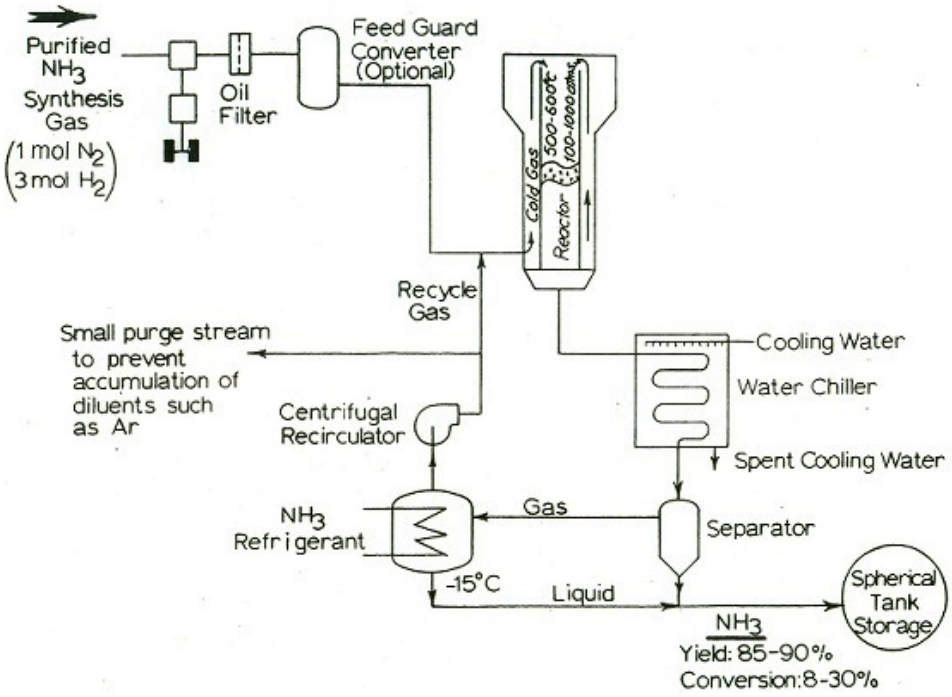
Important Instructions to examiners:

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 equivalen concept.

Q No.	Answer	marks	Total marks
1 a) (i)	Chemical reactions involved in manufacturing of sulfuric acid $S + O_2 \rightarrow SO_2$ $SO_2 + ½ O_2 \leftrightarrow SO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$	 ½ 1 ½	2
(ii)	Method of cement production a) Dry process b) Wet process	1 mark each	2
(iii)	Uses of acetylene a) In oxy-acetylene flame b) Manufacturing of raw material of polyurethane c) Manufacturing of vinyl chloride d) Manufacturing of Neoprene e) Manufacturing of Vinyl acetate	Half mark each for any four	2
(iv)	**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. We'll use the the equation for synthesizing ammonia to explore the factors which affect chemical equilibrium and apply Le Chatelier's principle: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + Heat$ Reaction is exothermic. That means that heat is given off as ammonia is synthesized in the forward reaction. So the reverse equation is endothermic and heat is absorbed when ammonia is decomposed. As a result, according to Le Chatelier's principle, if you add heat to a balanced equation the system will want to shift in the direction that removes heat from the system (endothermic) which is the reverse direction. So by increasing the temperature you would remove ammonia, it would decompose.	2	2

(v)	**Methods for manufacturing of HCl** a) Synthesis reaction (hydrogen and chlorine) b) Chlorination reaction c) Salt and acid	1 mark for any two	2
(vi)	**Methods for production of ammonium sulphate** a) Ammonia and sulfuric acid $2NH_3 + H_2SO_4 \rightarrow (NH_4)2SO_4$ b) Ammonia , carbon dioxide and gypsum $2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$ $(NH_4)2CO_3 + CaSO_4.2H_2O \rightarrow (NH_4)2SO_4 + CaCO_3 + 2H_2O$	1 mark for each	2
(vii)	**Uses of sulfuric acid** a) For manufacturing of Fertilizers b) Oil refining c) Metal processing d) Manufacturing of Rayon e) In Lead acid batteries f) Detergent manufacturing	Half mark each for any four	2
(viii)	**Biurete** It is the result of condensation of two molecules of urea and is a problematic impurity in urea-based fertilizers. $2\ CO(NH_2)_2 \rightarrow H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2 + NH_3$	1 1	2
1 b) (i)	**Raw material for cement** Portland cement consists essentially of compounds of lime (calcium oxide, CaO) mixed with silica (silicon dioxide, SiO_2) and alumina (aluminum oxide, Al_2O_3). The lime is obtained from a **calcareous** (lime-containing) raw material, and the other oxides are derived from an **argillaceous** (clayey)	4	4

