

## INTERCHAPTER E

# Nitrogen



A nitrogen production plant in Trinidad. The nitrogen is obtained by the fractional distillation of liquid air.

The most significant chemical property of elemental nitrogen,  $\text{N}_2(g)$ , is its lack of reactivity. Nitrogen, as  $\text{N}_2(g)$ , does not take part in many chemical reactions. Although nitrogen compounds are essential nutrients for animals and plants, only a few microorganisms are able to utilize elemental nitrogen directly by converting it to water-soluble compounds of nitrogen. The conversion of nitrogen from the free element to nitrogen compounds is one of the most important problems of modern chemistry and is called **nitrogen fixation**.

### E-1. Nitrogen Ranks Second Among Chemicals in Annual Production

Nitrogen (atomic number 7, atomic mass 14.0067) is a colorless, odorless gas that exists as a diatomic molecule,  $\text{N}_2(g)$ . The Lewis formula,  $:\text{N}\equiv\text{N}:$ , shows that  $\text{N}_2$  is a triple-bonded molecule, which accounts for its high bond strength and consequent lack of chemical reactivity. The principal source of nitrogen is the atmosphere, which is about 78%  $\text{N}_2(g)$  by volume at sea level. Pure nitrogen is produced by the fractional distillation of liquid air. Nitrogen boils at  $-196^\circ\text{C}$ , whereas oxygen, the other principal component of air, boils at  $-183^\circ\text{C}$ .

In terms of world industrial production, nitrogen is the second leading chemical (Appendix H). Over 26 million metric tons of nitrogen are produced from air each year in the United States. Nitrogen is also found in potassium nitrate,  $\text{KNO}_3(s)$  (saltpeter), and in sodium nitrate,  $\text{NaNO}_3(s)$  (Chile saltpeter). Vast deposits of these two nitrates are found in the arid northern region of Chile, where there is insufficient rainfall to wash away these soluble compounds. The Chilean nitrate deposits are about 300 kilometers long, 30 kilometers wide, and many meters thick. At one time the economy of Chile was based primarily upon the sale of nitrates for use as fertilizers. Nitrogen also occurs in all living organisms, both animal and vegetable. Proteins and nucleic acids, such as DNA and RNA, contain significant quantities of nitrogen.

Large quantities of nitrogen are stored and shipped as the liquid (Figure E.1) in insulated metal cylinders. Smaller quantities are shipped as the gas in heavy-walled steel cylinders. An alternative source is to heat an aqueous solution of ammonium nitrite that thermally decomposes according to the equation

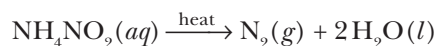
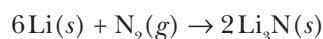


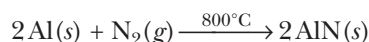
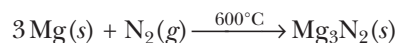
Figure E.1 Liquid nitrogen at its boiling point.

Ammonium nitrite is a potentially explosive solid, and so the aqueous ammonium nitrite solution is made by adding ammonium chloride and sodium nitrite, both stable compounds, to water. Even so, the solution must be heated carefully.

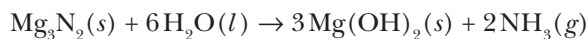
Lithium is the only element that reacts with nitrogen at room temperature:



Other reactive metals, such as the other alkali metals, magnesium, calcium, and aluminum, react at high temperatures to form **nitrides**:



When magnesium is burned in air, most of it is converted to the white magnesium oxide, but small yellow flecks of magnesium nitride also can be seen. Metallic nitrides react with water to form ammonia, one of the most important compounds of nitrogen:



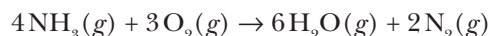
Ammonia,  $\text{NH}_3(g)$ , is a colorless gas with a sharp, irritating odor. It is the active ingredient in some forms of “smelling salts.” Over 10 million metric tons of ammonia are produced annually in the United States alone.

The ammonia molecule was the first complex molecule to be identified in interstellar space. Ammonia occurs in the galactic dust clouds of the Milky Way and, in the solid form, constitutes part of the rings of Saturn.

