**SUMMER–19 EXAMINATION**

**Model Answer**

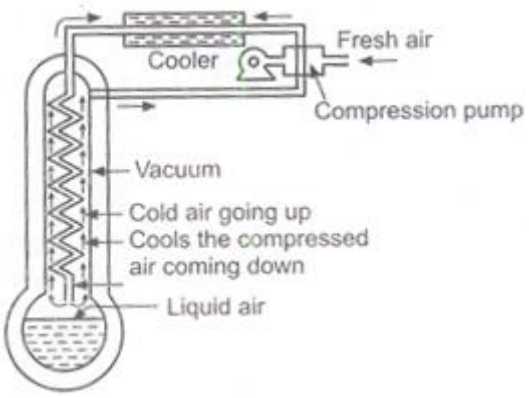
**Subject Name: Chemical Process Technology-I** **Subject Code:** 17314

**Important Instructions to examiners:**

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

| Q. No. | Sub Q. N | Answer | Marking Scheme |
|---|---|---|---|
| **1** | **A** | **Attempt any SIX** | **12** |
| | a | **Merits of contact process**<br>Can produce 100% concentrated acid and oleum<br>Large amount of acid can be manufactured.<br>**Demerits of contact process**<br>Catalyst can be poisoned if sulfur dioxide is not pure | 1<br><br><br><br><br>1 |
| | b | **Properties of sulfuric acid**<br>• Molecular weight: 98<br>• Melting point 10.5 $^{o}$C<br>• Boiling point 340$^{o}$C with decomposition<br>• Completely miscible with water with large heat of solution<br>• Formation of oleum with $SO_3$ | 1 mark each for any two |
| | c | **Uses of sulfuric acid**<br>a) For manufacturing of Fertilizers<br>b) Oil refining<br>c) Metal processing | 1 mark each for any two |

| | | | |
|---|---|---|---|
| | | d) Manufacturing of Rayon<br>e) In Lead acid batteries<br>f) Detergent manufacturing | |
| | d | **Reactions in sulfuric acid manufacturing**<br>$S + O_2 = SO_2$<br>$SO_2 + ½ O_2 = SO_3$<br>$SO_3 + H_2O = H_2SO_4$ | 2 |
| | e | Oleum or **fuming sulfuric acid**, is a solution of various compositions of sulfur trioxide in sulfuric acid. | 2 |
| | f | **Le Chatelier's Principle states**: when a change is introduced to a system in equilibrium, the equilibrium shifts in the direction that relieves the change. | 2 |
| | g | **Properties of chlorine (any 2)**<br>MW : 35, MP: – 101.5 $^oC$, BP : -34.4 $^oC$<br>It is a greenish yellow pungent smelling gas and is poisonous in nature. It causes headache if inhaled in small quantities. It dissolves in water to give chlorine water. It can be easily liquefied. It oxidizes, bleaches, disinfects.<br>**Properties of caustic soda (any 2)**<br>MW : 40, BP : 1390$^oC$, MP : 318 $^oC$ , Very soluble in water with high exothermic heat of reaction. | 1<br><br><br><br><br><br><br>1 |
| | h | **Hardening of cement**<br>Cement when mixed with sufficient quantity of water,the compounds present in cement reacts with water to form a cementitious crystalline structure that adheres to the sand and aggregates.This helps in binding the mass together and increases its strength till it becomes very hard. This is called hardening of cement. | **2** |
| 1 | **B** | **Attempt any TWO** | **8** |
| | a | **Cell notation for diaphragm cell** | 4 |

| | | | |
|---|---|---|---|
| | | Anode ↑ $Cl_2$ , C \| NaCl (aq) Cathode NaOH (aq) \| Fe, $H_2$ ↑<br>Cell reaction :<br>Anode : $Cl^- - e^- \rightarrow \frac{1}{2} Cl_2$<br>Cathode : $Na^+ + H_2O + e \rightarrow Na^+ + OH^- + \frac{1}{2} H_2$<br>Overall : $NaCl + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + \frac{1}{2} Cl_2$ | |
| | b | **Lindes Process**<br>Principle: the principle underlying is joule – Thomson effect which states that when a gas under pressure is allowed to expand suddenly through a small orifice into a region of low pressure it falls in temperature.<br>During expansion work is not done against external pressure but against internal attraction force between the molecules.<br>**Flow diagram:**<br>  <br><br>**Process description:**<br>Air free from $CO_2$ is compressed to about 200 atm pressure, and cooled by passing through a pipe surrounded by cold water. this cooled and compressed air passes through a spiral and escape through a small orifice or nozzle, when it is cooled by the above effect. This cooled air passes upwards surrounding the spiral pipe and cools the down coming air there in. The cooled air is further cooled by expansion and cooling is thus | 1<br>2<br>1 |

continued till it begins to condense.The up going air is compressed once again and is recirculated. Oxygen and nitrogen are separated from liquid air according to their boiling point.

c **Cement** 2

Cement is generic name for powdered material which initially have plastic flow when mixed with water but form a solid structure in several hours with varying degree of strength and binding properties which continue to improve with age.

**Composition of Portland Cement** 2

| **Compound** | **Formula** | **Shorthand form** |
|---|---|---|
| Tricalcium aluminate | $Ca_3Al_2O_6$ | $C_3A$ |
| Tetracalcium aluminoferrite | $Ca_4Al_2Fe_2O_{10}$ | $C_4AF$ |
| Belite or dicalcium silicate | $Ca_2SiO_5$ | $C_2S$ |
| Alite or tricalcium silicate | $Ca_3SiO_4$ | $C_3S$ |
| Sodium oxide | $Na_2O$ | N |
| Potassium oxide | $K_2O$ | K |
| Gypsum | $CaSO_4.2H_2O$ | $C\underline{S}H_2$ |

**2** **Attempt any TWO** **16**

a **Ammonia** 1

Raw Material:

Synthesis gas, Air

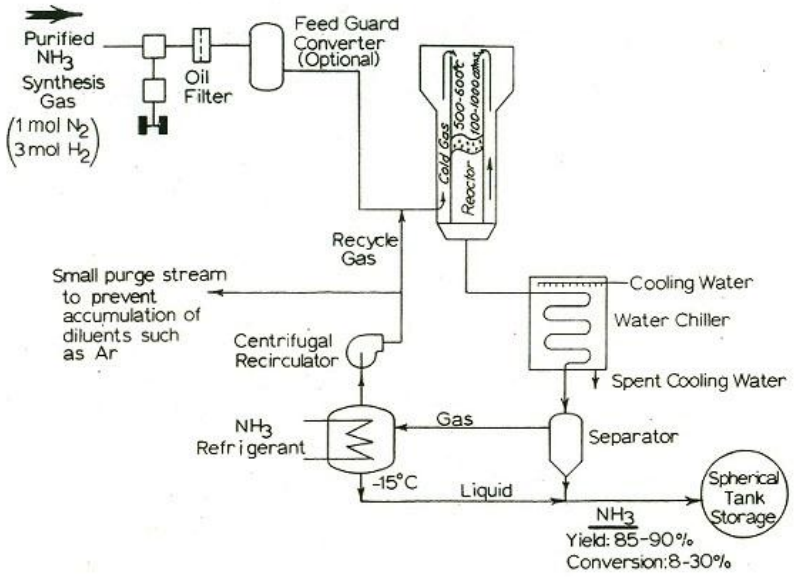
Reaction :

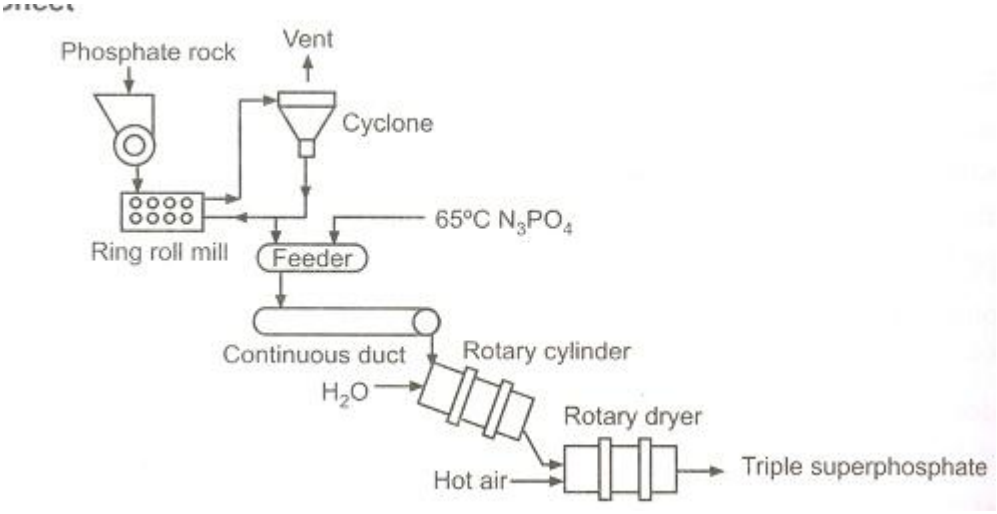
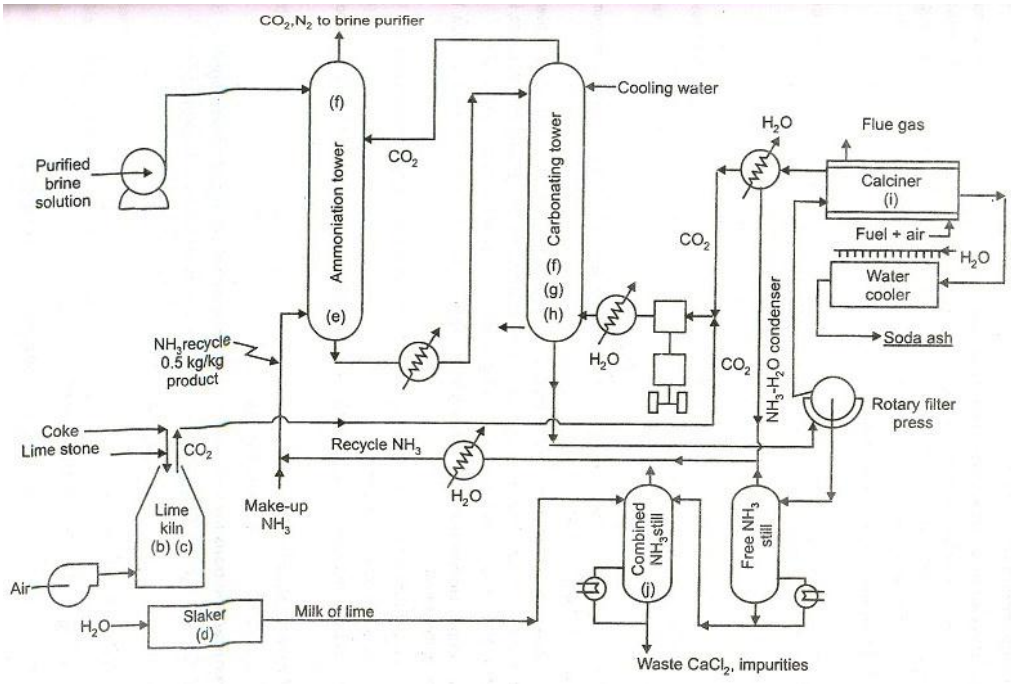
$N_2+3H_2 = 2NH_3$

Process

Ammonia synthesis gas is compressed to the operating pressure. It is send through a filter to remove compression oil and additionally through a high temperature guard converter to convert carbon monoxide, carbon dioxide to methane and remove traces of water vap, hydrogen sulfide. This is done by catalyst and suitable getter material.

The relatively cool gas is added along the outside of converter tube walls to provide

| | | | |
|---|---|---|---|
| | | cooling so that carbon steel can be used for the thick wall pressure vessel and internal tubes. The preheated gas flows next through the inside of the tubes which contain promoted porous iron catalyst at 550°C. The ammonia product with an 8-30% conversion depending on process condition is removed by condensation, first with water cooling and then ammonia refrigeration. The unconverted $N_2$-$H_2$ mixture is re circulated to allow 85-90% yield.<br>  <br> | 4<br><br>3 |
| | b | **Triple superphosphate**<br>This material is much more concentrated fertilizer then ordinary superphosphate it contains from 45 to 46% of available P2O5 of nearly three times the amount in the regular superphosphate.<br>Chemical reaction:<br>$CaF_2.3Ca_3(PO_4)_2 + 14H_3PO_4 \longrightarrow 10Ca(H_2PO_4)_2 + 2HF$<br>It is made by action of phosphoric acid on phosphate rock. The pulverized phosphate rock is mixed with phosphoric acid into a two stage reactor. The resultant slurry is sprayed into the granulator The product from the granulator is dried, screened, the oversize crushed and cooled again. Final product is conveyed to bulk storage where product is cured 4 to 6 weeks. During curing further reaction of acid and rock occurs which increases the availability of $P_2O_5$ for plants as food. Exhaust gases from granulator | 2<br><br>2 |

| | | | |
|---|---|---|---|
| | | and cooler are scrubbed with water to remove silicofluorides.<br>  <br> | 4 |
| | c | **Solvay process**<br>The overall reaction can be regarded as between calcium carbonate and sodium chloride:<br>$CaCO_3 + 2NaCl \longrightarrow CaCl_2 + Na_2CO_3$<br>However, calcium carbonate is too insoluble to react with a solution of salt. Instead the product is obtained by a series of seven stages.<br>  <br> | Rection-2<br>Diagram-3<br>Process-3 |

