A Simple Home-built Gas Liquefaction Cell

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Abstract: Liquefaction of gases offers deeper insight into the properties of various substances that are gaseous under normal conditions; however, the boiling temperatures of a number of gases are very low, preventing their liquefaction by means of standard laboratory techniques. A simple gas-liquefaction cell (designed by the authors) that can operate down to liquid-nitrogen temperature (77 K) is described in this paper. The properties of several liquefied (condensed) gases (e.g., ammonia, chlorine, nitric oxide, oxygen, and ozonized oxygen) are studied using this cell. The cell is also suitable for demonstration experiments.

Introduction

Chemistry, as well as physics, deals with the properties of matter. Both chemical and physical properties of a substance may show severe changes when the temperature or pressure are varied within certain limits. One well-known example is the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ [1–3], for which the color strongly depends on the temperature. Thus, when the temperature of the above gaseous mixture is decreased, the color fades continuously from very dark brown, through reddish-brown, to brownish-red. At about 295 K condensation occurs and the liquid has an orange-yellow color. Upon further decrease of temperature the liquid becomes yellow, pale-yellow, and finally freezes as a colorless solid, which is practically pure N_2O_4.

Similarly, the chemical reactivity may be shown to exhibit dramatic changes, depending on the state of aggregation of the reactants. Thus, solid potassium and liquid bromine combine so vigorously that a loud explosion occurs. (Caution: this reaction is dangerous and readers are not advised to try it.) The explosion results from a very fast reaction rate, interpreted in terms of a harpoon mechanism [4]. On the other hand, if solid potassium is placed in a cylinder filled with bromine vapor, no spectacular reaction (apart from KBr crust formation on the solid potassium surface) occurs. There are many other examples showing that, indeed, the physical and chemical properties of a substance are highly affected by the state of aggregation of the material in question.

In a number of cases it is possible to study the properties of substance in both the gaseous and liquid (or even solid) states. For instance, NO_2 (N_2O_4), N_2O_3, NOCl, CH_3CHO, etc. can easily be liquefied in an ice bath because their boiling temperatures are well above 273 K. SO_2, butane, and many other gases require somewhat lower temperatures, and liquefaction can be achieved using cryogenic mixtures (i.e., by adding NaCl, KNO_3, or NH_4Cl in the ice bath). A number of ordinary gases, however, have rather low boiling temperatures, for example, NH_3, chlorine, HCl, NO, and O_2 [5]. All of these can easily be liquefied (and most of them even solidified; see Table 1) using liquid nitrogen (LN_2). Unfortunately, to the best of our knowledge, no suitable laboratory liquefaction cells are commercially available (or, at least, are not available at a reasonable price). In what follows, we will first describe the construction of an inexpensive gas-liquefaction cell. Then, we will describe some experiments involving liquefaction of gases and the properties of those liquids and their solids will be discussed briefly. These experiments are suitable for demonstration purposes.

The Gas-Liquefaction Cell

In order to produce a gas-liquefaction cell that can be safely used for many years, we recommend the use of a best-quality hard (borosilicate) glass, which can survive rather abrupt temperature changes. Pyrex glass is inexpensive enough and meets the above requirements. The cell consists of three parts (see Figure 1).

Building the Cell. Three Pyrex glass (test)tubes of different diameters (we used tubes with diameters of ca. 1, 2, and 4 cm), two pairs of ground-glass joints that fit the selected tubes, a vacuum stopcock, a small funnel, and several ordinary glass tubes (i.d. ca. 3–4 mm) are needed. The parts are to be assembled (fused) exactly as shown in Figure 1. Avoid using glass tubes that are too long for part 1 of the cell and for connecting the stopcock to the outer Pyrex tube. We actually gave the drawing (as in Figure 1), where we marked the size of each part to the department’s glassblower and he constructed the cell in a couple of hours.

