

# 25

C H A P T E R

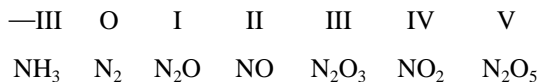
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## Nitrogen

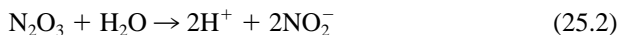
### 25.1 | GENERAL CONSIDERATIONS

The compounds of nitrogen are of great importance in water resources, in the atmosphere, and in the life processes of all plants and animals. The chemistry of nitrogen is complex because of the several oxidation states that nitrogen can assume and the fact that changes in oxidation state can be brought about by living organisms. To add even more interest, the oxidation state changes wrought by bacteria can be either positive or negative, depending upon whether aerobic or anaerobic conditions prevail.

Nitrogen can exist in seven oxidation states, and essentially all are of environmental interest.



Three forms combine with water to form inorganic ionized species that can reach high concentrations,

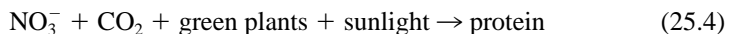


The respective water-soluble species formed, ammonium, nitrite, and nitrate, are of historical environmental concern in water, and their concentrations in drinking water supplies and surface waters have been regulated for decades.

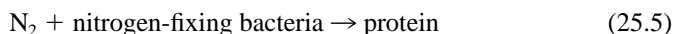
The other inorganic oxidation states,  $N_2$ ,  $N_2O$  (nitrous oxide),  $NO$  (nitric oxide), and  $NO_2$  (nitrogen dioxide) exist as gases that have somewhat limited solubility in water. Additionally, nitrogen is an important element in many organic chemicals. The reduced form  $N(III)$  is a major element in proteins and the amino acids of which they are composed, and in nucleic acids as well. Thus, nitrogen is essential to all life.

However, except for  $N_2$ , the major component of the earth's atmosphere, nitrogen compounds in all oxidation states can result in environmental problems of concern as will be discussed. Adding to the complexity, nitrogen is readily changed in oxidation state and in chemical form through natural biological, chemical, and photochemical processes. In order to help capture the beneficial uses of nitrogen while avoiding the harmful changes some of its forms can cause, environmental engineers and scientists need to have a good understanding of nitrogen chemistry and the nitrogen cycle. The nitrogen cycle is illustrated in Fig. 25.1.

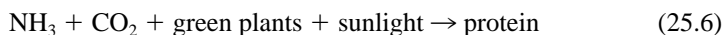
From the nitrogen cycle, it is seen that the atmosphere serves as a very large reservoir from which nitrogen is constantly removed by the action of electrical discharge, nitrogen-fixing bacteria and algae, and combustion processes. During electrical storms nitrogen is oxidized to  $NO$ , which is oxidized by ozone in the atmosphere to form  $NO_2$ .  $NO_2$  in turn is reduced back to  $NO$  by photolysis. This forward and backward reaction establishes a steady-state concentration between  $NO$  and  $NO_2$ , with  $NO$  generally being by far the dominant species. The two species together are generally referred to as  $NO_x$ . Combustion processes, such as in the internal combustion engine of automobiles, also lead to conversion of  $N_2$  to  $NO$  and  $NO_2$ . Other oxidative reactions with  $NO_2$  in the atmosphere lead to the conversion of  $NO_2$  to  $N_2O_5$ , which according to Eq. (25.3) can combine with water in the atmosphere to produce the nitrate of nitric acid, which reaches the earth's surface with falling rain. Nitrate is also produced by direct oxidation of nitrogen or of ammonia in the production of commercial fertilizers. The nitrate serves to fertilize plant life and is converted to proteins (organic nitrogen).



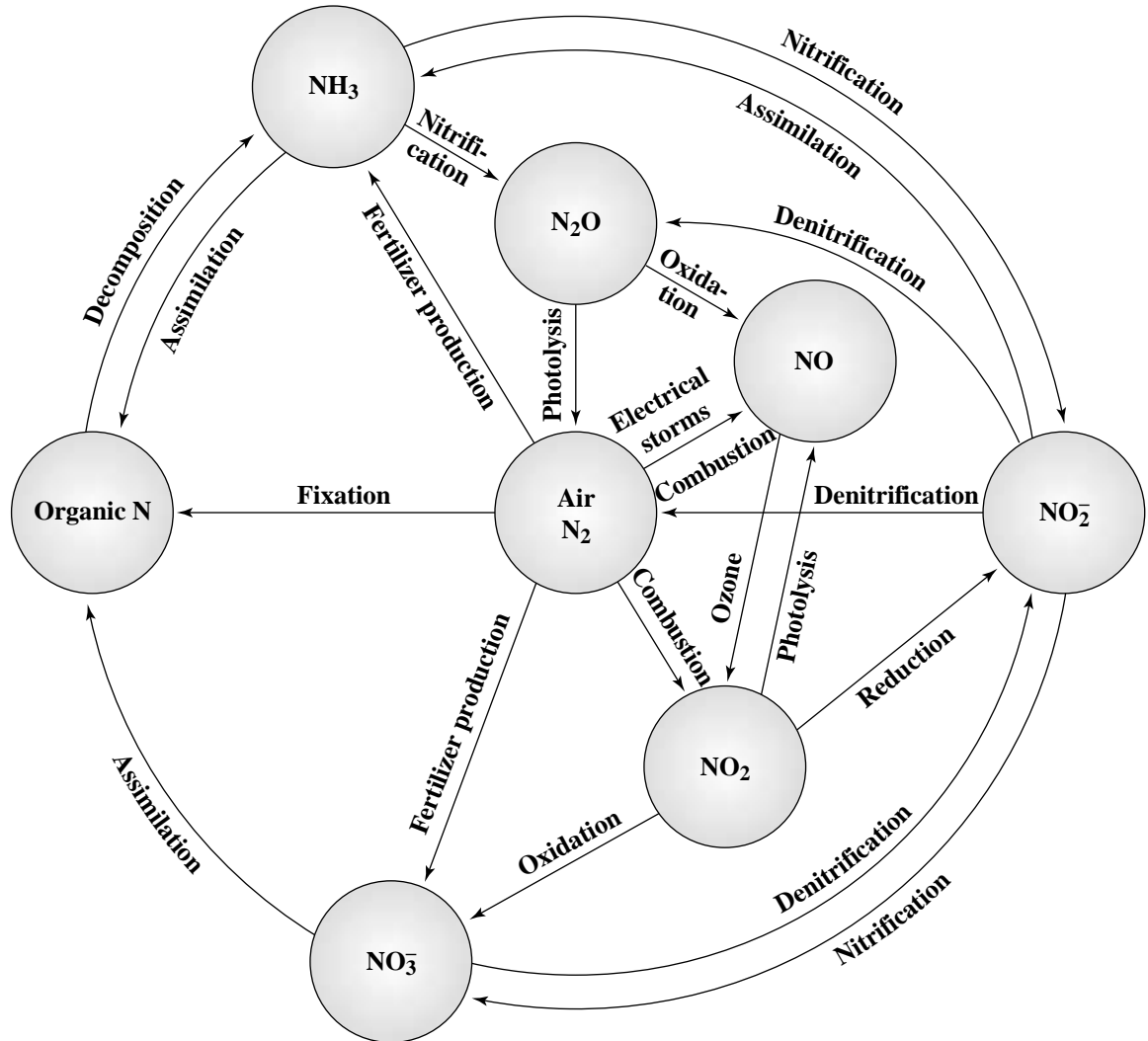
The major means by which atmospheric nitrogen enters the nitrogen cycle is through conversion to protein by nitrogen-fixing bacteria. This includes the photosynthetic *cyanobacteria*, which have many similarities to algae.



