Nitrogen in All Its Forms

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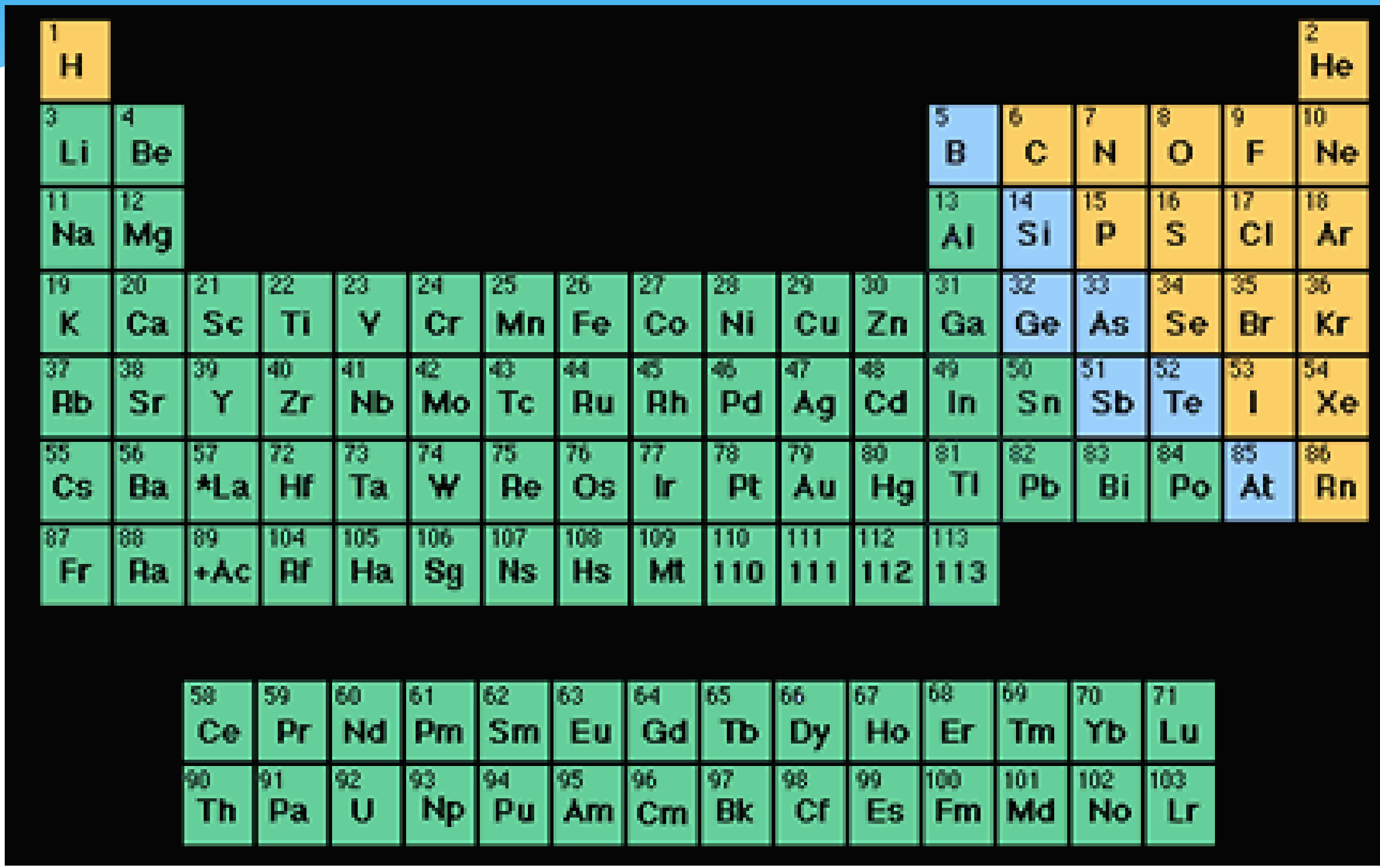
Nitrogen is in the Nonmetals Group



OXIDATION STATES OF NITROGEN

N has 5 electrons in valence shell ⇨7 oxidation states from –3 to +5

Increasing oxidation number (oxidation reactions) →

-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia** NH_4^+ **Ammonium** $R_1N(R_2)R_3$ **Organic N**	N_2	N_2O **Nitrous oxide**	**NO** **Nitric oxide** *free radical*	HONO **Nitrous acid** NO_2^- **Nitrite**	NO_2 **Nitrogen dioxide** *free radical*	HNO_3 **Nitric acid** NO_3^- **Nitrate** N_2O_5 **Nitrogen pentoxide**

← Decreasing oxidation number (reduction reactions)

* Three forms combine with water to form inroganic ionized species

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (25.1)$$

$$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^- \quad (25.2)$$

$$N_2O_5 + H_2O \rightarrow 2H^+ + 2NO_3^- \quad (25.3)$$

* The other oxidation states, N2, N2O and NO exist as gases that have limited solubility in water.
* Except N2, nitrogen compounds in all oxidation states can result in environmental problems

What does nitrogen do?

Nitrogen is an essential building block of biological molecules:

DNA is a blueprint for protein production.

DNA is expressed via the proteins it codes.

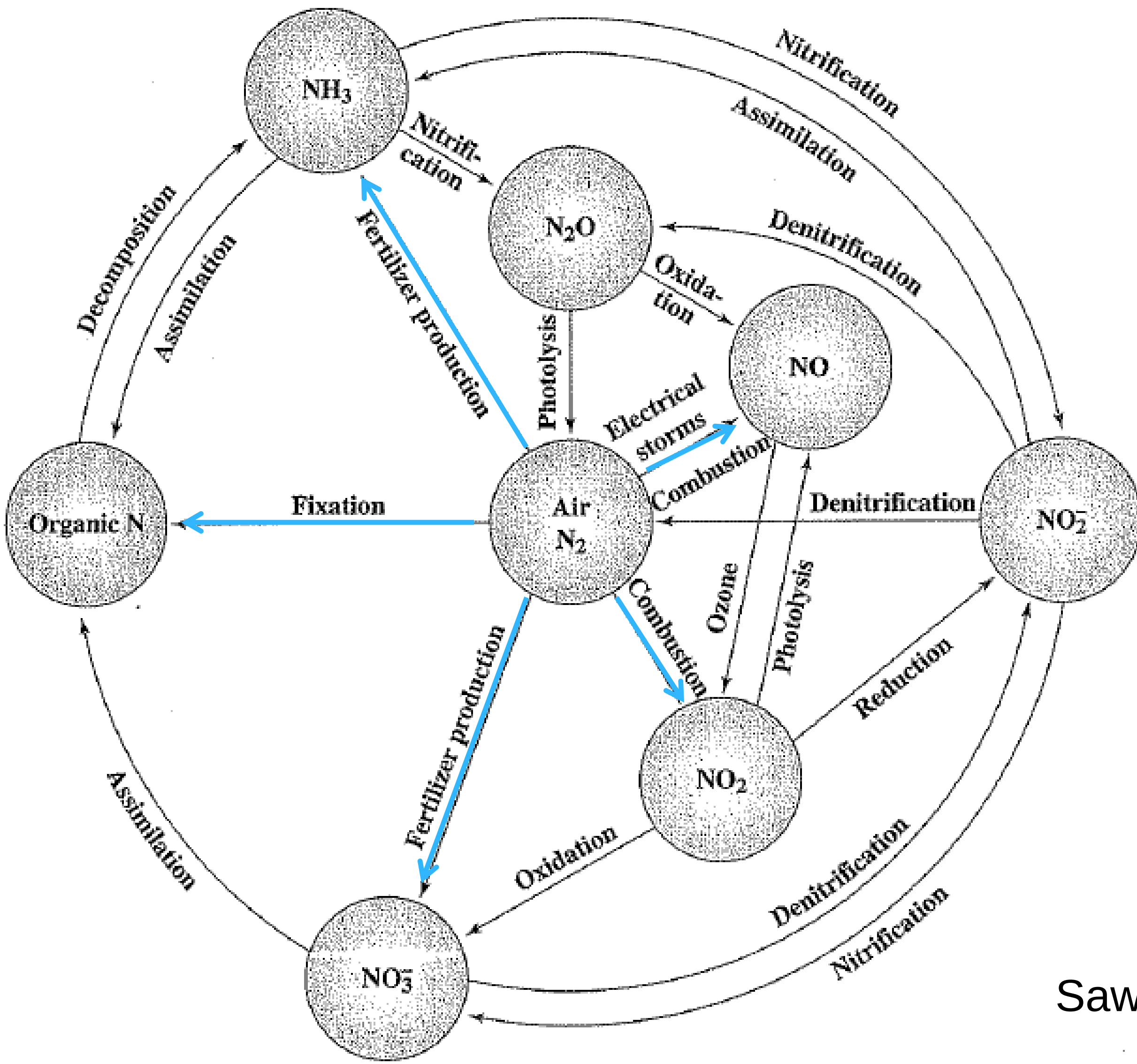
Proteins are made up of amino acids.