The process is known as the ammonia-soda process or the Solvay process, named after the Belgian industrial chemist who patented it in 186I. The various stages of the Solvay process are interlinked as can be seen from the diagram and description below.

**(1) Ammoniation of brine**

Ammonia gas is absorbed in concentrated brine to give a solution containing both sodium chloride and ammonia. $Na^+(aq)$, $Cl^-(aq)$, $NH_4^+(aq)$, $OH^-(aq)$ ions and $NH_3(aq)$ are present.

**(2) Formation of calcium oxide and carbon dioxide**

Kilns are fed with a limestone/coke mixture (13:1 by mass). The coke burns in a counter-current of pre-heated air:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^{\ominus} = -393 \text{ kJ mol}^{-1}$$

The heat of combustion raises the temperature of the kiln and the limestone decomposes:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +180 \text{ kJ mol}^{-1}$$

The gas, containing approximately 40% carbon dioxide, is freed of lime dust and sent to the carbonating (Solvay) towers. The residue, calcium oxide, is used in ammonia recovery (see step 7 below).

**(3) The Solvay Tower**

This is the key stage in the process. The ammoniated brine from step (1) is passed down through the Solvay Tower while carbon dioxide from steps (2) and (5) is passed up it. The Solvay Tower is tall and contains a set of mushroom-shaped baffles to slow down and break up the liquid flow so that the carbon dioxide can be efficiently absorbed by the solution. Carbon dioxide, on dissolving, reacts with the dissolved ammonia to form ammonium hydrogencarbonate:

$$NH_3(aq) + H_2O(l) + CO_2(g) \longrightarrow NH_4HCO_3(aq)$$

The solution now contains ions $Na^+(aq)$, $Cl^-(aq)$, $NH_4^+(aq)$ and $HCO_3^-(aq)$. Of the four substances which could be formed by different combinations of these ions,

sodium hydrogencarbonate ($NaHCO_3$) is the least soluble. It precipitates as a solid in the lower part of the tower, which is cooled. The net process is:

$$NaCl(aq) + NH_3(aq) + H_2O(l) + CO_2(g) \longrightarrow NaHCO_3(s) + NH_4Cl(aq)$$

A suspension of solid sodium hydrogencarbonate in a solution of ammonium chloride is run out of the base of the tower.

**(4) Separation of solid sodium hydrocarbonate**

The suspension is filtered to separate the solid sodium hydrogencarbonate from the ammonium chloride solution, which is then used in stage (7).

**(5) Formation of sodium carbonate**

The sodium hydrogencarbonate is heated in rotating ovens at 450 K so that it decomposes to sodium carbonate, water and carbon dioxide:

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

The carbon dioxide is sent back to the Solvay Tower for use in step (3). The product of the process, anhydrous sodium carbonate, is obtained as a fine white powder known as light sodium carbonate.

**(6) Formation of calcium hydroxide**

The last two stages, (6) and (7), are concerned with the regeneration of ammonia from ammonium chloride (made in step 3). The quicklime from step (2) is slaked with excess water giving milk of lime:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq/s)$$

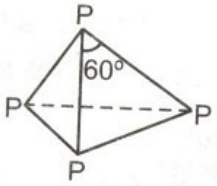
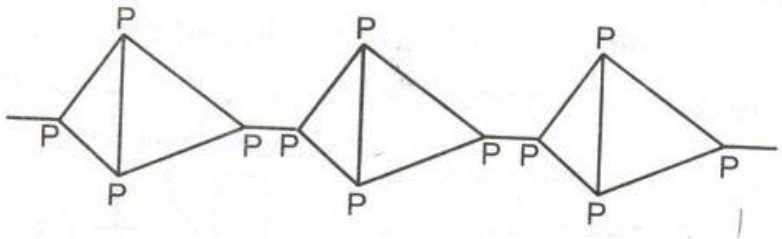
**(7) Regeneration of ammonia**

This calcium hydroxide suspension is mixed with the ammonium chloride solution left from step (4) and heated:

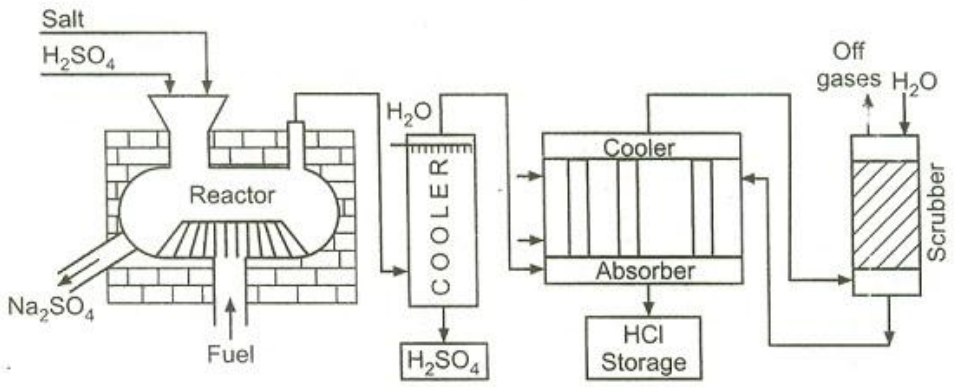
$$2NH_4Cl(aq) + Ca(OH)_2(aq/s) \longrightarrow CaCl_2(aq) + 2NH_3(g) + 2H_2O(l)$$