In addition, ammonia and ammonium compounds are applied to soils to supply plants with ammonia for further production of proteins. Urea is one of the popular ammonium compounds because it releases ammonia gradually.



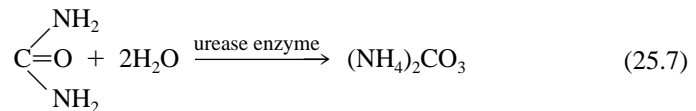
Animals and human beings are incapable of utilizing nitrogen from the atmosphere or from inorganic compounds to produce proteins. They are dependent upon plants, or other animals that feed upon plants, to provide protein, with the exception



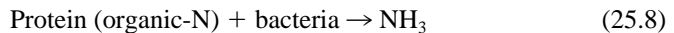
**Figure 25.1**  
The nitrogen cycle.

of ruminants. The multiple-stomached animals are capable of producing part of their protein requirement from carbohydrate matter and urea through bacterial action. Within the animal body, protein matter is used largely for growth and repair of muscle tissue. Some may be used for energy purposes. In any event, nitrogen compounds are released in the waste products of the body during life. At death the proteins stored in the body become waste matter for disposal. The urine contains the nitrogen resulting from the metabolic breakdown of proteins. The nitrogen exists in

urine principally as urea which is hydrolyzed rather rapidly by the enzyme urease to ammonium carbonate:

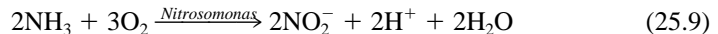


The feces of animals contain appreciable amounts of unassimilated protein matter (organic nitrogen). It and the protein matter remaining in the bodies of dead animals and plants are converted in large measure to ammonia by the action of heterotrophic bacteria, under aerobic or anaerobic conditions:

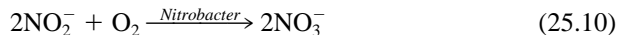


Some nitrogen always remains in nondigestible matter and becomes part of the nondigestible residue sink. As such it becomes part of the *detritus* in water or sediments, or the *humus* in soils.

The ammonia released by bacterial action on urea and proteins may be used by plants directly to produce plant protein. If it is released in excess of plant requirements, the excess is oxidized by the autotrophic nitrifying bacteria. One group (*Nitrosomonas*) convert ammonia under aerobic conditions to nitrite and derive energy from the oxidation:



The nitrite is oxidized by another group of nitrifying bacteria (*Nitrobacter*) to nitrate:



The nitrate formed may serve as fertilizer for plants. Nitrate produced in excess of the needs of plant life is carried away in water percolating through the soil because the soil does not have the ability to hold nitrate. This frequently results in relatively high concentrations of nitrate in groundwaters and is an extensive problem in Illinois, Iowa, and other midwestern states. Nitrification also can result in some production of  $\text{N}_2\text{O}$ .

Under anaerobic conditions nitrate and nitrite are both reduced by a process called *denitrification*. Nitrate is reduced to nitrite, and then reduction of nitrite occurs. Reduction of nitrite is carried all the way to ammonia by a few bacteria for protein formation, but mostly the nitrate is reduced to nitrogen gas, which escapes to the atmosphere. This constitutes a serious loss of fertilizing matter in soils when anaerobic conditions develop. Also, some denitrifying bacteria produce  $\text{N}_2\text{O}$  from nitrate reduction, and this too is a gas that leaves soil or water to enter the atmosphere.  $\text{N}_2\text{O}$  in the atmosphere can be reduced through photolysis to produce  $\text{N}_2$  and an excited state of oxygen, which oxidizes another portion of the  $\text{N}_2\text{O}$  to  $\text{NO}$ . We thus see that transformations of nitrogen occur in water, in soil, and in the atmosphere through a variety of chemical, photochemical, and biological processes.

## 25.2 | ENVIRONMENTAL SIGNIFICANCE OF NITROGEN SPECIES

While nitrogen is seen to be an essential component of all living things, excessive concentrations of certain nitrogen species in some compartments of the environment can lead to significant environmental problems. This is true of some nitrogen species in the atmosphere as well as in terrestrial and aquatic environments.