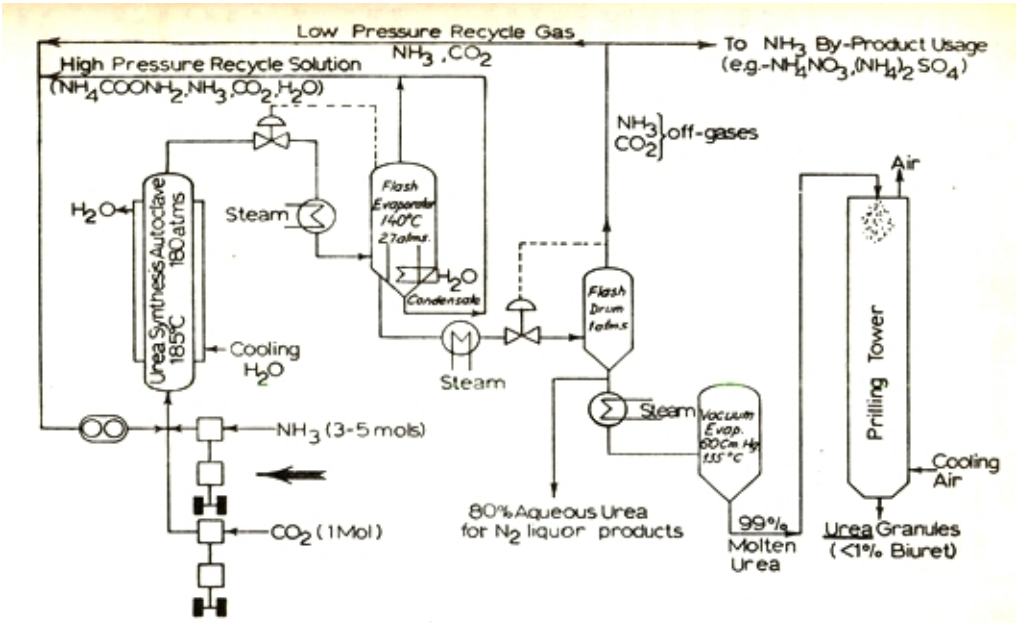
	material. Additional raw materials such as silica sand, iron oxide (Fe_2O_3), and bauxite containing hydrated aluminum, $Al(OH)_3$-may be used in smaller quantities to get the desired composition. The commonest calcareous raw materials are limestone and chalk, but others, such as coral or shell deposits, also are used. Clays, shales, slates, and estuarine muds are the common argillaceous raw materials. Marl, a compact calcareous clay, and cement rock contain both the calcareous and argillaceous components in proportions that sometimes approximate cement compositions. Another raw material is blast-furnace slag, which consists mainly of lime, silica, and alumina and is mixed with a calcareous material of high lime content. Kaolin, a white clay that contains little iron oxide, is used as the argillaceous component for white portland cement. Industrial wastes, such as fly ash and calcium carbonate from chemical manufacture, are other possible raw materials, but their use is small compared with that of the natural materials. The magnesia (magnesium oxide, MgO) content of raw materials must be low because the permissible limit in portland cement is 4 to 5 percent. Other impurities in raw materials that must be strictly limited are fluorine compounds, phosphates, metal oxides and sulfides, and excessive alkalies. Another essential raw material is gypsum, some 5 percent of which is added to the burned cement clinker during grinding to control the setting time of the cement. Portland cement also can be made in a combined process with sulfuric acid using calcium sulfate or anhydrite in place of calcium carbonate. The sulfur dioxide produced in the flue gases on burning is converted to sulfuric acid by normal processes.		
(ii)	(i) **Linde's method :** This process is based upon **Joule-Thomson effect** which states that "When a gas is allowed to expand adiabatically	2	4

	from a region of high pressure to a region of extremely low pressure, it is accompanied by cooling." (ii) **Claude's method :** This process is based upon the principle that when a gas expands adiabatically against an external pressure (as a piston in an engine), it does some external work. Since work is done by the molecules at the cost of their kinetic energy, the temperature of the gas falls causing cooling.	2	
(iii)	**Ammonia manufacturing**  	4	4
Q 2 a)	**Urea by ammonium carbamate method:** Chemical reaction: i) CO_2(carbon dioxide) + $2NH_3$ (ammonia) → $NH_4.COO.NH_2$ (ammonium carbamate) ii) $NH_4.COO.NH_2$ (ammonium carbamate) → $NH_2.CO.NH_2$ (urea) + H_2O	Rection-1 Diagram-4 Process-3	8

iii) Undesirable side reaction :

$NH_2.CO.NH_2$ (urea) $\rightarrow$ $NH_2.CO.NH.CO.NH_2$ (biuret) + NH_3

Flow diagram :

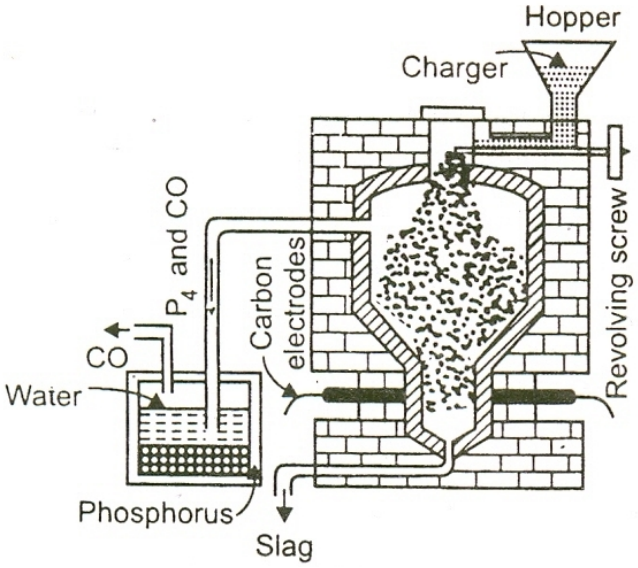


Process description :

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.		
b)	**Electro thermal process:** A mineral phosphate with sand and coke is charged in the electric furnace. It is heated upto 1400 to 1500 ^{o}C. Initially at 1150^{o}C, SiO_2 displace more volatile P_2O_5 from calcium phosphate. P_2O_5 is then reducing to phosphorous by coke at 1500^{o}C. following reaction takes place $Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$ $2P_2O_5 + 10C \rightarrow P_4 + 10CO$ $CaSiO_3$ 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-2 Diagram-3 Process-3	8

			
c)	The overall reaction can be regarded as between calcium carbonate and sodium chloride: $CaCO_3 + 2NaCl \longrightarrow CaCl_2 + Na_2CO_3$ However, calcium carbonate is too insoluble to react with a solution of salt. Instead the product is obtained by a series of seven stages. 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.	Rection-2 Diagram-3 Process-3	8

