

Natubhai V. Patel College of Pure & Applied Sciences

S. Y. B.Sc. (Industrial chemistry)

C-214: Chemical Process Industries

UNIT 1

SYLLABUS

Nitrogenous products – Manufacture and study of properties of synthetic nitrogen products and miscellaneous inorganic chemicals such as ammonia, hydrazine, iodine, fluorine, fluorocarbon and various types of nitrogenous fertilizers such as urea, ammonium sulphate, ammonium nitrate, calcium ammonium nitrate.

NITROGEN INDUSTRIES

1.0 INTRODUCTION

Nitrogen plays extremely important role in nature and human life without which a living cell cannot exist. Chilean saltpetre (NaNO_3) and nitrogen from air are significant source of fixed nitrogen. Nitrogen is one of the major ingredients for production of fertilizer. Soil takes up nitrogen in the form of ammonium or nitrate ions and forms amino acids with carbon compounds through the complex chemical system of plants. The amino acids are then converted into proteins and enzyme. The main sources of nitrogen are

- Fertilizers
- Organic nitrogen compounds formed in soil by recurring natural process
- Atmosphere

1.1 AMMONIA

It is of the most important nitrogenous material. It is a base from which all the nitrogen containing compounds are derived. Mostly is produced synthetically, but during some chemical processes obtained as by product.

1.1.1 Raw material

Basis: 1 tonne of NH_3

H_2 = 210 kg

Power = 850KWH

N_2 = 960 kg

Fuel gas for compressors = 3800K.cal

Catalyst = 0.2Kg

Cooling water = 12,500kg

1.1.2 Catalyst

Commercial synthesis of ammonia requires an **efficient catalyst**. Most widely used catalyst is **iron with added promoters** e.g. oxides of aluminium, zirconium or silicon at about 3% concentration and potassium oxide at about 1%. These prevent sintering and make the catalyst more porous. Iron catalysts lose their activity rapidly, if heated above 520°C . Also, is deactivated by contact with copper, phosphorous, arsenic sulphur and Carbon monoxide

1.1.3 Reaction



1.1.4 Manufacture

(a) Haber and Bosch Process

The manufacture of ammonia is carried out by passing a mixture of pure **Hydrogen** and **nitrogen** in the proportion of **3:1** by volume under pressure over a catalyst heated to an optimum temperature. The method was first developed by Haber and Bosch therefore known as Haber and Bosch Process.

Manufacturing consists essentially of six phases

1. Manufacture of reactant gases

2. Purification
3. Compression
4. Catalytic reaction
5. Recovery of ammonia formed and
6. Recirculation

Cost is greatly influenced by the pressure, temperature, catalyst, raw-materials purity and most importantly heat recovery and reuse. For achieving quality material at lower cost modification in Haber and Bosch Process are initiated.

(b) Modern method/ Killogg ammonia process

The flow diagram of modern method of ammonia manufacture is shown in figure

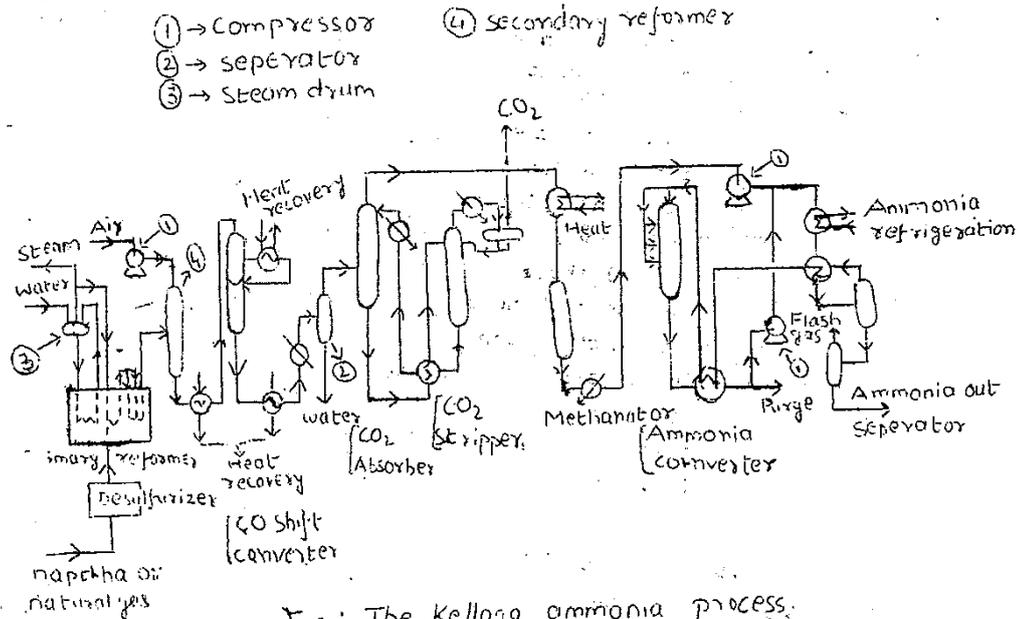


Fig. The Kellogg ammonia process.