### Atmospheric Concerns with Nitrogen Species

The three major environmental problems associated with nitrogen species in the atmosphere are photochemical smog, global warming, and stratospheric ozone depletion. Photochemical smog results when partially oxidized organic matter,  $\text{NO}_x$ , and sunlight come together under certain meteorological conditions, resulting in a series of complex chemical and photochemical reactions that lead to the production of high ozone concentrations and organic chemicals that together produce eye irritation, reduced air visibility, crop damage, and severe adverse health impacts in humans. The automobile has been a primary producer of two of the ingredients of photochemical smog, partially oxidized organic matter and  $\text{NO}_x$ . The most serious problems occur in dense urban areas where there are many automobiles.

Wide use of fossil fuels over the past century has resulted in an increase in atmospheric carbon dioxide, which acts as a blanket to prevent heat from radiating from the earth, a phenomenon, come to be known as the greenhouse effect, that is increasing the earth's temperature. However, the gaseous oxides of nitrogen also exhibit a greenhouse effect. While carbon dioxide is believed responsible for about 55 percent of the increased changes to the radiative temperature between 1980 and 1990, increased  $\text{NO}_x$  production from fuel and biomass combustion and particularly from denitrification ( $\text{N}_2\text{O}$ ) as a result of increased commercial fertilizer usage is estimated to be responsible for 6 percent of the increase.<sup>1</sup> While the amount of  $\text{NO}_x$  in the atmosphere would appear to be small compared with  $\text{CO}_2$ , one molecule of  $\text{N}_2\text{O}$  has a heat-trapping ability equivalent to 200 molecules of  $\text{CO}_2$ .

While  $\text{NO}_x$  is partially responsible for increased ozone production as part of photochemical smog production in urban areas near the earth's surface, it is somewhat surprising that it also plays a role in the destruction of ozone in the stratosphere. Stratospheric ozone plays a key role in protecting life on earth from the harmful effects of excessive ultraviolet radiation. The widespread use of chlorofluorocarbons (CFCs) is known to have resulted in significant destruction of the protective stratospheric ozone, but  $\text{NO}_x$  is playing a role as well.  $\text{N}_2\text{O}$  and  $\text{NO}_2$  are both converted to  $\text{NO}$  in the atmosphere, and  $\text{NO}$  reaching the stratospheres reacts with ozone to result in its depletion.

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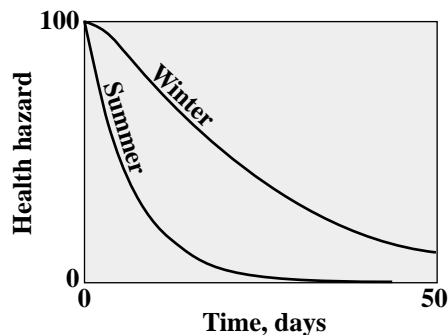
<sup>1</sup>R. Rosswall, "Greenhouse Gases and Global Change: International Collaboration," *Env. Sci. Tech.*, 25(4): 567, 1991.

## Aquatic Concerns with Nitrogen Species

**An Indicator of Sanitary Quality** It has long been known that polluted waters will purify themselves, provided that they are allowed to age for sufficient periods of time. The hazard to health or the possibility of contracting disease by drinking such waters decreases markedly with time and temperature increase, as shown in Fig. 25.2.

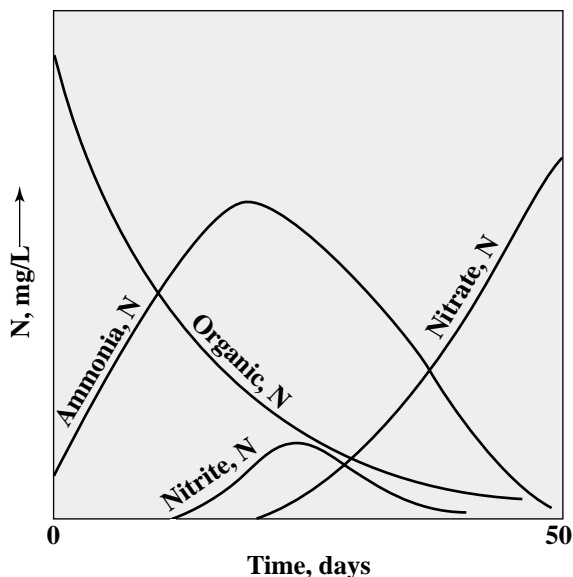
Prior to the development of bacteriological tests for determining the sanitary quality of water (about 1893), those concerned with the public health were largely dependent upon chemical tests to provide circumstantial evidence of the presence of contamination. The chloride test was one of these (see Sec. 21.2), but it gave no evidence of how recently the contamination had occurred. Chemists working with wastes and freshly polluted waters learned that most of the nitrogen is originally present in the form of organic (protein) nitrogen and ammonia. As time progresses, the organic nitrogen is gradually converted to ammonia nitrogen, and later on, if aerobic conditions are present, oxidation of ammonia to nitrite and nitrate occurs. The progression of events was found to occur somewhat as shown in Fig. 25.3, and more refined interpretations of the sanitary quality of water were based upon this knowledge. For example, waters that contained mostly organic and ammonia nitrogen were considered to have been recently polluted and therefore of great potential danger. Waters in which most of the nitrogen was in the form of nitrate were considered to have been polluted a long time previously and therefore offered little threat to the public health. Waters with appreciable amounts of nitrite were of highly questionable character. The bacteriological test for coliform organisms provides circumstantial evidence of much greater reliability concerning the hygienic safety of water, and it has eliminated the need for extended nitrogen analysis in most water supplies.

