# Cooling Gases

Phase Changes and Phase Diagrams

## Introduction

What happens to gases when the temperature is dropped way down? As this activity illustrates, it all depends on the gas.

### Concepts

- Condensation point
- Gas laws

- Intermolecular forces
- Phase change

## Materials

Gases such as carbon dioxide, helium, hydrogen, methane, and oxygen, 4-5 L of each	Paper towels, 2 Plastic bags, resealable, gallon-size, 5
Nitrogen, liquid, 1-L in Dewar flask	Rubber stoppers to fit test tubes, one-hole, 5
Water, in plastic cup	Saf-Cube <sup>™</sup> , 5-pint
Electrical tape	Scissors
Marker, permanent	Test tubes, large diameter, 5

## Safety Precautions

Use extreme care when handling liquid nitrogen. At atmospheric pressure, the temperature of liquid nitrogen is below its boiling point of  $-77 \text{ K} (-196 ^{\circ}\text{C})$ . Severe frostbite can result from contact with bare skin or clothing. Wear a pair of Zetex<sup>TM</sup> gloves when handling liquid nitrogen. When transporting liquid nitrogen in a car, prevent the filled Dewar flask from tipping and spilling its contents by placing it in a wide-based box. Surround the flask with packing material (i.e., crumpled newspapers) to stabilize and protect it. Carefully place the box on a flat and level surface in the car, such as the rear floorboard or the trunk rather than on the seat. Keep the car windows rolled down. This will prevent the displacement of oxygen from the car should the flask accidentally tip. The liquid nitrogen, liquid oxygen, liquid and solid methane and solid carbon dioxide used in this activity are all extremely cold and should be handled with proper precautions. Use Zetex<sup>TM</sup> gloves and never touch your skin directly to these substances or the test tubes in which they are in contact. Do not attempt to contain the condensed gases in the test tubes by means of a solid stopper, cork, or cap of any type. As the condensed gases warm, the pressure could cause the test tubes to rupture. Caution should be exercised when dealing with the flaming paper towels, especially the one soaked in liquid oxygen; it will burn at an alarming rate! Caution should also be exercised when burning the liquid methane. Remove all flammable materials and have a fire extinguisher available. Wear chemical splash goggles, Zetex gloves and a chemical-resistant apron. Wash bands thoroughly with soap and water before leaving the laboratory. Follow all laboratory safety guidelines. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

## Preparation

- 1. Cut off one of the bottom corners of one of the resealable bags. The hole made should be smaller than the wide end of the stopper (see Figure 1*a*).
- 2. Open the zipper of the bag and push one of the stoppers down into the hole so that the small end extends out of the hole. The fit should be tight (see Figure 1*b*).
- 3. Wrap the connection securely with 2–3 layers of electrical tape.
- 4. Press the air out and zipper the bag shut (see Figure 1*c*).
- 5. Repeat steps 1–3 with each of the plastic bags.
- 6. Label each bag with one of the names of the gases being used.





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## Procedure

- Fill the prepared bag labeled O<sub>2</sub> through the hole in the stopper with oxygen gas. *Note:* The bag should be completely filled and pillow shaped, but not filled to the point where the plastic might tear (see Figure 2a).
   *a. b. c.*
- Transfer the stopper securely into one of the test tubes. *Note:* To keep the gas from leaking out during this transfer, use one finger to push the plastic over the inside stopper hole (see Figures 2*b* and 2*c*).
- 3. Repeat steps 1–2 to fill each of the remaining bags respectively with each of the available gases.
- 4. Show the filled bags to the students, explain what substance each bag contains, and list on the board the melting/freezing and boiling/condensing points for each of the substances. Also list the temperature of the liquid nitrogen (see Table 1). Ask the students to predict what will happen to each of the gases when it is cooled in the liquid nitrogen.
- 5. Pour liquid nitrogen into the Saf-Cube to a depth of 3–4 cm (see Figure 3).
- 6. Place the test tubes all together in the container so that they extend down into the liquid nitrogen and their bags hang out over the top of the container (see Figure 4).
- 7. Observe for 5–10 minutes. This is a good time to discuss students' predictions, referring to Chart 1.
- 8. When no more changes are visible, remove the test tubes one at a time and observe their contents. Note that the bag of oxygen is

completely collapsed and that 4–5 mL of a pale blue liquid has condensed in the test tube. The methane bag has also collapsed, and 4–5 mL of a milky liquid has condensed in the test tube. The carbon dioxide bag has also collapsed, and 4–5 mL of a powdery white solid has formed inside the test tube. The hydrogen bag is only slightly collapsed and no liquid or solid can be seen in the test tube; the same observations can be made for the helium bag.