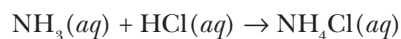
Unlike nitrogen, which is sparingly soluble in water, ammonia is very soluble in water. Over 700 milliliters of gaseous ammonia at  $0^\circ\text{C}$  and 1 bar will dissolve in 1 milliliter of liquid water. The solubility of ammonia in water can be demonstrated nicely by the **fountain effect**. This effect can be observed with the simple laboratory setup shown in Figure E.2. A dry flask is filled with anhydrous (“dry”) ammonia gas at atmospheric pressure. When just a few drops of water are squirted into the flask from a syringe, some of the ammonia dissolves in the drops. The pressure of the

ammonia falls below that of the atmosphere, and water is forced from the beaker, up the vertical glass tubing into the flask, producing a spectacular fountain.

Ammonia does not burn in air but will burn in pure oxygen according to



Certain compositions of ammonia and oxygen are explosive if sparked. Ammonia reacts with various acids to form ammonium compounds, which contain the  $\text{NH}_4^+(aq)$  ion. For example,



Household ammonia is an aqueous solution of ammonia together with a detergent. Many other ammonium compounds are important commercially, particularly as fertilizers.



**Figure E.2** An ammonia fountain demonstrates the large solubility of ammonia in water. The red color is due to a few drops of phenolphthalein indicator that has been added to the water in the beaker. Phenolphthalein is colorless in the neutral water, but turns red in the presence of the basic ammonia solution that forms in the flask.

## E-2. The Haber Process Is Used for the Industrial Production of Ammonia

Nitrogen fixation is the conversion of the free element to its compounds. Nitrogen fixation by microorganisms is an important source of plant nutrients. The most common of these nitrogen-fixing bacteria belong to the species *Rhizobium*. They invade the roots of leguminous plants such as alfalfa, clover, beans, and peas and form nodules on the roots of these legumes (Figure E.3). The relationship between *Rhizobium* and the host plant is symbiotic (mutually beneficial). The plant produces carbohydrates through photosynthesis, and *Rhizobium* uses the carbohydrate as fuel for fixing the nitrogen, which is incorporated into plant protein. Alfalfa is the most potent nitrogen-fixer, followed by clover, soybeans, other beans, peas, and peanuts. In modern agriculture, crops are rotated, that is, plantings of a nonleguminous crop and a leguminous crop are alternated from time to time on one piece of land. The leguminous crop is either harvested, leaving behind nitrogen-rich roots, or plowed into the soil, adding both nitrogen and organic matter. A plowed-back crop of alfalfa may add as much as 75 kilograms of fixed nitrogen to the soil per hectare (or about 400 pounds per acre).

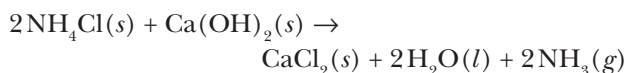
Because of its importance to agriculture, nitrogen fixation was a major application of modern chemistry; but because of the great strength of the nitrogen-nitrogen triple bond, it was also a major challenge.



**Figure E.3** Nitrogen-fixing nodules on the roots of a leguminous plant, soybeans. The nodules contain *Rhizobium*, a soil bacterium that converts atmospheric elemental nitrogen to water-soluble nitrogen compounds.

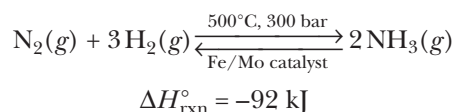


The large-scale demand for ammonia to make fertilizers and other nitrogen compounds requires an economical process for its production. The laboratory preparation of ammonia by reacting a metallic nitride with water is too expensive for large-scale use, as is the commonly used reaction of ammonium chloride with calcium hydroxide, given by

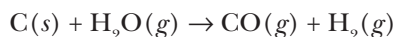


In this case, one of the starting materials,  $\text{NH}_4\text{Cl}(s)$ , is produced from ammonia in the first place.

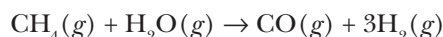
Since around 1913, ammonia has been produced commercially by the **Haber process**, developed by the German chemist Fritz Haber, in which nitrogen reacts directly with hydrogen at high pressure and high temperature:



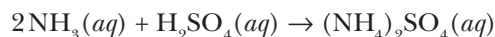
This reaction is favored by high pressure and low temperature, but it proceeds too slowly at low temperatures. Thus, the conditions represent a compromise between yield and rate. Originally, the hydrogen was obtained from the electrolysis of water, but now it is obtained either from the water-gas reaction (Interchapter C)



or from the steam re-forming of natural gas (Interchapter C)