In 1940 it was found that drinking waters with high nitrate content often caused methemoglobinemia in infants. From extended investigations in Iowa, Minnesota,



**Figure 25.2**

Surface waters; health hazard in relation to age of pollution.



**Figure 25.3**

Changes occurring in forms of nitrogen present in polluted water under aerobic conditions.

and Ohio, where the problem has been most acute, it has been concluded that the nitrate content should be limited.<sup>2</sup> For this reason, the U.S. EPA has set a maximum contaminant level requiring that the nitrate-nitrogen concentration not exceed 10 mg/L and the nitrite-nitrogen concentration not exceed 1 mg/L in public water supplies.

Methemoglobinemia is actually a result of interaction of nitrite with hemoglobin, the nitrite being formed from nitrate reduction in the digestive system. For this reason, a maximum contaminant level for drinking water has now been set for nitrite as well as nitrate. Nitrite can also interact with amines chemically (especially when chlorinating for disinfection<sup>3</sup>) or enzymatically<sup>4</sup> to form nitrosamines, which are strong carcinogens. The formation of N-nitrosodimethylamine (NDMA) by these processes has been found to result during wastewater treatment and has become an issue recently in wastewater reuse projects and contaminated groundwater supplies. Ammonia reacts with chlorine to form chloramines, which are slower-acting disinfectants than free chlorine as discussed in Sec. 20.2. Ammonia is sometimes added

<sup>2</sup>K. F. Maxcy. Report on Relation of Nitrate Nitrogen Concentration in Well Waters to the Occurrence of Methemoglobinemia in Infants. *Natl. Acad. Sci.-Research Council Sanit. Eng. and Environment Bull.*, 264, 1950.

<sup>3</sup>J. Choi and R. L. Valentine, "Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product," *Water Research*, **36**: 817-824 (2002).

<sup>4</sup>M. Alexander, "Biodegradation and Bioremediation," Academic Press, San Diego, 1994.

to drinking water supplies when a disinfection residual in water mains is desired as chloramines do not decompose as rapidly as chlorine.

**Nutritional and Related Problems** All biological processes employed for wastewater treatment are dependent upon reproduction of the organisms employed, as discussed in Sec. 6.6. In planning waste treatment facilities it becomes important to know whether the waste contains sufficient nitrogen for the organisms. If not, any deficiency must be supplied from outside sources. Determinations of ammonia and organic nitrogen are normally made to obtain such data.

Nitrogen is one of the fertilizing elements essential to the growth of algae. Such growth is often stimulated to an undesirable extent in bodies of water that receive either treated or untreated effluents, because of the nitrogen and other fertilizing matter contributed by them. Nitrogen analyses are an important means of gaining information on this problem.

**Oxidation in Rivers and Estuaries** The autotrophic conversion of ammonia to nitrite and nitrate requires oxygen, indicated in Eqs. (25.9) and (25.10), and so the discharge of ammonia nitrogen and its subsequent oxidation can seriously reduce the dissolved-oxygen levels in rivers and estuaries, especially where long residence times required for the growth of the slow-growing nitrifying bacteria are available. Also, these organisms are produced in large numbers by highly efficient aerobic biological waste treatment systems, and their discharge with the treated effluent can cause rapid nitrification to occur in waterways. Disinfection of effluents (e.g., with chlorine or ultraviolet light) minimized this problem. Nitrogen analyses are important in assessing the possible significance of the problem, and in the operation of treatment processes designed to reduce ammonia discharge.

**Control of Biological Treatment Processes** Determinations of nitrogen are often made to control the degree of purification produced in biological treatment. With the use of the BOD test, it has been learned that effective stabilization of organic matter can be accomplished without carrying the oxidation into the nitrification stage. This results in reducing time of treatment and air requirements where ammonia removal is not otherwise mandated.

Advantage is taken of denitrification for removing nitrogen from wastes where this is required to prevent undesirable growths of algae and other aquatic plants in receiving waters. Ammonia and organic nitrogen are first biologically converted to nitrite and nitrate by aerobic treatment. The waste is then placed under anoxic conditions, where denitrification converts the nitrite and nitrate to nitrogen gas, which escapes to the atmosphere. For denitrification to occur, organic matter, which is oxidized for energy while the nitrogen is being reduced, must be present. Methanol was a favorite form of organic matter, but, due to its increased cost, other materials including untreated wastewater itself are commonly used. When nitrification is required to protect oxygen resources in streams, advantage can be taken of the oxidizing potential of nitrate present in the plant effluent to reduce oxygen requirements for treatment. Here the nitrate-containing effluent is recycled back to be mixed with settled wastewater under anoxic conditions to effect some organic oxidation through denitrifica-

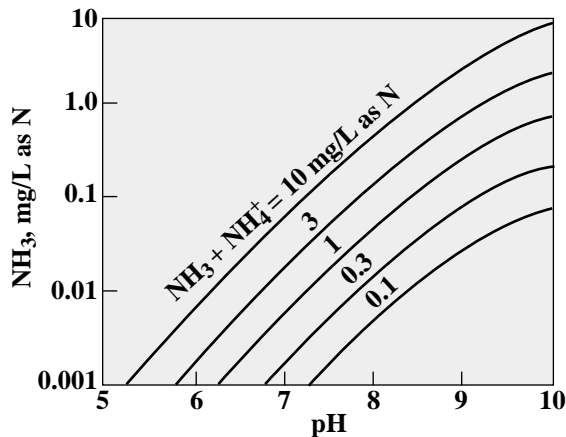


tion. The reduced quantity of organics remaining are then subject to the usual aerobic step, but now less oxygen is required for treatment. An additional advantage here is that nitrate is simultaneously removed in the denitrification step, which now occurs as a first step, rather than as the last step in the treatment train. The formation of  $N_2$  by denitrification is sometimes a problem in the activated sludge process of wastewater treatment. Prolonged detention of activated sludge in final settling tanks allows formation of sufficient nitrogen gas to buoy the sludge, if nitrates are present in adequate amounts. This is often referred to as the “rising” sludge problem. As this discussion suggests, analyses for nitrogen forms in wastewater treatment can be of great importance in process control and in achieving overall treatment objectives.

