications*; Saunders: Philadelphia, 1998, p 747.

All Web sites accessed February 1998.

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*Spring Shock* refers to a flow of acidic water into lakes and streams that occurs during snowmelt in the spring. Acid impurities in the snow contribute to the low pH. Acid snow is similar to acid rain, except that instead of being distributed through the ecosystem as it falls, snow piles up all winter long and then melts over a short period of time. The majority of the resulting water forms runoff, passing directly into lakes and streams. The increase in acid concentration (lowering of pH) is harmful to fish, especially during the spring when many species of fish spawn. The overall process is complex and not completely understood, but you can simulate the effect with vinegar, a dilute solution of acetic acid in water. What happens when frozen vinegar melts? Why?



### Try This

You will need: clear cider vinegar or white distilled vinegar; an ice cube tray; a plastic bag or plastic wrap; a freezer; a large plastic or glass funnel; support for the funnel such as a ring stand with ring clamp; 12 small containers such as beakers, plastic bottles, or plastic zip-lock bags; a timer; labels; a marking pen; and a pH meter. If you are working at home and will transport the samples to school for measurement with a pH meter, you must be able to close and tightly seal the containers. Plastic bottles with screw caps or plastic zip-lock bags work well. It will take two or three days to complete this activity.

- \_\_\_ 1. Pour clear cider vinegar or white distilled vinegar into a clean, dry ice cube tray. Put the tray into a plastic bag or cover with plastic wrap and set it in a freezer. Leave the tray of vinegar in the freezer at least overnight.
- \_\_\_ 2. Label the containers 1–12.
- \_\_\_ 3. Place 6 frozen vinegar cubes in a large clean dry funnel and suspend the funnel above the first container. (If you are working in the laboratory, use a ring stand to support the funnel. If you are working at home, you can suspend the funnel in a hole cut in one end of a sturdy shoe box. Place the container inside the box under the funnel. Another alternative is to place an open plastic zip-lock bag inside a tall drinking glass, with the opening of the bag folded over the rim of the glass. Support the funnel in the mouth of the glass so that the liquid is collected in the bag.)
- \_\_\_ 4. Set a timer for 30 minutes. After 30 minutes, remove the container beneath the funnel and replace it with the next container. Reset the timer for another 30 minutes.
- \_\_\_ 5. Measure and record the pH of the liquid collected, or cap/seal the container to take to school for pH measurement. Follow your instructor's directions for the proper operation of the pH meter.
- \_\_\_ 6. Repeat steps 4 and 5 until all the frozen vinegar has melted. This will take 5 or 6 hours. The time required will depend on the size of the vinegar cubes and the temperature of the room where you are working.
- \_\_\_ 7. Make a plot with pH of the sample on the *y*-axis and total time elapsed in minutes on the *x*-axis.
- \_\_\_ 8. Measure the pH of a sample of vinegar that has not been frozen and add it to your plot.

### Questions

- \_\_\_ 1. Compare the appearance and texture of the frozen vinegar with that of ordinary ice cubes.
- \_\_\_ 2. How does the pH of the vinegar melt change over time? How does the pH of vinegar compare with that of the melted cubes at the start of melting? at the end of melting? Explain what is happening to the acetic acid and water as the frozen vinegar melts.

### More Things To Try:

Take a can of frozen apple juice concentrate from a freezer. Scoop the concentrate into a funnel suspended over a clean, clear, colorless container. Observe the color of the melting juice as a function of time. If you are working in lab, do not taste or drink the melted juice. If you are working at home with clean kitchen implements and containers, you can add water to the melt according to the package directions, and drink the juice.

### Information from the World Wide Web

1. <http://www.epa.gov/acidrain/ardhome.html>
2. <http://www.qesn.meq.gov.qc.ca/ssn/acidrain/web.htm>

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