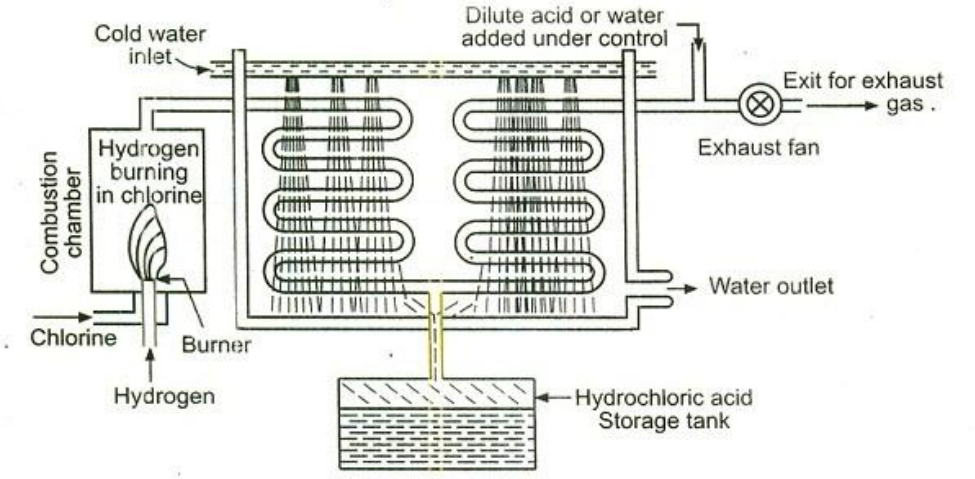
The ammonia is thus recovered, and sent back to step (1). Calcium chloride is the only by-product of the whole process.

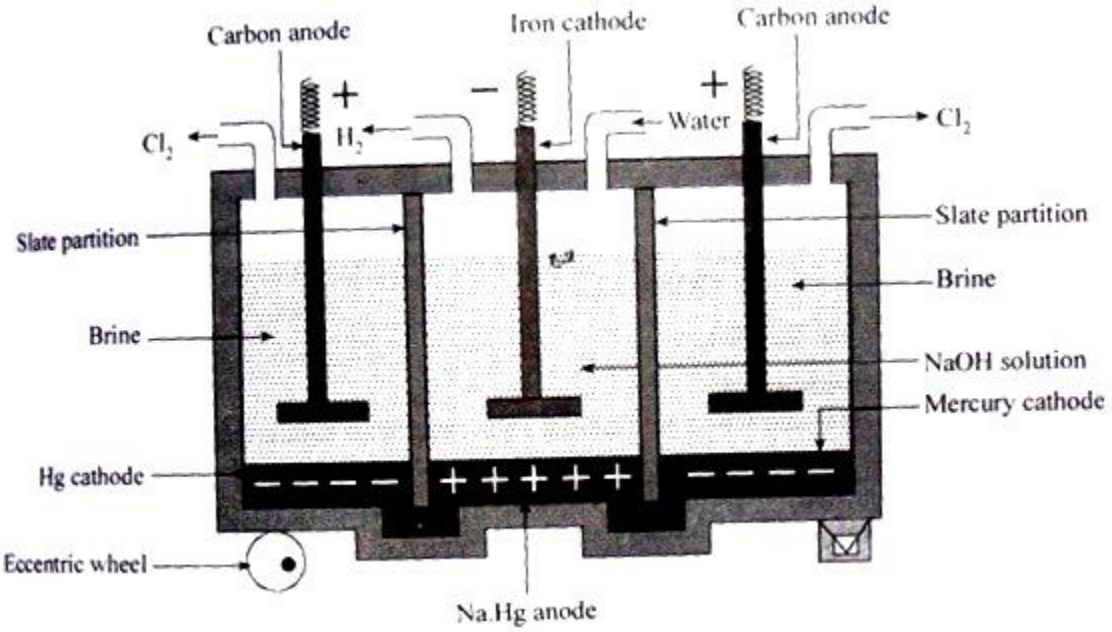
The overall process is an elegant one. In theory, the only raw materials are limestone and brine. Inevitably, there are losses of ammonia, and these are made up for by

| | | | |
|---|---|---|---|
| | | addition of extra supplies, as required in step (1) | |
| **3** | | **Attempt any FOUR** | **16** |
| | a | **Electro thermal process:**<br>A mineral phosphate with sand and coke is charged in the electric furnace. It is heated upto 1400 to 1500 $^oC$.<br>Initially at 1150$^oC$, $SiO_2$ displace more volatile $P_2O_5$ from calcium phosphate. $P_2O_5$ is then reducing to phosphorous by coke at 1500$^oC$. following reaction takes place<br>$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$<br>$2P_2O_5 + 10C \rightarrow P_4 + 10CO$<br>$CaSiO_3$ from molten slag is periodically removed through hole. Vapors of Phosphorous and carbon monoxide are send to the tank where cold water is placed. Phosphorous vapors are condensed to white phosphorous and carbon monoxide is escaped. | Rection-1 mark and Process-3 marks |
| | b | **Structure**<br>Yellow phosphorous<br>  <br><br>Red phosphorous<br>  <br><br>**Properties of white phosphorous:**<br>MW =60<br>MP = 44.1$^oC$<br>BP = 280 $^oC$<br>Stored under water due to reaction with oxygen. | 1<br>1<br>2 |