Amino acids have a carboxylic **acid** on one end and an **amine** (nitrogen) group on the other.

The largest single source of *nitrogen* is in the *atmosphere*.

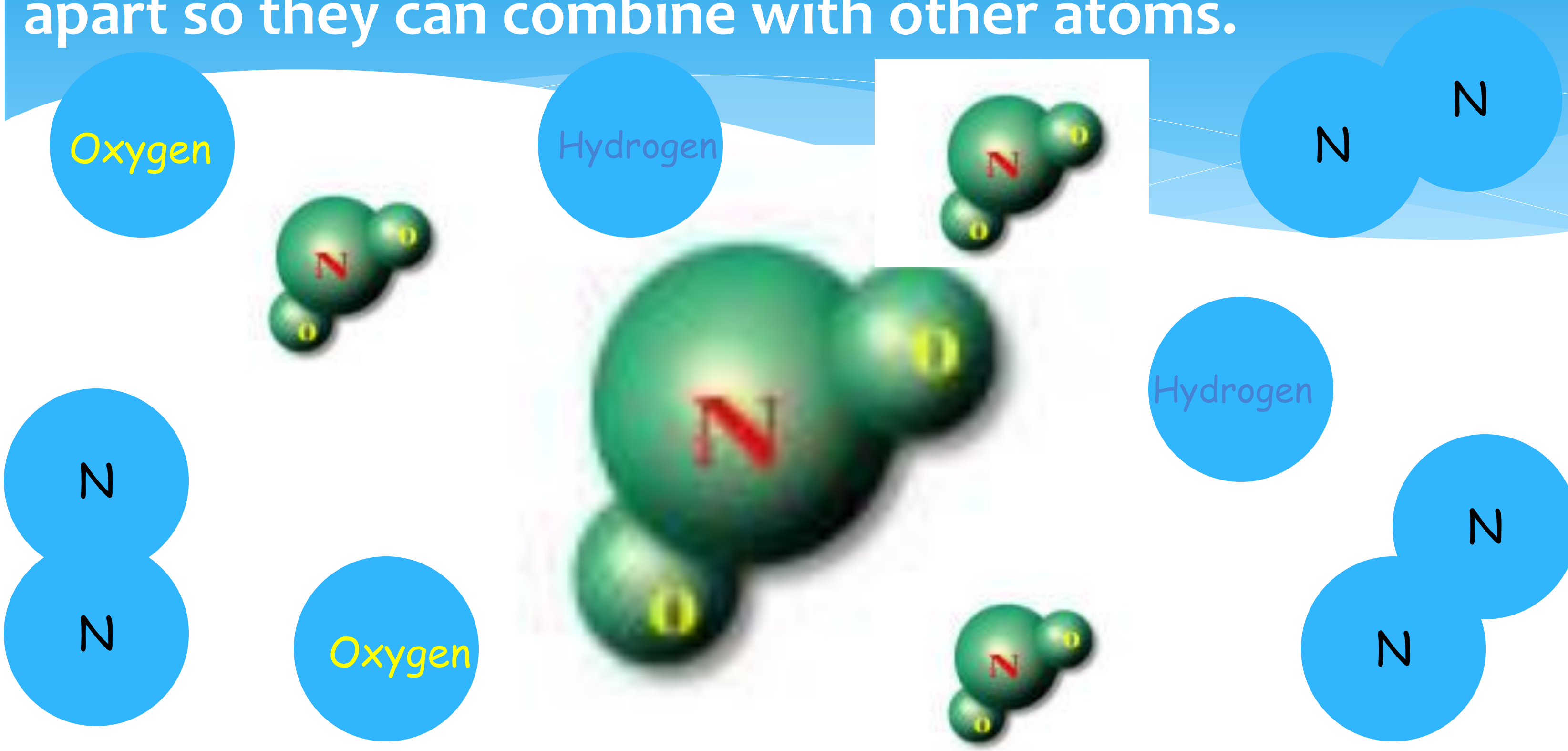
Nitrogen makes up 78% of our air!

Nitrogen Cycle



Sawyer, 2003

"***Nitrogen Fixation***" **is the process that causes the strong two-atom nitrogen molecules found in the atmosphere to break apart so they can combine with other atoms.**



Nitrogen gets "*fixed*" when it is combined with oxygen or hydrogen.

There are three ways that nitrogen gets "fixed"!

(a) Atmospheric Fixation

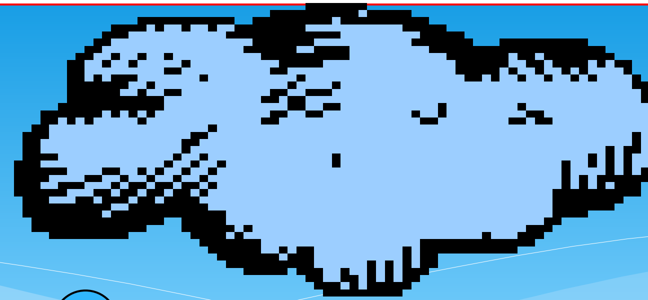
(b) Industrial Fixation

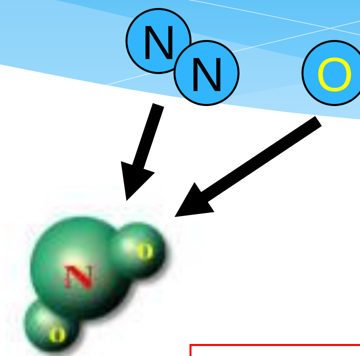
(c) Biological Fixation

Bacteria

Lightning "fixes" Nitrogen!

Atmospheric Fixation
(Only 5 to 8% of the Fixation





The enormous energy of *lightning breaks nitrogen molecules apart* and enables the nitrogen atoms to combine with oxygen forming *nitrogen oxides* *(N_2O)*. Nitrogen oxides dissolve in rain, forming nitrates. *Nitrates (NO_3)* are carried to the ground with the rain.

(N_2O)

(NO_3)

Nitrogen combines with Oxygen

Nitrogen oxides forms

Nitrogen oxides dissolve in rain and change to nitrates

$$NO_3^- + CO_2 + \text{green plants} + \text{sunlight} \rightarrow \text{protein} \qquad (25.4)$$

Plants use nitrates to grow!

Industrial Fixation

Under great pressure, at a temperature of 600 degrees Celcius, catalyst, *atmospheric nitrogen* (N_2) and *hydrogen* are combined to form *ammonia* (NH_3). Ammonia can be used as a *fertilizer*.