Cell Operation. Prior to use, the cell should be assembled and evacuated via the stopcock of the cooler (the stopcock to the right of part 3 in Figure 1). High vacuum is necessary to minimize thermal conductivity. After evacuation, the cell is mounted on a stand. The gas inlet tube (upper left of the transmitter, part 1, Figure 1) is connected to the supply of the gas to be liquefied. Then, the cell is splashed with liquid nitrogen (use a polystyrene cup) through the funnel of the cooler (part 3, Figure 1) several times. After thermal equilibrium is approached, LN_2 is added to an optimal level. This level depends on the properties of the gas used. Gases with relatively high boiling and freezing temperatures will require the level of LN_2 to be kept rather low (lower than the bottom of the receiver; see Figure 1, part 4). This is the case with Cl_2 and NH_3. On the other hand, oxygen can be efficiently liquefied with the cooler half-filled with LN_2. Proper operation of the cell requires some experience and some knowledge about the properties of the gas being used. In principle, it is

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Table 1. Melting (T_m) and boiling (T_b) temperatures of some gases that may be used in the demonstration

Gas	T_m, K	T_b, K
N_2	63.1	77.3
O_2	64.7	90.1
O_3	81.4	161.2
NO	109.5	121.3
HCl	158.5	188.2
Cl_2	173.1	239.2
NH_3	195.4	239.7

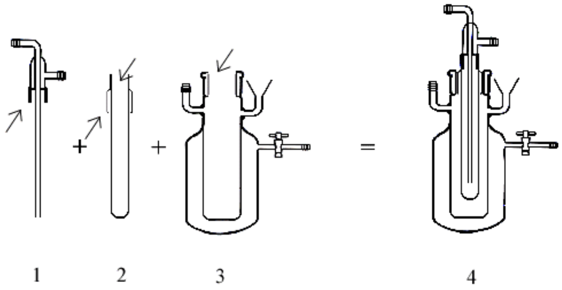

Figure 1. The parts of the liquefaction cell (1, gas transmitter; 2, receiver; 3, cooler) and the assembled liquefaction cell, 4. The arrows indicate parts that must be made of ground glass. The part marked by an upper arrow on the receiver should match that marked on the transmitter and that marked with lower arrow on the receiver should match that marked on the cooler.

always better to start the experiment with a low level of LN_2 in the cooler and then slowly increase it where necessary. Wherever possible, we strongly recommend that a gas be first stored in a rubber balloon or be collected in a gas reservoir (or suitable vessel under water), that will provide easy manipulation at a later time (see safety tips in the supporting material). The cell can be modified by adding a thermocouple thermometer to allow for precise temperature monitoring.

After prolonged operation, water vapor may condense on the outer walls of the cooler. A thin layer of glycerol or liquid soap will prevent this condensation. Alternatively, the observation can be performed with the lower part of the liquefaction cell (the cooler) dipped in a rectangular-walled glass vessel filled with water.

Demonstrations

The Liquefaction of Ammonia. Gaseous ammonia is easily generated by slow addition of a saturated solution of NH_4Cl in concentrated NH_4OH (use a separatory funnel) to solid NaOH in a Würtz flask. The gas is dried by passing it through a U-tube filled with $CaSO_4$ (possibly containing some $CaSO_4{\cdot}\frac{1}{2}H_2O$), prepared previously by dehydration of the dihydrate at ca. 450 K. We used pieces of blackboard chalk. (Be aware that $CaCO_3$ is sometimes used as a chalk material, so an identity check of the material, for instance, by testing with HCl, is necessary.) Please note that other convenient drying agents (such as P_2O_5, H_2SO_4 and $CaCl_2$) may not be used in this case, because they react with the ammonia gas. A slow stream of dry ammonia was passed through the liquefaction cell, keeping the level of LN_2 low. Very soon, droplets of liquid ammonia appeared on the wall of the receiver. After about 10 min it was possible to collect 1–2 cm^3 of ammonia, as a colorless liquid.

