A Pair of Experiments with Liquid Nitrogen

MILOŠ ROTTER
Charles University in Prague, Faculty of Mathematics and Physics

Abstract

We add another two experiments with liquid nitrogen to our series described in previous years. They demonstrate phase transitions: creation of solid nitrogen and condensation of liquid oxygen using liquid nitrogen.

How to make solid nitrogen

If we lower the pressure of vapour above the surface of a boiling liquid by pumping it with a suitable vacuum pump, the temperature of the liquid decreases. It is because we intensively withdraw molecules which possess the highest energy that allowed them to leave the liquid. Molecules remaining in the liquid have lower and lower internal energy and thus a decreasing temperature. Liquid nitrogen at standard pressure (p_a = 101.325 kPa) boils at a temperature of T_b = 77.35 K. If its temperature is decreased to T_s = 63.15 K, which corresponds to a pressure of p_s = 12.5 kPa (triple point), a phase transition takes place and nitrogen becomes solid. Specific heat capacity of liquid nitrogen is equal to $c_p \approx 2\ \mathrm{kJ{\cdot}kg^{-1}{\cdot}K^{-1}}$, latent heat of vaporization at these temperatures is about $L \approx 200\ \mathrm{kJ{\cdot}kg^{-1}}$ [1, 2]. Thus we consume about 14% of liquid for cooling. The wastage of liquid is actually higher because natural evaporation of liquid nitrogen that is not thermally insulated must be taken into account.

Solid nitrogen is created in form of snow; it converts to compact ice at even lower temperatures. Solid nitrogen exists in two crystal modifications at the pressure of saturated vapour. The α phase has a hexagonal structure and an unfixed orientation of N_2 molecules. Solid nitrogen converts to the β phase that has a face centered cubic structure with N_2 molecules oriented in direction of space diagonals at a temperature of 36.61 K.

One needs a vacuum pump to prepare solid nitrogen. We use an oil sealed rotary vacuum pump with a pumping speed of 1.5 m^3/hour with a venting valve on the inlet that allows beginning pumping at a low speed (an aspirator would be also sufficient). For the vacuum chamber one can use a glass jar with a screw lid such as from yoghurt, see Fig. 1. One glues a tube into a hole drilled in the lid with some epoxy and connects the tube to the vacuum pump with a rubber hose. A plastic box from a photo film is put in the jar and liquid nitrogen is carefully poured into it using a funnel. We wait for the evaporation of nitrogen to settle down, close the lid and start pumping with open venting valve. We gradually decrease the pressure in the jar until we reach the triple point and remaining liquid nitrogen turns into solid in the form of a snow plug that jumps out of the box. Solid nitrogen has approximately half the heat capacity of liquid and thus it melts gradually in the poorly thermally insulated jar.

Fig. 1 A jar for the preparation of solid nitrogen

How to get liquid oxygen

Liquid oxygen is made in a similar way as liquid nitrogen from the air using liquefiers, heat pumps working usually in the reversed Kirk's (Philips') cycle [1]. Larger amounts of liquid oxygen are used in metallurgy or chemistry and also in rocket engineering. Oxygen is a very active oxidant and it must be treated under very strict safety instructions. Commonly used lubricants, most plastic materials and also some metals, such as aluminium, magnesium or titanium and their alloys burn easily in atmosphere with a high concentration of oxygen. Only a small amount of energy originating for example from friction or a physical shock is sufficient for ignition or even explosion. For this reason we avoid using oxygen in laboratory if it is not necessary. Dripping of liquid oxygen drops on skin is accompanied by biting pain due to rapid oxidation.

We will show how to safely prepare a small amount of liquid oxygen and demonstrate its physical properties. We avoid namely using common gas cylinders that can be manipulated only by specially trained personnel.

Oxygen forms diatomic molecules in its basic form. It turns from gas to liquid at standard pressure at T_b = 90.188 K, it reaches its triple point at a temperature of T_t = 54.39 K and a pressure of $p_t \approx$ 150 Pa. Thus it is not surprising that after some time a significant amount of oxygen condenses from ambient air into an open container with liquid nitrogen. This is pronounced mainly by a blue hue if the liquid. Such mixture of liquid nitrogen and oxygen can certainly be dangerous because it makes a strong oxidant. Polystyrene foam vessels which are very convenient for short-term usage of liquid nitrogen should not stay uncovered at least with a freely laid lid for a longer time. The well flammable polystyrene along with liquid oxygen may become the beginning of a very dangerous fire.

We can obtain a small amount of liquid oxygen directly from the air using a simple tool, see Fig. 2.