(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:

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

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:

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

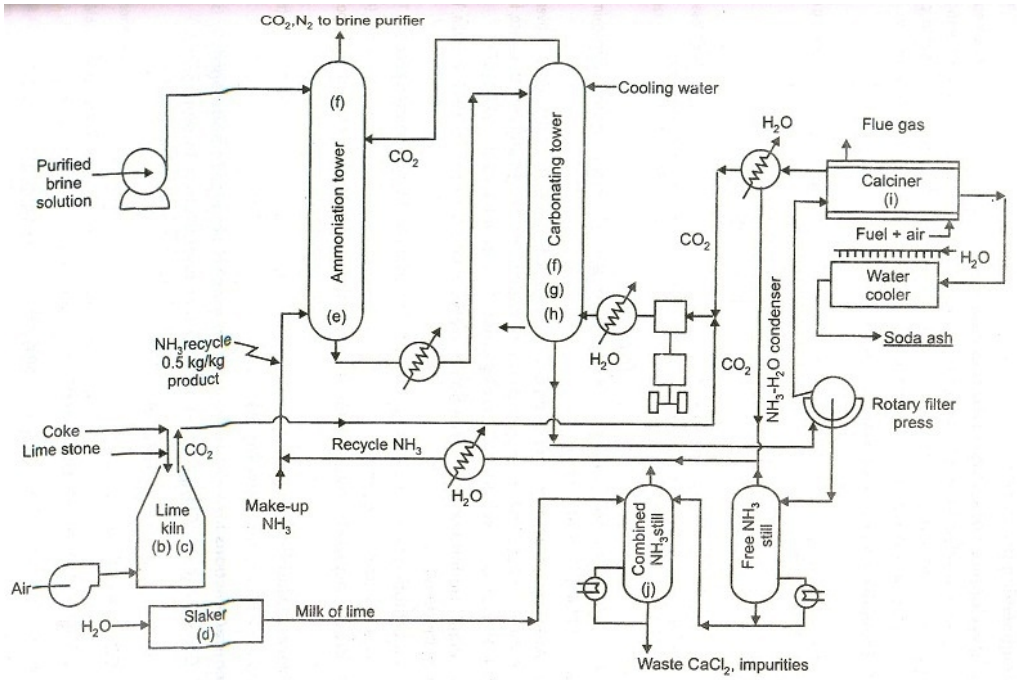
(7) Regeneration of ammonia

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

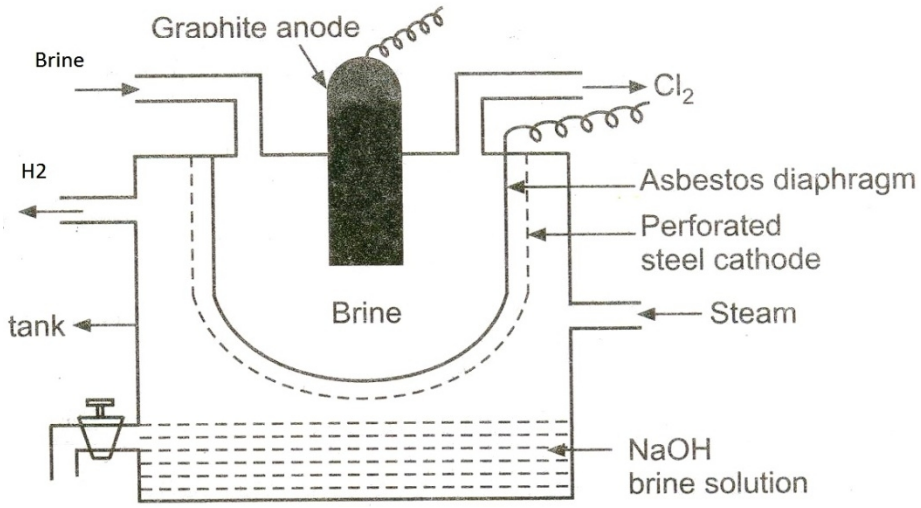
$$2NH_4Cl(aq) + Ca(OH)_2(aq/s) \longrightarrow CaCl_2(aq) + 2NH_3(g) + 2H_2O(l)$$