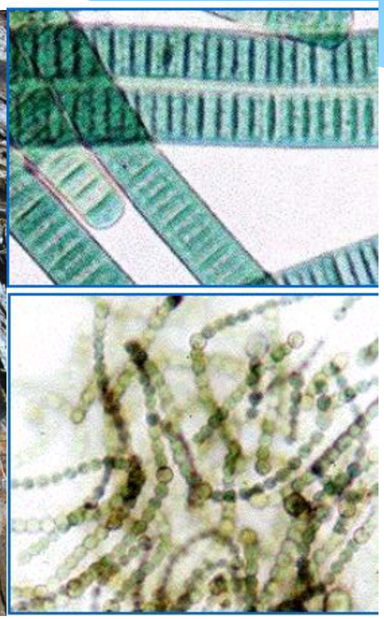
Industrial Plant combines nitrogen and hydrogen

Ammonia is formed

Ammonia is used a fertilizer in soil

Biological Fixation

There are two types of Nitrogen Fixing Bacteria"



Free Living Bacteria (Diazotrophs)

("fixes" 30% of N_2)

Symbiotic Relationship Bacteria

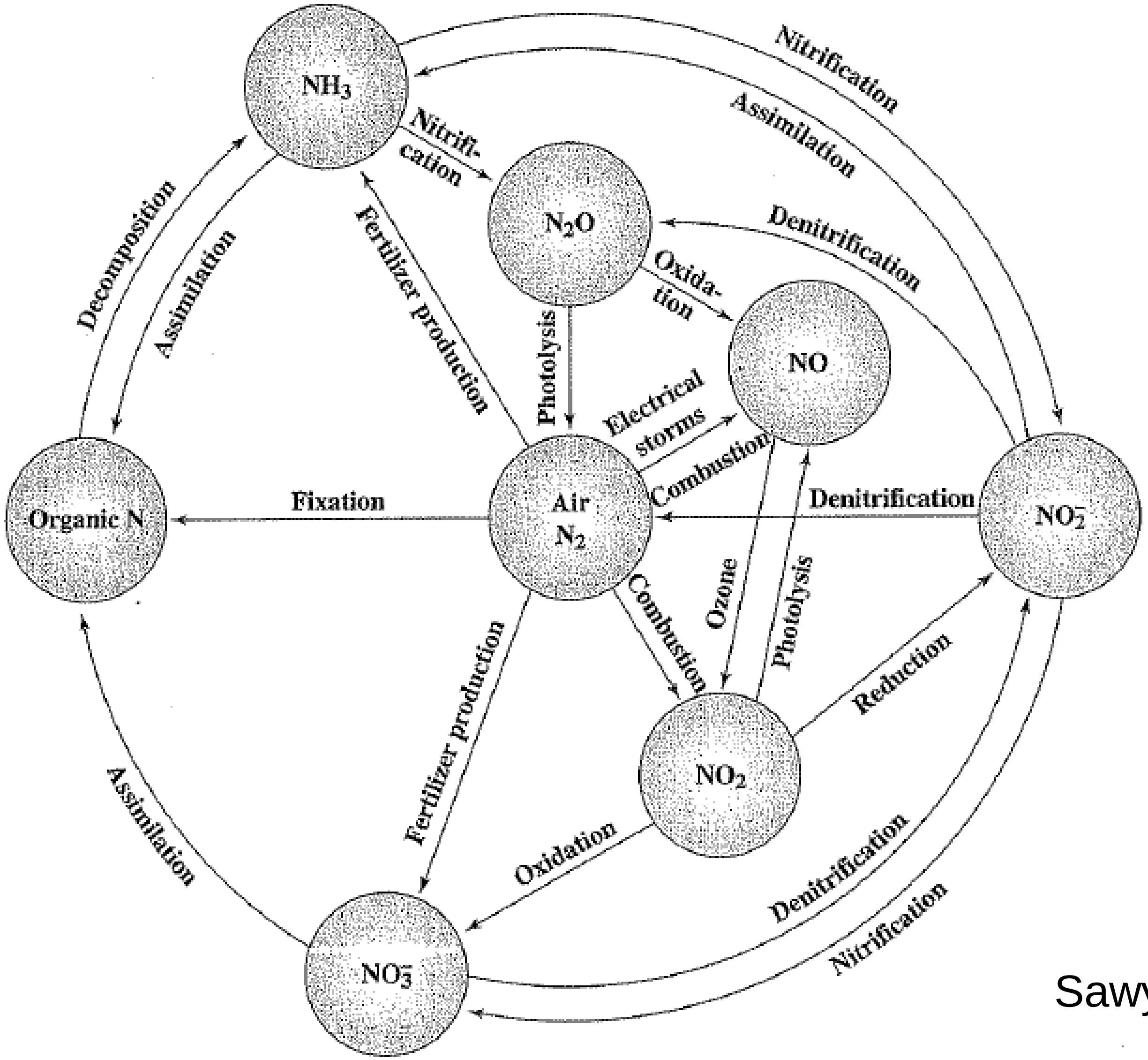
("fixes" 70% of N_2)

$$N_2 + \text{nitrogen-fixing bacteria} \rightarrow \text{protein} \quad (25.5)$$

Symbiotic Relationship Bacteria

Bacteria live in the roots of legume family plants and provide the plants with *ammonia (NH_3)* in exchange for the plant's carbon and a protected home.

Nitrogen Cycle



Sawyer, 2003

Biology rules

The biological importance of amino acids results in both opportunities and problems for nitrogen.

1. To make amino acids, plants need nitrogen. (Animals mostly absorb the amino acids from what they eat – plants!)
2. When organisms die, their decay releases the nitrogen back into the environment.

Aquatic & soil systems

Plants need to acquire nitrogen from the environment and incorporate it into its amino acid production.

Not all forms of nitrogen can easily be incorporated.

"Good Nitrogen" – The Plant Perspective

For a plant, nitrogen must be in a form the plant can absorb and use.

What properties would a molecule need to have?

1. Water soluble
2. Membrane permeable

“Good Nitrogen”

NH_4^+ ($NH_3 + H_2O$)

NO_3^-

Other forms of nitrogen aren’t directly usable, but “nitrogen-fixing bacteria” can make them usable.

Bad Nitrogen

NO and NO_2 (sometimes called NO_x)

They are responsible for acid rain, ozone depletion and are greenhouse gases.

They are the products of combustion of nitrogen containing compounds.

Biodegradation of waste

* Urea rapidly hydrolyzes:

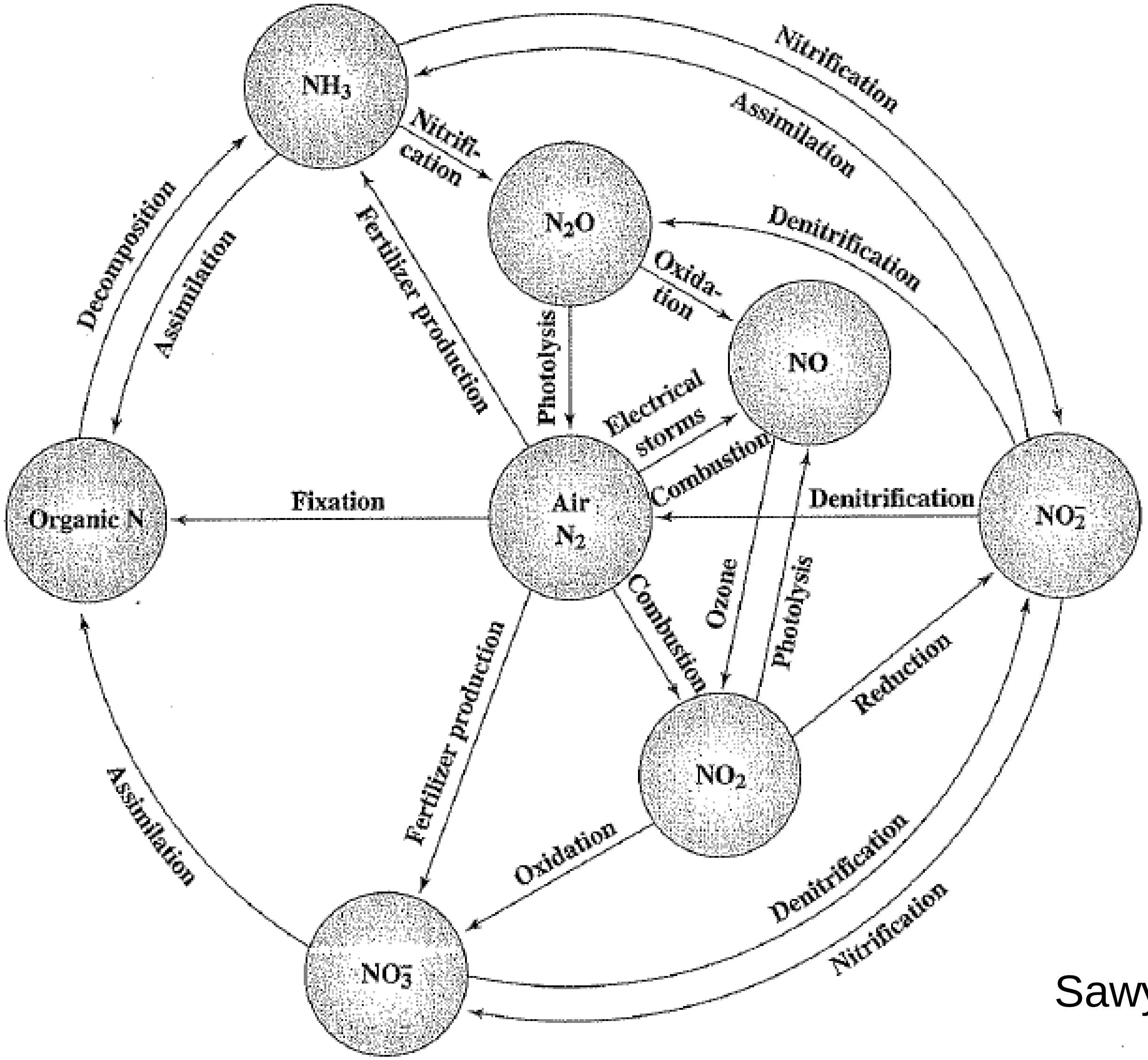
$$C(=O)(NH_2)_2 + 2H_2O \xrightarrow{\text{urease enzyme}} (NH_4)_2CO_3 \qquad (25.7)$$

* The feces of animals contain appreciable amounts of unassimilated protein matter (organic nitrogen)

$$\text{Protein (organic-N)} + \text{bacteria} \longrightarrow NH_3 \qquad (25.8)$$

* Some nitrogen always remains in nondigestible matter and becomes a part of the nondigestible residue sink.

Nitrogen Cycle



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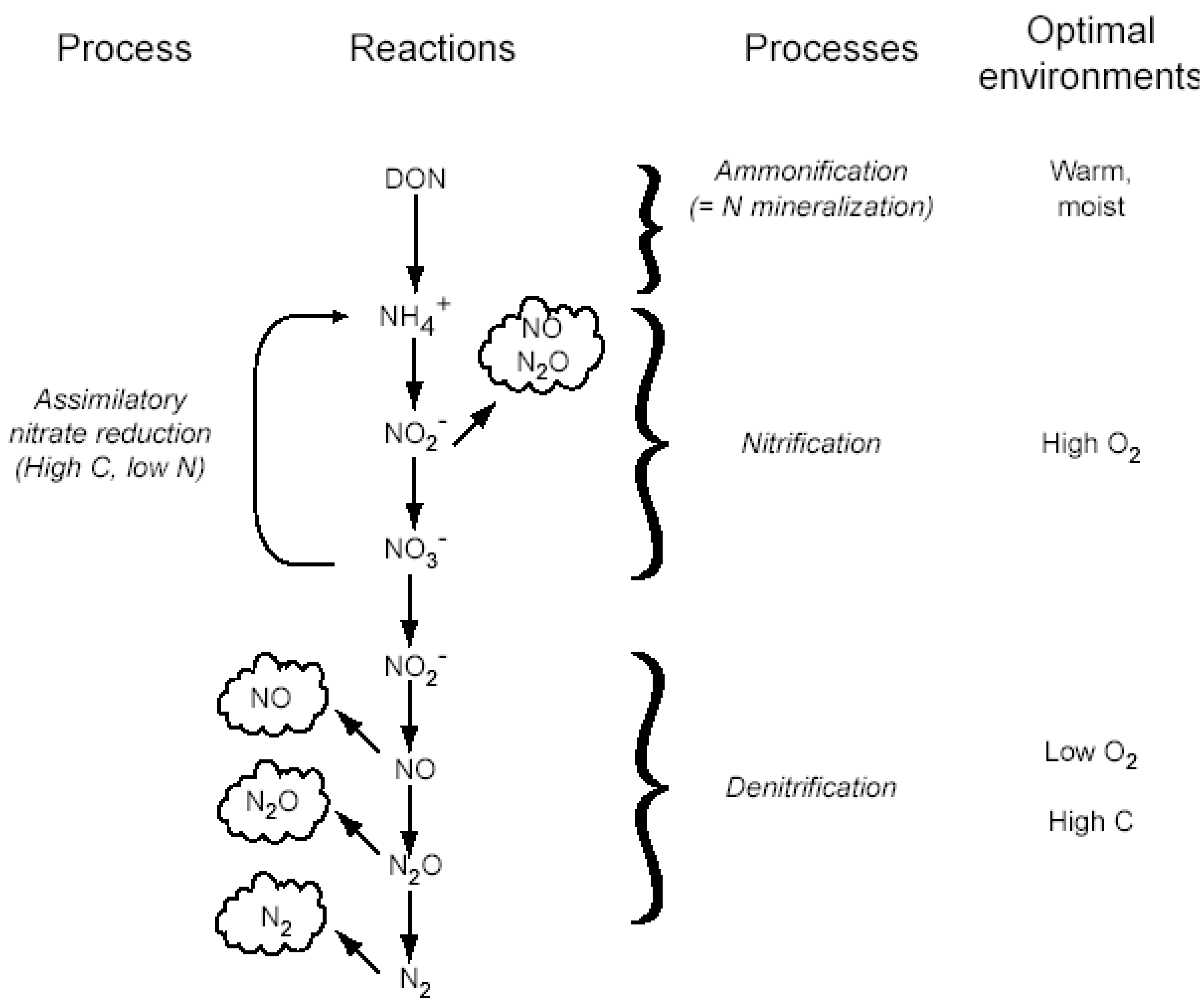
Nitrification

* $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$
  * Two-step process conducted by chemoautotrophic bacteria:
    * First step conducted by AOB, $NH_4^+ \rightarrow NO_2^-$, ammonia mono-oxygenase, need O_2
    * Second step conducted by *NOB*, $NO_2^- \rightarrow NO_3^-$
  * Controls:
    * NH_4^+
    * O_2
    * Slow growth of nitrifiers

Nitrification and denitrification occur under different conditions.