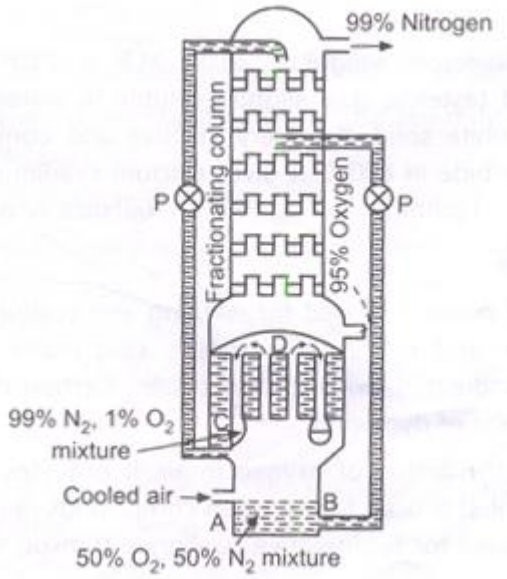
<table>
<tr><td></td><td>c</td><td>Difference between wet process and electric furnace process:
<table>
<tr><th>Wet Process</th><th>Electric furnace process</th></tr>
<tr><td>1. High grade phosphate rock is used</td><td>Low grade phosphate rock is used</td></tr>
<tr><td>2. Cost of plant is low</td><td>Cost of plant is high</td></tr>
<tr><td>3. Comparatively low pure acid is obtained</td><td>Highly pure acid can be obtained</td></tr>
<tr><td>4. This process doesn’t get affected by rate of electricity</td><td>This process is economical in those places where electricity is quite cheap</td></tr>
<tr><td>5. Phosphate rock is finely ground and prepulped in the mixing tank with cooled recycled H3PO4 from the slurry cooler</td><td>Phosphate rock ground and sized. Rock and sand mixed with coke, sintered and introduced into electric furnace</td></tr>
<tr><td>6. Reaction temperature is comparatively low</td><td>Reaction temperature is high</td></tr>
</table></td><td>1 mark for any 4</td></tr>
<tr><td></td><td>d</td><td>Principle involved in manufacturing of caustic soda<br>The process of electrolysis involves using an electric current to bring about a chemical change and make new chemicals. The electrolysis of brine is a large-scale process used to manufacture chlorine from salt. When an electric current is passed through salt water, the negative chloride ions, Cl-, migrate to the positive anode and lose their electrons to become chlorine gas.<br>(The chlorine atoms then pair up to form $Cl_2$ molecules.) Meanwhile, sodium ions, Na+, are drawn to the negative cathode. But they do not pick up electrons to become sodium metal atoms as they do in molten salt, because in a water solution the water molecules themselves pick up electrons more easily than sodium ions do. At the cathode the hydroxide ions, together with the sodium ions that are already in the solution, constitute sodium hydroxide, which can be recovered by evaporation.</td><td>4</td></tr>
<tr><td></td><td>e</td><td>HCL by Salt and Sulphuric acid method:<br>Both reactions involve the displacement of volatile acid from salt. The equilibrium can</td><td>1mark reaction,</td></tr>
</table>

| | | | |
|---|---|---|---|
| | | be displaced in desired direction by choice of condition i.e. promoting volatilization of HCl. The high temperature process is superior to vacuum for this purpose. To promote reaction rate it is desirable to have temperature sufficiently high to keep at least one of the reacting component in liquid condition. There is no difficulty in first stage of decomposition but second stage required temperature of about 400 ˚C to liquefy $NaHSO_4$. The higher limit to temperature is the attack of corrosive relative mass on furnace. The product and unconverted $H_2SO_4$ is send to further processing in which there is recovery of $H_2SO_4$ by cooling and HCL is recovered as main product from absorber.<br><br>$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$<br>$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$<br><br>  <br><br><br>OR<br>**Synthesis process:**<br>The process generates hydrogen chloride by burning chlorine in a few percent excess of hydrogen; chlorine and hydrogen are obtained as by products during manufacture of caustic soda.<br><br>$H_2 + Cl_2 \longrightarrow 2\ HCl$ | 1mark process and 2 mark diagram. |

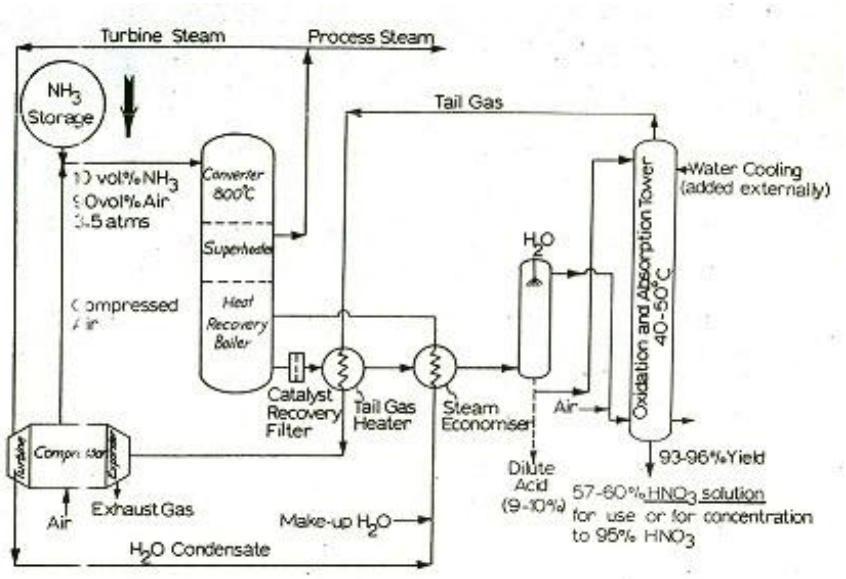
| | | | |
|---|---|---|---|
| | |  <br>Dry hydrogen is made to burn in acid resisting burner fitted in a combustion chamber lined with silica bricks. Dry chlorine is passed into the combustion chamber when hydrogen burns in an atmosphere of chlorine to give HCl<br>The gas is passed through a cooler cooled by water spray and then through absorber through which water flows down in controlled quantities.<br>The absorber is also cooled by a spray of cold water to remove the heat of absorption of HCl in water. The solution of HCl flows into storage tank below.<br>An exhaust fan on the extreme right pumps out the waste gases which escape in the atmosphere. | |
| | f | **Mercury Cell**<br>In the mercury-cell process, also known as the Castner–Kellner process, a saturated brine solution floats on top of a thin layer of mercury. The mercury is the cathode, where sodium is produced and forms a sodium-mercury amalgam with the mercury. The amalgam is continuously drawn out of the cell and reacted with water which decomposes the amalgam into sodium hydroxide, hydrogen and mercury. The mercury is recycled into the electrolytic cell. Chlorine is produced at the anode and bubbles out of the cell. Mercury cells are being phased out due to concerns about mercury poisoning from mercury cell pollution such. | 2 |

| | | | |
|---|---|---|---|
| | |  | 2 |
| **4** | | **Attempt any FOUR** | **16** |
| | a | **Ammonical brine** is brine solution saturated with ammonia.<br><br>The purified brine is allowed to percolate down the ammonia tower in which ammonia gas is passed through the bottom in a counter current fashion. The brine solution thus takes up the necessary amount of ammonia and liberates heat. The gas which escapes solution in the tank is absorbed by the brine falling down the tower. Some carbon dioxide is also absorbed by ammonia, as a result of which some insoluble carbonate is also precipitated. The ammoniated brine is allowed to settle, coded to about 30°C and pumped to the carbonating tower. | 1<br><br>3 |
| | b | **Mixed fertilisers are more popular**<br>Mixed fertilizers are more popular because Mixed fertilizers are capable of supplying all or several elements needed for plant nourishment. All the three major plant nutrients are made available in one and the same material. There is saving of time and labor. The residual effects will not be there. The fertilizer mixtures are usually prepared taking into account the acidic or alkaline nature of the ingredients, and other chemical reactions. Hence, some of the residual effects like acidity will not be there. Usually mixed fertilizer | 4 |