In the process **natural gas** is used for production of nitrogen and hydrogen. The purified nitrogen and hydrogen is thus reacted to give ammonia gas. In commercial production sulphur free natural gas is mixed with steam in the volume based ratio of **3.7:1** and compressed to **40atm**. The mixture is preheated with the recycled flue or effluent gases and fed into the furnace. At **800-850°C** in the presence of **iron catalyst** promoted with other metal oxides conversion of methane takes place with the formation of CO. The residual gas is mixed with air and fed into shaft converter to get complete conversion. The waste heat is utilized for the steam generation and generation of ethanolamine which are used in CO₂ and H₂S removal. The exit gas containing poison was regenerated in the methanator at 280-350°C which ultimately used for heating the feed water.

Purified N₂ and H₂ mixture was compressed to **300atm at 320 to 380°C** in the presence of catalyst converted to NH₃. 14-20% conversion per pass was achieved. NH₃ condensed and separated from exit gas, whereas unconverted N₂ and H₂ gases were recycled along with the fresh gases.

Ammonia synthesis is being exothermic the process requires an effective temperature control system at every stage of reaction.

(c) Latest method

The manufacture of ammonia may be carried out by the **partial oxidation** of hydrocarbon (derived from naphtha, natural gas or coal) by oxygen enriched air in the presence of catalyst. CO is removed by passing through ammonical solution of cuprous formate. The remaining N₂ and H₂ gas are utilized for the manufacture of ammonia by Haber process.

1.1.5 Uses

- Ammonia is major raw material for fertilizer industries.
- It is used during the manufacture of
 1. Nitro compounds

to maximize the use of energy by "stripping" the product liquor by contacting it with incoming carbon dioxide and by using some of the heat of formation of carbamate to bring about the endothermic decomposition and the rest to generate process steam. Figure shows a flowchart for the process.

Liquid ammonia, gaseous carbon dioxide and recycle materials meet in a **heat exchanger-reactor** at a pressure of **14 MPa at 170 to 190°C** to form carbamate, with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mixture of unreacted reactants and carbamate flows to the decomposer. The stoichiometric ratio of CO₂/NH₃ conversion to urea is essentially about 55%, but by using an excess of CO₂ (or NH₃) the equilibrium can be driven as high as 85%. The reactor must be heated to force the reaction to proceed. The flowchart shows a decomposer followed by a stripper in which CO₂ is introduced; these are at substantially identical pressures, requiring no gas recompression only a small liquid recycle pump. For all the unreacted gases and un-decomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400kPa). The reagents are reacted and pumped back into the system. Evaporation and prilling or granulating produces the final product. Overall, over 99% of both CO₂ and NH₃ are converted to urea, making environmental problems minimal. Carbamate is highly corrosive to both ordinary and stainless steel, but with oxygen present, 300 series stainless steel resist it very well, so some air is introduced along with CO₂ reagent to reduce system corrosion.

1.2.4 Properties

Nitrogen percent	46%
Solubility, g/100ml water at 25°C	119
Melting point	132.7°C
Particle size	95% - 8 mesh , 16 mesh
Hygroscopic point, %	72
Sp. Gravity @20.4°C	1.335
Bulk density, lb/ft ³	42-45

1.2.5 Uses

- As a fertilizer
- As a protein food supplements for ruminant
- As an ingredient in the manufacture of resins, plastics, adhesive, coatings
- Textiles anti-shrink agents and ion exchange resins
- In melamine production
- It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid and phthalocyanines.

1.3 AMMONIUM NITRATE

Ammonium nitrate is important nitrogenous fertilizer. Ammonium nitrate plants are found in most of the fertilizer producing countries.

1.3.1 Raw material

- Ammonia
- Nitric acid

Both of these are usually produced at the same installation. Particularly all nitric acid is made by oxidizing ammonia and absorbing the resulting nitrogen oxides in water.

1.3.2 Manufacture

There are three important methods of producing of ammonium nitrate

- Crystallization
- Flaking
- Prilling

The latest and most important method is prilling. Modern ammonium nitrate prilling plant consists of the following operations.