Atmospheric Concerns with Nitrogen Species

* Photochemical smog
  * Partially oxidized org. matter + NOx + Sunlight→ O3+Org. Chemicals
  * Produce eye irritation, reduced air visibility, crop damage, health impacts on humans
  * e.g. automobiles
* Global warming
  * NOx production from fuel and biomass combustion
  * NOx production from Denitrification
  * Amount of NOx emission wrt CO2 is very low, N2O=200xCO2 global warming contributor
* Stratospehric ozone depletion
  * N2O and NO2 are converted to NO in atm.
  * NO reacts with O3 in stratosphere

Aquatic Concerns with Nitrogen Species

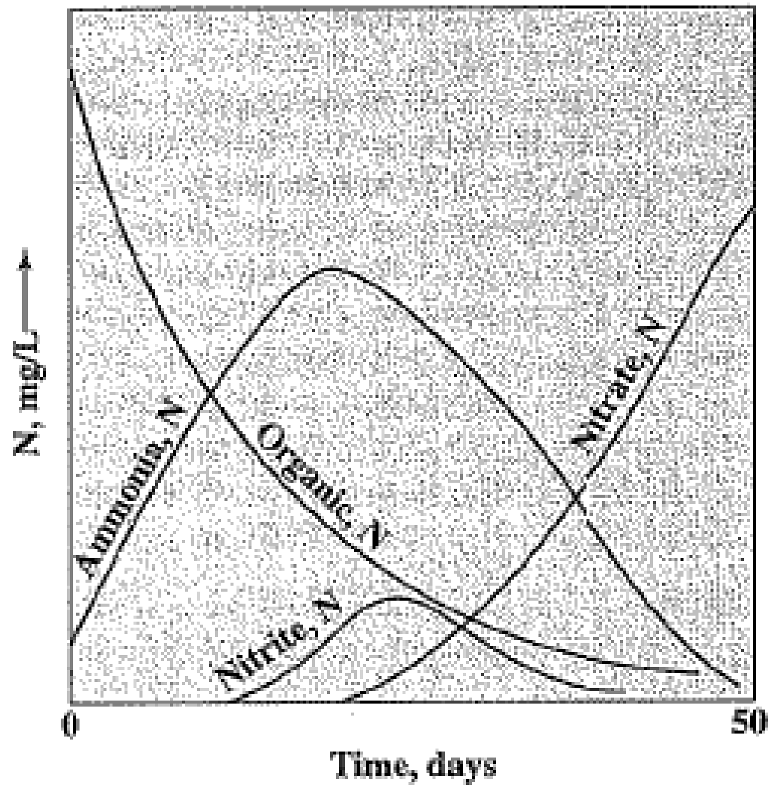


Figure 25.3
Changes occurring in forms of nitrogen present in polluted water under aerobic conditions.

Biodegradation of waste

In polluted waters, as organic contamination is biodegraded, ammonia concentration peaks early and then decreases during biodegradation. Nitrite peaks later and then tails off even quicker. Nitrate rises later in the process.

Nitrogen profiles

Looking at the RELATIVE concentrations of different nitrogen compounds can give you some indication of where in its natural evolution a water system is.

Limits

NO_3^- - EPA limit of 10 mg/L

NO_2^- - EPA limit of 1 mg/L

NO2 binds to hemoglobin causing methemoglobinemia in infants

Interact with amines to form nitrosamines, which are strong carcinogens

Important issues related with water

* Ammonia is sometimes added to drinking water supplies when a disinfection residual in water mains is desired.
  * Ammonia + Cl_2 → Chloramines
* During biological wastewater treatment sufficient nitrogen should be present for bacterial growth.
* Discharge of nitrogen containing species may deplete DO in receiving bodies.
* Unionized ammonia is toxic

Important issues related with water

* Sequence of anoxic- oxic tanks are important for biological nitrogen removal.

Testing for ammonia

3 main tests:

1. **Phenate Addition – Direct and Distilled**
2. **Volumetric Analysis**
3. **Ammonia Selective Electrode**
4. Nessler Method-removed from Standard Methods

Phenate addition

Adding an alkaline phenol (C_6H_5OH) solution along with hypochlorite (ClO^-) and a manganous salt (Mn^{2+}).

The manganese is a catalyst for the reaction:

$$2\ C_6H_5OH + ClO^- + NH_3 \longrightarrow C_{12}H_9NO_2 + \ldots$$

$C_{12}H_9NO_2$

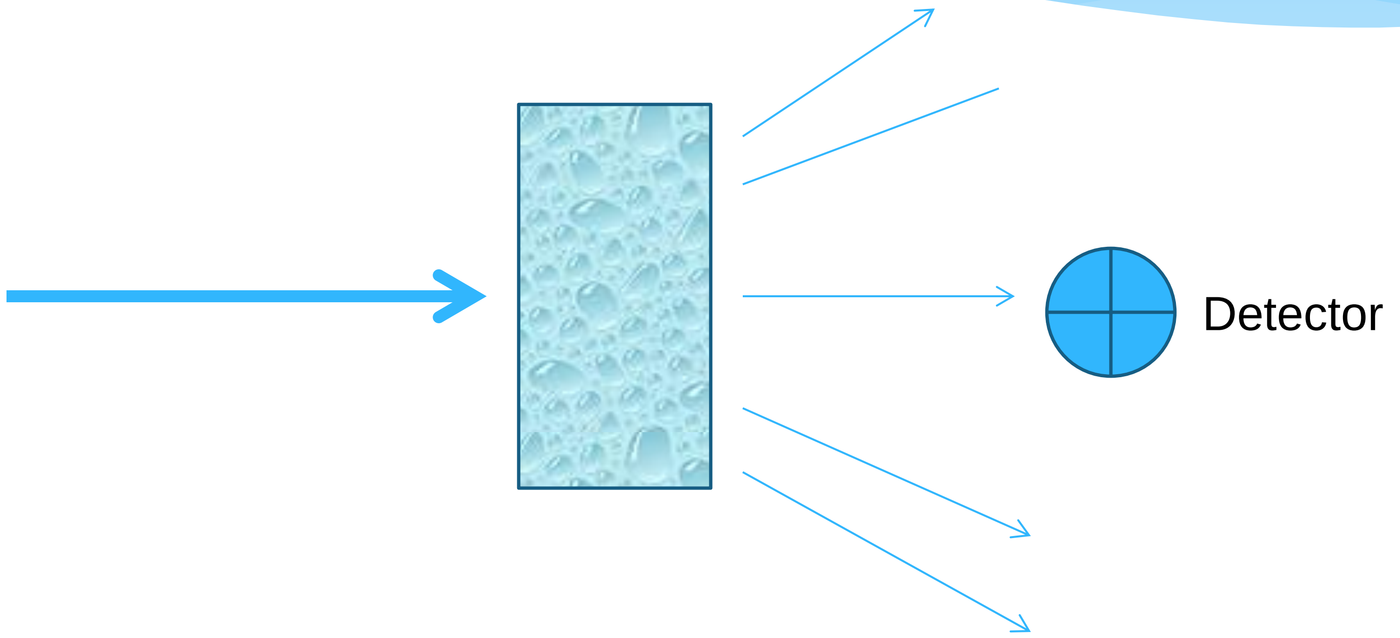
Indophenol (short for indigo phenol) is a very blue dye. It can be quantified via colorimetry.