In some states, ammonia-nitrogen limitations have been imposed because of suspected toxic effects upon fish life. It is well known that un-ionized ammonia is toxic but that the ammonium ion is not. Since the relationship between the two is pH-dependent,



a discussion is in order. Figure 25.4 shows the relationship between free ammonia and ammonium ion that exists for several concentrations of ammonia nitrogen over the pH range of interest in most natural waters. Free ammonia in concentrations above about 0.2 mg/L can cause fatalities in several species of fish. Applying the usual safety factor, a National Research Council Committee has recommended that no more than 0.02 mg/L free ammonia be permitted in receiving waters.<sup>5</sup> From this



**Figure 25.4**

The effect of pH and ammonia nitrogen concentration ( $NH_3 + NH_4^+$ ) on the concentration of free ammonia in water.

<sup>5</sup>Committee on Water Quality Criteria, “Water Quality Criteria, 1972,” Superintendent of Documents, Washington, DC, 1972.

and the data presented in Fig. 25.4, it appears that ammonia toxicity will not be a problem in receiving waters with pH below 8 and ammonia-nitrogen concentrations less than about 1 mg/L.

Control of ammonia for the given reasons is generally accomplished by nitrification. In some cases, limitations are placed upon the amount of total nitrogen that can be present in an effluent. This condition can be met by removal of ammonia in some instances, but more often it requires nitrification and denitrification. Because of these new requirements, methods of measuring all forms of nitrogen have become important.

## 25.3 | METHODS OF ANALYSIS

Nitrogen exists in four forms that are of interest in water resources. These are the forms located in the outer ring of the nitrogen cycle (Fig. 5.1). These are ammonia, nitrite, nitrate, and organic nitrogen. A discussion of the determination of each form is required. Because of differences in the amounts present in potable and polluted waters, methods applied to water may differ somewhat from those applied to wastewaters. It is customary to report all results in terms of nitrogen so that values may be interpreted from one form to another without use of a factor.

### Ammonia Nitrogen

All nitrogen that exists as ammonium ion or in the equilibrium



is considered to be ammonia nitrogen. Essentially four different methods for determining ammonia nitrogen are included in “Standard Methods”: two colorimetric procedures, a volumetric procedure, and an instrumental method using an ammonia-selective membrane probe.

**By Direct Nesslerization** This historical colorimetric method, which yields a yellow color from the reaction of Nessler’s reagent with ammonia, has now been dropped from “Standard Methods” because Nessler’s reagent contains mercury. Use of analytical methods that result in waste analytical solutions that contain the hazardous chemical mercury are no longer being favored if satisfactory alternatives are available.

**By Direct Phenate Addition** The phenate method is now the standard colorimetric procedure for ammonia. It involves the addition of an alkaline phenol solution together with hypochlorite and a manganous salt. The manganese catalyzes the reaction involving phenol, hypochlorite, and ammonia to produce indophenol, which has an intense blue color. This procedure is subject to similar interferences as with Nesslerization. Ammonia nitrogen can be determined over a range of 0.02 to 2 mg/L by an automated phenate procedure.

**By Distillation** The phenate procedure is subject to serious error from extraneous color and turbidity. Thus, direct application is impractical to use on many samples. The distillation procedure is used to separate the ammonia from interfering sub-

stances, and measurement of ammonia nitrogen can then be made in a number of ways, including the phenate procedure.

Ammonium ion exists in equilibrium with ammonia and hydrogen ion, as shown in Eq. (25.11). At pH levels above 8, the equilibrium is displaced far enough to the right so that ammonia is liberated as a gas along with the steam produced when a sample is boiled, as follows:



Removal of ammonia allows the hydrogen ions released in the decomposition of ammonium ion to accumulate in the residue, and a decrease in pH will result unless a buffer is present to combine with the hydrogen ions. A borate buffer is added to maintain the pH in a range of 9.5 in order to displace the equilibrium far to the right. Higher pH levels are not recommended because of the danger of some ammonia being released from organic sources at the temperature of boiling water. Experience has shown that essentially all the free ammonia will be expelled from solutions whose pH is maintained at 9.5 by the time 200 mL of water has been distilled when samples of 500 to 1000 mL are used. The distillate is collected by passage of the vapor through a condenser and then into an acid solution contained in a flask. The acid solution converts the free ammonia in the vapor to ammonium ion [the reverse of Eq. (25.12)], which cannot volatilize from the condensate solution. The acid solution used depends upon the analysis that follows. A boric acid solution is used for analyses by titration, and a dilute sulfuric acid solution for analyses by the phenate or membrane probe procedures. The titration and membrane probe procedures are described in the following sections on volumetric analysis and the ammonia-selective electrode.

For water samples that contain small amounts of ammonia nitrogen, the usual procedure is to measure the amount of nitrogen in the distillate by the phenate method. The calculation of ammonia nitrogen in terms of milligrams per liter must take into consideration the volume of distillate as well as the sample size. Many analysts find it convenient to distill an amount that exceeds 200 mL to avoid close attention at the end of the distillation. The calculation can be made, provided that the volume of distillate is known, by the following method:

$$\text{mg/L NH}_3\text{-N} = \frac{V_D}{V_{DA}} \times A \times \frac{1000}{s} \quad (25.13)$$

where  $V_D$  = mL of distillate

$V_{DA}$  = mL of distillate actually analyzed

$A$  = mg of  $\text{NH}_3\text{-N}$  found in the analyzed portion of the distillate