Ammonia binds to many components of soil and is easily converted to usable plant food. Concentrated aqueous solutions of ammonia or pure liquid ammonia can be sprayed directly into the soil (Figure E.4). Ammonia is an inexpensive fertilizer that is high in nitrogen. The increased growth of plants when fertilized by ammonia is spectacular. For some purposes it is more convenient to use a solid fertilizer instead of ammonia solutions. For example, ammonia combines directly with sulfuric acid to produce ammonium sulfate:



Ammonium sulfate is the most important solid fertilizer in the world. Its annual U.S. production exceeds 2.6 million metric tons. The primary fertilizer nutrients are nitrogen, phosphorus, and potassium, and fertilizers are rated by how much of each they contain. For example, a 5-10-5 fertilizer has 5% by mass total available nitrogen, 10% by mass phosphorus [equivalent to the form  $\text{P}_2\text{O}_5(s)$ ], 5% by mass potassium [equivalent to the form  $\text{K}_2\text{O}(s)$ ], and 80% inert ingredients. The production of fertilizers is one of the largest and most important industries in the world.

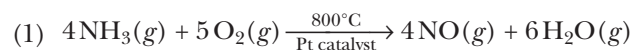


**Figure E.4** Spraying ammonia into the soil. Liquid ammonia, called anhydrous ammonia, is used extensively as a fertilizer because it is cheap, high in nitrogen, and easy to apply.

### E-3. Nitric Acid Is Produced Commercially by the Ostwald Process

Shortly after the Haber process was put into large-scale production, World War I, with its great demand for munitions, started. Explosives and munitions are produced from nitric acid and nitrates, and at the beginning of the War the major source of nitrates was Chile. Germany recognized that this transoceanic supply was going to be difficult to maintain (one of the first naval battles of World War I was fought between Britain and Germany off the coast of Chile) and directed its attention to the production of nitric acid from ammonia.

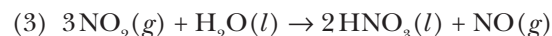
In the early 1900s, the German chemist Wilhelm Ostwald showed that nitric acid could be produced from ammonia by a sequence of reactions that is now known as the **Ostwald process**. The first step in this process is the conversion of ammonia to nitrogen oxide according to



The second step involves the oxidation of  $\text{NO}(g)$  to  $\text{NO}_2(g)$ :

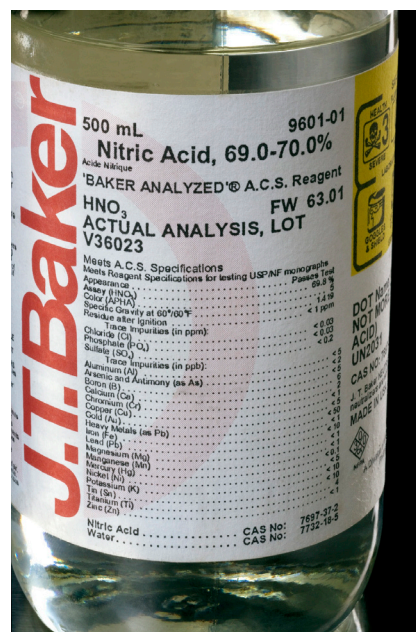
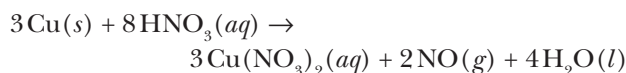


In the final step, the  $\text{NO}_2(g)$  is reacted with water to yield nitric acid:



The  $\text{NO}(g)$  evolved is recycled back into step 2. The large-scale availability of ammonia from the Haber process enabled the Ostwald process to be run on an industrial scale.

Laboratory-grade nitric acid is approximately 70%  $\text{HNO}_3$  by mass with a density of  $1.42 \text{ g}\cdot\text{mL}^{-1}$  and a concentration of 16 M (Figure E.5). The U.S. annual production of nitric acid is over six million metric tons. The greatest use of nitric acid is in the production of ammonium nitrate for fertilizers. It is also used in the production of explosives such as trinitrotoluene (TNT), nitroglycerine, and nitrocellulose (gun cotton), and in etching and photoengraving processes to produce grooves in metal surfaces. For example, dilute nitric acid readily reacts with copper metal:

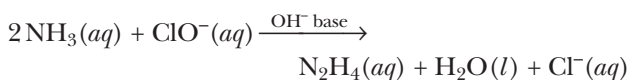


**Figure E.5** Label from a bottle of concentrated nitric acid.

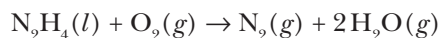
In contrast, copper metal does not react directly with hydrochloric acid. The reaction equation above does not involve the liberation of hydrogen gas, as in the reaction of, say, zinc metal with hydrochloric acid.