Interference

Colorimetric analysis is subject to possible errors from:

1. Native color – other “blue” species
2. Turbidity – scattered light

Scattered Light



Phenate addition with distillation

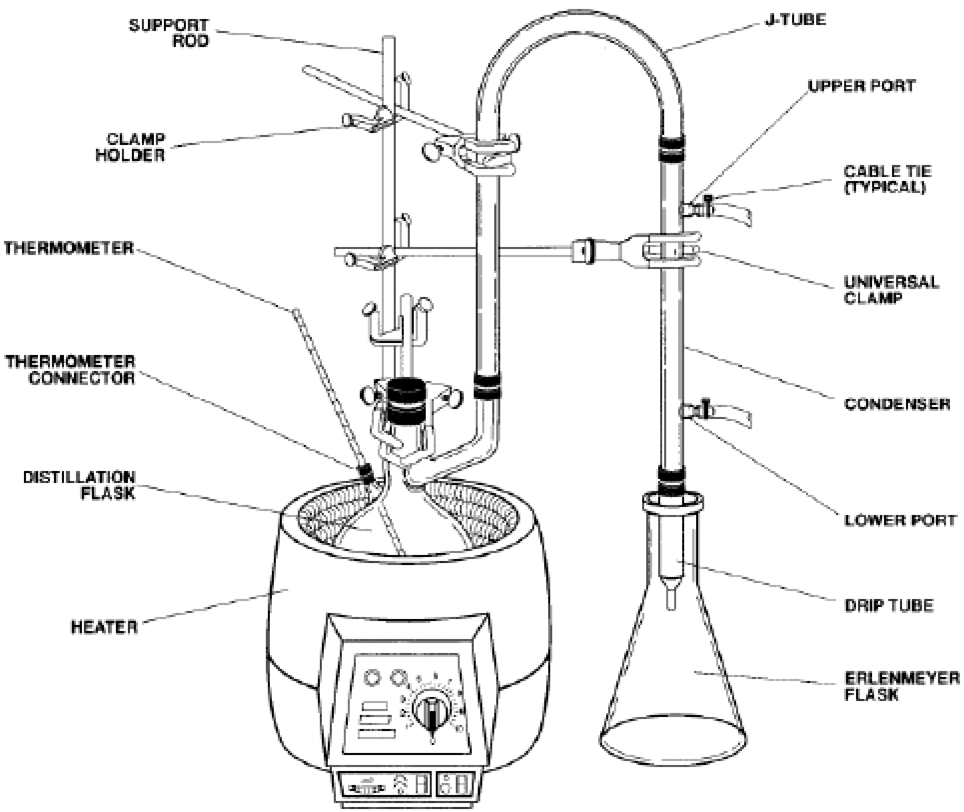


Figure 2 General Purpose Distillation Apparatus Assembly

To prevent interference, the waste water sample can first be distilled. The ammonia is volatile and will be distilled off early with some water as long as the pH stays in the 9.5 range.

How would you keep the pH steady?

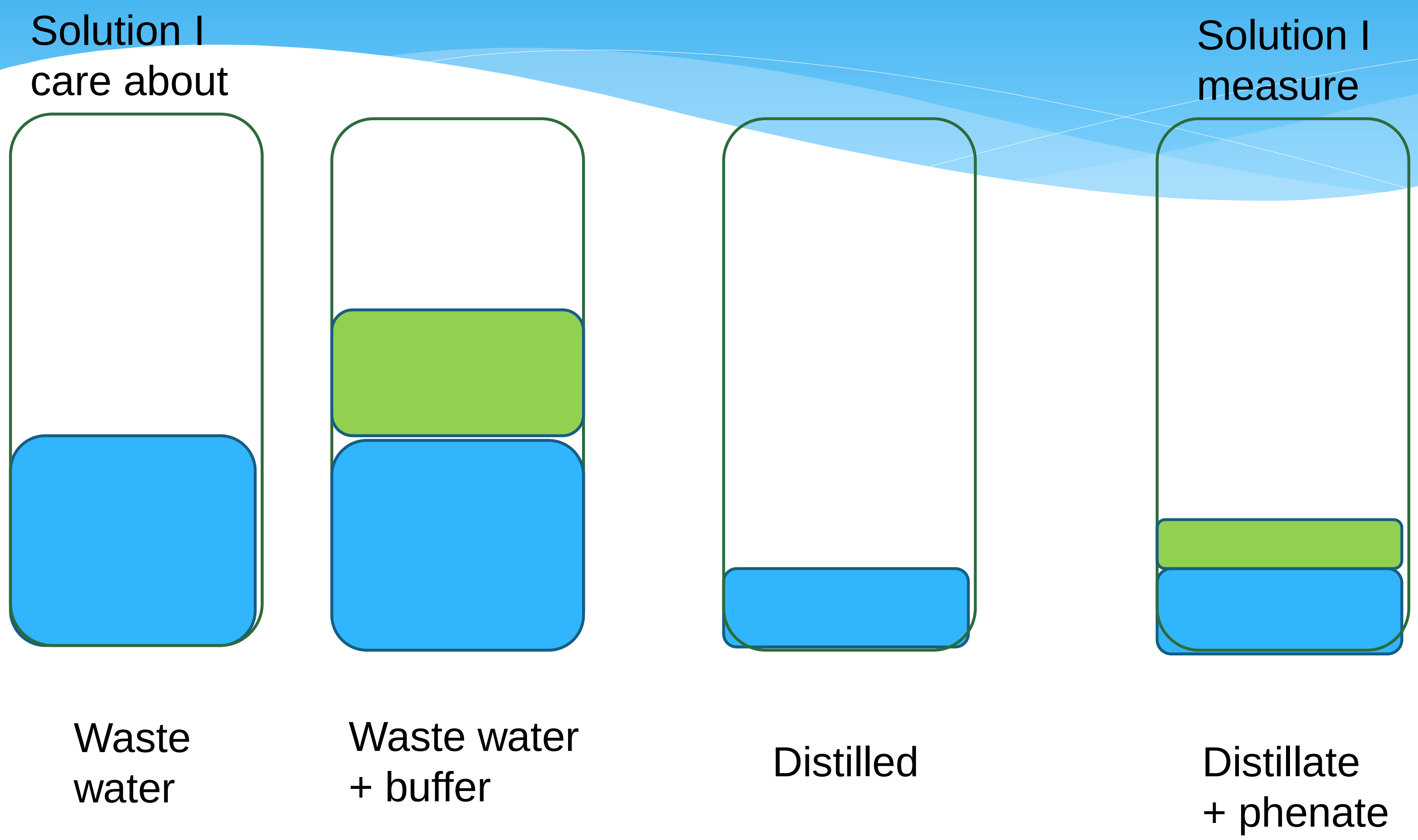
Add a buffer (standard borate buffer has pH=9.5)

Phenate Addition after Distillation

So, you would take the original sample (say 1 L), add buffer, and then distill off approximately 20-50% of the sample. Since the ammonia comes off early, 99% of it has been distilled off in the first 20% of the distillate.

Then you can do the phenate addition and the colorimetric analysis.

You need to correct the value for "concentration"!!!


Solution I
care about
Solution I
measure
Waste
water
Waste water
+ buffer
Distilled
Distillate
+ phenate

Sample Problem

1000 mL of waste water is mixed with 1000 mL of a standard borate buffer (pH =9.5). The resulting sample is distilled until 500 mL of distillate is collected. Phenate addition and colorimetric analysis of the distillate determines the indophenol concentration to be 1.2×10^{-4} M. What is the ammonia concentration of the waste water?

Solution

$$\frac{1.2 \times 10^{-4} \text{ mol indo}}{1 \text{ L}} = \frac{1.2 \times 10^{-4} \text{ mol } NH_3}{1 \text{ L}}$$

$$\frac{1.2 \times 10^{-4} \text{ mol } NH_3}{1 \text{ L}} * \frac{17.1 \text{ g } NH_3}{1 \text{ mol } NH_3} = \frac{0.00205 \text{ g}}{1 \text{ L}}$$

2.05 mg/L

Dilution is the solution

2.05 mg/L is NOT the answer

$\frac{2.05\ mg\ NH_3}{L\ ANALYZED}$ NOT $\frac{2.05\ mg\ NH_3}{L\ waste\ water}$

We did stuff before we analyzed it.