➤ **Neutralization**

Heated ammonia vapour and 60-80% nitric acid (prepared by oxidation of ammonia) are introduced at the base of a neutraliser tower operating under a pressure of 3-5 atmosphere and through which neutralized solution is recycled. The neutralization reaction is exothermic



➤ **Evaporation**

Solution obtained from the neutralizer contains about 83% NH_4NO_3 . This solution is allowed to pass through heater supplied with steam from the neutralizer. Means are provided to recover ammonia flashed off the neutralizer with the steam. The heated solution from the heater is then passed to a vacuum evaporator when its concentration increased to about 95%, 83% solution is drawn off at this point and used in making solution.

➤ **Prilling**

The concentrated solution is now sprayed into prilling tower. The falling solution in the tower is cooled by an ascending current of air; the prilling towers are quite high, up to 185 ft. The solution is sprayed through spray nozzles in such a manner that the liquid breaks up into drop of uniform and adequate size. The prills solidify sufficiently as they reach the bottom of tower. They must be handled carefully until they are dried.

➤ **Drying and Finishing**

It is very difficult to dry the prills of ammonium nitrate, because it is deliquescent in nature. The drying temperature must be low to avoid melting.

Various, methods of drying are available. In one method, the material is cooled to below 90°F and the remaining moisture is removed in a second dryer.

In other method known as short tower prilling, ammonium nitrate solution concentrated to about 99.5% rather than the usual 95% is prilled in the usual way in a short tower, making use of the fact that strong solution solidifies faster. The last trace of water may be removed by the process of evaporation than removing it in dryers. However, the quality of ammonium nitrate obtained by this method is not as good as it should be.

➤ **Handling**

The latest practice is to store in bulk in buildings equipped with dehumidification equipments.

➤ **Explosive nature**

A major drawback of ammonium nitrate is its explosive nature. It is very sensitive to heat and shock. The risk of explosion may therefore be avoided by mixing it with chalk. A mixture of NH_4NO_3 and CaCO_3 called nitro-chalk contains 16% nitrogen and does not explode. Ammonium nitrate can therefore be used safely by avoiding contact with oxidisable material keeping fire and open flames away and prompt disposal of bags.

1.3.3 Properties

The most important properties of ammonium nitrate (which are of great value in the fertilizer field) are given in the following table:

Percent of nitrogen	35%		
Solubility, g/100gm water			
0°C	118		
100°C	843		
Melting point	170.4°C		
Particle size	95% - 6 mesh, 16 mesh		
Hygroscopic point	59.4		
Specific gravity, 20.4°C	1.725		
Crystal state	State	Temp. °C	System
	1	170 to 125	Cubic
	2	155 to 84	Tetragonal
	3	84 to 32	Rhombic
	4	32 to - 18	Rhombic
	5	Below - 18	Tetragonal

1.3.4 Uses

- Over 80% of the world wide ammonium nitrate production goes into fertilizers
- Minor amounts to other uses, mainly to industrial explosive.

1.4 AMMONIUM SULPHATE

Ammonium sulphate containing **21% nitrogen** is another important nitrogenous fertilizer. It can be obtained **as a by-product** or may be **manufactured synthetically**. Ammonium sulphate is obtained as a by-product; in the steel industry in which ammonia (another by-product)-from coke ovens is absorbed in sulphuric acid.

Ammonium sulphate is also manufactured by reacting synthetic ammonia with sulphuric acid.

Waste streams from various chemical and metallurgical industries are other sources of ammonium sulphate e.g. ammonia leaching of ores, production of pigments and synthetic fibres, manufacture of caprolactam etc produce by product; solutions containing ammonium sulphate.

Flue gases are another source of the ammonium sulphate. The metallurgical smelters and coal burning power plants liberate large quantities of SO₂ that pollute the atmosphere. The sulphur dioxide is collected and converted into sulphuric acid, Ammonium sulphate is then produced by passing ammonia gas through 60% sulphuric acid placed in lead lined vats at about 60°C the crystals of ammonium sulphate separate out on cooling.



1.4.1 Manufacture

From by-product

Manufacture of by-product ammonium sulphate may be carried out by passing cleaned **coke oven gases** into an **absorption column**, counter current to a re-circulating stream of saturated solution of ammonium sulphate. A **96-98% sulphuric acid** is now introduced into the stream at another point. The **neutralisation** takes place and the effluent solution containing ammonium sulphate is passed to a **crystalliser**, where crystals of ammonium sulphate separate out on cooling. The crystals are separated either by filtering or by centrifuging and then dried. The mother liquor overflowing from the crystalliser is acidified and recycled to the absorber.

In an **old saturation process** ammonium sulphate is produced by passing coke oven gas and sulphuric acid into a vat containing a saturated solution of ammonium sulphate and then setting out the crystal.