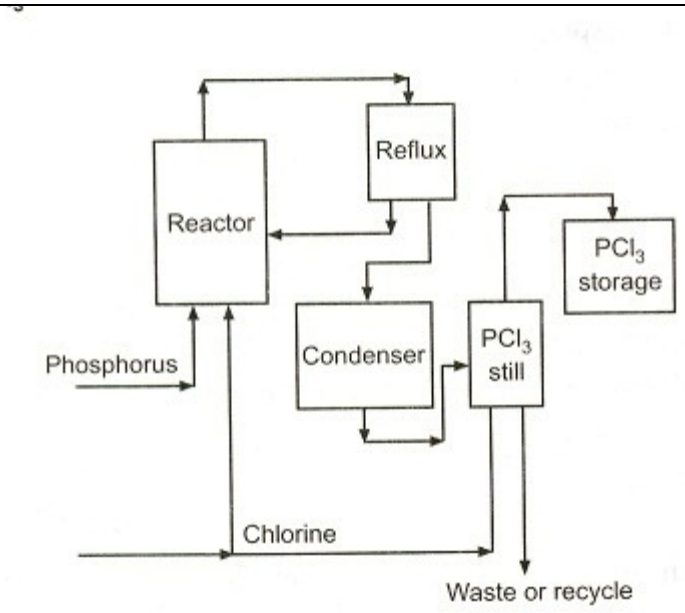
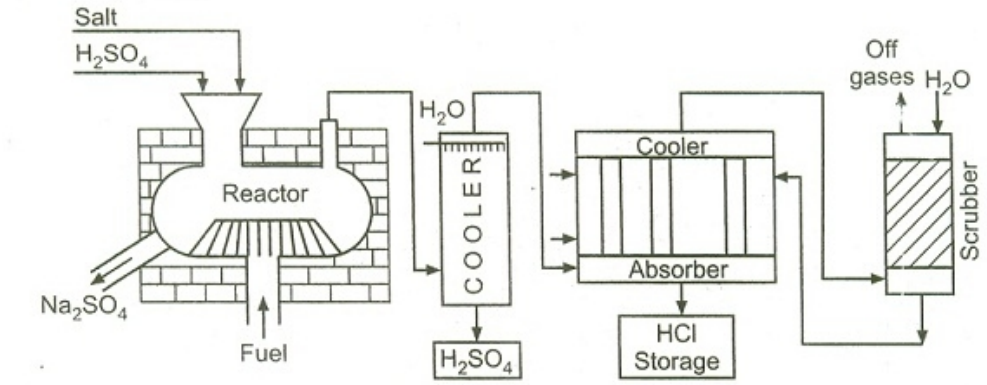
The ammonia is thus recovered, and sent back to step (1). Calcium chloride is the only by-product of the whole process.

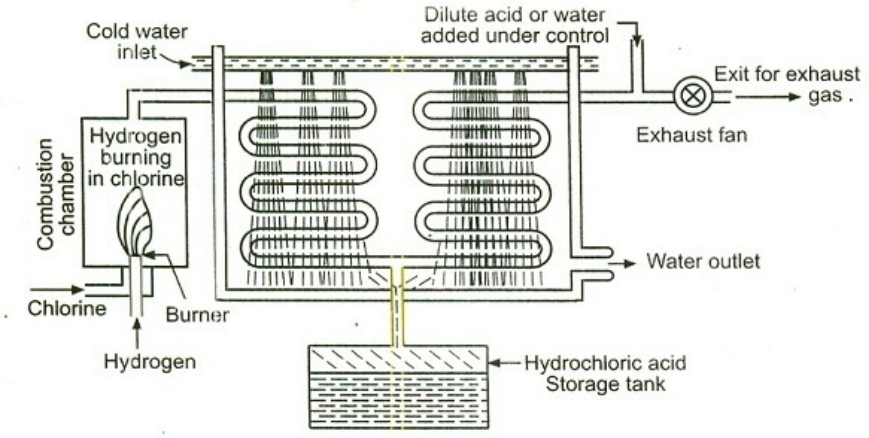
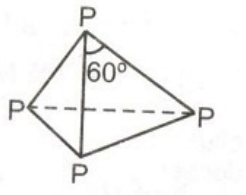
The overall process is an elegant one. In theory, the only raw materials are limestone and brine. Inevitably, there are losses of ammonia, and these are made up for by addition of extra supplies, as required in step (1).

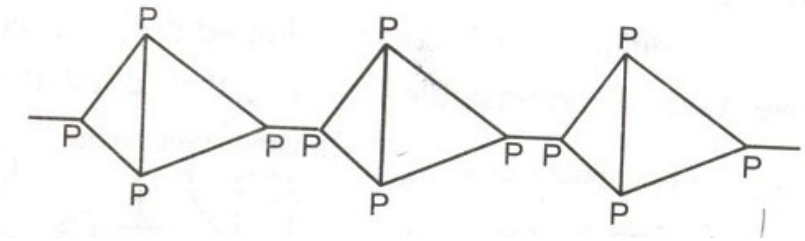


Q3 a)	**Nelson cell** The cell consists of U –shaped perforated steel cathode lined outside with asbestos paper and suspended in rectangular iron tank. A carbon anode is dipped in brine placed in the cathode. On passing the electric current,Cl_2 is liberated at the anode and led out through an outlet above and compressed into steel cylinders. Sodium ions penetrate through the asbestos paper and along with hydroxyl ions formed by the reduction of H_2O at cathode, form NaOH. Steam is injected in the cathode compartment for forming NaOH solution. NaOH is collected in the outer tank H_2 is drawn off through the exit of the top	2	4

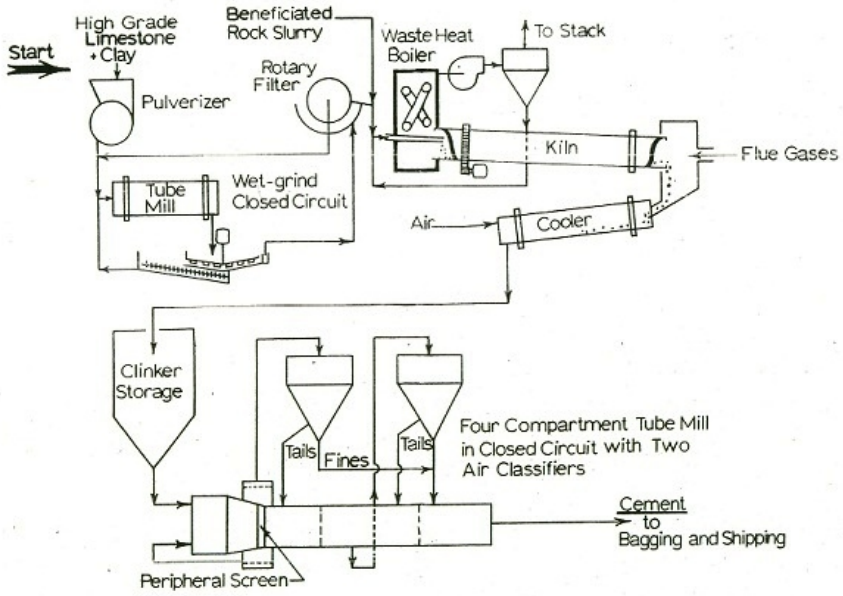
	and collected as a by product.  	2	
b)	**Phosphorous trichloride** $P_4 + 6\ Cl_2 \rightarrow 4PCl_3$ Phosphorus trichloride is prepared by direct union of phosphorus and chlorine,the reaction being exothermic and spontaneous. Liquid phosphorus and chlorine gas are fed into a reactor.PCl3 formed is partly refluxed in the reflux and apart is passed through a condenser and then to a still for distillation and finally for storage.	2 2	4

