SUSTAINABILITY PROFILE: Ammonia

The industrial production of ammonia (NH_3) from nitrogen (N_2) in the air and hydrogen (H_2), usually derived from natural gas (CH_4) is, practically speaking, one of the most important reactions known to humankind.

Nitrogen is a key element in living systems (along with carbon, hydrogen, and oxygen and to a less degree phosphorus and sulfur). Nitrogen is found in proteins and nucleic acids, two key molecules of life. Dry air is 78% nitrogen in the form of N_2. It is also 21% O_2, 0.9% Ar, and other trace gases—often pollutants. While the element nitrogen is abundant on earth as gaseous N_2 in the atmosphere, N_2 is not readily accessible to living systems in that form. N_2 with its triple bond is very stable. We call atmospheric $N_2(g)$ unaccessible nitrogen because it cannot be directly used by most organisms. Organisms use nitrogen in the form of nitrates (NO_3^-) and ammonia (NH_3).

In nature some atmospheric N_2 is converted to nitrogen monoxide or nitric oxide (NO) by lightning in a reaction with atmospheric O_2.

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$$

NO reacts further with oxygen to form nitrogen dioxide (NO_2) and nitric acid (HNO_3) in the atmosphere and eventually ends up as mineral nitrates (NO_3^-) in the soil and in rocks. The process of converting biologically unaccessible N_2 to these sorts of biologically more accessible nitrogen compounds is known as nitrogen fixation. Similar reactions occur in naturally occurring combustion processes such as forest and grassland fires. Anthropogenic combustion (combustion in power plants and in internal combustion engines in cars, trucks, trains, ships, and planes) also produces these compounds. These nitrogen containing oxides are known collectively as NO_x's. While this fixation process is valuable in making nitrogen accessible to organism, NO_x's are largely considered undesirable air pollutants. They are responsible for photochemical smog and are a part of the chemical pathway that produces ozone (O_3) in the lower atmosphere (the troposphere). In the troposphere O_3 is a pollutant that causes respiratory disease.

Certain bacteria and archaebacteria are able to convert atmospheric N_2 to ammonia using a molybdenum containing enzyme called nitrogenase. These bacteria are often symbiotically associated with legume plants. Other soil bacteria convert ammonia and ammonium ion to nitrites and nitrates. Some bacteria convert these compounds back into N_2. These process together with the abiotic processes described in the previous paragraph are known as the nitrogen cycle (see Figure 1). Nitrogen waste from organism as well as nitrogen containing decomposition products from dead organisms also enter this cycle. The symbiotic association of nitrogen-fixing bacteria with

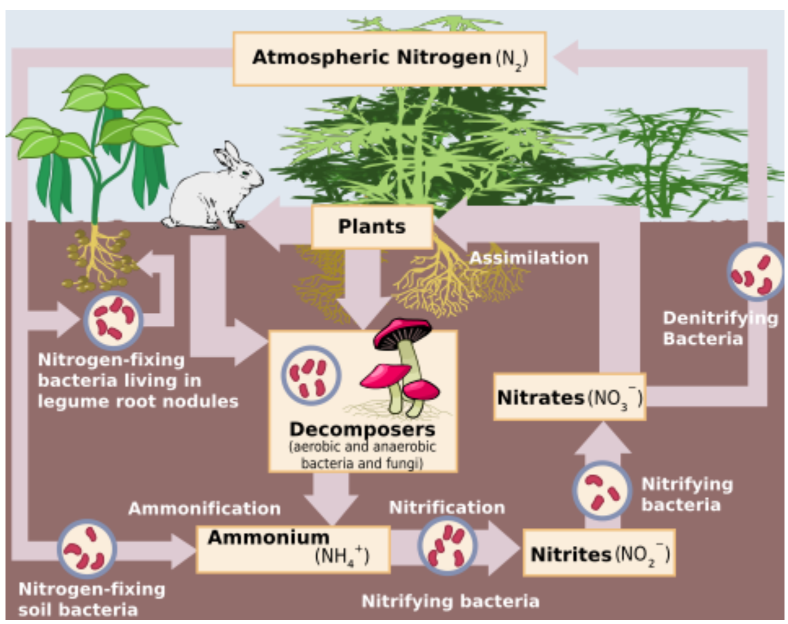

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FIGURE 1 – THE BIOTIC NITROGEN CYCLE

legumes is the basis for traditional crop rotation farming methods where the growing of legumes such as soybeans which replenish nitrogen in the soil is alternated with the growing of corn and wheat which deplete the soil of nitrogen.