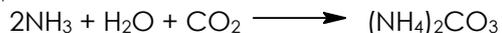
Synthetic Manufacture: Ammonium sulphate **made with manufactured ammonia** is called **synthetic ammonium sulphate**. Both **saturator's and crystallizers** are also employed in the synthetic manufacture of ammonium sulphate. The heat of reaction of anhydrous ammonia and concentrated sulphuric acid obtained by contact process is very high. Hence water evaporated from the crystallizer must be returned either by means of a condenser or by addition of water.

Sulphuric acid may also be obtained as a by-product from alcohol manufacture, nitrating process, alkylation in petroleum refining and benzene production. The acid obtained by such processes is called spent acid and contains a large number of impurities.

Ammonium sulphate is dried throughoutly to prevent caking. Free sulphuric acid is removed either by washing on a centrifuge or filter or by neutralising with weak ammonia solution.

Ammonium sulphate from gypsum or anhydrite (CaSO₄.2H₂O)

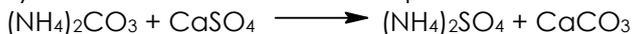
A new method which is used at Sindri in India consists of passing a concentrated **aqueous solution of ammonia** down a **tower packed with aluminium rings** against a current of CO₂, so as to form ammonium carbonate.



Ammonia is manufactured by Haber process and CO₂ is manufactured by heating limestone.



Now proper proportion of finely ground **gypsum or anhydrite** is fed into the aqueous solution of **ammonium carbonate** in large tanks, whereby calcium carbonate is precipitated gradually as a result of double decomposition.



CO₂ and NH₃ are passed until all the gypsum is converted into CaCO₃. The resulting CaCO₃ is separated by filtration and the ammonium sulphate solution is evaporated and crystallised in vacuum. CaCO₃ is used as a raw material for the manufacture of cement.

1.4.2 Action of (NH₄)₂ as fertilizer

It reacts with lime present in the soil to form ammonium hydroxide which is oxidised by air with the help of nitrosifying bacteria into nitrous acid. The latter is then converted into nitrites. The nitrous acid and nitrites also undergo oxidation by means of air in presence of nitrosifying bacteria and form nitric acid and nitrate.

1.4.3 Properties

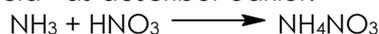
Properties of fertilizer grade ammonium sulphate are given in the following table.

Percent of nitrogen	20-21%
Solubility, g/100gm water	
32F	70.6
912F	103.8
Melting point	513°C
Specific gravity, 20.4°C	1.769
Bulk density	50
Particle size	28% + 16 mesh

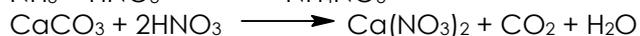
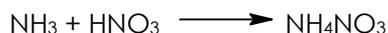
1.5 CALCIUM AMMONIUM NITRATE

Calcium nitrate contains 15.5 percent nitrogen and its manufacturing process involves reaction of lump **limestone** with **concentrated nitric acid**, addition of **ammonia to neutralise excess of acid**, evaporation of the resulting solution, and prilling or flaking the melt. The resulting product is a double salt, 5Ca(NO₃)₂NH₄NO₃ called calcium ammonium nitrate and is more useful than the single salt calcium nitrate.

Calcium ammonium nitrate contains **19% nitrogen** and is manufactured in India particularly at Nangal. Ammonium nitrate is first prepared by the reaction of ammonia and nitric acid as described earlier.



Ammonium nitrate so obtained contains some unreacted nitric acid which is neutralised by adding calcium carbonate (obtained as a by-product, in the manufacturing of ammonium sulphate) on cooling grains of calcium ammonium nitrate separate out.

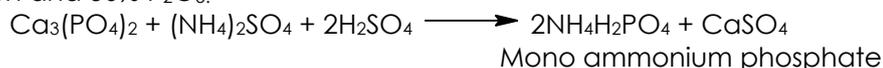


The granules of calcium ammonium nitrate are finally coated with thin layer of soap stone powder, which acts as a protective coating and prevents the absorption of moisture during storage and transportation. CO₂ is obtained as a by-product.

1.6 AMMONIUM PHOSPHATE

1.6.1 Mono Ammonium Phosphate

Mono ammonium phosphate is prepared today by the action of **sulphuric acid** on **mixtures of calcium phosphate and ammonium sulphate**. As a result, mono ammonium phosphate is formed, along with slurry of CaSO₄. The phosphate is separated from the slurry and crystallised to get fine crystals of mono ammonium phosphate containing about 12% nitrogen and 50% P₂O₅.