9. The test tubes may all be warmed back to room temperature, the bags re-inflated with the respective gases, and the demonstration may be repeated indefinitely with no refilling necessary. Alternatively, the following extensions may be used to show some further properties of some of the substances.

Gas	mp(K)	bp(K)	
H <sub>2</sub>	14	21	
Не	1	4	
N <sub>2</sub>	63	77	
O <sub>2</sub>	55	90	
CH <sub>4</sub>	91	109	
CO,	195 (sublimes)		

**Table 1.** Melting/freezing points (mp) and boiling/condensing points (bp) for hydrogen helium, nitrogen, oxygen, methane and carbon dioxide.







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Chart 1. Graphic representation of Table 1, showing the stable states at various temperatures (at 1 atm. pressure) for hydrogen, helium, nitrogen, oxygen, methane and carbon dioxide. The black vertical line represents 77 K, the temperature of liquid nitrogen.

## Extensions

#### Oxygen is paramagnetic

Hold a strong magnet alongside the bottom of the oxygen test tube and observe how the liquid oxygen is attracted toward it. Move the magnet up the side of the test tube and note how the liquid climbs up the inside wall. The stronger the magnet, the more pronounced this effect.

#### Oxygen supports combustion

Fill a cup with water, and have it available to extinguish flames. Take two 10 cm  $\times$  20 cm sheets of paper towel and twist them both into long, tight rolls. Holding one of the rolls with a pair of crucible tongs, light one end to show how the paper burns in air. Extinguish the flame in the cup of water. Remove the stopper from the oxygen test tube and use the tongs to lower the second paper towel roll down into the liquid oxygen. Tip the test tube back and forth to fully wet the paper towel with the liquid oxygen. Remove the roll with tongs and light the end to show how much faster it burns when saturated with oxygen. *Caution:* The burning is much faster and hotter.

#### Methane is combustible

Place just a few mL of water in a plastic cup (depth should be no greater than 6–8 mm). Remove the stopper from the methane test tube, and observe as the methane begins to boil. Using a clamp to hold the test tube, light the methane gas escaping at the mouth. Lower the very bottom tip of the test tube briefly into the water to warm it slightly, and observe the increased size of the flame. Remove it from the water to diminish the flame. *Caution:* If left in the water for more than a second or two, the flame can get quite high. *Further precaution:* Never leave an open test tube of liquid methane in the liquid nitrogen for any extended period of time (more than 40–50 seconds). Oxygen from the air will eventually begin to condense and mix with the liquid methane. If this should happen or you suspect it may have inadvertently happened, do not attempt to light the gas escaping from the test tube, it may represent a combustible mixture and backfire into the test tube. Instead, allow the methane/oxygen mixture to boil off under a fume hood and away from and ignition source. *Note:* To avoid this potential hazard, keep the test tube securely stoppered while in the liquid nitrogen, so that no air can enter.

#### Solid carbon dioxide

Fill a cup with water. Remove the stopper from the carbon dioxide tube. Dip the test tube in the water briefly to loosen the solid carbon dioxide (dry ice). Turn the tube upside-down and shake out the dry ice (gently tap the tube on the lab table if necessary). Observe as the solid  $CO_2$  sublimes.

## Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. Excess liquid nitrogen may be allowed to evaporate in a well ventilated area.