Dilution is the solution

$\frac{2.05 \text{ mg } NH_3}{\text{L analyzed}}$ * 0.500 L analyzed = 1.025 mg NH_3

There must have been a total of 1.025 mg NH_3 in the sample analyzed. That ammonia was originally in 1 L of the waste water.

$\frac{1.025 \text{ mg } NH_3}{\text{1 L waste water}}$ = 1.025 mg NH_3/L

THAT'S the answer!

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

where V_D = mL of distillate

V_{DA} = mL of distillate actually analyzed

A = mg of NH_3–N found in the analyzed portion of the distillate

s = mL of sample used for distillation

Ion selective electrode

There are ammonium selective ions. (They have a membrane permeable only to the ammonium ions). Works like a pH meter – an electrode that is selective of H^+.

You just stick in the probe and read a voltage. The voltage is directly proportional to the concentration. (like a pH meter!)

Other Nitrogen species

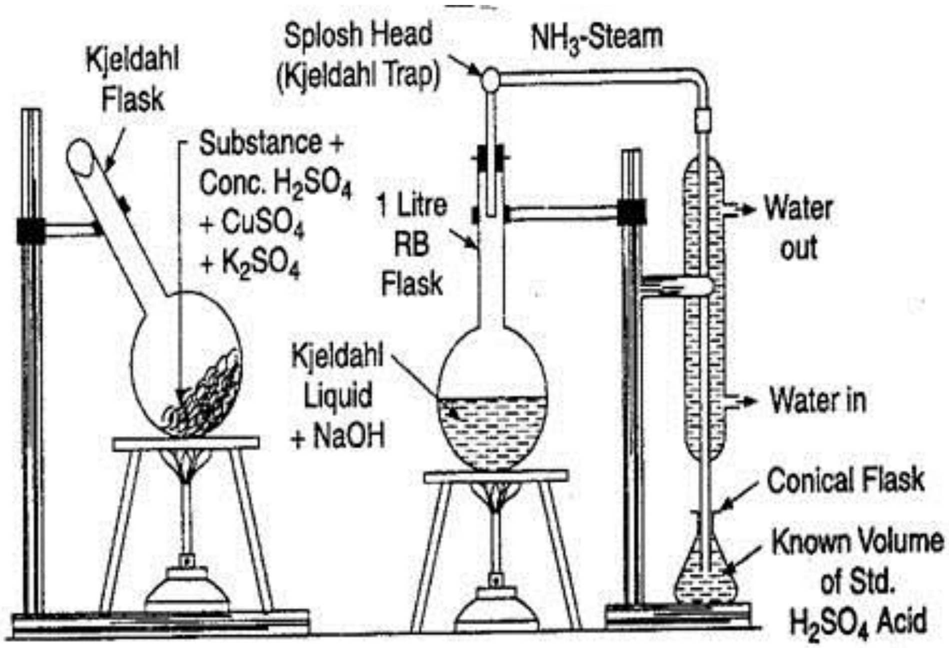
You can test for:

1. Organic nitrogen – bound in proteins
2. Nitrite
3. Nitrate
4. Total Nitrogen

Organic nitrogen measurement

* All nitrogen present in organic compounds (e.g. Amines, amides, aminoacid, nucleic acid etc.)
* Organic nitrogen in domestic wastewater→proteins and their degradation products: polypeptides and aminoacids
* Destruction of the organic portion by oxidation frees the nitrogen as ammonia.
* The Kjeldahl method employing sulfuric acid is standard procedure.

Kjeldahl Method



Boil to clear + 20 min

Sulfuric acid as oxidizing agent

A concentrated salt-copper mixture to hasten the oxidation of resistant organic matter

Oxidation proceeds rapidly at temperatures slightly higher than the boiling point of H_2SO_4 (340°C)

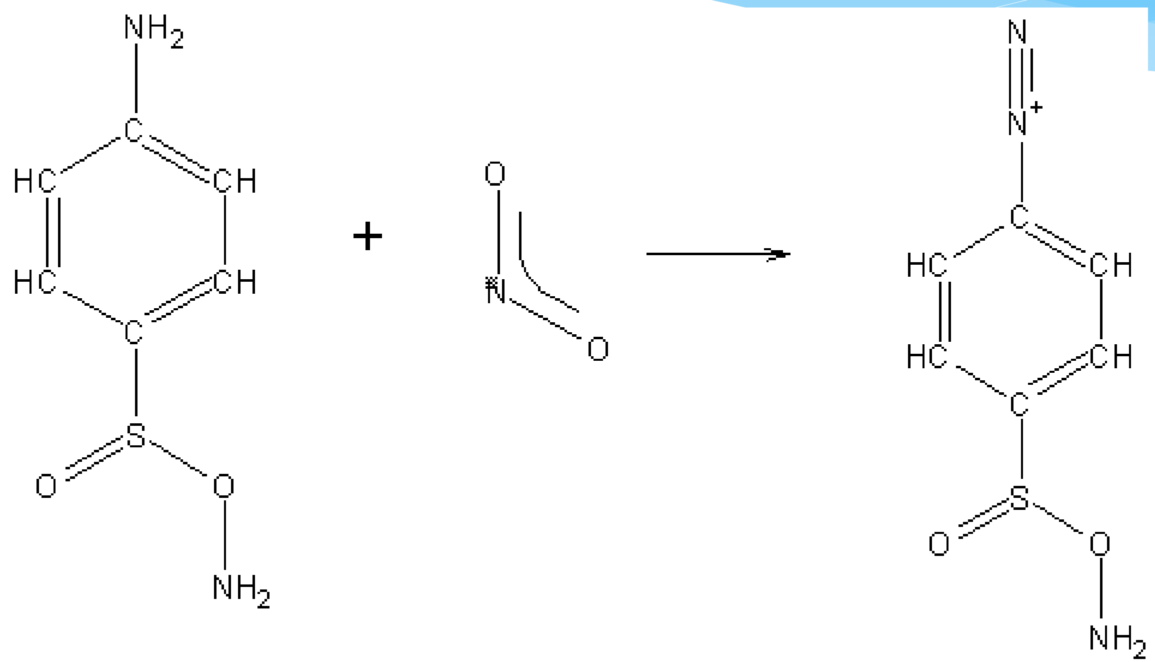
K_2SO_4 to increase boiling water to 360-370 °C

Nitrite-Nitrogen

- Seldom appears at concentrations > 1mg/L
- Measurement:
  - Colorometric-Diazotization method
  - Ion chromotography

