

A Molecular Explanation of How the Fog Is Produced when Dry Ice Is Placed in Water

Thomas S. Kuntzleman,^{*,†} Nathan Ford,[†] Jin-Hwan No,[†] and Mark E. Ott[‡]

[†]Department of Chemistry, Spring Arbor University, Spring Arbor, Michigan 49283, United States

[‡]Department of Science, Jackson College, Jackson, Michigan 49201, United States

S Supporting Information

ABSTRACT: Everyone enjoys seeing the cloudy white fog generated when solid carbon dioxide (dry ice) is placed in water. Have you ever wondered what physical and chemical processes occur to produce this fog? When asked this question, many chemical educators suggest that the fog is produced when atmospheric water vapor condenses on cold carbon dioxide gas that sublimates through the water. But this explanation is incorrect, as shown by Luck and co-workers in an article previously published in *J. Chem. Educ.* Herein, we extend this previous work by presenting some simple experiments and explanations that provide a model for how the fog forms when dry ice is placed in water. Many of these experiments can be carried out using materials found at the pharmacy, grocery store, or hardware store. The explanations involved draw from many concepts taught in general chemistry such as vapor pressure and Le Châtelier's principle.

KEYWORDS: General Public, Elementary, Middle School Science, High School, Introductory Chemistry, First-Year Undergraduate, General, Demonstrations, Physical Chemistry, Public Understanding, Outreach, Textbooks, Reference Books, Phases, Phase Transitions, Diagrams



When solid carbon dioxide (dry ice) is placed in water a thick, white fog forms. This demonstration is easy to do and it captivates most observers. Many children are familiar with the phenomenon, as it is routinely done at Halloween and birthday parties, during chemistry outreach events, and in science classrooms. Because the dry ice-in-water-fog (DIWF)¹ is both easy and generates great curiosity, it is not surprising that many variations on this experiment have been reported by chemical educators.^{2–7}

Witnesses of this experiment at our outreach events⁸ often ask how the fog forms when dry ice is placed in water. When first asked this question, we had no answer. Aware of a paper published in this journal,² we knew enough to inform inquirers that the water in the fog did not come from atmospheric water vapor, but rather from the bulk water into which the dry ice is placed. However, we did not know the pertinent physicochemical processes involved in the formation of the fog. One published paper describes energy transfer in this experiment,⁹ but otherwise the literature is silent on the mechanism of fog formation. Therefore, in this article we endeavor to describe on the molecular level what may be happening in this demonstration. That level of understanding can be inferred from how dry ice interacts with other liquids. We present some experiments and propose a simple mechanism to describe how the DIWF forms.

■ PEDAGOGY

In-class investigations of and discussion on the experiments and models described herein could provide a means for teachers to align their curriculum with several Science and Engineering Practices described in the Next Generation Science Standards (NGSS).^{10,11} The NGSS outline several scientific practices including Asking questions, Developing and using models, Planning and carrying out investigations, Analyzing and interpreting data, and Constructing explanations. That these practices are to be integrated *into* the content being taught rather than being treated separately embodies a significant difference between the NGSS and previously released standards. As such, it might be useful for teachers to present the experiments and models presented herein when discussing concepts such as phase changes, vapor pressure, and/or Le Châtelier's Principle.

■ EXPERIMENTAL SETUP FOR MEASUREMENTS OF FOG DENSITY

In order to compare how effective one experimental condition is to another in producing a "fog", one needs some semiquantitative way of measuring what we call "fog density". Our device consists of a 500 mL round-bottom flask containing ~200 mL of a particular liquid. This flask contains two openings. A pellet of dry ice (9–10 g) is dropped into the

liquid through one opening, which is immediately sealed. The fog formed exits the flask through the second opening, onto which is attached a bottomless plastic cuvette. It is important to note that the fog formed in these experiments comprises liquid condensate that has the same chemical composition as the bulk liquid into which the dry ice is placed. For example, when dry ice is placed into acetone, a fog of condensed acetone vapor is formed.⁵

The relative “fog density” is measured with an LED (any color) light source and light sensor situated around the cuvette. Fog density is defined as¹²

$$\text{Fog Density} = -\log\left(\frac{I}{I_0}\right) \quad (1)$$

where I_0 is the intensity of incident light and I is the intensity of light that travels through the fog. This experiment may alternatively be conducted in a simpler fashion using ~15 mL of liquid in a 100 mL graduated cylinder with the LED light source and light sensor positioned at the top of the graduated cylinder.