1.6.2 Diammonium Phosphate

It is prepared by a **continuous process** in which **anhydrous ammonia gas** and almost **pure phosphoric acid** are passed into saturated mother liquor containing mono ammonium phosphate. The temperature is kept at about **60-70°C** and pH at about 6.0. The heat of reaction vaporises water from the liquor and crystal of pure diammonium phosphate are formed. These are centrifuge washed and dried.

Mono ammonium phosphate is used in quick dissolving fertilizer and as a fire retarding agent for wood, paper and cloth.

1.7 HYDROGEN CYANIDE

It is a relatively new commercial chemical, its importance increases due to the rapid growth of methyl methacrylate, acrylonitrile and other chemicals.

1.7.1 Manufacture

Hydrogen cyanide can be manufacture in several ways; one of the **earliest methods** involves the **action of sulphuric acid on sodium cyanide**. Process which is convenient for small quantities. Sodium cyanide may also be produced by reaction **sodium carbonate** with **carbon and nitrogen** or by **reacting soda lime with charcoal** or by passing **ammonia and carbon monoxide** through **molten sodium** to form a mixture of sodium cyanide and carbon dioxide.

Hydrogen cyanide may be obtained from hydrogen, nitrogen and carbon by passing the two gases through an electric arc formed by two carbon electrodes. The conversion is low even at **2,000°C** hence the reaction is not of commercial importance.

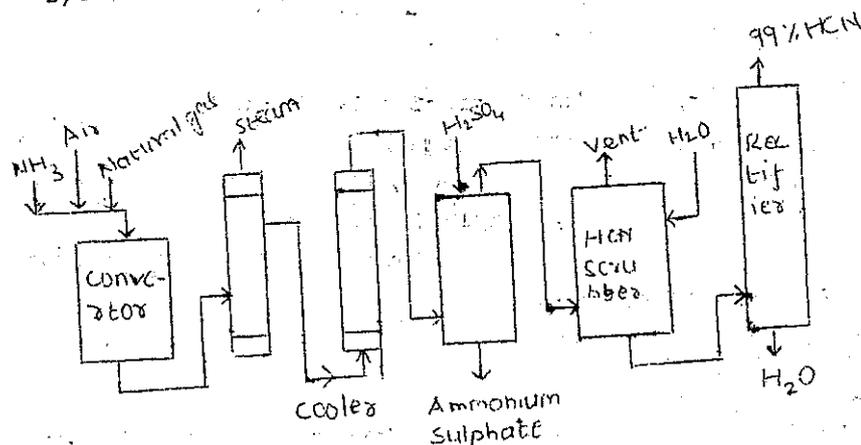
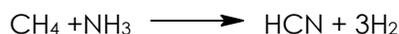
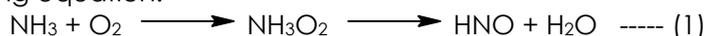


Figure: Hydrogen cyanide Synthesis

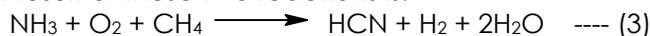
Formamide has been dehydrated to produce hydrogen cyanide and water. Today, however, **most hydrogen cyanide** is produced by the **action of ammonia with methane and air**, since the reaction will proceed, only if sufficient heat is supplied, the air is used to burn the methane and produce the heat required. The reaction of methane with ammonia is as follow.



The formation of hydrogen cyanide requires the **addition of heat** (-60 kcal/mol). The reaction of methane, air and ammonia is believed to proceed in accordance with the following equation.



The net result of these two reactions is:



Equation (2) evolves 66 k.cal/mole, the other reaction is also exothermic and the heat effect is 144 k. Cal. liberated per mole of hydrogen cyanide produced.

Reaction (2) & (3) occurs at very high rates below **850°C**. Temperature above **1100°C** are necessary to **promote** reaction (1) at a significant rate. The feed composition for the converter which is selected to meet the demand of equation (3) is as follow:



Some **side reactions** occur and produce carbon monoxide and hydrogen which are in turn partially consumed by oxygen to give carbon dioxide and water.

1.7.2 Properties

- Hydrogen cyanide is toxic gas
- It has a melting point of -140°C
- It can be liquefied to colourless liquid by cooling to 26°C .
- It is soluble in cold water, alcohol and ether.
- It forms explosive mixture with air.

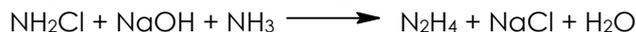
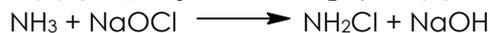
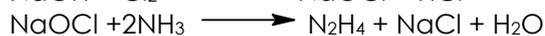
1.7.3 Uses

Hydrogen cyanide is used principally in the manufacture of methyl methacrylate, acrylonitrile, sodium cyanide, adiponitrile, chalcates, acrylic acid, ferrocyanide pigments and in the production of tertiary alkyl amines. These materials are obtained by adding HCN to tertiary olefins by hydrolysis of the formids produced.