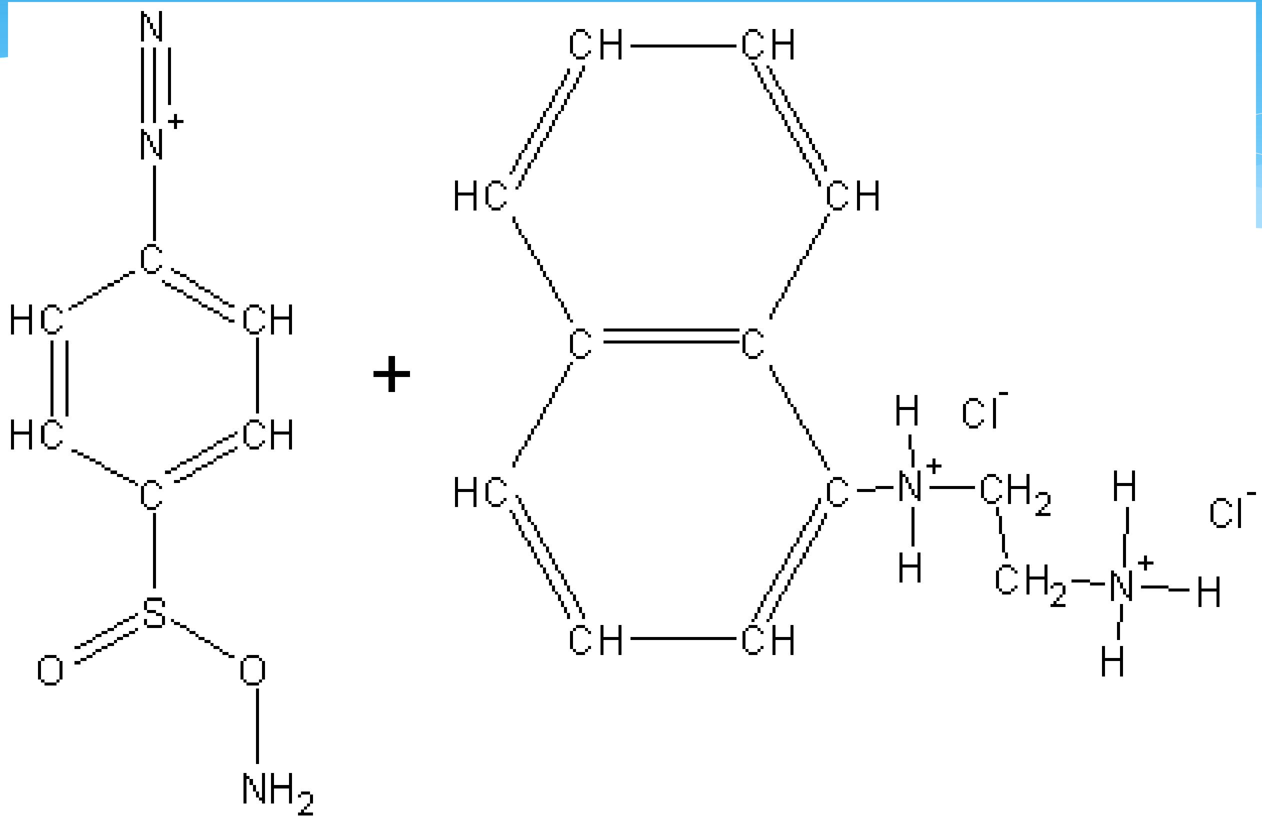
Diazotization Method

Unbalanced (there's some water and protons)



Sulfanilamide nitrite a diazonium salt

Then we add color…

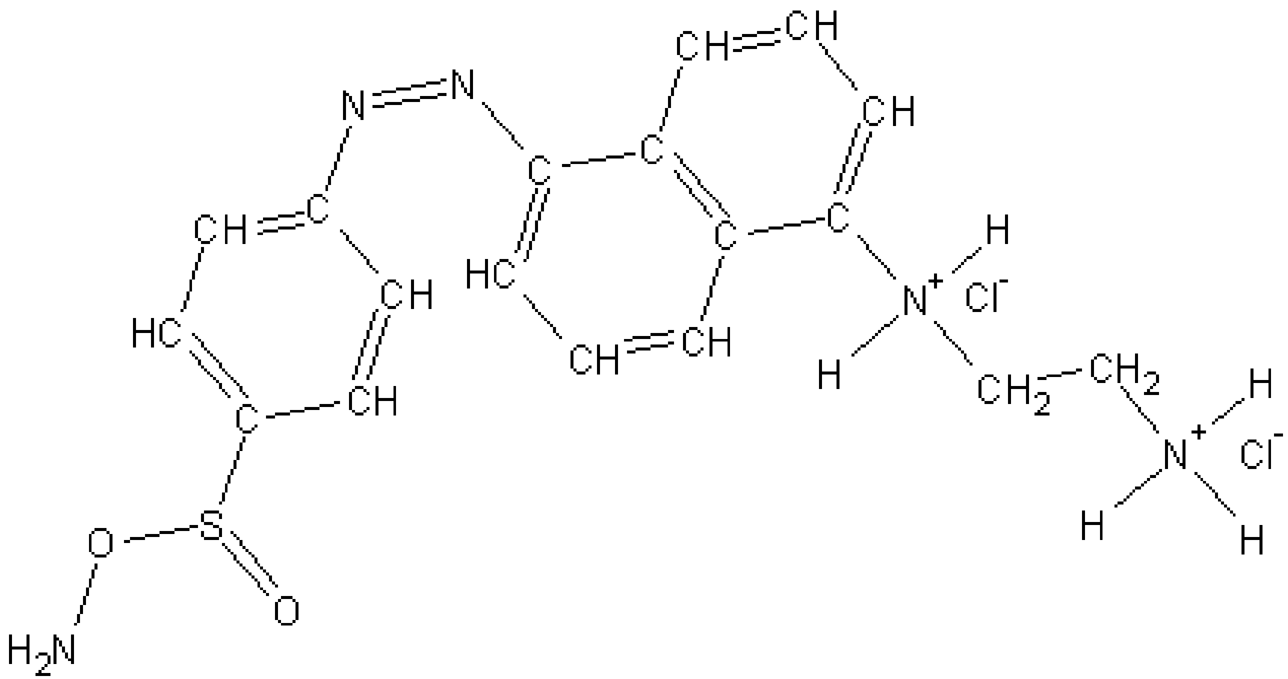


Diazonium salt

N-(1-naphthyl)-ethylenediamine dihydrochloride

The actual colored compound.

This is “pink”



Once you have color, you can do colorimetry!

Make a calibration curve.

Compare your solution to the calibration curve.

Nitrate nitrogen measurement

* Screeening with ultraviolet spectrometry
  * Nitrate ions absorb UV at 220 nm
  * Any material that absorb UV at this region interfere with results (e.g. Nitrite, hegzavallent Chromium, many different org. Matter)
* Ion chromotography
  * Expensive
* Nitrate electrode method
  * Rapid
  * Chloride and bicarbonate cause interference
  * Not sensitive at low concentrations
* Cadmium Reduction Method

Cadmium Reduction Method

- A filtered sample with added NH4Cl-EDTA solution is passed through a specially prepared column containing amalgamted Cd granules
- Nitrate is reduced to nitrite by Cd
- Nitrite is analyzed by Diazotization Method.

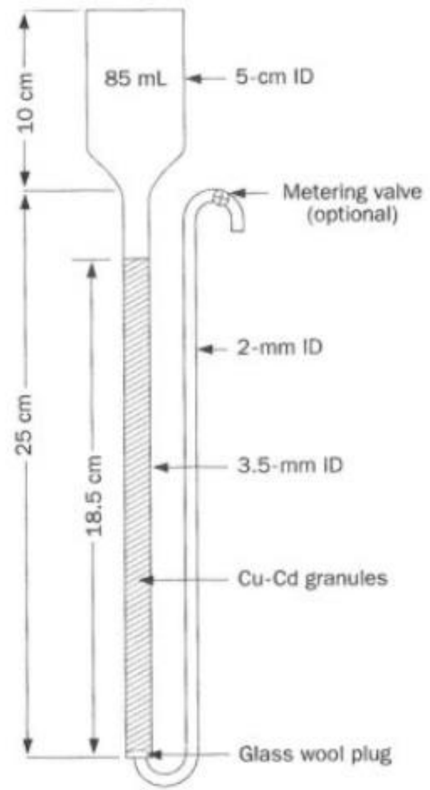


Figure 4500-NO_3^-:1. Reduction column.

Nitrogen

* Total nitrogen (TN) =Ammonia-Nitrogen + Nitirite-Nitrogen + Nitrate-Nitrogen + Organic Nitorgen
* Total Kjeldahl Nitrogen (TKN)=OrganicNitrogen + Ammonia-Nitrogen