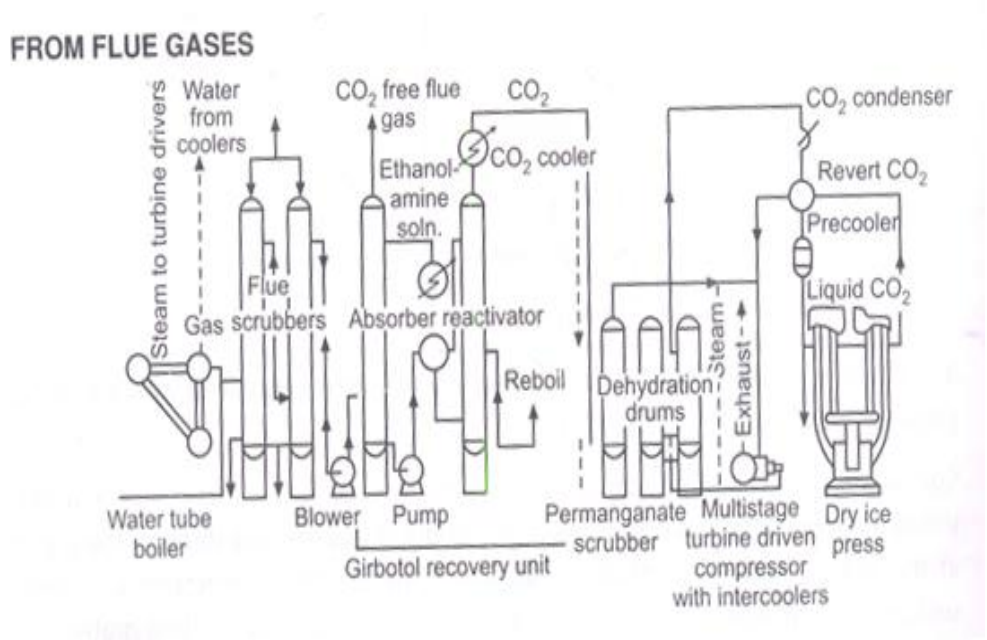
| | | | |
|---|---|---|---|
| | | are prepared to suit a group of crops and soils | |
| | c | **Phosphorus pentachloride**<br>Phosphorus pentachloride is prepared in two stages. 1) Preparation of phosphorous trichloride 2) Chlorination of Phosphorus trichloride.<br>Phosphorous trichloride is prepared by direct reunion of phosphorus and chlorine, the reaction being exothermic and spontaneous.<br>$P_4 + 6Cl_2 \longrightarrow 4\ PCl_3$<br>Liquid phosphorous and chlorine gas are fed in reactor. $PCl_3$ formed is partly refluxed in the reflux and a part is passed through a condenser and then to a still for distillation and finally for storage.<br>It is analyzed for elemental phosphorus. Based on this analysis, additional chlorine is introduced to remove traces of unreacted phosphorus.<br>Phosphorus pentachloride is conveniently prepared by passing excess of dry chlorine over liquid phosphorus trichloride in a tank cooled by a freezing mixture. $PCl_3$ is added drop by drop into it. The unused chlorine is removed by another tube and recycled again.<br>$PCl_3 + Cl_2 \longrightarrow PCl_5$ | 1<br><br><br><br><br>1<br><br><br><br><br><br>2 |
| | d | **Use of soda ash**<br>• Glass manufacturing<br>• Soap/detergents<br>• Pulp and paper<br>• Desulfurization<br>• Textile processing<br>**Reactions in Carbonating tower**<br>$CO_2 + OH = HCO_3^-$<br>$CO_2 + H_2O = HCO_3^- + H^+$<br>$Na^+ + Cl^- + NH_4^+ + HCO_3^- = NH_4 + Cl^- + NaHCO_3$ | ½ mark each for any four<br><br><br><br><br><br>2 |
| | e | **Properties of $H_2$ gas**<br>• Molecular wt is 2.016<br>• melting point of -259.14 °C | 2 |

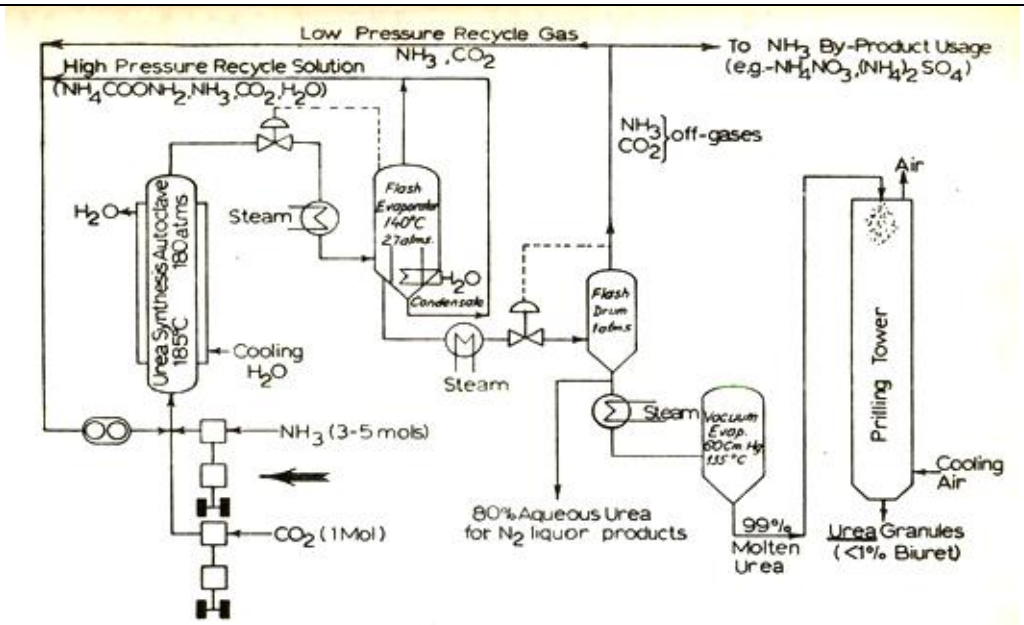
| | | | |
|---|---|---|---|
| | | • boiling point of -252.87 °C<br>• highly flammable and will burn in air at a very wide range of concentrations between 4 percent and 75 percent by volume.<br>• Hydrogen gas can also explode in a mixture of chlorine<br>• Hydrogen is a colorless, odorless gas<br>• Once ignited it burns with a pale blue, almost invisible flame.<br>• The vapors are lighter than air.<br>**Uses of hydrogen (four)**<br>1. Hydrogenation of oil<br>2. Ammonia production<br>3. Fuel<br>4. Methanol production<br>5. Coolant in power generator | 2 |
| | f | **Claudes Process**<br>**Principle:** when a cooled compressed gas is allowed to some external work e.g. pushing the piston of gas engine, it falls in temperature.<br>**Flow diagram:**<br>  <br> | 1<br>2 |

