NITROGEN

Nitrogen occurs uncombined in the atmosphere making 78% by volume. Only a small fraction of the gas is removed and returned normally (nitrogen cycle). It is removed from the atmosphere by biological fixation and by oxidation to nitric oxides during lightening and returned to the atmosphere by bacterial action. In the combined state it is found as $NaNO_3$ and proteins. It is obtained commercially by fractional distillation of liquefied air.

Nitrogen is a diatomic gas where the two atoms are linked by a triple bond made up of one sigma and two pi bonds. The bond energy is 994 kJ mol. The bond is so strong that at ordinary temperatures the energy required to break the bond cannot be supplied and hence it is inert. However it reacts at high temperatures, the reactions are mostly endothermic due to the high bond energy.

1. Nitrogen and hydrogen react at 450 - 500 °C and 250-300 atm pressure in the presence of iron catalyst to give ammonia.*
2. At high temperatures it combines with oxygen to give nitric oxide.*
3. When heated with metals nitrogen forms nitrides. Burning magnesium continues to burn in nitrogen to give white magnesium nitride*

Uses of nitrogen

1. It is used in making ammonia, cyanamide and cyanides
2. To provide inert atmosphere for food storage (in packaging- to increase shelf life) and in certain industrial processes.(e.g Pb-Na alloy, nylon, vitamin A, semi-conductors.)
3. Liquid nitrogen is used as a refrigerant- for frozen food and to preserve cornea, blood, quick freezing chicken to avoid formation of large ice crystals

Laboratory preparation of ammonia

Ammonia is prepared in the laboratory by heating an ammonium salt with an alkali, the stronger base displacing the weaker base.

Manufacture - Haber's Process

Ammonia is manufactured by the reaction of nitrogen and hydrogen at high temperatures and pressures.

$$N_2 + 3H_2 \leftrightharpoons 2NH_3 \qquad {}^\wedge H = -92\ kJ$$

The reaction attains equilibrium. It is accompanied by a decrease in the number of moles of gases and hence according to Le Chatelieur's a high pressure would favour a better yield. At the same time a high pressure would increase the concentration, increasing the frequency of collision and raise the rate of reaction as well. Thus a high pressure will favour a better yield and better rate. But with very high pressures the process becomes costly as stronger plants must be built to withstand high pressures and maintenance too will be expensive. A pressure of 250 - 300 atm is used nowadays.

The reaction is exothermic According to Le Chatelieur's principle a low temperature will favour a better yield. Low temperature will increase the working life of the catalyst also (less likelihood of being poisoned). But at low temperatures the number of molecules having the energy of activation as well as the frequency of collision would be low resulting in a low rate of reaction. A compromise is reached between high yield in a long time and lower yield in a shorter time. A temperature of 500 °C is found to be optimum.

In order to increase the rate of reaction a catalyst of finely divided iron is used with K_2O and Al_2O_3 as promoters

The raw materials for the process are air and hydrocarbons. Nitrogen is obtained by the fractional distillation of liquid air and hydrogen from hydrocarbons by steam reforming. (Coal and water would replace the natural gases soon as they are being depleted.) The gases are thoroughly purified to remove any CO, sulphur compounds, water and carbon dioxide, as these would poison the catalyst.

Nitrogen and hydrogen mixed in the ratio of the stoichiometry of the reaction 1:3 by volume is compressed to 250- 300 atm. and passed into a heat exchanger to heat up the reacting gases. The gases are then passed into a catalyst chamber maintained at 450 - 500 °C. The catalyst needs to be heated only at the beginning. Then the heat of the reaction will maintain the temperature. The hot gases leaving the converter then pass through the heat exchanger. The gaseous products are then cooled and ammonia liquefied out. The reacted gases are then recycled.