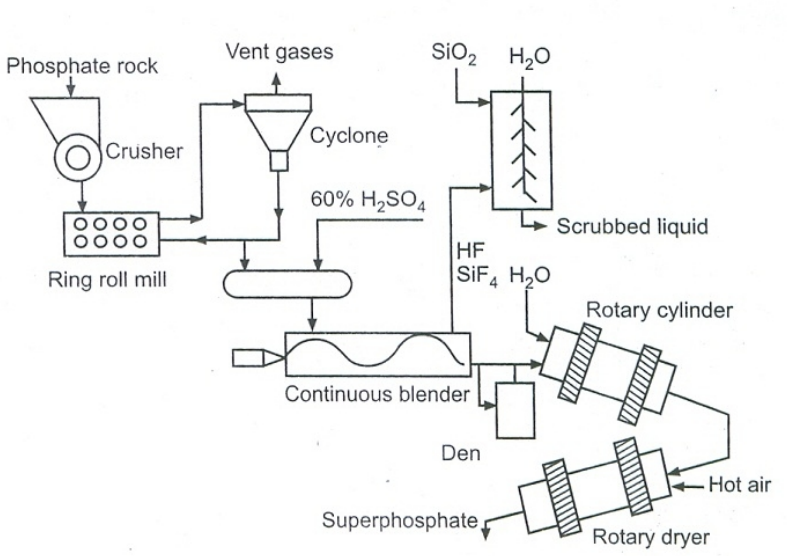
			
c)	**HCL manufacturing** 	4 for any one fig.	4

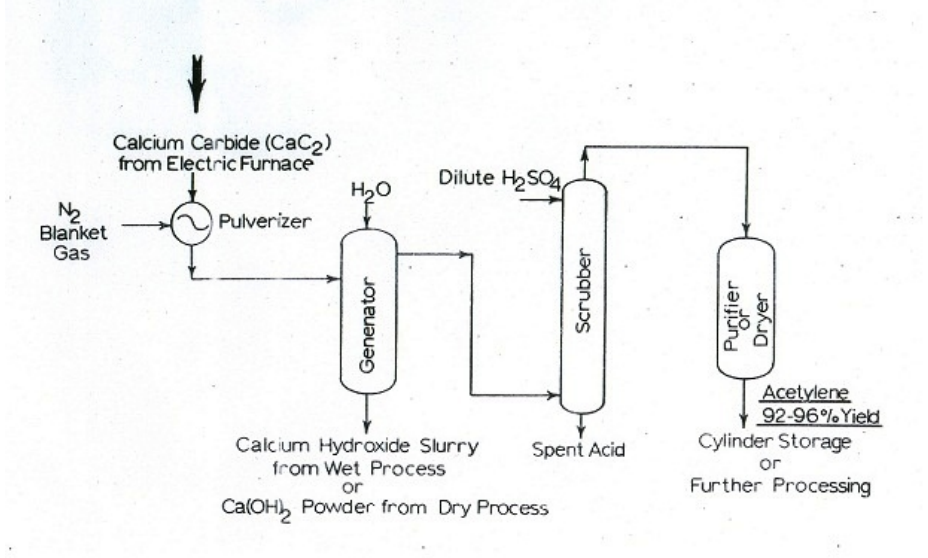
			
d)	**Uses of phosphorous** • Used to prepare • phosphoric acid • phosphate builders for detergents • fertilizer • animal feed • pesticides • gasoline lube oil additives • fireworks • flame retardants • matches **Structure** Yellow phosphorous 	1 mark each for any two uses 1	4

	Red phosphorous 	1	
e)	Reaction for phosphoric acid $Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO4 + 3(CaSO_4.2H_2O)$ Reaction for phosphorous penta chloride $PCl_3 + Cl_2 \rightarrow PCl_5$	2 2	4
f)	Reaction for sodium carbonate $CaCO_{3\,(s)} + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$ Reaction for caustic soda $NaCl + H_2O \rightarrow NaOH + 1/2H_2 + ½\ Cl_2$	2 2	4
Q 4 a)	**Methods for the production of carbon dioxide** i)From flue gases ii) From fermentation process iii) From limestone **CO2 from flue gas** Flue gases resulting from burning carbonaceous material. They are cooled, purified and washed by passing through two water scrubbers the scrubbers contain washing soda. Sodium carbonate is absorbed in absorber by countercurrent selective absorption in aqueous solution of`etanolamines,CO	1 3	4