Accessible nitrogen containing compounds such as nitrates and ammonia are used as fertilizers in agriculture. Applying these compounds to the soil increases the yield of crops even in the absence of crop rotation techniques. Natural sources of these compounds are mineral deposits of potassium nitrate (saltpeter) and other mineral nitrates and guano, seabird and bat excrement, which contain uric acid ($C_5H_4N_4O_3$), urea ($NH_2C(=O)NH_2$), and ammonia. Around 1900 these materials were being mined in an unsustainable way to increase the yield of food crops in such a way that scientist began to worry about whether or not global food production could sustain the world's population, then at 1.6 billion.

These nitrogen containing compounds are not only useful as fertilizers, but they are also used in manufacturing explosives. Nitrates react to form nitrogen gas with the rapid expansion of the gaseous product. The chemical equation of gunpowder combustion is:

$10KNO_3(s) + 3S(s) + 8C(s) \rightarrow 2K_2CO_3(s) + 3K_2SO_4(s) + 6CO_2(g) + 5N_2(g)$.

TNT (2,4,6-trinitrotoluene), invented in1863 is synthesized from the organic molecule toluene with nitric acid. Detonation of TNT is from the following exothermic and gas producing reactions:

$2C_7H_5N_3O_6(s) \rightarrow 3N_2(g) + 5H_2(g) + 12CO(g) + 2C$
$H_2(g) + CO(g) \rightarrow H_2O(g) + C(s)$
$2CO(g) \rightarrow CO_2(g) + C(s)$

Dynamite, invented by Alfred Nobel in 1867, is made from glycerin or glycerol (CH_2OH-$CHOH$-CH_2OH) and nitric acid. It undergoes explosive decomposition in the following reaction:

$2C_3H_5N_3O_9(l) \rightarrow 5H_2O(g) + 6CO_2(g) + 3N_2(g) + 1/2O_2(g)$

This reaction is highly exothermic ($\Delta H = -1414$ kJ/mol) and with the production of 7.25 moles of gas per mole has a high entropy.

It was the application in explosives that led to the development of the Haber-Bosch process for the synthesis of ammonia from nitrogen gas and methane. The reaction is an equilibrium reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The uncatalyzed rate is slow, but because the reaction is exothermic ($\Delta H^\circ = -91.8$ kJ/mol), increasing the temperature drives the reaction toward the reactants. Increasing the pressure drives the equilibrium toward ammonia production because of the 4:2 mole ratio of reactants to products. The reaction uses an iron-based catalyst.

Fritz Haber Public Domain

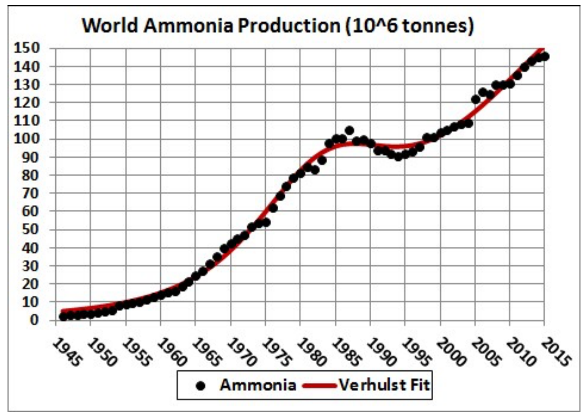
The German chemist Fritz Haber developed this reaction during World War I because the allies were blocking access by Germany to the natural sources of nitrogen compounds used in explosives. Haber is the father of chemical warfare and was involved in the development of various chemical agents used to kill people. See this 9:40 video highlighting the evils that Fritz

Haber unleashed upon the world. Carl Bosch was a German industrial chemist who with Haber enabled the large-scale production of ammonia.