SOURCE OF THE FOG

Bulk Water Solutions

A persistent misconception regarding the DIWF is that it forms from atmospheric water vapor condensing on cold carbon dioxide gas on the surface of the bulk water. However, as reported previously in this journal,² atmospheric water is not the source of the DIWF. Rather, the water in the DIWF comes from the bulk water into which the dry ice is placed. To prove this, a precisely known mass of water (about 100 g) at room temperature is poured into a 250 mL graduated cylinder. A dry ice pellet of known mass is placed carefully (to avoid splashing) into the water. After the dry ice has completely sublimed, the mass of the water remaining in the graduated cylinder is determined. It is consistently observed that the mass of water in the cylinder is less than was present at the beginning of the experiment (Figure 1, closed circles). A linear relationship exists between the mass of dry ice added to the water and the mass of water that escapes the cylinder as a fog. The slope of this line indicates that about 0.1 g of water escapes from the

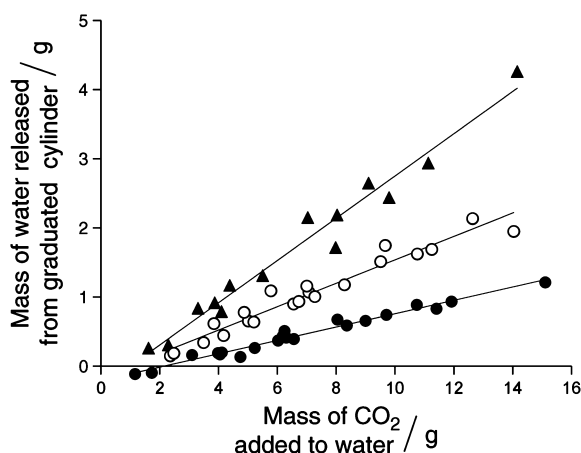


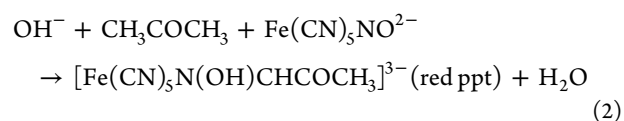
Figure 1. Water loss from a graduated cylinder into which dry ice is placed. Water initially at room temperature (closed circles), 50 °C (open circles), or 90 °C (closed triangles). The water temperature drops over the course of the experiment.

graduated cylinder for every gram of dry ice that is added. These results are consistent with the notion that the water in the graduated cylinder is the source of the condensed water vapor in the DIWF. The results for elevated temperatures will be discussed later.

Other Bulk Liquids

When dry ice is placed in various organic liquids, thin, evanescent fog materializes. If the source of the DIWF is the bulk water into which dry ice is placed, might not the source of the thin fog produced when dry ice is placed in another liquid be the very liquid into which the dry ice is placed? If so, the fog produced when dry ice is placed in ethanol, for example, should be composed of condensed ethanol droplets. The general assumption—indeed a misconception—is that the fogs are always composed of water. It is therefore instructive to demonstrate that when dry ice is placed in liquids other than water, the fog produced does not consist of water but of condensed vapor originating from the bulk liquid into which the dry ice is placed.

When dry ice is placed in ethanol a strong, sweet odor indicative of ethanol is observed. Furthermore, if a DIEF is passed through a digital alcohol breathalyzer, a positive result is recorded. These simple experiments provide evidence that the DIEF is composed, not of water, but of condensed ethanol vapor. Furthermore, when dry ice is placed in glycerin heated to ~150 °C, a sticky white DIGF emanates from the hot glycerin. The fog observed in this experiment is reminiscent of that made in fog machines. These are produced from condensed vapor of hot polyalcohols.⁴ Lastly, dry ice placed in acetone produces a DIAF composed of condensed acetone vapor. To show this, a drop of 0.8 M KOH is added to the test square of a ketone test strip (which contains sodium nitroprusside in acid buffer). When this strip is placed in a DIAF, the color of the strip changes from yellow to red. This color change is diagnostic for acetone according to the following reaction:^{13,14}



The DIAF produced when dry ice is placed in acetone is very thin and does not last long. Therefore, the same basic ketone test strip may need to be immersed in multiple DIAFs, produced one after another in separate beakers of fresh acetone to record a positive result.

