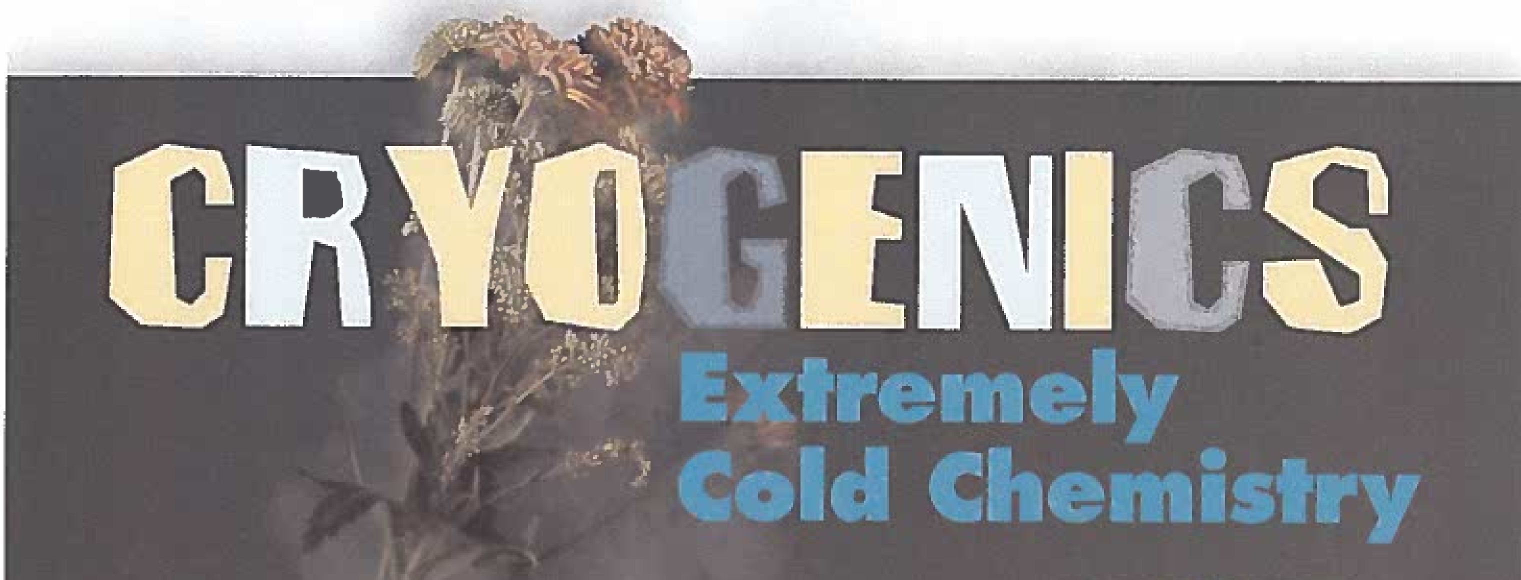

CRYOGENICS
Extremely Cold Chemistry

By Brian Rohrig

Everyone knows that chemistry is really cool, but cryogenics takes it to the extreme!

If a racquetball is dipped into liquid nitrogen and then dropped on the floor, it will shatter like glass. So will hot dogs, flowers, green peppers, and many other common objects. The properties of many substances change drastically when subjected to extreme cold. The fascinating branch of science that deals with extremely low temperatures (below –150 °C) is known as cryogenics.

How do you make something that cold?

The very low temperatures used in cryogenics are achieved by removing almost all of the thermal energy contained within a material. Thermal energy refers to the internal movement of the substance's molecules. What we call the "temperature" of something is actually a measure of the average kinetic energy possessed by the molecules of that substance. Kinetic energy is energy of motion. It depends on both the mass of the molecule and its velocity. For molecules moving with the same velocity, more massive molecules have higher kinetic energy. Just think, would you rather be hit with a ping-pong ball or a bowling ball? For a given molecule, the faster it is moving, the greater its kinetic energy. If you like mathematical equations, the equation for the kinetic energy of a moving object is

$$KE = \frac{1}{2} mv^2$$

The coldest possible temperature—at which there is no thermal motion—is absolute zero (0 K or –273.15 °C). Although it is theoretically impossible to actually reach absolute zero, we can get very, very close. In fact, scientists have succeeded in achieving temperatures just a few billionths of a degree above absolute zero.

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When a bouquet of flowers is submerged in super cold liquid nitrogen, it quickly freezes and becomes so brittle that it shatters when struck on a tabletop.