## Tips

- Prepare a sixth bag and label it  $N_2$ . Form a ladle out of a Styrofoam cup. Wearing Zetex gloves, dip the ladle into the Saf-Cube of liquid nitrogen. Pour a few milliliters of liquid nitrogen into a sixth test tube and proceed as in Step 2. Shake the test tube if necessary to fill the bag with nitrogen gas. If liquid nitrogen remains in the tube after the bag is filled, remove the tube (keeping the bag sealed as in Figure 2*b*) and pour the liquid nitrogen back in the Saf-Cube.
- To observe solid methane, leave the stoppered test tube in the liquid nitrogen for 20–25 minutes (see *Discussion* section below).

## Discussion

Helium and hydrogen are comprised of very small, nonpolar particles with extremely weak forces of attraction (known as Van der Waal forces) occurring between them. The temperature required to condense them into liquids is far lower than that of liquid nitrogen (77 K). The particles in the test tubes do slow down, and exert less pressure, thus the bags of helium and hydrogen do collapse slightly. *Note:* By Charles' Law, one would expect the gas samples to collapse to about one-fourth their initial volume (with the temperature decreasing from about 300 K to about 77 K), but only the portion of the gas inside the test tube gets cooled to 77 K; the decrease in bag volume would be much more pronounced if the entire bag could be submerged in liquid nitrogen!

Oxygen consists of much larger molecules which, although nonpolar, have strong enough intermolecular forces to give oxygen a condensing/boiling point higher than that of nitrogen. Hence liquid nitrogen at its boiling point is cold enough to condense the oxygen. The blue color of liquid oxygen is the result of molecule pairs cooperatively absorbing specific frequencies of light. In the gaseous state, the oxygen molecules are too spread apart for this cooperation to occur.

Methane has strong enough intermolecular forces not only to condense at liquid nitrogen temperatures, but also to freeze. The condensing of methane takes place rather quickly, yet the freezing is a much slower process (once the methane has condensed, its temperature is much closer to that of the liquid nitrogen, and so the heat transfer out of the methane is not as rapid). The cloudiness of the liquid methane is caused by the suspension of small crystals of solid methane throughout; indeed the longer the methane is allowed to cool in the liquid nitrogen, the cloudier the liquid gets, eventually freezing into a waxy-looking plug after 20–25 minutes. (*Reminder:* Keep the methane test tube securely stoppered while it is left in the liquid nitrogen.) That solid methane should have a waxy appearance is not surprising given that methane and paraffin are, after all, both in the same general category of compounds, namely alkanes.

Of all the substances discussed, carbon dioxide has by far the strongest intermolecular forces of attraction, and thus condenses at the highest temperature. Most intriguing, however, is that carbon dioxide condenses directly from a gas to a solid, with no stable liquid state in between. This is not to say that liquid  $CO_2$  cannot exist; it is just not stable at standard pressure. At higher pressures, above the triple point of  $CO_2$  of 5.1 atm, liquid  $CO_2$  can be observed as a stable phase. Indeed, a pressurized  $CO_2$  fire extinguisher can be tilted back and forth to hear the sloshing around of the liquid  $CO_2$  inside.

## Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
 Evidence, models, and explanation

 Content Standards: Grades 5–8
 Content Standard A: Science as Inquiry
 Content Standard B: Physical Science, properties and changes of properties in matter

 Content Standards: Grades 9–12
 Content Standard A: Science as Inquiry
 Content Standard A: Science as Inquiry
 Content Standard B: Physical Science, structure and properties of matter

## Reference

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Atkins, P. W.; Molecules; W. H. Freeman: New York, 1987.

## Flinn Scientific—Teaching Chemistry<sup>TM</sup> eLearning Video Series

A video of the *Cooling Gases* activity, presented by Bob Becker, is available in *Phase Changes and Phase Diagrams*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

## Materials for *Cooling Gases* are available from Flinn Scientific, Inc.

Catalog No.	Description
AP8560	Dewar Flask, Large, 4-L
GP6077	Test Tubes, Heavy-Walled, 25 × 200 mm
AP2305	Rupper Stoppers, One-Hole, #5
AP6011	Tape, Electrical, 60 ft
AB1005	Bags, Zipper-Lock, 12" × 15", Pkg/50
AP3240	Zetex <sup>™</sup> Gloves, 11" Length
SE051	Saf-Cube <sup>™</sup> , 5-Pint

Consult your Flinn Scientific Catalog/Reference Manual for current prices.