EFFECT OF INCREASING THE SOLUTION VAPOR PRESSURE

Dropping dry ice into warmer liquids intuitively would be expected to produce a thicker fog with more liquid escaping. With water initially heated to 50 °C there is a release of about 0.2 g of water per gram of dry ice (Figure 1, open circles); if the water is heated to 90 °C, around 0.3 g of water escapes per gram of dry ice (Figure 1, closed triangles). Since the vapor pressure (VP) of water increases with temperature (Table 1), water with a higher VP induces a thicker DIWF. To further demonstrate the effect of increasing VP on the thickness of the resulting fog, room temperature and hot glycerin may be used. Pellets of dry ice are placed into separate 250 mL graduated cylinders, one filled with 100 mL of glycerin at room temperature and another filled with 100 mL of hot glycerin at ~150 °C. Because the VP of hot glycerin is over 10,000 times

Table 1. Vapor Pressure of Liquids at Various Temperatures^{15,16}

liquid	vapor pressure/torr
water at 25 °C	23.8
water at 50 °C	92.5
water at 90 °C	525
glycerin at 25 °C	0.0003
glycerin at 150 °C	4.5
acetone at 25 °C	231
ethanol at 25 °C	59
methanol at 25 °C	127
hexane at 25 °C	152
isopropanol at 25 °C	45

higher than the VP of glycerin at room temperature (Table 1), a sticky white DIGF, composed of condensed glycerin vapor, emanates from former but not the latter. While bubbling occurs in the room temperature glycerin, no fog is observed.

■ EFFECT OF SUBLIMATION TYPE AND CO₂ BUBBLE SIZE

The previous experiments demonstrate that increasing the VP of the liquid produces thicker dry ice fogs. This might lead one to suggest that a thick, persistent fog should form when dry ice is placed into any liquid with high VP, such as acetone or ethanol (Table 1). However, thin, transient fogs are produced when dry ice is placed in these liquids (Figure 2, green and red

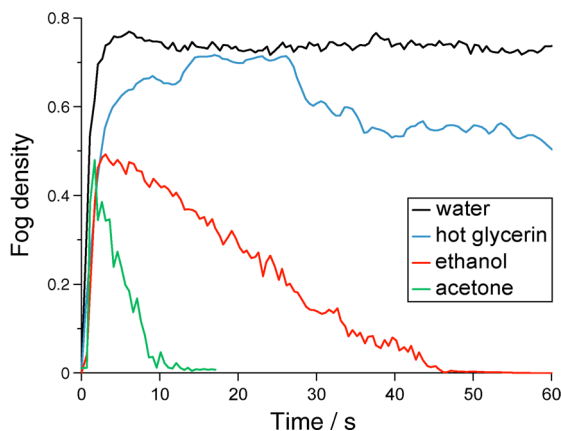


Figure 2. Fog densities resulting when 9–10 g of dry ice is placed into 200 mL of various liquids. Hot glycerol at 150 °C, all other liquids at 25 °C. Results for methanol, isopropanol, and hexane (data not shown) are similar to those observed for acetone and ethanol.

traces). In contrast, dry ice in water or hot glycerin forms dense and long-lasting fogs (Figure 2, black and blue traces, respectively). One possible explanation for the difference involves the type of sublimation that dry ice undergoes when placed into various liquids. Two types of sublimation are observed when dry ice is placed in various liquids.⁹ The first type, called nucleate state sublimation, is characterized by rapid sublimation of dry ice and evolution of numerous, tiny CO₂ bubbles. By contrast, in film state sublimation, a large CO₂ bubble forms a thin, insulating film around the dry ice. The dry ice sublimates slowly during film state sublimation. When dry ice is added to ethanol (high VP), tiny bubbles that are characteristic of nucleate state sublimation form (Figure 3, left tube); a thin and transient DIEF forms. Similar results are



Figure 3. Bubble sizes observed when dry ice is added to liquids. Ethanol (left tube), water (center tube), and room temperature glycerin (right tube). Small bubbles indicative of nucleate state sublimation also form in acetone, hexane, methanol, and isopropyl alcohol (data not shown).