A small piece of sodium or potassium metal (match-head size, thoroughly dried and freed of the inevitable corrosion coating) is added to the liquid. The piece dissolves quickly, and the color changes to very dark blue. Allowing ammonia to evaporate brings on changes in the viscosity of the solution. After a while, the solution begins to crawl up the wall of the cell; this is followed by a color change from dark blue to a brass metallic luster. These changes are due to complex processes, including the formation of solvated electrons and are thoroughly described elsewhere [6].

When the ammonia is completely gone, a fine, highly reflecting film of sodium (or potassium) metal can be seen. The film is firmly adhered to the wall and can survive as such for up to an hour. This may be considered as evidence that one of the possible reactions in the system,

$$Na(s) + NH_3(g) \rightarrow NaNH_2(s) + \tfrac{1}{2}H_2(g) \qquad (1)$$

is indeed very slow and may be neglected during the time needed for this experiment. Ca, Sr, or Ba can be used instead of Na or K [6, 7].

This experiment should be performed last if liquefaction of several gases is planned for the demonstration because the receiver must be flushed with ethanol or water (to eliminate the traces of sodium or potassium) and dried before reuse; the drying is time-consuming.

Liquefaction of Chlorine. Chlorine was generated by slow addition of concentrated hydrochloric acid (from a separatory funnel) to solid potassium permanganate in a Würtz (side-armed) flask. The gas was dried by passing through a U-tube filled with $CaCl_2$, then passed to the liquefaction cell. To dispose of the excess chlorine gas, the gas outlet tube leading out of the cell (upper-right tube of transmitter) should be connected to a wash-bottle filled with a solution of $Na_2S_2O_3$.

As in the previous experiment, during liquefaction, the LN_2 level should be low, because of the relative high freezing and boiling temperatures of Cl_2. In a few minutes, a considerable amount of liquid chlorine can be collected. The liquid chlorine has a very intense yellow color. Potassium metal spontaneously ignites in a chlorine atmosphere. Addition of a small piece of potassium to the liquid chlorine (and a comparison of that reaction with the extremely vigorous one, when potassium is added to liquid bromine) is not recommended, however. The whole cell may explode or implode causing injury to the demonstrator and audience. The following experiment, on the other hand, is completely safe. A few crystals (up to 100 mg) of solid iodine is added to liquid chlorine (or, better, in a receiver containing both liquid and solid chlorine). Contrary to our expectations, the iodine appeared to be virtually insoluble in the liquid. The cell was left to warm up for a few minutes (no liquid nitrogen was added). After the solid chlorine melted, the liquid becomes muddy and soon a pale yellow precipitate (probably ICl_3) forms. If all the liquid is evaporated, a yellow solid residue is obtained. If it is left at room temperature for a longer period (a few hours) the solid changes color continuously, probably as a result of decomposition:

$$ICl_3(s) \rightarrow ICl(s) + Cl_2(g) \qquad (2)$$

The reaction product is soluble in $CHCl_3$, so the receiver can be splashed several times with chloroform to clean it for the next experiment and dried with a stream of gaseous nitrogen or air.

Liquefaction of Nitric Oxide. High purity nitric oxide can be prepared by the following redox reaction:

$$FeCl_2(aq) + 2HCl(aq) + NaNO_2(aq) \rightarrow$$
$$FeCl_3(aq) + NaCl(aq) + H_2O(l) + NO(g) \qquad (3)$$

A solution of $NaNO_2$ is placed in a long neck separatory funnel and is added slowly to the mixture of HCl and $FeCl_2$ solutions in a Würtz flask. A brown gas is formed, due to the instantaneous reaction of NO with oxygen:

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad (4)$$

After the air is thoroughly displaced with NO (NO is colorless), the gas is collected in a gas reservoir for later use. Collect about 2 dm^3 of NO gas.