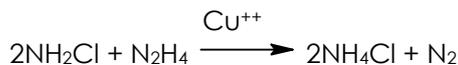
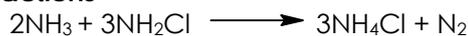
1.8 HYDRAZINE

1.8.1 Manufacture

Hydrazine (N_2H_4) becoming more important as an industrial chemical. Its manufacture involves the following reaction.



Side reactions



Glue and gelating are used to prevent these side reaction.

The process carried out in the **liquid phase** is outlined in figure. **Sodium hydroxide** and **chlorine** are mixed in **cooler reactor system** to produce sodium hypochlorite.

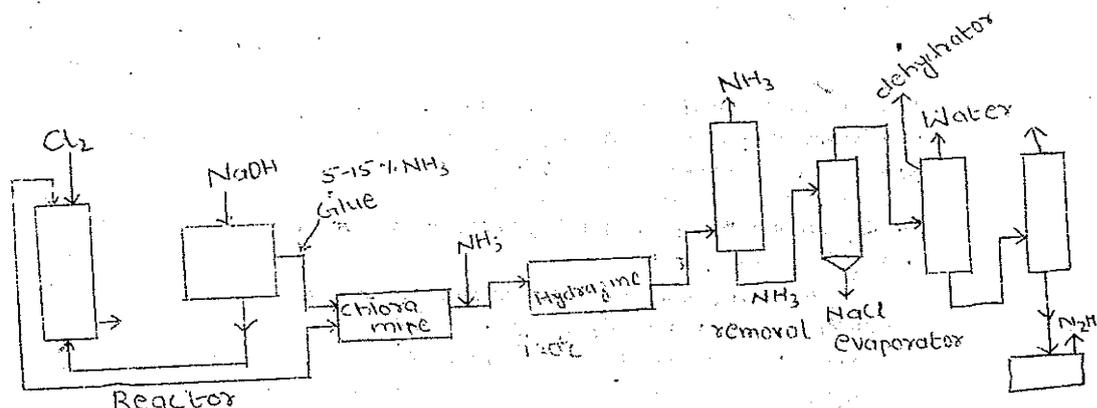


Figure: Hydrazine manufacture

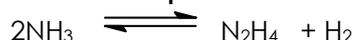
Glue is added to this solution as an **inhibitor** until the mixture is viscous; a dilute solution of ammonia (5 to 15%) is added until a mole ratio of 3 ammonia to 1 hypochlorite is obtained. The mixture forms chloramine, which when reacted with anhydrous ammonia is a ratio of 20-30 to 1 produce hydrazine. The temperature reaches 130°C . The effluent from the hydrazine reactor is fed to ammonia removal still where excess ammonia is taken off overhead. The tails are fed to an evaporator where concentrated sodium chloride is removed. The vapours from the evaporator are dehydrated in three columns in the first column the hydrazine is dehydrated until the water hydrazine mixture approaches the hydrated $\text{NH}_2\text{NH}_3\text{OH}$ in the second column, aniline is used as a dehydrating agent, the water being removed, over

head with aniline. A third column is required to remove, the aniline from the hydrazine. 98% hydrazine is produced. An overall **yield** of about **70%** is obtained.

Synthesis efficiency was increased by operating with dilute system but operating cost increase because of the low concentrations. In some cases anhydrous hydrazine is obtained by dehydrating with 50% caustic. Pressure less than atmospheric are used to reduce its composition however this may permit air linkage and result decomposition of the hydrazine to nitric oxide, water and ammonia.

1.8.2 Other processes

- It is produced by **nitration of urea** giving nitrourea, which in turn can be hydrogenated to the semicarbazide. When this is reacted with ammonia one mole of hydrazine is obtained along with one mole of urea.
- In **another process**, hydrazine is obtained by reacting urea with a carbonyl forming metal such as iron or nickel at 132 to 150°C.
- **Still another process** is based on the reaction:

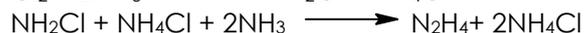
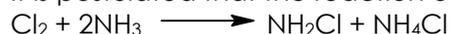


In this process ammonia is passed through an extended glow discharge highly turbulent flow and effective cooling is required. Alkyl compounds are effective in increasing the yield of hydrazine.

Anhydrous hydrazine is also formed by the following reaction



It is postulated that the reaction occurs in stages.