While Haber may have been motivated by the war effort and the munitions application of ammonia synthesis, the industrial synthesis of ammonia was recognized to be the solution to the looming shortages of natural sources of accessible nitrogen compounds used in fertilizers. Haber was awarded the 1919 Nobel Prize in Chemistry and Bosch in 1931.

Ammonia production by the Haber-Bosch process enables half of modern food production and thought to be responsible for the Green Revolution (along with pesticides and higher yield food crop strains) that increased agricultural production around the globe and enabled the feeding of our now near 8 billion human population. Before Haber-Bosch scientists were worried about sustaining a population of less than 2 billion. Interestingly, 50% of the nitrogen in the human body was produced by the Haber-Bosch process.

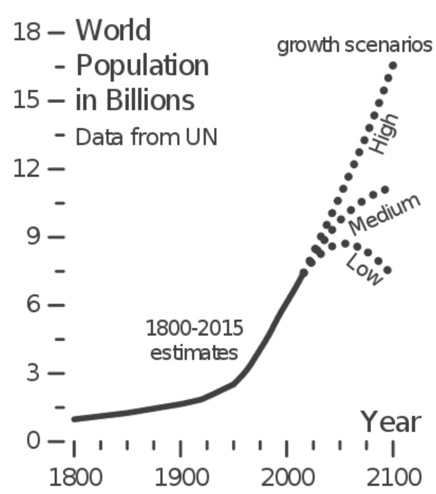
https://www.census.gov/popclock/



Global Ammonia Production Graph by L.David Roper
http://www.roperld.com/science/minerals/Ammonia.jpg

175 million tonnes of ammonia are produced each year. This puts ammonia in the top 10 industrially produced chemicals. 3-5% of the world's natural gas goes to ammonia production. This amounts to 1-2% of the world's energy supply. See this 5:18 video and this 9:49 video about the Haber process and its importance.

The benefits of the industrial production of ammonia for feeding 8 billion people is indisputable. However, there are significant other environmental problems created by the use and overuse of fertilizers. Over half of the nitrogen compounds applied as fertilizers is lost to waterways via runoff or to the atmosphere due to inherent volatility (as with ammonia) or to the action of microbes converting these compounds to volatile compounds such as N_2 or nitrous oxide (dinitrogen monoxide, N_2O). Fertilizers in waterways result in rapid growth of cyanobacteria, green algae, and diatoms and deplete the river, lake, or ocean of oxygen. These hypoxic (low oxygen) conditions result in dead zones where aquatic and marine life cannot be supported. N_2O is a greenhouse gas 300x more potent than CO_2 (emitting 1 tonne of N_2O is the equivalent of emitting 300 tonnes of CO_2). About 10 million tonnes of N_2O were emitted in 2016 (compared to 35 billion tonnes of CO_2). With a 300x greenhouse gas potency, 10 million tonnes of N_2O are equivalent to 3 billion tonnes of CO_2. This is around 6% of total greenhouse gas emissions.



World Population Estimates
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Learning Goal

Explain the Haber process for the production of ammonia and its importance in the history of explosives and food production. (15.6 + this handout + three YouTube videos)

Study Questions

1. What are the two most important applications of ammonia (NH_3) in modern society?
2. What is the difference between “fixed” (accessible) and “unfixed” (inaccessible) nitrogen? What substance(s) are “fixed” forms of nitrogen? What substance(s) are “unfixed” forms of nitrogen?
3. How is Le Chatelier’s principle involved with this reaction? What is the effect of temperature, pressure, changing concentrations, etc. on the $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ reaction
4. What fraction of accessible nitrogen found in living systems is the result of the Haber-Bosch process?
5. What are at least two negative effects of the overuse of fertilizers?