There are several ways to remove energy from a substance. One way is through evaporation. Evaporation is an endothermic (energy absorbing) process. Perspiration is important in cooling the body. But sweating by itself does not cool you. It is the evaporation of sweat on your skin that cools you, since evaporation requires energy. If evaporation occurs rapidly, like when alcohol is placed on your skin, the cooling effect is even greater.

Simply allowing gases to pass through a small opening can often cool them. This phenomenon is known as the Joule-Thomson effect. As the gas passes through the opening and expands, the molecules get further apart. This means that some of the attractive forces that exist between the molecules must be broken. The breaking of these attractive forces requires energy, and as this energy is removed from the gas, its temperature drops. You've probably seen a demonstration of this effect and didn't realize it. The pressurized (but room temperature) CO_2 inside a CO_2 fire extinguisher undergoes a Joule-Thomson expansion when it passes out through a special nozzle. As a result, when the extinguisher is activated, a very cold white mist of frozen and gaseous CO_2 shoots out and helps extinguish fires. Much of the cryogenic liquid production (and refrigeration for that matter) done today relies on some version of the Joule-Thomson effect for cooling.

PHOTODISC

Cryogenic applications generally do not depend on the specific properties of the liquefied gases themselves, but rather on the very cold temperatures of the liquids. The most commonly used cryogenic liquid is nitrogen. Because the atmosphere contains 78% nitrogen, it is the most easily obtained and the most commonly used gas. A relatively nonreactive gas, nitrogen will not burn, which eliminates some safety concerns.

In order to transport any cryogenic fluid, special containers are required. A special flask known as a Dewar flask (named after the British chemist) is needed. A Dewar flask is composed of two metal or glass cylinders that are separated by a vacuum. Because heat cannot easily be transferred through a vacuum, liquids within a Dewar flask can stay cold for long periods. The lids are also never threaded because some fluid always evaporates in the Dewar. If this gas cannot escape, pressure can build in the flask and cause it to explode.

One of the most widely used applications of cryogenic technology involves food preservation. However, most foods cannot simply be immersed in liquid nitrogen or they will become very hard and brittle and shatter if dropped. Improper freezing can also cause foods to turn into mush when thawed, due to extensive cell damage.

Cryogenic foods

Cryogenic freezing systems used for foods are extremely complex. They must be cooled gradually, often by first using the vapors of liquid nitrogen. Once the food is completely frozen, it can be transported long distances and thawed without damage.

All McDonald's hamburger patties are cryogenically frozen and then thawed after being shipped to individual restaurants. Airline food is often cryogenically frozen and then thawed before being served on the airplane. Pizzas, poultry, cakes, some fruits and vegetables, and TV dinners are often cryogenically frozen.

Dippin' Dots Ice Cream, marketed as the ice cream of the future, is made by instantly freezing droplets of ice cream mixture within liquid nitrogen. This results in perfectly formed tiny spheres of ice cream, and the large surface area of these spheres is designed to enhance the intensity of the taste. In 2002, the Dippin' Dots Company used 4.9 million gallons of liquid nitrogen to make 1.9 million gallons of ice cream! This averages out to 2.58 gallons of liquid nitrogen per gallon of ice cream. However, the exact method used to make the Dippin' Dots is a trade secret.

DIPPIN' DOTS, INC.

Cryosurgery

Have you ever had a wart "burned" off with liquid nitrogen at the doctor's office? In a typical scenario, the doctor comes into the examination room with a cup of this strangely effervescent liquid and carefully applies it to the wart. The wart freezes and turns white briefly. Even though it feels like a burn, the doctor is actually performing a simple type of cryosurgery. After a few treatments, the wart disappears.

Cryogenic liquid milestones

1877: Louis Paul Cailletet makes the first cryogenic liquid, oxygen (−183 °C). Later that year, Raoul Pierre Pictet liquefies nitrogen (−196 °C).

1898: Sir James Dewar liquefies hydrogen (−253 °C).

1908: The most difficult gas to liquefy, helium (−269 °C) is made by Heike Kamerlingh Onnes.

Cryosurgery is an exciting application of cryogenics that has emerged within the past 30 years. It uses extreme cold to kill cells. Hemorrhoids, cervical polyps, and many types of skin cancer can often be effectively treated by the application of extreme cold to the affected area.