#### E-4. Nitrogen Forms Many Important Compounds with Hydrogen and Oxygen

The most important nitrogen-hydrogen compounds are ammonia,  $\text{NH}_3(g)$ , hydrazine,  $\text{N}_2\text{H}_4(l)$ , and hydrazoic acid,  $\text{HN}_3(aq)$ . Hydrazine is a colorless, fuming, reactive liquid. It is produced by the **Raschig synthesis**, in which ammonia is reacted with the hypochlorite ion (household bleach is sodium hypochlorite in water) in basic solution according to



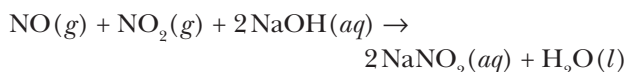
The reaction of hydrazine with oxygen,



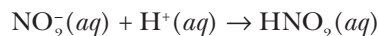
is accompanied by the release of a large amount of energy; hydrazine and some of its derivatives are used as rocket fuels (Chapter 14).

Nitrous acid,  $\text{HNO}_2(aq)$ , is prepared by reacting equal amounts of nitrogen oxide and nitrogen dioxide with a basic solution [for example,  $\text{NaOH}(aq)$ ]:

Household bleach should never be mixed with household ammonia because toxic and explosive chloramines, such as  $\text{NH}_2\text{Cl}(l)$  and  $\text{NHCl}_2(l)$ , are produced as by-products.

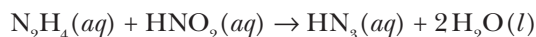


Addition of acid to the resulting solution yields nitrous acid:



Salts of nitrous acid are called nitrites. Sodium nitrite,  $\text{NaNO}_2(s)$ , is used as a meat preservative. The nitrite ion combines with the hemoglobin in meat to produce a deep red color. The main problem with the extensive use of nitrites in foods is that the nitrite ion reacts with amines in the body's gastric juices to produce compounds called nitrosamines [such as  $(\text{CH}_3)_2\text{NNO}(l)$ , dimethylnitrosamine], which are carcinogenic.

The reaction of nitrous acid with hydrazine in acidic solution yields hydrazoic acid:



Hydrazoic acid is a colorless, toxic liquid and a dangerous explosive. Its lead and mercury salts,  $\text{Pb}(\text{N}_3)_2(s)$  and  $\text{Hg}(\text{N}_3)_2(s)$ , which are called **azides**, are used in detonation caps; both compounds are dangerously explosive. Sodium azide,  $\text{NaN}_3(s)$ , is used as the gas source in automobile air safety bags,



(the sodium metal formed is reacted with  $\text{KNO}_3(s)$  and  $\text{SiO}_2(s)$  to form an inert alkaline silicate powder and thus avoid a potential sodium fire).

Nitrogen forms a number of oxides (Table E.1). Dinitrogen oxide (nitrous oxide), also known as **laughing gas**, was once used as a general anesthetic,

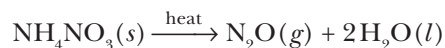
TABLE E.1 The oxides of nitrogen

Formula	Systematic name	Description
$\text{N}_2\text{O}(g)$	dinitrogen oxide (nitrous oxide)	colorless, rather unreactive gas
$\text{NO}(g)$	nitrogen oxide (nitric oxide)	colorless, paramagnetic, reactive gas
$\text{N}_2\text{O}_3(g)$	dinitrogen trioxide	dark blue solid (b.p. $3.5^\circ\text{C}$ ); dissociates in gas phase to $\text{NO}$ and $\text{NO}_2$
$\text{NO}_2(g)$	nitrogen dioxide	brown, paramagnetic, reactive gas; dimerizes reversibly to $\text{N}_2\text{O}_4$
$\text{N}_2\text{O}_4(g)$	dinitrogen tetroxide	colorless gas (b.p. $21^\circ\text{C}$ ); dissociates reversibly to $\text{NO}_2$
$\text{N}_2\text{O}_5(s)$	dinitrogen pentoxide	colorless, ionic solid; unstable as a gas