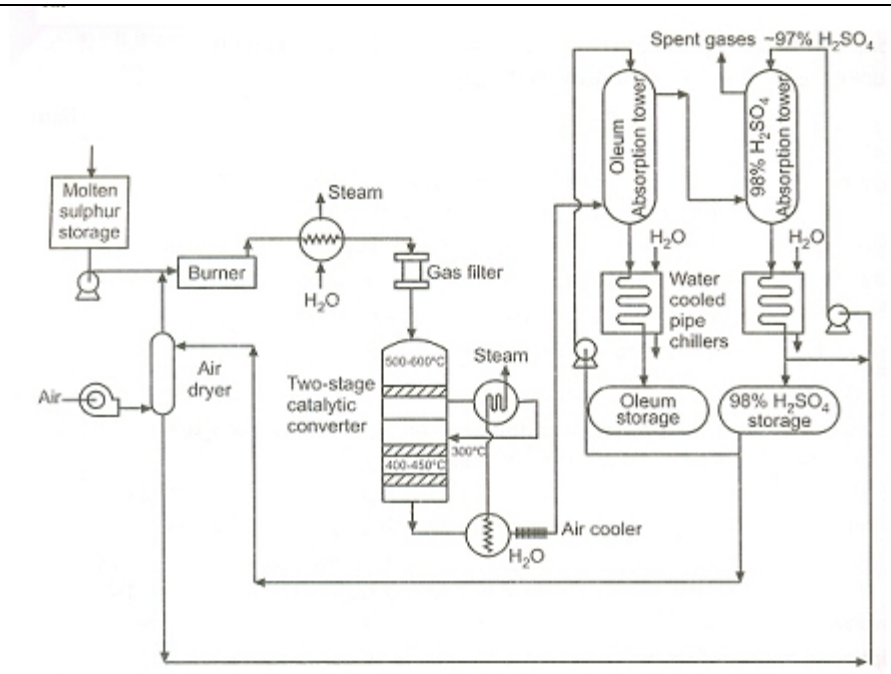
	and steam pass through a reactivvator then through co2 cooler to condense steam which returns to tower as a reflux. Co2 now passes through a permagnate scrubber, where traces of H2S & amines are removed. It is dried by passing it through dehydration drums. Finally CO2 is condensed,cooled in pre cooler and sent to liquid CO2 receiver for liquefaction. **From fermentation process** 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 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.		
b)	**Wet process for cement manufacturing**	4	4

			
c)	**Single super phosphate** Manufacturing of Single Super Phosphate is based on the simplest chemical reaction amongst chemical fertilizers. The major raw materials required are phosphate rock and sulphuric acid. The Rock Phosphate contains Tri Calcium Phosphate which is insoluble in water and hence cannot be taken by the plant. The Rock Phosphate is reacted with dilute Sulphuric Acid. The product of reaction is Mono Calcium Phosphate which is soluble in water. This soluble phosphate can be easily consumed by the plants. Rock phosphate is ground very fine (93% passing through 100 mesh). The measured / weighed quantity of Rock phosphates is fed into lead lined mixer, where it is neutralized with dilute sulphuric acid. The reaction is very fast in the beginning and the material is fine slurry which thickens quickly. The material is discharged in the den where the material slowly solidifies. The den discharge is fitted with den cutter which cuts the solid cake to powder. The Fluorine based gases are liberated which are sucked by ID fan and scrubbed in	2	4

	multi stage conventional scrubbers &venturi Scrubbers. The material gets cured in a few days time. Reaction $[Ca_3(PO_4)_2]_3CaF_2 + 7H_2SO_4 = 3CaH_4(PO_4)_2 7CaSO_4 + 2HF$  	2	
d)	**Acetylene** Pulverized calcium carbide is added to acetylene gas generator in which quantity of water used is sufficient to discharge the calcium hydroxide as lime slurry containing 85-90% water. The temperature is kept below 90^oC and 2 atm in the gas generator. The impure acetylene from generator which contains traces of ammonia, sulfides and phosgene is scrubbed with acid solution. It is further purified and dried with silica gel.	2 2	4

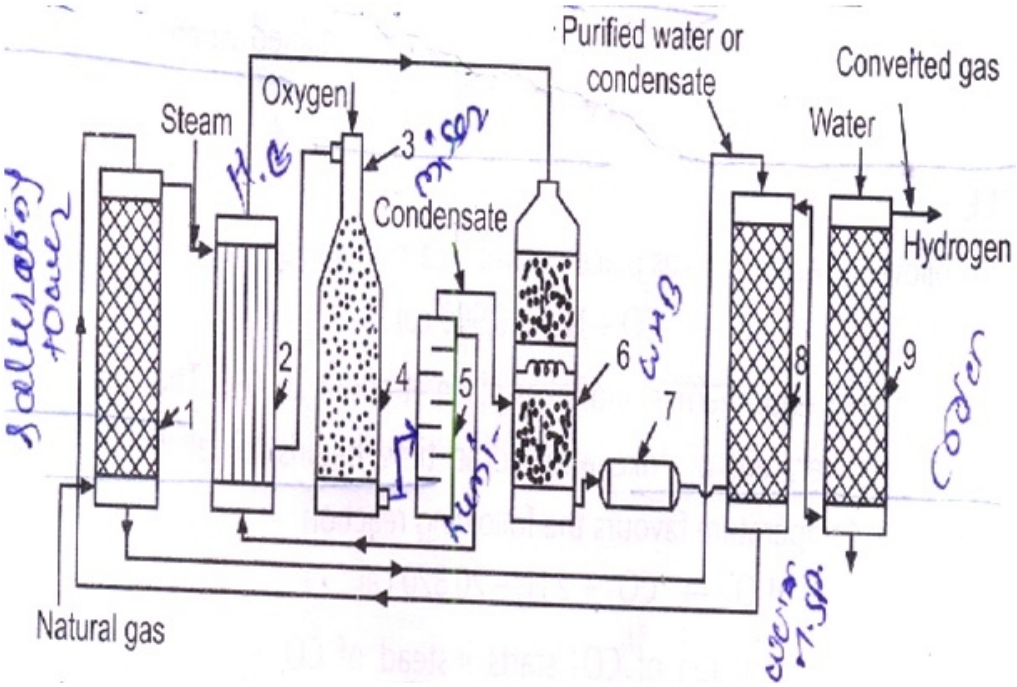
			
e)	Reaction for soda ash $CaCO_{3\,(s)} + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$ Reaction for HCL i) from synthesis process $H_2 + Cl_2 \rightarrow 2HCl$ ii)From salt & sulphuric acid $2Nacl + H_2SO_4 \rightarrow 2HCL + Na_2SO_4$	2 2	4
f)	Chlorine • PVC manufacturing • PCl_3 and PCl_5 manufacturing • HCl manufacturing • paper mills for bleaching the pulp • bleaching of textiles • sterilization of municipal water supplies	2	4