| | | | |
|---|---|---|---|
| | | **Process description:**<br>Air freed from $CO_2$ is dried, compressed and passes through a pipe surrounded by cold oxygen and nitrogen, where it is cooled. Cooled and compressed air is allowed to do work in an expansion engine where it is further cooled.<br>This cooled air enters the plant and rises through iron tubes surrounded by liquid oxygen. a part of the air gets liquefied and collects. the condensation is 50% N2,50%O2 .the gas which escape condensation passes downwards through side tubes surrounded by liquid oxygen and condenses. The condensation being 99% $N_2$ and 1% $O_2$<br>The condensed liquid is pumped to the top of fractionating column, while the bottom liq. Is pumped to a level slightly above the fractionating column, where it meets an upward current of gases. the liq is wormed up a little as it comes down and loses a volatile constituents more and more. i.e. $N_2$ bye evaporation and gets gradually richer in $O_2$ . similarly up going gases loses more and more $O_2$ by condensation due to cooling and gets richer in $N_2$.by the time gases rich the top, it is 99% pure $N_2$ which escape to the exit provided. Liq $O_2$ evaporate as it cools the air and escape to the exit indicated | 1 |
| **5** | | **Attempt any TWO** | **16** |
| | a | **Nitric Acid Production**<br>Raw material<br>Ammonia, air, water<br>Reaction<br>$4NH_3+5O_2 = 4NO +6H_2O$<br>$2NO+O_2 = 2NO_2$<br>$3NO_2+H_2O=2HNO_3+NO$<br>Ammonia and air are compressed and send to the catalytic converter. Ammonia is oxidized and converted into nitric oxide. Large heat is evolved which is utilized to run turbine by producing steam and gas expander. Both are connected to the compressor. | 2<br>3 |

| | | | |
|---|---|---|---|
| | | Hence compressor does not require external energy source. NOx gases after heat recovery is send through cooler condenser where it is cooled by cooling tower water. Some part of acid is converted into liquid form. Both liquid and gas are send to absorption tower at different feed plates. Air is provided from the bottom to complete oxidation of NO. Water is fed from the top of the tower. Nitric acid (60%) is collected at the bottom. Tail gases from the absorber are used to run gas expander after heating.<br>  <br> | 3 |
| | b | **Method for production of $CO_2$**<br>• From Fermentation process<br>• From Flue gas<br>• From Calcination of limestone<br>• Ethylene oxide production<br><br>**$CO_2$ by fermentation process**<br>Gas from fermenter is send to compressor. With a dry-running piston compressor the fermentation carbon dioxide is compressed to one sixteenth of the original gas volume. After the $CO_2$ compressor it is send to drying unit . It consists of two adsorption tanks | 2<br><br>6 |

| | | | |
|---|---|---|---|
| | | filled with drying agent molecular sieves In order to remove the residual moisture from the gas, the carbon dioxide flows through one tank while the other tank is regenerated by heater. In the gas purifier, installed after the drying unit and also consisting of two vessels, substances influencing odor and taste are removed. By compression and condensation the storage volume is reduced to such an extent that temporary storage of even very large quantities of carbon dioxide requires little space. The compressed gas is liquefied in the condenser and then collected in a storage tank.<br>**OR**<br>**Manufacturing of $CO_2$ by flue gas: Process description**:<br>Fflue gases result from burning carbonaceous material are cooled, purified and washed by passing through two water scrubbers contain $Na_2Co_3$.<br>($Na_2Co_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$)<br>The reaction to left is formed by heating $NaHCO_3$.$CO_2$ is absorbed in absorber by counter current selective absorption. in aq.solution of ethanolamine $CO_2$ and steam passed through reactivator and then through $CO_2$ cooler to condensed steam which returns to the tower as reflux.$CO_2$ passes through permagnet scrubber where traces of $H_2S$ amines are removed it is dried by passing it through dehydration drums. finely $CO_2$ is condensed cooled in precooler and sent to liquid $CO_2$ receiver for liquefaction. | |

| | | | |
|---|---|---|---|
| | |  | |
| | c | **Urea by Montecatini Process:**<br>**Chemical reaction:**<br>i) $CO_2$(carbon dioxide ) + $2NH_3$ ( ammonia) → $NH_4.COO.NH_2$ (ammonium carbamate)<br>ii) $NH_4.COO.NH_2$ (ammonium carbamate) → $NH_2.CO.NH_2$ ( urea) + $H_2O$<br>iii) Undesirable side reaction :<br>$NH_2.CO.NH_2$ (urea) → $NH_2.CO.NH.CO.NH_2$ (biuret) + $NH_3$<br>**Flow diagram :** | Rection-1<br>Diagram-4<br>Process-3 |