TABLE E.2 Some important compounds of nitrogen

Compound	Uses
ammonia, $\text{NH}_3(g)$	fertilizers; manufacture of nitric acid, explosives; synthetic fibers; refrigerant
nitric acid, $\text{HNO}_3(l)$	manufacture of fertilizers, explosives, lacquers, synthetic fabrics, pharmaceuticals, and dyes; oxidizing agent; metallurgy; ore flotation
ammonium nitrate, $\text{NH}_4\text{NO}_3(s)$	fertilizer; explosives; herbicides and insecticides; solid rocket propellant
sodium cyanide, $\text{NaCN}(s)$	extraction of gold and silver from their ores; insecticide; fumigant; manufacture of dyes and pigments
sodium azide, $\text{NaN}_3(s)$	inflate automobile airbags

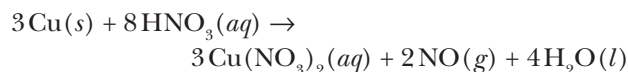
but its primary use now is as an aerosol and canned whipped cream propellant. Dinitrogen oxide can be produced by a cautious thermal decomposition of  $\text{NH}_4\text{NO}_3(s)$ :



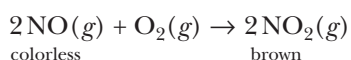
The reaction is potentially explosive, with the evolution of nitrogen, oxygen, and water. Consequently, often an equal mixture of potassium nitrate and ammonium chloride is used:



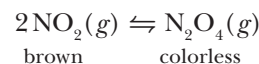
Nitrogen oxide (also called nitric oxide and nitrogen monoxide) is produced in the oxidation of copper by 6 M nitric acid according to



Nitrogen oxide is a highly toxic gas. It is a by-product of incomplete combustion and is one of the components of automobile exhaust and air pollution. To limit its role in smog, automobiles use catalytic converters to reduce  $\text{NO}(g)$  to  $\text{NO}_2(g)$  and  $\text{N}_2(g)$  (see Figure 14.9). Although  $\text{NO}(g)$  is colorless, this reaction produces a brown gas if it is run in a vessel that is open to the atmosphere. The brown gas results from the rapid production of nitrogen dioxide by the reaction described by



In the gas phase, nitrogen dioxide reversibly dimerizes to form dinitrogen tetroxide:



Because this reaction is exothermic, an increase in temperature results in the formation of more  $\text{NO}_2(g)$  and, hence, a more reddish-brown mixture (see Chapter 19).

Despite its toxicity, nitrogen oxide also plays an important role in biology. Plants use nitrogen oxide to defend against pathogens, and macrophages use it to kill invading bacteria. In 1998 the Noble Prize in Medicine was awarded to Robert F. Furchgott, Louis J. Ignarro, and Ferid Murad for showing that nitrogen oxide also functions as an important chemical messenger in the cardiovascular system.

Some commercially important nitrogen-containing compounds are given in Table E.2.

## TERMS YOU SHOULD KNOW

nitrogen fixation E1  
 nitride E1  
 fountain effect E2  
 Haber process E3  
 Ostwald process E4  
 Raschig synthesis E5  
 azide E5  
 laughing gas E5



## QUESTIONS

E-1. Discuss what is meant by nitrogen fixation.

E-2. What percentage of air (by volume) is  $\text{N}_2(g)$  at sea level?

E-3. To produce small quantities of  $\text{N}_2(g)$  from the thermal decomposition of  $\text{NH}_4\text{NO}_2(aq)$ , an aqueous solution containing equal amounts of  $\text{NH}_4\text{Cl}(aq)$  and  $\text{NaNO}_2(aq)$  is used instead of  $\text{NH}_4\text{NO}_2(aq)$ . Why?

E-4. Which is the only element that reacts with  $\text{N}_2(g)$  at room temperature?

E-5. When magnesium is burned in air, yellow flecks can be found in the product. What are they?

E-6. Briefly describe the Haber process.

E-7. Using balanced chemical equations, outline the Ostwald process.

E-8. What are azides? How are they made?

E-9. Why should you never mix household ammonia and household bleach?

E-10. What is “laughing gas”?

E-11. Give the chemical formula for each of the following compounds:

- |                      |                      |
|----------------------|----------------------|
| (a) ammonia          | (f) nitrogen dioxide |
| (b) nitric acid      | (g) sodium azide     |
| (c) sodium nitrite   | (h) lithium nitride  |
| (d) dinitrogen oxide | (i) ammonium nitrate |
| (e) nitrogen oxide   | (j) hydrazine        |