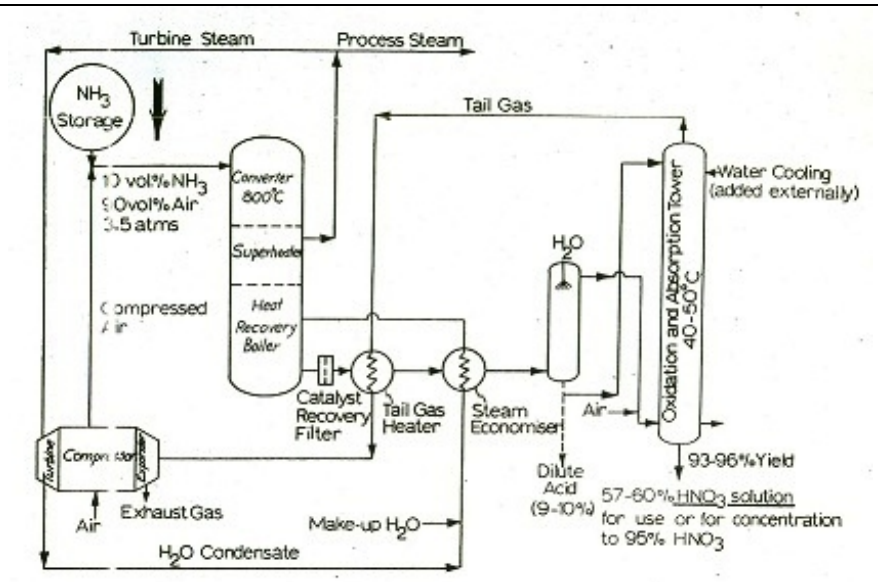
	Oxygen • High purity oxygen is used for welding &cutting operations • open hearth furnace • steel production • industrial oxidation process Nitrogen • It is used to provide protective atmosphere to prevent oxidation of metal. • It is used for nitrogen compounds .Liquid nitrogen is used for refrigerative cooling in transportation industry.	1 1	
Q5 a)	**Sulfuric acid production** $S + O_2 = SO_2$ $SO_2 + ½ O_2 = SO_3$ $SO_3 + H_2O = H_2SO_4$ Description: Molten sulfur is oxidized with air in burner. Heat produced is recovered in waste heat boiler. Gas stream containing 7-10% SO_2 and 11-14 % O_2 preheated by convertor gas and send to first stage reactor . The reacted temp is 500-600^o C contained 30% catalyst and convert about 80% of SO_2. The converter product exchange heat at 300^{o}C and sent to second stage where yield is increased to 97% at 400-450^{o}C .The product gases are cooled to 150^{o}C by water and air heat exchanger and absorbed in oleum fed at rate to allowed not over 1% rise in acid strength. Final scrubbing is done with lower strength.	Rection-2 Diagram-3 Process-3	8

			
b)	**Production of hydrogen** Hydrogen from natural gas: Natural gas mainly methane is converted into hydrogen by mixing it with steam and passing the mixture over a catalyst nickel with alumina at 800-900^oC . The natural gas is passes through a saturating tower saturated with water vap. At the exit steam is added and the steam gas mixture directed to the heat exchanger at 500-600^oC .The gas mixture goes to mixture chamber where O_2 is introduced .This is entered at 450^0C to methane convertor , After adding the catalyst at 800^o C passed to humidifier where water vap. is added to reduce the temp. upto 750^o C .The gases passes through heat exchanger which gives a heat to the gas going to the mixture chamber converted at 400^o c and entered at carbon monoxide convertor. The gases are send to waste heat boiler, water tower spray and	Rection-1 Diagram-3 Process-4	4

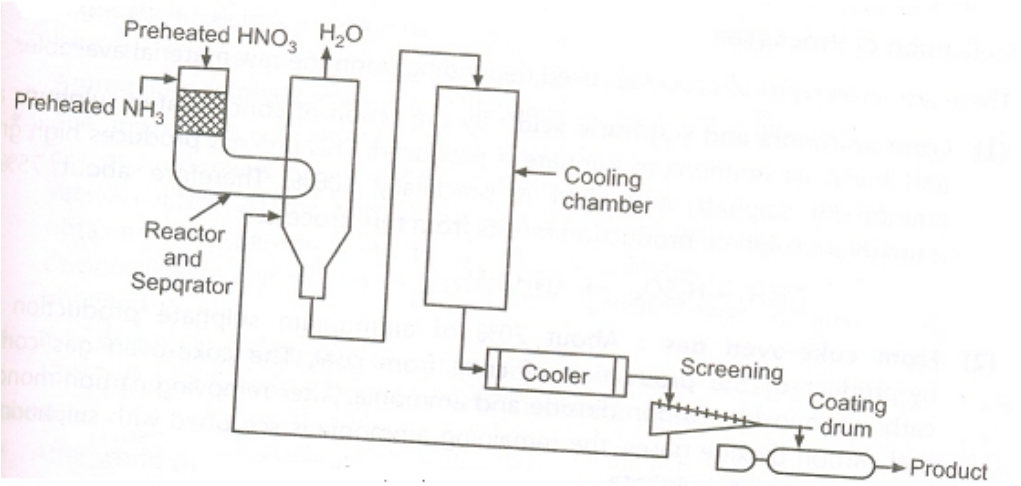
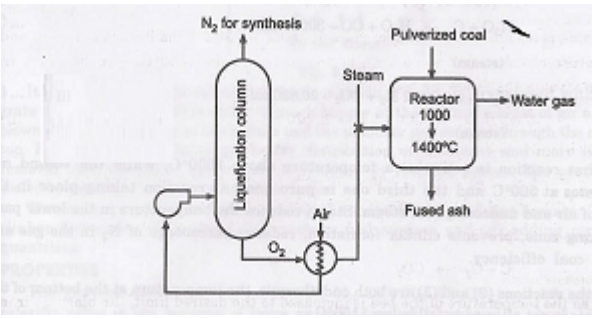
cooler for removal of CO_2.