In this method it is not necessary to wait until equilibrium is reached as the unreacted gases can be

42

Properties of ammonia

Ammonia is colourless gas with a characteristic pungent odour. It is trigonal pyramidal in shape with an appreciable dipole moment. It has appreciable hydrogen bonding and hence can be easily liquefied by compression. Ammonia dissolves in water readily and the aqueous solution is commonly referred to as ammonium hydroxide although NH_4OH molecules are not present. In the solution ammonia is hydrogen bonded to water and from the hydrate few OH^- ions are formed. Thus aqueous ammonia is weak base. However it precipitates all the insoluble metallic hydroxides from the aqueous solution of their salts.

Industrial importance of ammonia and compounds derived from ammonia.

Ammonia forms the basis of nitrogen industry, which covers a wide range of substances ranging from fertilizers, explosives, plastics and synthetic fibres,

to manufacture nitric acid
to manufacture fertilizers like ammonium nitrate, ammonium sulphate ammonium dihydrogen phosphate and urea. aqueous ammonia as a fertilizer for acidic soil..
in the manufacture of nylon and rayon
to produce a reducing atmosphere in metallurgy. (ammonia is heated to give inert nitrogen and reducing atmosphere of hydrogen
aqueous ammonia as a grease remover for window cleaning
to manufacture ammonium chloride (used in dry cells and as flux during soldering) and ammonium carbamate (main constituent of smelling salt).

Uses of nitric acid

In the production of fertilizers: ammonium nitrate, potassium nitrte.
to manufacture explosives: guncotton, TNT, nitroglycerine, ammonium nitrate, picric acid
in the manufacture of Terylene and nylon
to manufacture nitrates: barium and strontium nitrate for fireworks and flares, silver nitrate for photography.

The environmental consequences of nitrate fertilizers.

All fertilizers have to be soluble in water to be absorbed by plants. The nitrogen fertilizers especially nitrates are highly soluble in water and are easily leached by it. The rapid leaching necessitates repeated application leading to high concentration of nitrates in waterways, which leads to rapid growth of aquatic plants especially the algae. The algae soon blankets the surface of the water cutting off sunlight from reaching the submerged aquatic plants, resulting in reduced photosynthesis and lowering of oxygen concentration which ultimately leads to their death. The decomposition of the dead organisms causes further lowering of oxygen concentration resulting in the death of almost all the aquatic fauna except those that can survive in very low oxygen concentration.

The environmental impact of nitrogen oxides

Whenever there is high temperature atmospheric nitrogen and oxygen combine to form nitric oxide. At low temperatures nitric oxide then combines with the atmospheric oxygen to form nitrogen dioxide. The NO and NO_2 are referred to as nitrogen oxides, NO_x and considered together. At much lower temperatures the nitrogen dioxide dimerises to give dinitrogen tetroxide.*

High temperature prevailing during lightening is able to supply the high energy of activation required for the endothermic reaction. The main artificial sources of nitrogen oxides are motor vehicles (40%) coal and oil-fired power stations (30%) and industrial burning of fossil fuels (20%).

During the burning of fuels in internal combustion engines due to the high temperature (around 2000K) prevailing, the endothermic oxidation of nitrogen from the air occurs. The nitric oxide formed undergoes further aerial oxidation to form nitrogen dioxide. The NO_2 dissolves in water to form nitrous and nitric acids. The nitrous acid is further oxidised too nitric acid later by air. These acids cause acidity in the atmosphere. In addition to their contribution to acid rain they cause respiratory problems, interfere with nitrogen cycle and play a part in the formation of photochemical smog. Thus the nitrogen oxides are serious pollutants

Moreover the oxides of nitrogen NO and NO_2 catalyse the oxidation of sulphur dioxide to sulphur trioxide

SULPHUR

Sulphur is a yellow solid, melting point 119°C and boiling point 444°C. It is found as S_8 molecules, which form a puckered ring. Sulphur burns in air with a blue flame forming the sulphur dioxide and little of sulphur trioxide.