$s$  = mL of sample used for distillation

**By Volumetric Analysis** When samples contain more than 2 mg/L of ammonia nitrogen, as is the case with domestic and many industrial wastes, the concentration can be determined by titration with a standard solution of sulfuric acid after distillation and absorption of ammonia in boric acid as previously described. The chemistry involved is as follows: First, boric acid is an excellent buffer. It

combines with ammonia in the distillate to form ammonium and borate ions, as shown in the equation:



This causes the pH to increase somewhat, as was discussed under buffer action in Sec. 4.6, but the pH is held in a favorable range for absorption of ammonia by the use of an excess of boric acid. The ammonia may then be measured by back titration with a strong acid such as sulfuric acid. Actually, the acid measures the amount of borate ion present in the solution as follows:



When the pH of the boric acid solution has been decreased to its original value, an amount of strong acid equivalent to the ammonia has been added. The titration is most easily conducted by potentiometric methods which eliminates the need for internal indicators. The proper pH for the end point is best determined by diluting the specified volume of boric acid solution with ammonia-free distilled water in an amount equal to the volume of distillate desired and measuring the pH of the mixture.

Many water chemists prefer to use a N/14 or 0.0714 N, solution of sulfuric acid for the measurement of ammonia nitrogen. Since each milliliter of 0.0714 N acid is equivalent to 1.0 mg of nitrogen, its use eliminates the need for the 0.28 factor required when 0.020 N acid is used. Furthermore, much smaller volumes of 0.0714 N acid are needed for titration, an important factor in conserving reagent and preventing undue dilution of the sample during titration.

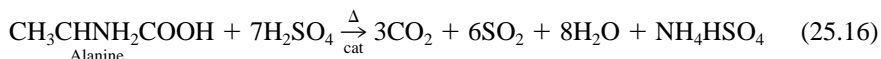
**By Ammonia-Selective Electrode** This approach makes use of a gas-permeable membrane probe as discussed in Sec. 12.3. The sample pH is raised above 11 to convert ammonium to the ammonia form, which diffuses through the membrane and changes the pH of the internal solution. This change is measured by an internal pH glass electrode and is interpreted in terms of sample ammonia nitrogen concentration using a calibration curve. The calibration curve must be prepared with a standardized ammonia solution. In an alternate approach, the change in pH following addition of measured amounts of a standardized ammonia solution to the sample can be used, rather than a calibration curve, to determine the ammonia nitrogen concentration of a sample.

## Organic Nitrogen

All nitrogen present in organic compounds may be considered organic nitrogen. This includes the nitrogen in amino acids, nucleic acids, amines, amides, imides, nitro derivatives, and a number of other compounds. Most of these have very little significance in water analysis unless specific industrial wastes are involved.

Most of the organic nitrogen that occurs in domestic wastes is in the form of proteins or their degradation products: polypeptides and amino acids. Therefore, the methods employed in water analysis have been designed to ensure measurement of these forms without particular regard to other organic forms. Actually, most forms except the nitrogen in nitro compounds are measured by the methods used.

Most organic compounds containing nitrogen are derivatives of ammonia, and thus the nitrogen has an oxidation state of  $-3$ . Destruction of the organic portion of the molecule by oxidation frees the nitrogen as ammonia. The Kjeldahl method employing sulfuric acid as the oxidizing agent is standard procedure. A concentrated salt-copper mixture is used to hasten the oxidation of some of the more resistant organic materials. The reaction that occurs may be illustrated by the oxidation of alanine ( $\alpha$ -aminopropionic acid). In the reaction, carbon is oxidized to carbon dioxide, while the sulfate ion is reduced to sulfur dioxide. The amino group is released as ammonia but, of course, cannot escape from the acid environment and is held as an ammonium salt.



The oxidation proceeds rapidly at temperatures slightly above the boiling point of sulfuric acid ( $340^\circ\text{C}$ ). The boiling point of the acid is increased to about  $360$  to  $370^\circ\text{C}$  to enhance the rate of oxidation by addition of sodium or potassium sulfate.

The complete digestion of organic matter is essential if all organic nitrogen is to be released as ammonia. A misinterpretation often occurs as to what conditions exist when digestion is complete, and some explanation seems in order. This can best be done by listing the changes that samples undergo during digestion.

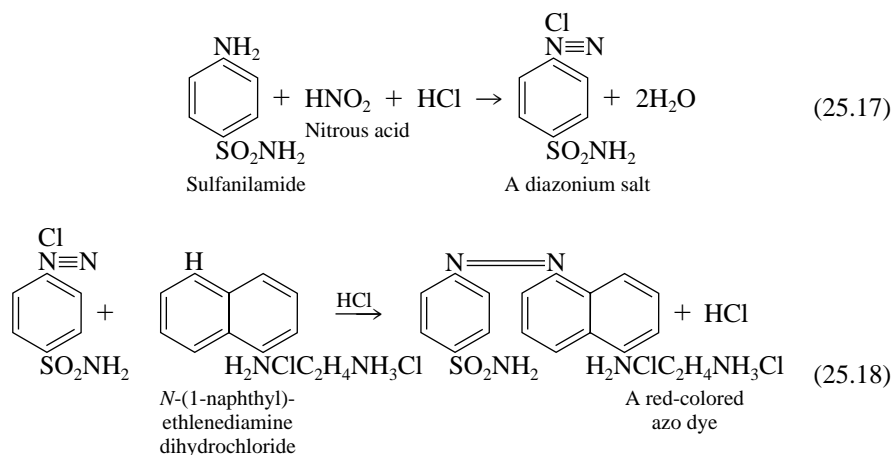
1. Excess water is expelled, leaving concentrated sulfuric acid to attack the organic matter.
2. Copious white fumes form in the flask at the time sulfuric acid reaches its boiling point. Digestion is just beginning at this stage.
3. The mixture turns black, owing to the dehydrating action of the sulfuric acid on the organic matter.
4. Oxidation of carbon occurs. Boiling during this period is characterized by extremely small bubble formation due to the release of carbon dioxide and sulfur dioxide.
5. Complete destruction of organic matter is indicated by a clearing of the sample to a "water-clear" solution.
6. Digestion should be continued for at least 20 min after the samples appear clear to ensure complete destruction of all organic matter.