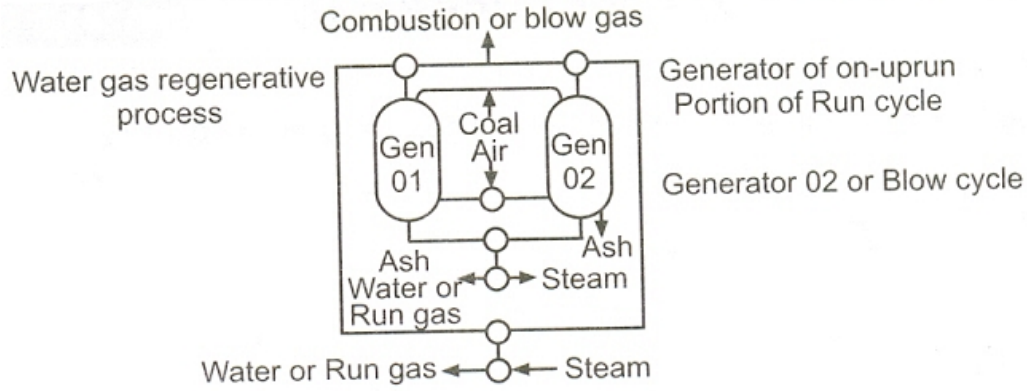
$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$



c)	 Raw material Ammonia, air, water Reaction $4NH_3+5O_2 = 4NO +6H_2O$ $2NO+O_2 = 2NO_2$ $3NO_2+H_2O=2HNO_3+NO$ Ammonia and air are compressed and send to the catalytic converter. Ammonia is oxidized and converted into nitric oxide. Large heat is evolved which can de utilized to run turbine by producing steam and gas expander. Both are connected to the compressor. 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	Rection-2 Diagram-3 Process-3	8

	heating.		
Q6 a)	**Uses** i)**Acetylene:** • For welding and gas cutting due to it's highest temp. with O_2 . o For Mfg. of Vinyl chloride, o Neoprene, o Vinyl acetate , ii)**Water gas** : as fuel gas and as a source of industrial hydrogen .	2 2	4
b)	**Dry process for Portland cement:** The dry process is used when the raw material is either cement rock or blast furnace slag. The calcareous raw material and argillaceous are crushed separately by jaw or roller crusher(primary crushing) The material is dumped to huge bins The raw material is mixed by automatic weighing machines then it is fed to grinding mill, pulverized then to rotary kiln . Rotary kiln is 50-80m long and having three times diameter kiln is inclined and rotate one revolution per minute. Temperature maintained in the kiln is 1400-1500^{o} C . The product obtained is known as clinker removed from the lower end of the kiln then ground with 2% gypsum to obtained Portland cement.	4	4
c)	**Ammonium nitrate**	4	4

			
d)	**Water gas** Reactions- $C+ O_2 \rightarrow CO_2$ $C+H_2O \rightarrow CO+H_2$  Process Description- Nitrogen is separated from air by liquefaction process. The correct ratio of steam oxygen and coal is added to reactor to yield water gas as shown in the above flow dig. As continuous supply of all reactants are taking place at temperature of 1000 to 1400 ^oC product is formed and fused ash is removed continuously. OR **By regenerative process**	1 3 marks for any one process	4

	In this process two gas generators are used. While first generator is producing water gas other is in regeneration process. It is called as blow period. As both generators are used alternatively continuous supply of gas is available.  		
e)	**Physicochemical principle used in ammonia process** 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. We'll use the the equation for synthesizing ammonia to explore the factors which affect chemical equilibrium and apply Le Chatelier's principle: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + Heat$ Reaction is exothermic. That means that heat is given off as ammonia is synthesized in the forward reaction. So the reverse equation is endothermic and heat is absorbed when ammonia is decomposed. As a result, according to Le Chatelier's principle, if you add heat to a balanced equation the system will want to shift in the direction that removes heat from the system (endothermic) which is the reverse direction. So by increasing the temperature you would remove ammonia, it would decompose. **Urea process**	2	4

	The equilibrium ratio and rate of synthesis depend upon pressure, temperature and chemical composition. As vapor pressure of ammonium carbamate is very high and moreover the overall result of synthesis reaction is decrease in gas volume. , the equilibrium yield grows with pressure. The process rate and actual yield also grow rapidly with pressure due to increase in process driving force i.e. concentration of gas phase reactant.	2	
f)	**Phosphoric acid** : $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow H_3PO_4 + 3(CaSO_4.2H_2O)$ Side reaction: $CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO.2H_2O$ $6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$ **Triple super phosphate**: $[Ca_3(PO_4)_2]3CaF_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)2H_2O$	2 2	4