High temperature and pressure speeds up the reaction. The larger the ratio of ammonia to chlorine, the better the yield.

1.8.3 Stabilization

Hydrazine, hydrazine hydrate or mixture of these with water are decomposed by contact with metals such as iron, It has also been shown that solutions containing 95% N_2H_4 by weight are associated with its potential acidity. The latter property is also associated with its corrosiveness organic compounds of the type $\text{R}_1\text{SO}_2\text{NHR}^2\text{OOR}^3$ (where R_1 is hydrocarbon R_2 is an aliphatic or aryl radical and R_3 is sodium, potassium or ammonium ore) are inhibitors. Substituted ammonium radicals such as aniline, organic sulfides, sodium carbonate and zinc oxide at concentration of 0.2 to 5% by wt will also inhibit decomposition.

1.8.4 Properties

- Hydrazine is a colourless liquid that boils at 113.5°C.
- It has melting point: 1.4°C
- Sp. Gravity: 1.014 at 15°C
- It forms a sparingly soluble sulphate ($\text{NH}_2\text{.NH}_2\text{.H}_2\text{SO}_4$) and the chloride.
- It is a powerful reducing agent
- Very poisonous even through the skin.

Hydrazine Hydrate ($\text{H}_2\text{NNH}_2\text{.H}_2\text{O}$)

- It is obtained by fractional distillation from water.
- The hydrate boils at 119°C and is still liquid at -40°C
- It has a specific gravity of 1.03 at 21°C.

1.8.5 Uses

Hydrazine is used as a scarangar for oxygen in boiler feed water treatment and as a high energy fuel. It is also used for making blowing agents for forming rubbers and plastics, for the production of maleic hydrazide.

1.9 IODINE

1.9.1 Historical and raw material

It was in 1811 that **Courtois**, a salt peter manufacturer of Paris, obtained a beautiful violet iodine vapour from the mother liquors left from the recrystillization of certain salts. Iodine was later found to exist almost universally in nature. It is present as iodates (0.05 to

0.15%) in the Chilean salt. It occurs in sea water from which certain sea weeds extract and concentrate it within their cells. Iodine has been made from these by weeds by the Kelp-burning process.

1.9.1 Uses

- Iodine is converted to chemical compounds such as KI, NaI etc.
- Iodine, for medicinal, photographic and pharmaceutical purposes is usually in the form of alkali iodides prepared through the agency of ferrous iodide.
- It is also employed in the manufacture of dyes and as germicides.
- Simple iodine derivative of hydrocarbon such as iodoform have an antiseptic action, organic compounds containing iodine have been used as rubber emulsifier, chemical, antioxidant and dyes and pigment.

1.10 FLUORINE AND FLUORO CHEMICAL

1.10.1 Fluorine

A pale greenish yellow gas of halogen is the most chemically active non metal element. It occurs in combined form and is second only to chlorine in abundance among the halogen. The chief fluorine containing minerals of commercial significance are fluorspar, fluorapatite and cryolite.

1.10.2 Historical

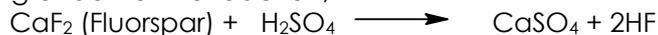
Fluorine was discovered by Scheele in 1771 but it was not until 1886 that it was isolated by H. Moissan.

1.10.3 Manufacture

Fluorine gas is generated by the electrolysis of KHF_2 under varying conditions of temperature and electrolyte.

Composition

Both aqueous and anhydrous hydrofluoric acid is prepared in heated kilns by the following endothermic reaction,



The hot gaseous hydrogen fluoride is either absorbed in water, or liquefied; refrigeration is employed to obtain the anhydrous product needed for fluorocarbon manufacture and other uses.

1.10.4 Uses

Elemental fluorine is costly and has comparatively limited usage. The element is employed in making sulphur hexafluoride (SF_6) for high voltage insulation and for uranium hexafluoride. Fluorine is used directly or combined with heavier metals (Cobalt, Silver, Cerium) and halogen (Cl & Bromide).

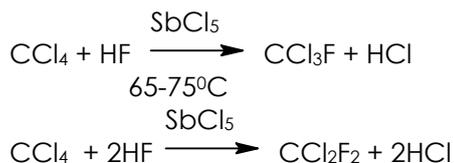
It is also employed in the preparation of inorganic fluorides, elemental fluorine and many organic fluoride and non fluorine containing compounds. Aqueous hydrogen fluoride is used in the glass, metal and petroleum industries. Three of the most unusual plastics known as are Teflon, Kel F and Fluorothene products formed by the polymerization of chlorofluoro ethylene. It is also consumed in the smelting and refining of secondary aluminium.