Once the organic nitrogen has been released as ammonia nitrogen, it may be measured in a manner similar to that described in the discussion of ammonia nitrogen. The excess sulfuric acid must be neutralized and the pH of the sample adjusted to about 11. Under such conditions, the equilibrium shown in Eq. (25.12) is displaced greatly to the right, and ammonia can be distilled with ease. The ammonia nitrogen in the vapor is collected as in the distillation procedure described for ammonia nitrogen, and further analysis is conducted by any of the procedures there described. Calculation of organic nitrogen is made in the same manner as for ammonia nitrogen.

## Nitrite Nitrogen

Nitrite nitrogen seldom appears in concentrations greater than 1 mg/L, even in waste-treatment-plant effluents. Its concentration in surface waters and groundwaters is normally much below 0.1 mg/L. For this reason sensitive methods are needed for its measurement. The colorimetric procedure provides this sensitivity. However, another standard procedure is an instrumental approach using ion chromatography as described in Sec. 12.4. Several anions can be determined simultaneously on a single sample by ion chromatography, but the colorimetric procedure is cheaper and preferred when analysis for nitrite alone is desired or nitrite concentrations are especially low.

In the colorimetric procedure a modification of the Griess-Ilosvay diazotization method is used. This employs the use of two organic reagents: sulfanilamide and *N*-(1 naphthyl)-ethylenediamine dihydrochloride. The reactions involved may be represented as follows:



Under acid conditions nitrite ion as nitrous acid reacts with an amino group of sulfanilamide to form a diazonium salt that combines with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to a bright-colored, pinkish-red azo dye. The color produced is directly proportional to the amount of nitrite nitrogen present in the sample, and determination of the amount can be made by comparison with color standards or by means of photometric measurement. Photometric measurement is preferred because standards for visual comparison are not permanent and must be prepared each time analyses are performed.

## Nitrate Nitrogen

Obtaining reliable nitrate nitrogen analysis is difficult. In recent years several procedures have been developed. All have limitations with which the analysts must be familiar. The ultraviolet spectrophotometric procedure can be used for initial screening to help decide on initial sample dilutions if needed and what particular method

of analysis is most appropriate. This screening procedure and four standard methods are described in the following.

**Screening by Ultraviolet Spectrophotometry** Nitrate ions in water absorb ultraviolet radiation with a wavelength of 220 nm. For this reason optical methods of analysis as described in Sec. 12.2 can be used to measure nitrate. The method is quite sensitive but requires a spectrophotometer that can be operated in the ultraviolet range. Any materials that absorb 220 nm radiation will interfere in this analysis. This includes nitrite, hexavalent chromium, and many different organic compounds. Thus, this method is generally used only for screening; caution in the use of this method for other than simple screening is required.

**Ion Chromatographic and Capillary Ion Electrophoresis Methods** The ion chromatographic procedure described in Sec. 12.4 is highly useful for analysis with nitrate nitrogen concentrations greater than about 0.2 mg/L. In this way many of the normal interferences in nitrate analysis can be avoided. The procedure also permits the simultaneous analysis for other anions in the sample. The disadvantage of this procedure is the cost for purchase and maintenance of the instrument. The capillary ion electrophoresis method, also described in Sec. 12.4, is similar to the ion chromatographic method in permitting analysis for other ions, but its operating costs are significantly less. Ultraviolet absorption is used for detection.

**Nitrate Electrode Method** The nitrate electrode is a liquid membrane electrode as described in Sec. 12.3 and can detect the presence of nitrate nitrogen down to concentrations of about 1 mg/L. The advantage of the electrode method is that once calibrated, analysis for nitrate is rapid. Also, the electrode is readily adapted to continuous monitoring and to automatic process control. Disadvantages are that several common ions such as chloride and bicarbonate cause interference, and the electrode is not sensitive with the lower nitrate concentrations frequently encountered.

**Cadmium Reduction Method** The cadmium reduction method offers a highly sensitive procedure for nitrate analysis. A filtered sample with added  $\text{NH}_4\text{Cl}$ -EDTA solution is passed through a specially prepared column containing amalgamated cadmium granules. During passage, nitrate is quantitatively reduced by the cadmium to nitrite. The nitrite produced is determined by the diazotization method previously described. Since nitrite originally present in the sample is also measured, this procedure in effect measures the sum of nitrate plus nitrate nitrogen. In order to determine the nitrate concentration, a separate analysis of nitrite alone is required, and this value is subtracted from the results of the cadmium reduction procedure. Because of the sensitivity of the diazotization method for nitrite, nitrate concentrations as low as 0.01 mg/L can be detected. Samples with nitrate nitrogen concentrations greater than 1 mg/L can also be measured if the samples are diluted prior to passage through the cadmium column. A standard nitrate solution should be passed through the column on occasion to establish that quantitative conversion of nitrate to nitrite is being obtained. If not, then the column should be reactivated or the sample flow rate should be adjusted to obtain quantitative conversion. This procedure has successfully been used in an automated method of analysis.