A slow stream of nitric oxide is passed from the gas-reservoir through a U-tube filled with $CaCl_2$ to the liquefaction cell until the brown color of NO_2 completely disappears. At this point, the outlet tube out of the cell (upper-right tube of the transmitter) should be closed (preventing excess gas from entering the atmosphere.) and LN_2 is carefully added. The LN_2 should only touch the bottom of the receiver in order to avoid overcooling of the gas. In a few minutes NO gas condenses as a colorless liquid. The color, however, can be pale yellow-green due to NO_2/N_2O_3 impurities. Further cooling freezes the liquid into a white solid. Both the liquid and the solid consist of cyclic N_2O_2 dimers in the cis form [8]. Alternatively, in the presence of NO_2/N_2O_3 impurities, white and orange regions are seen in the solid phase. It is questionable whether the orange color is due to "...the asymmetrical dimer...observed to be formed as a red solid in the presence of HCl or other Lewis acids" [7] or due to "...a trans form and possibly another cis form...detected in smaller concentrations in un-annealed solid phase of N_2O_2" [8].

Liquefaction of Oxygen and Ozonized Oxygen. The fastest, safest, and most convenient way to obtain these gasses is to take oxygen gas directly from a gas cylinder into a rubber balloon with an attached glass stopcock. Alternatively, oxygen may be generated from $KClO_3$ with ~5% MnO_2 (acting as a catalyst) according to the reaction:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g) \qquad (5)$$

The generated oxygen should be collected in a gas reservoir.

The oxygen is then passed through the liquefaction cell, which is immediately cooled with LN_2. (It is necessary to dry the gas if it is generated and collected in a gas reservoir.) If the LN_2 level is high enough (as it may be, in this case) 2–3 cm^3 of liquid oxygen are collected in the receiver within 5–10 minutes. Liquid oxygen has a pale blue color. If a strong electromagnet is available, it may be interesting to check the liquid oxygen paramagnetic properties. The magnet should first be cooled with liquid nitrogen to prevent rapid boiling of the liquid oxygen.

After completion of this demonstration, it is a good idea to repeat it, first passing the oxygen through an ozonizer. (We used a simple lab-made ozonizer.) The procedure is exactly the same as above. The liquefied ozonized oxygen has a violet-blue color. By repeated fractionation (allowing the liquid to evaporate partly and then liquefying another portion of gas) the liquid is ozone enriched, as evidenced by its darker color.

As suggested by a reviewer of this manuscript, large quantities of oxygen could be liquefied by attaching tubing from a gas cylinder to a stoppered side-arm flask, which is immersed in a Dewar flask filled with liquid nitrogen. Simple and effective demonstrations of burning steel wool or a cigarette in liquid oxygen can easily be performed in this way.

Safety Tips and Disposal

Wear safety goggles or face shield during this experiment. Appropriate gloves are also recommended when working with liquid nitrogen and with large quantities of other liquefied gases (e.g. liquid oxygen, argon etc).

Beware that chlorine is a poisonous gas. (It was actually used in World War I). NO is also highly toxic, as well as ozonized oxygen, hydrogen chloride and ammonia (although to a substantially lesser degree). **Never breathe in any of these gases. Never collect more than 1–2 cm^3 of liquid chlorine, nitric oxide, ammonia, hydrogen chloride etc.** Liquefaction of these gases should be done in a hood. In case of accident (e.g., poisoning due to inhalation etc.) consult a physician immediately.

In all cases where the inlet tube is directly connected to the gas-generation equipment special care must be taken to prevent freezing of the gas and thus obstruction of the in-cell gas outlet tube (bottom tube of transmitter) because in unfavorable cases (for instance, if there is no safety tube in the gas-generation apparatus) there is a risk of explosion and injury of the experimenter. It is important to note that a separatory funnel, when the stopcock is open, acts as a safety tube. Bubbling of gas through the funnel may be considered as a strong indication of obstruction of the gas outlet tube. In such cases, carefully remove the separatory funnel and disassemble the apparatus.

It is strongly recommended that the disposal of most of these gases (apart from oxygen and ozonized oxygen) should be done by chemisorption using wash-bottles filled with suitable reagents. This procedure should also be done in a hood.

Conclusion

The liquefaction cell described here can be easily built in a couple of hours by an experienced glassblower. The experiments that can be performed using the cell are very interesting; they attract the attention of students and significantly increase their understanding of the properties of substances and of chemistry.

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