1.11 FLUORO CARBONS

These are compounds of carbon, Fluorine and chlorine with little or no hydrogen. Fluorocarbons containing two or more fluorine on a carbon atom are characterized by extreme chemical inertness and stability. The volatility and density are greater than those of the corresponding hydrocarbons.

1.11.1 Manufacture

Fluorocarbons are/made from **chlorinated hydrocarbons** by reacting them with **anhydrous hydrogen fluoride** using **antimony pentachloride** catalyst. The fluorocarbons, trichlorofluoromethane, dichlorodifluoromethane and chlorodifluoromethane compose 90% of fluorocarbon production.



Difluoromonochloromethane is made by substituting chloroform for the carbon tetrachloride.

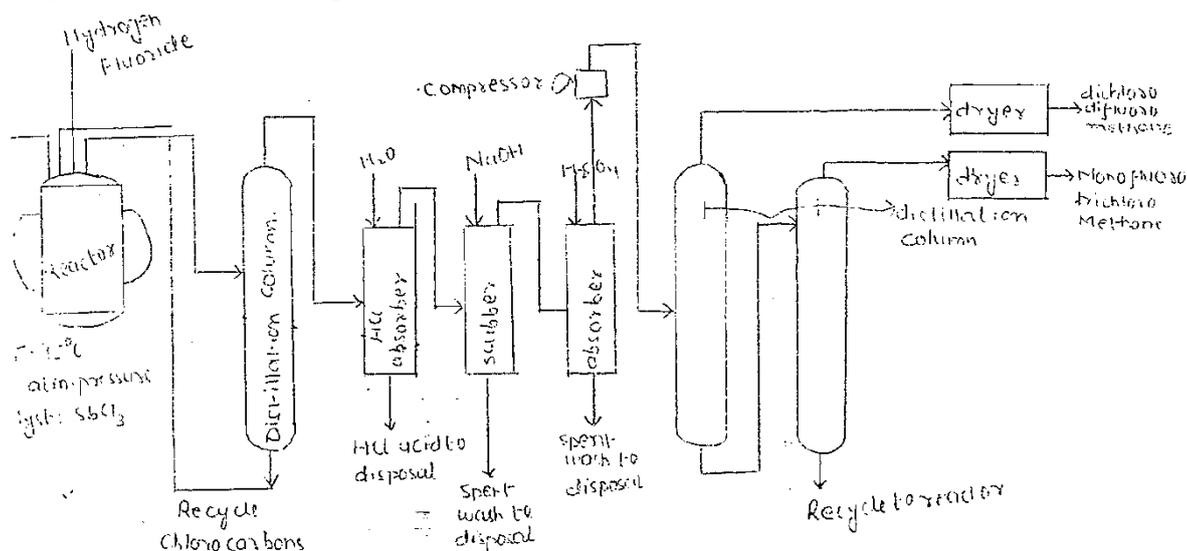
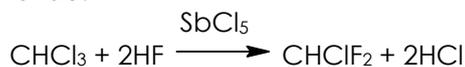


Fig: Production of FluoroCarbons (Flow Chart)

The fluorocarbon process shown in the figure may be divided into following co-ordinated sequences

- Anhydrous hydrogen fluoride and carbon tetrachloride are bubbled through molten antimony pentachloride. These reactions are slightly endothermic and take place in a steam jacketed atmospheric/pressure reactor at 65 to 95°C.
- The gaseous mixture of fluorocarbon and unreacted chlorocarbon is distilled to separate and recycle the chlorocarbon to the reaction.
- Waste hydrogen chloride is removed by absorption.
- The last traces of hydrogen chloride and chlorine are removed in caustic scrubbing tower.

1.11.2 Uses

The major use as a refrigerants (46% of the production) and remainder goes into over 100 different important applications, including plastic films, elastomers, lubricants, textile-treating agents, solvents and fire extinguisher product. It is also used as foam blowing agent, fluoro-polymers and aerosol propellants.

1.12 EXERCISE

1. With the help of simplified flow chart, describe the manufacture and uses of following
 - Urea
 - Calcium ammonium nitrate
 - Fluorocarbon
2. What care should be taken in handling of ammonium nitrate? Enlist various methods of preparation and explain anyone in detail.

3. Give detail preparation, properties and uses of following
 - Ammonium sulphate
 - Ammonia
4. With the help of flow diagram discuss manufacture of hydrogen cyanide
5. Using neat and clean flow diagram discuss the manufacture of hydrazine
6. Write a notes on
 - Ammonium phosphate
 - Calcium ammonium nitrate

1.13 FURTHER READING

1. Industrial chemistry by B. K. Sharma
2. Shreve's chemical process industries by George T. Austin