CHAPTER 17

NITROGEN

DANIEL RUTHERFORD IS CREDITED with the discovery of nitrogen in 1772. Like Priestley, Rutherford did not recognize his substance as a new element. It was Antoine Lavoisier who correctly identified nitrogen as an element and named it ***azote*** meaning "without life". The name ***nitrogen*** was suggested by Jean-Antoine-Claude Chaptal in 1790 when it was recognized that it was one of the elements present in nitric acid. The name is also based on the Greek word ***nitron*** which means ***to form***.

Like oxygen, nitrogen, N_2, is a colorless, odorless, and tasteless gas with a very low solubility in water. Interestingly, nitrogen molecules give the orange-red, blue-green, indigo and deep violet colors to the dawn sky. The melting point of N_2 is -209.86 ^oC and its boiling point is -195.8 ^oC. Liquid nitrogen is colorless. The density of nitrogen is 1.145 g/L at 25 ^oC and 1 atm — 3% less than air.

Nitrogen occurs chiefly in the atmosphere, where is constitutes 78% of air. The rest of air is made up of oxygen (21%), argon (about 1%) and traces of carbon dioxide, water vapor and a dozen other gases. The mass of the atmosphere is approximately 5 x 10^{18} kg, so there is a limitless supply of nitrogen. Very little nitrogen is found in minerals or crustal rocks.

Nitrogen is obtained by the fractional distillation of air. Nitrogen is ranked second among industrial chemicals in terms of commercial production with over 20 billion kilograms produced per year in the USA. Four other nitrogen-containing compounds, all originally produced from nitrogen, also appear in the Top 15.

The main use of nitrogen is as an inert blanket in the iron and steel industry as well as in related metallurgical and chemical activities where an inert atmosphere is required. Another important, large-scale use of nitrogen blankets is in the glass industry. One third of the nitrogen produced is liquefied for use as a refrigerant. Liquid nitrogen is maintained at its normal boiling point, 77.2 K. Liquid nitrogen is used to freeze rubbery or sticky substances so they can be ground or milled. Freeze grinding is even used to make hamburger. Liquid nitrogen is used to quick-freeze foods and to maintain refrigeration of frozen foods as they are transported over the highway.

By its nature, nitrogen is not very reactive. At room temperature, reactions of nitrogen are extremely limited. Certain bacteria living on the root nodules of soybeans, peas, beans and similar plants ***fix*** nitrogen, that is, convert nitrogen into a variety of compounds and ultimately amino acids. Other than these reactions occurring with bacteria, only the alkali metals, and especially lithium reacts with nitrogen at room temperature

$$6\ Li(s) + N_2(g) \rightarrow 2\ Li_3N(s)$$

At elevated temperatures, nitrogen reacts with all of the alkali metals and alkaline earth metals. For example, when magnesium powder is burned in air, magnesium oxide is produced as the primary product with small amounts of magnesium nitride as a byproduct:

$$2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$$

$$6\ Mg(s) + N_2(g) \rightarrow 2\ Mg_3N_2(s)$$

Nitrogen also reacts with oxygen at the elevated temperatures found in the automobile engine:

$$N_2(s) + O_2(g) \rightleftharpoons 2\ NO(g)$$

The forward reaction is not thermodynamically favored, but at elevated temperatures an equilibrium mixture of the two gases exist. When the temperature is suddenly dropped, as occurs for the stream of gases exiting an engine, the NO(g) is locked in and cannot easily revert to nitrogen and oxygen for kinetic reasons. The role of the automotive catalytic converter is to facilitate the reverse reaction.

Suitability

Both high school and university-level chemistry students, with the background skills listed below, would be able to do this experiment. This chapter describes the preparation of nitrogen but does not include any specific experiments with the gas due to its limited reactivity. Several experiments are suggested and referred to below, but no experiments, unique to nitrogen, are included in this chapter.

Background skills required

Students should be able to:

- generate a gas as learned in Chapter 1.
- measure quantities of liquid reagents.
- use a balance.

Time required

Students should be able to prepare nitrogen in about 15 - 20 minutes.

Before students arrive

Each experiment will consume 5 - 7 mL 5 mL 0.5 M $NaNO_2$(aq), but we suggest that the volume estimation be based on 8 – 10 mL per experiment. Prepare a bottle of approximately 0.5 M $NaNO_2$(aq) by dissolving 8.1 g solid $NaNO_2$ in 250 mL water.

Website

This chapter is available on the web at website:

http://mattson.creighton.edu/Microscale_Gas_Chemistry.html

Instructions for your students

PREPARATION OF NITROGEN[1]

General Safety Precautions

Always wear safety glasses. Gases in syringes may be under pressure and could spray liquid chemicals. Follow the instructions and only use the quantities suggested.

Toxicity

Nitrogen is non-toxic; it is a simple asphyxiant if inhaled in very large quantities. We will not be generating large quantities of nitrogen.