observed when dry ice is added to the other high VP liquids (acetone, hexane, methanol, or isopropanol; data not shown). In contrast, large bubbles characteristic of film state sublimation⁹ (Figure 3, right tube) form and surround dry ice added to room temperature glycerin (very low VP), but no DIGF is formed. Finally, when dry ice is added to water (moderate VP) large bubbles characteristic of film state sublimation form and surround the dry ice (Figure 3, center tube). In addition, a thick DIWF is observed within these bubbles even before they completely separate from the dry ice! Taken together, these observations suggest that in order to form a thick and stable fog, dry ice should be placed in a liquid that has a high enough VP and also allows for film state sublimation. Given the result with the still relatively low VP heated glycerin, film state sublimation clearly is the more important factor. Of the liquids pictured only water has both these characteristics and a thick white fog is observed within the large bubbles formed in water. In water and glycerin, a film of CO₂ vapor insulates the dry ice pellet from the surrounding bulk liquid in a manner similar to the way boiling liquids are insulated from very hot surfaces via the Leidenfrost effect. This is consistent with previous work showing that water forms an insulating vapor layer at the dry ice–water interface.¹⁷

It is easy to demonstrate that the large bubble, which accompanies film state sublimation, effectively insulates dry ice from the surrounding liquid, whereas the small bubbles which accompany nucleate state sublimation do not. To do so, 50 g of a chosen liquid at room temperature is placed in a 125 mL Erlenmeyer flask, and a temperature sensor connected to a digital data acquisition system is immersed in the liquid. Once the temperature reading is stable, a 7.0 g pellet of dry ice is placed in the liquid. The temperature and the time required for the dry ice pellet to completely sublime away is recorded (Table 2). In the liquids in which the dry ice undergoes film state sublimation (water and glycerin), it requires longer than 6 min for the dry ice to sublime away. In the case of water, a CO₂

Table 2. Time for dry ice to sublime in various liquids^a

liquid	sublimation time/s
water	410 ± 30
glycerin	1200 ± 100
acetone	17 ± 3
ethanol	90 ± 5
methanol	30 ± 5
hexane	60 ± 5
isopropanol	150 ± 10

^aA 7.0 g pellet of dry ice placed in 50 mL of each respective liquid at 20 °C.

vapor film encases the dry ice pellet and insulates the bulk liquid from the cold pellet of dry ice. This causes the temperature of the water to drop slowly (Figure 4, dashed

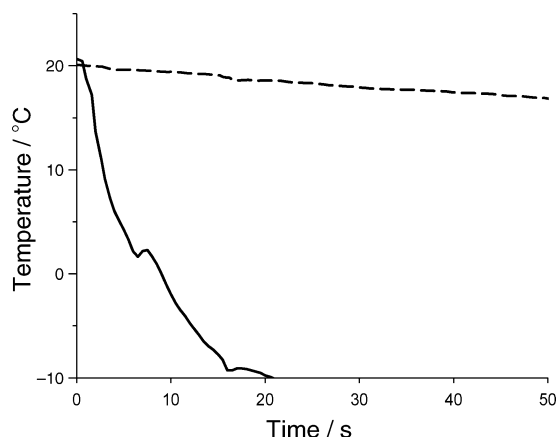
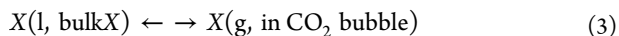


Figure 4. Temperature of 50 g of liquid to which a 7.0 g pellet of dry ice is added (at $t = 0$ s): water (dashed trace) and acetone (solid trace). Data for acetone not shown after the dry ice has completely sublimed away.

trace). On the other hand, in liquids in which the dry ice undergoes nucleate state sublimation (acetone, hexane, methanol, ethanol, isopropanol), the dry ice completely sublimates away in less than 2.5 min (Table 2). In the case of acetone, a very large number of tiny bubbles are formed. These tiny bubbles do not form a CO₂ vapor film that insulates the dry ice pellet from the surrounding bulk liquid. Because the liquid acetone and solid dry ice are in direct physical contact in many regions, the acetone easily and quickly transfers energy to the dry ice. As a result, the temperature of the acetone (Figure 4, solid trace) drops very quickly upon addition of dry ice, and the dry ice pellet simultaneously sublimates away in less than 30 seconds.