Sulphur dioxide

Sulphur dioxide may be prepared in the laboratory by reacting a sulphite with any strong dilute acid.*
It is formed when sulphur and compounds of sulphur burn in air
The molecule is angular in shape with strong dipole - dipole attraction and hence can be liquefied easily by compression. The gas dissolves in water readily to form sulphurous acid and sets up equilibrium (aq)

$$SO_2(g) + H_2O \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3(aq) \rightleftharpoons SO_3^{2-}(aq) + 2H^+(aq)$$

Sulphur dioxide is a poisonous gas and has a suffocating odour. In small amounts it is used to preserve food. It preserves food by killing the microorganisms and also by preventing oxidation of the foodstuff. i.e as a germicide and as an anti -oxidant.

Harmful effects of sulphur dioxide

Sulphur dioxide enters the atmosphere mainly during the combustion of sulphur contaminated carbonaceous fuel, especially coal. The fractions of crude oil though refined still contains some sulphur and when these fractions are burnt sulphur dioxide is released Sulphur dioxide is also released when sulphides ores are smelted.

1 Sulphur dioxide is the main cause of acid rain. The gas has a corrosive effect on many building materials, metals and paper
2 It is also found to be responsible for the formation of the smog.
3 Sulphur dioxide causes irritation to the eyes and the respiratory tract and aggravates respiratory diseases like asthma, emphysema and chronic bronchitis. It also stimulates contraction of the airways, making it difficult to breathe.
4 Destroys the leaf tissue in plants by inhibiting the enzymes responsible for photosynthesis

Sulphur dioxide dissolves in water to give sulphurous acid, which later gets oxidised to sulphuric acid. These acids are the main cause of acid rain. The NO_x from the exhaust fumes of motor vehicles catalyse the oxidation of sulphur dioxide to sulphur trioxide contributing further to the acidity of the rain

- Acid rain lowers the pH of water in the lakes and streams killing aquatic plants and animals, damages the forest cover, makes a number of poisonous metallic ions soluble from rocks and soil, destroys stonework in building and accelerates of corrosion of metalwork.

Manufacture of sulphuric acid. Contact Process

The raw materials are sulphur (sulphide ores) air and water. Sulphur dioxide is first obtained by burning sulphur (or roasting sulphide ores) in dry air. The gas is mixed with excess air and thoroughly purified to remove dust particles and any traces of arsenic, as they would poison the catalyst. It is then dried by passing over concentrated sulphuric acid. The gaseous mixture is passed through heat exchanger to raise its temperature and then over beds of vanadium (V) oxide preheated to 450-500°C at atmospheric pressure.* The passage through catalyst chamber and heat exchanger is repeated to lower the temperature and ensure better yield. The sulphur trioxide from the heat exchanger is finally passed into an absorption tower, where concentrated sulphuric acid is sprayed. The sulphur trioxide dissolves forming oleum,* which is cooled and diluted with appropriate amount of water to obtain sulphuric acid.*

- The gas is not absorbed in water, as the reaction is highly exothermic producing an `acid mist'
- Though platinum is a more efficient catalyst it is more expensive and also easily poisoned
- The burning of sulphur is so exothermic that the energy released (298kJ mol^{-1} is more than sufficient to supply the energy requirement of the entire process. The rest is marketed
- Concentrated sulphuric acid containing 98% by mass of the acid has a density of 1.84 g cm^{-3} and boils at 338°C

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \text{^} H = -197 \text{ kJ}$$

The conversion of sulphur dioxide to sulphur trioxide attains equilibrium. It is accompanied by a decrease in the number of moles of gases and hence according to Le Chatelieur's a high pressure would favour a better

The reaction is exothermic According to Le Chatelieur's principle a low temperature will favour a better yield. Low temperature will increase the working life of the catalyst (less likelihood of being poisoned) as well as the plant (lower rate of corrosion rate will be high). But at low temperatures the reaction rate would be too low. Hence a compromise of 450- 500°C is used. A good rate is ensured by using a catalyst of vanadium pentoxide

Uses of sulphuric acid.

manufacture of fertilizers: ammonium sulphate, super- phosphate , triple phosphate, potassium sulphate
manufacture of non soapy detergents., paper, rayon and other polymers; pickling of metals
as electrolyte in lead accumulators; Refining of petroleum; Manufacture of drugs and paints and pigments