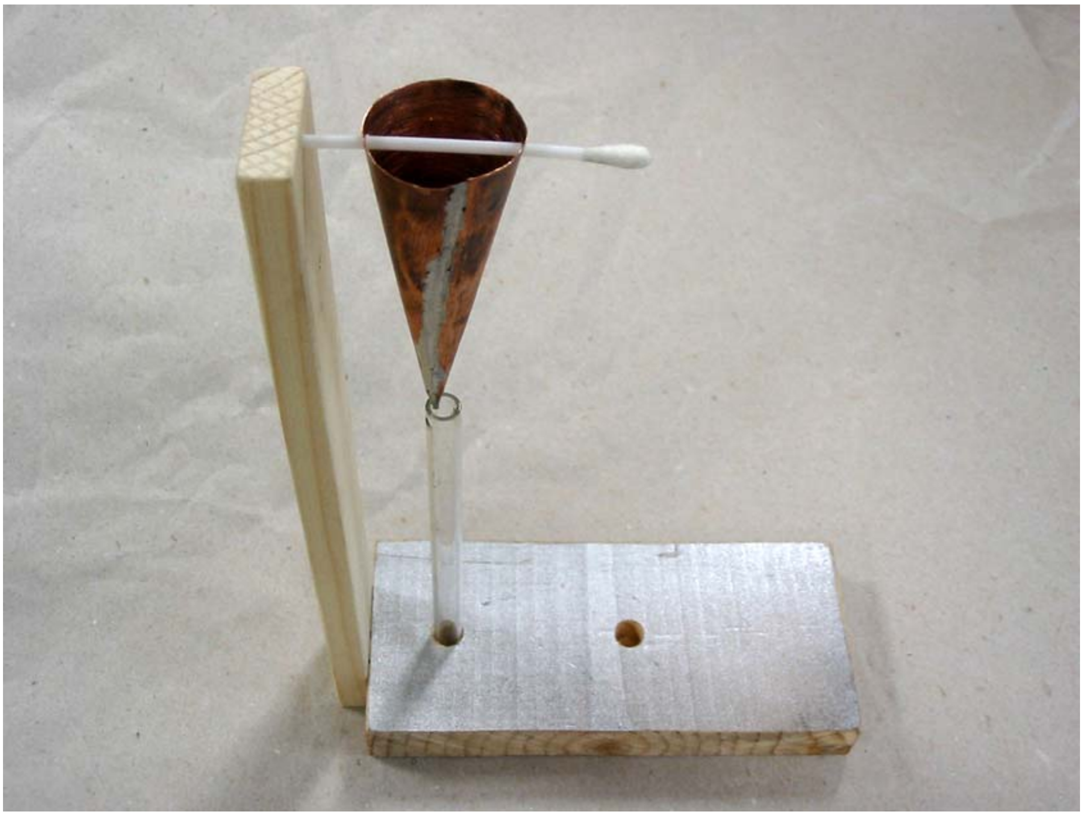

Fig. 2 Tool for liquefying oxygen from ambient air

We pour liquid nitrogen in a cone coiled from a copper sheet with a thickness of 0.3 mm or so and soldered with common Pb-Sn solder. Liquid oxygen condenses on the outside of the cone and drips into a test tube. There occur fewer and fewer droplets because the surface of the cone is getting covered with ice that grows from the water vapour contained in the air. It is needed to evaporate more than two times the amount of liquid nitrogen to get a certain amount of liquid oxygen. Oxygen heat of condensation is $L = 213\ \mathrm{kJ \cdot kg^{-1}}$, specific heat capacity of gas oxygen is $c_p = 0.91\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$ and the gas must be cooled from room temperature down to 90 K. Oxygen in the test tube evaporates quickly but we can prove its presence with a fired wooden skewer that we blow out before sticking it into the test tube. The skewer flames up again in the test tube. We can catch the drops with a cotton bud on a skewer. The oxygen saturated bud deflagrates rapidly above the flame of the candle.

If we put a permanent magnet, best made from NdFeB alloy, from side near to the dripping droplets, the droplets are pulled to the magnet that gets covered with a layer of liquid. Thus we prove a strong paramagnetism of liquid oxygen. Relative susceptibility of liquid oxygen has an unusually high value of $\chi = + 3 \cdot 10^{-4}$. It was first measured by James Dewar along with J. A. Fleming in 1898. It was allowed by modern computational methods of molecular dynamics to prove that the magnetic moment of the O_2 molecule is due to the unpaired electrons in molecular orbitals.

We can obtain a larger amount of liquid oxygen using pure medical oxygen that is sold for emergency medical situations in small metal vessels containing 8 liters of gas at a pressure of about 1 MPa (thus they are not classified as high-pressure gas cylinders and can be manipulated without restrictions). We inflate a toy balloon or football bladder (which is a rarity nowadays) with gaseous oxygen as one can see in Fig. 3.

Fig. 3 Balloon with attached test tube

An inflated balloon has a volume of about 1.3 l. We attach a test tube to it which we immerse in liquid nitrogen bath. About 1.5 ml of liquid oxygen condenses into the test tube in several minutes (the ratio of the volume of evaporated oxygen at room temperature to the volume of liquid is about $V_g/V_l = 845$). The test tube in our experiment has an inner diameter of 6 mm and thus we can see an approximately 5.5 cm tall column of nicely bluish liquid with which we can also demonstrate magnetic and oxidizing properties of liquid oxygen.

The bluish colour of liquid oxygen is due to formation of molecular orbitals of the O_2 molecule. Wide absorption bands are observed in the visible part of the absorption spectrum of O_2 that let pass only the blue part of passing white light. Yet, wavelengths of transitions between elementary energetic states of the O_2 molecule correspond only to weak lines in the infrared part of the spectrum [3]. To explain the origin of observed distinct absorption bands one must presume that one photon causes simultaneous transitions of two electrons to excited states in two different molecules. Other lines originate from an admixture of molecular vibrational transitions. A pair of molecules that take part in this process do not have to be bound. It is sufficient that they collide with each other.

If we fill the balloon with dry air only instead of pure oxygen, we also obtain liquid oxygen through this process but only about a fifth of the amount. We can also obtain several millilitres of liquid oxygen in about twenty minutes if we immerse a glass vessel into liquid nitrogen and let a weak current of dry air flow through it at a low pressure.

We have thus supplemented the existing set of experiments with liquid nitrogen [4] with demonstration of some thermodynamic phase transitions of cryogenic liquids.

Reference

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