## Total Nitrogen

*Total nitrogen* in water is taken to mean the sum total of the concentrations of ammonia, nitrite, nitrate, and organic nitrogen. The gaseous forms of nitrogen, including  $N_2$ , are not included in the total. The concentration of  $N_2$  in water is generally quite high, roughly 15 to 20 mg/L, due to equilibrium with  $N_2$  in the atmosphere as indicated in Fig. 22.1. However, because it is so nonreactive, it plays little role in water quality considerations associated with nitrogen. Knowledge of the concentration of the individual four forms of nitrogen present in water is generally more important than their “total value,” and thus the analytical procedures for individual species will always be of importance. The total can be readily obtained from their summation. Nevertheless, “Standard Methods” now contains analytical procedures that provide measurement of the “total nitrogen” content. This may be useful for obtaining a quick overview of the total nitrogen present, or as a method of determining the concentration of a particular species by difference when concentrations of the other three are known. For example, the normal Kjeldahl digestion procedure for determining organic nitrogen can be avoided if one knows the total nitrogen concentration and the concentration of the three inorganic forms. Organic nitrogen concentration is then equal to the total minus the sum of the three inorganic forms. Of course, the error in the organic nitrogen determination then reflects the errors inherent in all the other analyses combined as discussed in Chap. 10, and whether this error is acceptable needs to be evaluated.

The “Standard Methods” procedure for total nitrogen analysis involves the oxidation of ammonia, nitrite, and organic nitrogen to nitrate, and subsequent reduction of the nitrate to nitrite using the cadmium reduction procedure followed by the sensitive colorimetric diazotization method for nitrite already discussed. For the original oxidation of reduced nitrogen forms to nitrate, an alkaline digestion solution containing persulfate ( $S_2O_8^{2-}$ ) is mixed with the sample and heated under pressure at 100 to 110°C. This results in release of organic nitrogen as ammonia and oxidation of the reduced inorganic nitrogen forms to nitrate, while reducing the persulfate sulfur (VII) to sulfate sulfur (VI). The procedure offers speed and simplicity over the Kjeldahl method and lends itself to automated methods that are available commercially.

## 25.4 | APPLICATION OF NITROGEN DATA

At the present time, data concerning the nitrogen compounds that exist in drinking water supplies are used largely in connection with disinfection practice. The amount of ammonia nitrogen present in a water determines to a great extent the chlorine needed to obtain free chlorine residuals in breakpoint chlorination and determines to some extent the ratio of monochloramine to dichloramine when combined chlorine residuals are involved. Nitrate and nitrite determinations are important in determining whether water supplies meet U.S. EPA maximum contaminant levels for the control of methemoglobinemia in infants.



Nitrogen data are important in connection with wastewater treatment. By controlling nitrification when not required, aerobic-treatment costs can be kept at a minimum. When nitrogen oxidation is required, then understanding nitrogen changes through nitrification and denitrification is essential for process control. Ammonia and organic nitrogen analyses are important in determining whether sufficient available nitrogen is present for biological treatment. If not, they are needed to calculate the amounts that must be supplied from outside sources, an important economic consideration in many instances.

Where wastewater sludges are sold for their fertilizing value, the nitrogen content of the sludges is a major factor in determining their value for such purposes.

The productivity of natural waters in terms of algal growths is related to the fertilizing matter that gains entrance to them. Nitrogen in its various forms is a major consideration. Also, reduced forms of nitrogen are oxidized in natural waters, thereby affecting the dissolved-oxygen resources. For these reasons nitrogen data are often part of the information needed in stream-pollution-control programs.

## PROBLEMS

- 25.1** In what forms does nitrogen normally occur in natural waters?  
**25.2** Discuss the significance of nitrogen analysis in water pollution control.  
**25.3** Analyses for various forms of nitrogen were made at three points in a stream as follows:

Point	Location	DO, mg/L	Nitrogen, mg/L			
			Org-N	NH <sub>3</sub>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
1	Point of waste discharge	7	3	4	0	0
2	5 km downstream	2	1	2	1	3
3	10 km downstream	0	1	0	0	2

On the basis of your knowledge of the nitrogen cycle, explain the processes involved in the relative changes in each nitrogen form, as well as the decrease in total nitrogen in moving downstream from point 1 to point 3.

- 25.4** Would you expect to find the highest concentration of each of the following in raw domestic wastewater or in the effluent from an aerobic biological waste treatment plant? Why? (a) Organic-N; (b) NH<sub>3</sub>-N; (c) NO<sub>2</sub><sup>-</sup>-N; (d) NO<sub>3</sub><sup>-</sup>-N.  
**25.5** What biological processes might be used to reduce the total nitrogen content of a wastewater?  
**25.6** What limit is placed on the nitrogen content of drinking water and why?  
**25.7** What is NO<sub>x</sub> and what environmental problems are associated with it?  
**25.8** What is the general source of N<sub>2</sub>O in the environment, and what environmental problems can it cause?  
**25.9** What are the oxidation states of nitrogen, and what environmental problem or problems may be associated with each?  
**25.10** What environmental problems may be associated with ammonia discharge to a river?

- 25.11** Why might one wish to suppress nitrification in a biological wastewater treatment plant? Is it always a good idea to do this? Why?
- 25.12** How can advantage be taken of the need to nitrify a wastewater in order to reduce the oxygen demand for treatment?
- 25.13** Of what significance is ammonia nitrogen in water disinfection?
- 25.14** What four analytical methods can be used for ammonia nitrogen measurements?
- 25.15** How may organic nitrogen concentration in a wastewater be determined?
- 25.16** Describe the chemistry of the colorimetric method for nitrite determination.
- 25.17** What methods are available for analysis of nitrate nitrogen?
- 25.18** Describe two procedures for determining total nitrogen in a water sample.
- 25.19** Determine the total nitrogen concentration in mg/L of a water sample containing 0.25 mM ammonia, 0.02 mM nitrite, 0.75 mM nitrate, and 1.3 mg/L organic nitrogen.
- 25.20** Determine the total nitrogen concentration in mg/L of a water sample containing 1.3 mg/L ammonia, 0.25 mg/L nitrite, 15.1 mg/L nitrate, and 0.9 mg/L organic nitrogen.
- 25.21** The total nitrogen concentration of a water sample is found to be 11.2 mg/L. How might the organic nitrogen content be determined without chemical analysis for the organic nitrogen content of the sample? What is the advantage and disadvantage of your method over direct chemical analysis for organic nitrogen?

## REFERENCES

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