Syringe Lubrication

We recommend lubricating the black rubber seal of the plunger with silicone oil.

Equipment

Microscale Gas Chemistry Kit (Chapter 1)

Chemicals

0.14 g solid HSO_3NH_2 (sulfamic acid)

5 mL 0.5 M $NaNO_2$(aq)

These quantities of reagents will produce approximately 60 mL of N_2. The production of N_2 is relatively fast and it typically takes about 15 seconds to fill a syringe. A trace of reddish NO_2 is often observed at first but soon disappears. The reaction is:

$$HSO_3NH_2(s) + NaNO_2(aq) \rightarrow N_2(g) + H_2O(l) + NaHSO_4(aq)$$

Nitrogen is generated by the In-Syringe Method described in Chapter 1 and summarized here:

Instructions

1. Wear your safety glasses!
2. Make sure the syringe plunger and barrel are a good combination for each other and that the plunger moves with reasonable ease in the barrel without binding or sticking.
3. Measure out 0.14 g sulfamic acid. Place the sulfamic acid directly into the vial cap to prevent loss.
4. Fill the syringe barrel with water. Place your finger over the hole to form a seal.
5. Float the vial cap containing the solid reagent on the water surface.

[1] Content for this chapter first appeared as "Microscale Gas Chemistry, Part 4. Experiments with Oxygen and Nitrogen" Mattson, B. M.; Lannan, J. ***Chem13 News***, **254**, January, 1997.

6. Lower the cap by flotation. Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents.

7. Install the plunger while maintaining the syringe in a vertical position.

8. Fill the weighing dish with 0.5 M $NaNO_2(aq)$. Draw 5 mL of this solution into the syringe.

9. Push the syringe cap over the syringe fitting.

10. Shake the device up and down in order to mix the reagents. Gently help the plunger move up the barrel.

11. Remove the syringe cap with the syringe held "cap-up". Assume contents are under positive pressure.

12. Rotate the syringe and discharge the liquid reagent into the plastic cup. Immediately cap the syringe to prevent loss of gas.

13. Wash away contaminants. Nitrogen-filled syringes must be "washed" in order to remove traces of unwanted chemicals from the inside surfaces of the syringe before the gases can be used in experiments. Remove the syringe cap and draw 5 mL water into the syringe. Cap the syringe and shake to wash inside surfaces. Remove cap and discharge water only (no gas), and recap the syringe. Repeat these washing steps if necessary.

Disposal of nitrogen samples

Unwanted nitrogen samples can be safely discharged into the room.

Clean-up and storage.

At the end of the experiments, clean the syringe parts, caps and tubing with water. Rinse all parts with distilled water if available. Be careful with the small parts because they can easily be lost down the drain. **Important:** Store plunger out of barrel unless both are completely dry.

EXPERIMENTS WITH NITROGEN

There are relatively few actual reactions that can be attempted with nitrogen-filled syringes. Nitrogen can be shown to be an inert gas by performing some of the reactions for oxygen in conjunction with performing the same reaction with nitrogen. In particular, from Chapter 4 (Oxygen), the following experiments stand out as those that would be interesting to perform with two different gases, oxygen and nitrogen:

- Experiment 1. Traditional test for oxygen
- Experiment 2. Oxygen supports combustion
- Experiment 5. Steel wool burns in oxygen

Nitrogen could be used in an experiment analogous to Experiment 3 in Chapter 2 (Carbon dioxide extinguishes fires).

Nitrogen could be used with the following experiments from Part 2:

- Chapter 6. Mystery Gas. Nitrogen could round out the series of gases by adding a fourth gas to the original three, hydrogen, oxygen and carbon dioxide. Nitrogen would make the laboratory experiment more challenging.
- Chapter 9. Molar Mass. Nitrogen gives good results in this experiment. Using prepared samples of nitrogen and Calculation Method II, we reported that the molar mass of nitrogen was determined to be 28.6 $^{+}/_{-}$ 0.4, just 1.9% away from the actual molar mass.
- Chapter 10. Limiting Reagent. This experiment could be modified to work with nitrogen production.
- Chapter 11. Barometric Pressure. This experiment could be modified to work with nitrogen instead of hydrogen. We have tried this and the results are not as good as they are for hydrogen. As a twist, however, the experiment could utilize the known barometric pressure to determine by experiment a value for the ideal gas law constant.

Summary of Materials and Chemicals Needed for Chapter 17. Preparation of Nitrogen

Equipment required

This list summarizes all of the equipment necessary to perform this experiment.

Item	For 5 pairs	For 10 pairs
Gas Kit (See Chapter 1)	5	10
top-loading balance	2 - 3	3 - 5

Chemicals required

Item	For 5 pairs	For 10 pairs
0.5 M $NaNO_2(aq)$	40 mL	80 mL
sulfamic acid, $HSO_3NH_2(s)$	2 g	4 g