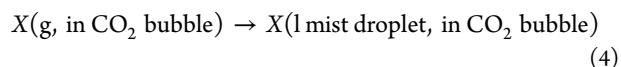
DISCUSSION

The following processes are proposed for the formation of the fog produced when dry ice is placed into a liquid. First, the submerged, subliming dry ice forms bubbles in the bulk liquid. Because at first the bubble contains only pure CO₂, bulk liquid molecules evaporate from the surface of the fluid/bubble interface into the CO₂ bubble:



In these equations, X represents molecules originating from the bulk liquid into which the solid dry ice is placed. If the

vaporized X molecules in the CO₂ bubble are able to cool enough, they condense into a fog within the CO₂ bubble:



By LeChâtelier's principle, when X vapor molecules condense into a fog in the CO₂ bubble (eq 4), more bulk liquid molecules evaporate into the dry ice bubble (eq 3). These molecules also condense (eq 4) to form an even thicker fog. The condensation of the vaporized liquid into a fog occurs while the CO₂ bubble is in contact with the solid dry ice, because vaporized X molecules within the bubble must be cooled considerably to condense. Thus, bulk liquid molecules evaporate into the CO₂ bubble, which remains in contact with the dry ice. Equations 3 and 4 occur on a very rapid time scale—even before the bubble separates from the solid dry ice (See Figure 3, middle test tube). Once the fog-filled bubble separates from the solid dry ice, it floats to the surface of the liquid where it pops open to release its cloudy contents into the atmosphere.

To relate these proposed processes with the experiments presented here, it is useful to categorize liquids into groups. While it is likely that many liquid physical properties not considered here (such as viscosity and surface tension) play a role in fog formation, these groupings are based only on relative VP and whether dry ice undergoes film state or nucleate state sublimation when immersed in the liquid (Table 3). Group 1

Table 3. Liquids Categorized by Relative VP and Type of Sublimation Dry Ice Undergoes When Immersed in the Liquid

liquid type	relative VP	sublimation type	fog observed	example(s)
Group 1	very low	film-state	none	room temperature glycerin
Group 2	low to high	film-state	thick and persistent	water, hot glycerin
Group 3	moderate to high	nucleate-state	thin and transient	acetone, alcohols

liquids are categorized by very low VP and film state sublimation, Group 2 liquids by low to high VP and film state sublimation, and Group 3 liquids by moderate to high VP and nucleate-state sublimation. In the experiments presented here, only Group 2 liquids have the properties necessary to form heavy, enduring fogs.

The Group 1 liquid glycerin (at room temperature) did not form any observable fog when dry ice was placed in it (Figure 3, right tube). To form a fog inside a dry ice bubble, molecules at the bulk liquid/CO₂ bubble interface must first evaporate into this bubble (eq 3). This process does not appreciably occur when dry ice is placed in room temperature glycerin because of its very low VP (Table 1). Therefore, no fog is observed when dry ice is placed in glycerin at room temperature. In contrast, the VP of Group 2 and Group 3 liquids is sufficiently high to allow the liquid molecules to evaporate into any CO₂ bubbles formed within the bulk liquid (eq 3). These vaporized molecules can then condense into a fog (eq 4), causing more evaporation into the bubble (eq 3). Why is it, then, that Group 2 liquids form thick, persistent fogs while Group 3 liquids form thin, transient ones (Figure 2)? The difference lies in the size of the bubbles that form when dry ice sublimates in these different liquid groups. In the nucleate-state sublimation that occurs in a Group 3 liquid, an enormous number of tiny bubbles rapidly

form around and separate from the solid dry ice (Figure 5). These tiny bubbles maintain very little contact with the solid

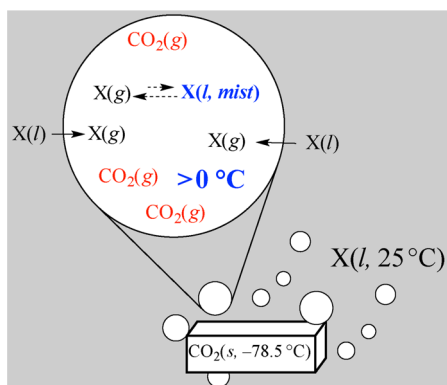


Figure 5. Nucleate-state sublimation that occurs within a Group 3 liquid leads to direct contact between CO_2 (s) and X(l) and minimal fog formation. All bubbles contain CO_2 (g), X(g) , and X(l) as indicated in the expanded bubble.