Traditionally, cryosurgery has been used for external conditions that make it easy to apply a cryogenic substance. However, recent advances have shown that cryosurgery can also be effective in the treatment of prostate cancer, liver cancer, and tumors of the bone, brain, and spinal cord. It is sometimes used in conjunction with other treatments such as radiation and surgery.

An internal tumor is treated by applying an extremely cold liquid, such as liquid nitrogen, directly to the tumor by means of a specialized instrument known as a cryoprobe. Only a small incision is needed to insert the cryoprobe, and the surgeon is guided to the exact location of the tumor by ultrasound. Cryosurgery is much less invasive than other forms of surgery, involving minimal bleeding and scarring. It is much less expensive than traditional surgery, and recovery time is much faster.

While generally considered highly effective at treating external conditions, the jury is still out on its effectiveness at treating internal tumors. Early results are promising, but more study is needed to determine the long-term effectiveness of cryosurgery in treating internal malignant tumors.

You've got what in your freezer?

Another important application of cryogenics involves the storage of certain blood products in liquid nitrogen, such as bone marrow and plasma. Umbilical cord blood—a rich source of stem cells—has been successfully stored in liquid nitrogen for 15 years.

Human embryos, sperm, and eggs can be kept frozen indefinitely in liquid nitrogen, with no harm to the DNA. Bull semen is commonly transported in liquid nitrogen before being used for the artificial insemination of cows. A company known as Geneti-Pet will even keep your pet's blood cryogenically frozen if you believe that technology will eventually advance to the point where an identical pet can be cloned from its DNA!

A related field to cryogenics is cryonics, which is generally regarded with skepticism by most scientists. Cryonics involves freezing the entire human body after death in a large vat of liquid nitrogen. The idea is to keep the body *cryopreserved* until science advances sufficiently to bring a person back from the dead.

The body of legendary baseball great Ted Williams is housed at the Alcor Life Extension Foundation in Scottsdale, AZ. His head and body are actually stored in separate containers. He is joined by 12 other corpses, 37 frozen heads, and a few frozen pets. It has been reported that many other celebrities, such as Woody Allen and Michael Jackson, have expressed an interest in being cryonically frozen after death. But Walt Disney was never cryonically preserved, as has often been erroneously reported.

Interested, but not a wealthy celebrity? For a reduced rate, you can have just your head preserved. Are you worried about … uh … freezer burn among other things? You should be. There is no scientific evidence whatsoever that the dead can be revived after long-or even short-term storage in liquid nitrogen.

Other cryogenic applications

Are you looking to improve your golf game? Cryogenics might be able to help. NASA first discovered in the 1960s that deep-freezing could change the internal structure of steel and other metals. Known as cryogenic tempering, golf clubs can be treated with liquid nitrogen. This is done by placing the golf clubs in a specialized chamber, subjecting them to the vapors of liquid nitrogen, and gradually cooling the clubs to a temperature of –184 °C. After being exposed to this temperature for 24 hours, the clubs are then gradually warmed back to room temperature. This process is claimed by some to reduce vibration when the ball is struck, resulting in up to a 6% increase in distance compared to untreated clubs.

Refrigerated liquid nitrogen.

In industry, liquid nitrogen is commonly used to shrink-fit metal parts. When cooled, metals contract, and when they warm again, they expand. When assembling a product using metal rivets, for example, shrink-fitting can be used. The rivets are first immersed in liquid nitrogen and put into place.

Cryogenic golf ball? Not quite. A golf ball frozen in liquid nitrogen will sometimes split in half on its own. It worked one out of two times for us.

As the rivets warm, they expand, ensuring a very tight fit.

Rockets could not be launched without the use of cryogenic fluids. To launch a rocket, two components are needed: fuel and an oxidizer. The very first liquid-fueled rocket used gasoline as the fuel and liquid oxygen as the oxidizer. Most rockets launched since then still use liquid oxygen, but the fuel has changed. The main engines of the Space Shuttle use a combination of two cryogenic fluids: liquid hydrogen and liquid oxygen.

Magnetic Resonance Imaging (MRI) scanners use very intense magnetic fields generated by superconducting magnets cooled with liquid helium (–269 °C or 4.2 K). These magnetic fields are used to create an internal image of the body, which can then be used to diagnose many diseases, especially those of the brain and central nervous system. Many lives have been saved as a result of this technology, which would not be possible without cryogenics.

Brian Rohrig teaches chemistry at the Eastmoor Academy in Columbus, OH. His most recent article for *ChemMatters*, "Matches—Striking Chemistry at Your Fingertips", appeared in the December 2002 issue.