**Process description :**

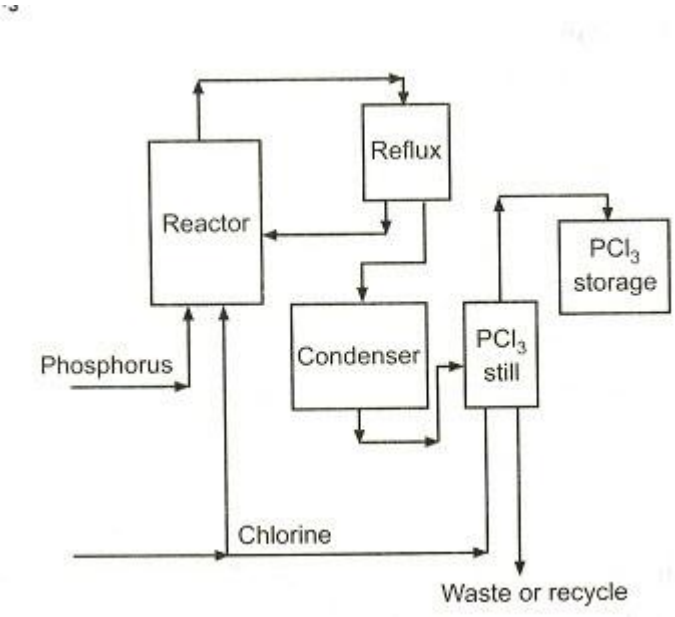
Ammonia and carbon dioxide are compressed separately and added to the high pressure autoclave which must be water cooled due to highly exothermic reaction. The average residence time in the autoclave, which is operated on a continuous basis, is 1.5 to 2 hrs. a mixture of urea, ammonium cabamate, water and unreacted $NH_3$ and $CO_2$ results.

This liquid effluent is let down to 27 atms and feed to a special flash evaporator containing gas liquid separator and condenser. unreacted $NH_3$, $CO_2$ and water as a solution are removed and recycled. An aqueous solution of carbamate urea is passed to the atmospheric flash drum where further decomposition of carbamate takes place. The off gases from this step can either be recycled or sent to ammonia process for making chemical fertilizers.

The 80% aqueous urea solution can be used as it is or sent to a vacuum evaporator to obtained molten urea containing less than 1% water. The molten mass is them sprayed into prilling or granular solidification tower. To avoid formation of biuret in percentage > 1% , the temperature must be kept just above the melting point for processing time of 1-2 seconds in this phase of the operation.

| 6 | | Attempt any FOUR | 16 |
|---|---|---|---|
| | a | **Use of Oxygen (Four)**<br>• For human breathing<br>• For life supporting system at space<br>• In hospital<br>• In Smelting of iron ore into steel<br>• For the production of ethylene oxide<br>• In oxy acetylene flame<br>**Use of Nitrogen (Four)**<br>• As a modified atmosphere, pure or mixed with carbon dioxide, to nitrogenate and preserve the freshness of packaged or bulk foods<br>• For the production of ammonia<br>• In incandescent light bulbs as an inexpensive alternative to argon<br>• In fire suppression systems for Information technology<br>• In the manufacture of stainless steel<br>• In the case-hardening of steel by nitriding<br>• In some aircraft fuel systems to reduce fire hazard<br>• To inflate race car and aircraft tires<br>• Liquid nitrogen as refrigerent | 2<br>2 |
| | b | **Advantages of high alumina cement**<br>• Rapid Hardness<br>• Initial setting time 3 hrs and final setting time 5 hrs<br>• It does not expand on setting.<br>• Great resistance to corrosion,<br>**Disadvantages of high alumina cement**<br>• Strength diminishes when comes in contact with traces of lime<br>• It is costly<br>• Evolves great heat during setting. | 2<br>2 |

| | | | |
|---|---|---|---|
| | | • Does not have greater strength in tropical climate | |
| | c | **Properties of ammonia (Four)**<br>• MW = 17<br>• MP = -77.73 $^{o}$C<br>• BP = -33.34 $^{o}$C<br>• Ammonia is a colorless gas.<br>• It is highly soluble in water<br>• Ammonia is irritating to the skin, eyes, nose, throat, and lungs.<br>**Industrial applications of ammonia (any four)**<br>1. For production of urea<br>2. For production of nitric acid<br>3. For production of ammonium nitrate<br>4. For production of ammonium phosphate<br>5. As refrigerant | 2<br>2 |
| | d | **Producer gas principle**<br>Producer gas, mixture of flammable gases (principally carbon monoxide and hydrogen) and nonflammable gases (mainly nitrogen and carbon dioxide) made by the partial combustion of carbonaceous substances, usually coal, in an atmosphere of air and steam. Producer gas has lower heating value than other gaseous fuels, but it can be manufactured with relatively simple equipment; it is used mainly as a fuel in large industrial furnaces.<br>Producer gas is generally made from coke, or other carbonaceous material such as anthracite. Air is passed over the red-hot carbonaceous fuel and carbon monoxide is produced. The reaction is exothermic and proceeds as follows:<br><br>Formation of producer gas from air and carbon:<br>$C + O_2 \rightarrow CO_2$, +97,600 calories<br>$CO_2 + C \rightarrow 2CO$, -38,800 calories<br>$2C + O_2 \rightarrow 2CO$, +58,800 calories | 4 |

| | | | |
|---|---|---|---|
| | | Reactions between steam and carbon:<br>$H_2O + C \rightarrow H_2 + CO$, -28,800 calories<br>$2H_2O + C \rightarrow 2H_2 + CO_2$, -18,800 calories<br>Reaction between steam and carbon monoxide:<br>$H_2O + CO \rightarrow CO_2 + H_2$, +10,000 calories<br>$CO_2 + H_2 \rightarrow CO + H_2O$, -10,000 calories | |
| | e | **Phosphorous trichloride** is prepared by direct reunion of phosphorus and chlorine, the reaction being exothermic and spontaneous.<br>$P_4 + 6Cl_2 \longrightarrow 4\ PCl_3$<br>Liquid phosphorous and chlorine gas are fed in reactor. $PCl_3$ formed is partly refluxed in the reflux and a part is passed through a condenser and then to a still for distillation and finally for storage.<br>It is analyzed for elemental phosphorus. Based on this analysis, additional chlorine is introduced to remove traces of unreacted phosphorus.<br>  <br> | 2<br>2 |
| | f | **Biurete**<br>It is the result of condensation of two molecules of urea and is a problematic impurity in urea-based fertilizers. Biuret it is very harmful for certain crops like pineapple, Citrus, | 2 |

| | | | |
|---|---|---|---|
| | | Tobacco and coffee which are sensitive to Biuret. Chlorosis occurs on the leaf of the plants, when Biuret more than 1.5%.Fertilizer grade urea contains the impurity biuret which is toxic to the plant especially when applied as a leaf dressing. Biuret more than 1.5 % can damage the root of the plant and also useful bacteria and chock the capillary of the root cell, Nitrogen carrying capacity will be reduced.<br><br>**Reaction**<br><br>$2\ CO(NH_2)_2 \rightarrow H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2 + NH_3$ | 2 |