dry ice. As a result, these bubbles do not remain at low temperature for long, which limits the ability of vaporized liquid molecules to condense into a fog. Further, Group 3 liquid molecules within the bulk liquid come into direct physical contact with dry ice, causing rapid cooling of the bulk liquid and subliming of the dry ice (Figure 4, solid trace). Because the dry ice does not last long in these liquids, a long-lived fog cannot be maintained. By contrast, in the film-state sublimation that occurs in a Group 2 liquid, sublimed CO_2 vapor flows around the solid dry ice in a large bubble, physically separating the solid dry ice from the bulk liquid (Figure 6). This film of CO_2 vapor insulates the solid dry ice from the surrounding liquid, causing slow dry ice sublimation and cooling of the bulk

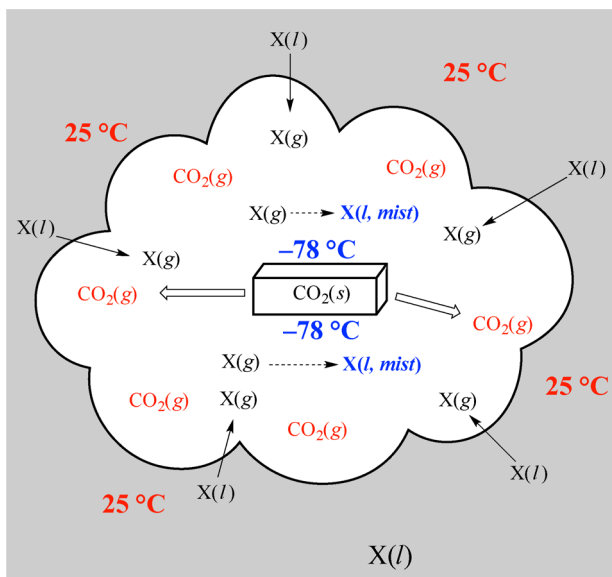


Figure 6. Film-state sublimation within a Group 2 liquid leads to a thick fog. A large CO_2 bubble (thick black line) forms an insulating barrier between the solid dry ice (center block) and surrounding liquid. Open arrows, sublimation of dry ice; solid thin arrows, evaporation of bulk liquid into bubble; broken thin arrows, condensation of vaporized liquid into fog. Note that the bubble size is greatly exaggerated for clarity.

liquid (Figure 4, dashed trace). (It should be noted that film state sublimation is most easily observed by submerging a large pellet of dry ice in glycerin at room temperature. The bubbling occurs slowly enough that one can easily observe the vapor film that completely surrounds the dry ice pellet.)

The slow dry ice sublimation allows for long-term fog production. In addition, the insulating CO_2 vapor film allows vaporized liquid molecules to come into contact with a large amount of cold CO_2 vapor from the dry ice, causing massive condensation (eq 4). Concomitant with the condensation of vapor, more bulk liquid evaporates, contacts cold CO_2 gas, and condenses. This process continues to form a rich, dense fog within the bubble. After the bubble separates from the dry ice, it rises to the surface, bursts open, and releases the fog produced.

CONCLUSION

Placing dry ice in water to form a fog is a simple and familiar demonstration, yet it is also interesting and dramatic. While the experiment is easy to perform, the processes involved in fog formation are complex. However, these processes can be elucidated with simple experiments and concepts familiar to most students of chemistry. Indeed, our students of general chemistry find these experiments to be thought provoking. For example, students are routinely surprised to discover that the water in a DIWF originates from bulk water, or that a DIAF is comprised of acetone and not water. Students also find it interesting that the processes posited (eqs 3 and 4) are analogous to atmospheric cloud formation during the water cycle.

The processes predicted herein explain why a fog forms when dry ice is placed in hot, but not room-temperature glycerin. The proposed mechanisms also explain why thicker fogs form in hot versus cold water and why thin, wispy fogs form in acetone, hexane, and alcohols. On the basis of the hypothesized processes involved in the formation of these fogs, it is predicted that dense fogs should form when dry ice undergoes film-state sublimation in any liquid with sufficiently high VP. Other liquid characteristics are likely to play a role in the formation of dry ice fogs. In the spirit of the NGSS, we hope that others ask questions and carry out investigations to construct some explanations of how other liquid physical properties affect the formation of dry ice fogs.

ASSOCIATED CONTENT

Supporting Information

Video footage of the experiment described in Figure 3 and also slow motion video footage of dry ice in water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tkuntzle@arbor.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Jackson Community Foundation for financial support and Emeric Schultz for helpful discussion. We would also like to thank the reviewers of this manuscript and the *Journal of Chemical Education's* editorial and production staff for

great feedback and suggestions that served to greatly improve this article.

■ REFERENCES

- (1) Throughout this paper, the abbreviation DIXF will be used for dry ice-in-X-fog ($X = W$ for water, A for acetone, E for ethanol, and G for glycerin) to distinguish among the fogs produced when dry ice is added to these various liquids.
- (2) Kohli, M.; Luck, R. L.; Ohtamaa, V. The Source of the Cloud Produced upon Adding Dry Ice to Water. *J. Chem. Educ.* **1998**, *75*, 60.
- (3) Wally, L. M.; Levinger, N. E.; Grainger, D. W. Employing Popular Children's Literature To Teach Elementary School Chemistry: An Engaging Outreach Program. *J. Chem. Educ.* **2005**, *82*, 1489–1495.
- (4) Vitz, E.; Lyle, K. S. Fog Machines, Vapors, and Phase Diagrams. *J. Chem. Educ.* **2008**, *85*, 1385–1388.
- (5) Bent, H. A. Carbon Dioxide: Its Principal Properties Displayed and Discussed. *J. Chem. Educ.* **1987**, *64*, 167–171.
- (6) Shakhshiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; The University of Wisconsin Press: Madison, WI, 1983; Vol. 2, pp 114–120.
- (7) Harris, D. C. *Quantitative Chemical Analysis*, 6th ed.; W.H. Freeman and Company: New York, 2003; p 240.
- (8) Kuntzleman, T. S.; Baldwin, B. W. Adventures in Coaching Young Chemists. *J. Chem. Educ.* **2011**, *88*, 863–867.
- (9) Aoki, K.; Sawada, M.; Akahori, M. Freezing due to Direct Contact Heat Transfer Including Sublimation. *Int. J. Refrig.* **2002**, *25*, 235–242.
- (10) For more information on the Science and Engineering Practices in the NGSS, see: <http://www.nextgenscience.org/sites/ngss/files/Appendix%20F%20%20Science%20and%20Engineering%20Practices%20in%20the%20NGSS%20-%20FINAL%20060513.pdf> Accessed Jun 2014.
- (11) Cooper, M. M. Chemistry and the Next Generation Science Standards. *J. Chem. Educ.* **2013**, *90*, 679–680.
- (12) Battan, L. J. *Cloud Physics: A Popular Introduction to Applied Meteorology*; Dover Publications, Inc.: Mineola, NY, 1962; p 12.
- (13) Fraser, J.; Fetter, M. C.; Mast, R. L.; Free, A. H. Studies with a Simplified Nitroprusside Test for Ketone Bodies in Urine, Serum, Plasma and Milk. *Clin. Chim. Acta* **1965**, *11*, 372–378.
- (14) Loach, K. W.; Turney, T. A. The Acetone Complex of Nitroprusside Ion. *Clin. Chim. Acta* **1961**, *18*, 179–183.
- (15) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 93rd ed.; CRC Press: Boca Raton, FL, 2012.
- (16) Mokbel, I.; Sawaya, T.; Zanolta, M.-L.; Naccoul, R. A.; Jose, J.; de Bellefon, C. Vapor–Liquid Equilibria of Glycerol, 1,3-Propanediol, Glycerol + Water, and Glycerol + 1,3-Propanediol. *J. Chem. Eng. Data* **2012**, *57*, 284–289.
- (17) Antonini, C.; Bernagozzi, I.; Jung, S.; Poulidakos, D.; Marengo, M. Water Drops Dancing on Ice: How Sublimation Leads to Drop Rebound. *Phys. Rev. Lett.* **2013**, *111*, 1–5.