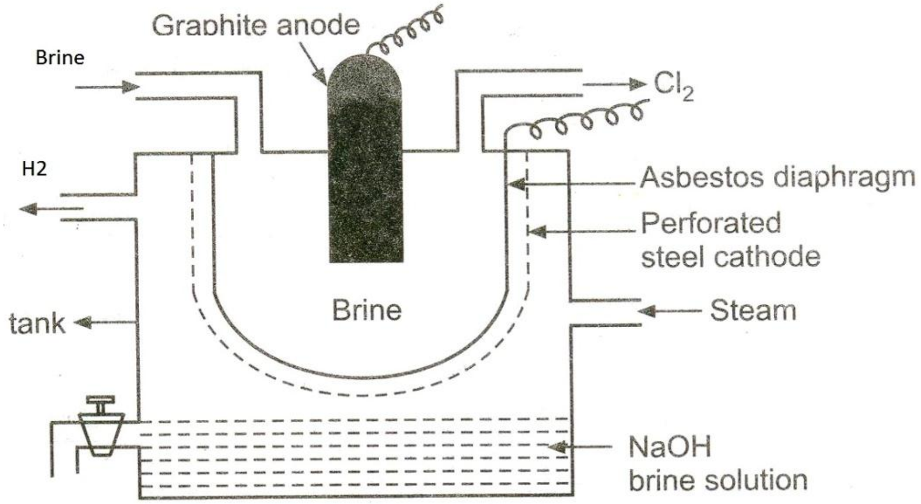
Summer-17 EXAMINATION
Model Answer

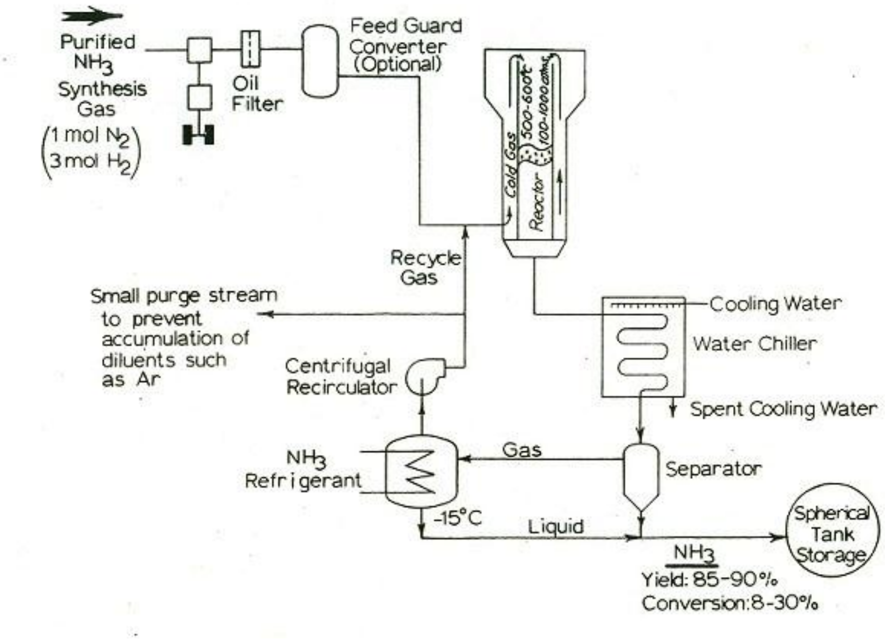
Important Instructions to examiners:

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 one quivalent concept.

Q No.	Answer	Marks
1A	**Attempt any six**	**12**
a)	Air Drying: Air is dried by passing air drying tower where sulfuric acid is used as hygroscopic agent to remove moisture from air in sulfuric acid plant.	2
b)	**Uses of sulfuric acid (any two)** a) For manufacturing of Fertilizers b) Oil refining c) Metal processing d) Manufacturing of Rayon e) In Lead acid batteries f) Detergent manufacturing	2
c)	If SO_3 dissolved directly in water, then a large amount of heat is evolved. This heat gives a dense form of minute particles of H_2SO_4. These particles do not easily condense down.	2
d)	**Reactions in sulfuric acid manufacturing** $S + O_2 = SO_2$ $SO_2 + ½ O_2 = SO_3$ $SO_3 + H_2O = H_2SO_4$	2
e)	Heat available from sulfur oxidation reaction is recovered in waste heat boiler to produce steam in sulfuric acid plant.	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)	**Calcination:** is a thermal treatment process in presence of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The	2

	calcination process normally takes place at temperatures below the melting point of the product materials. For example, in limestone calcination, a decomposition process, the chemical reaction is $CaCO_3 \rightarrow CaO + CO_2(g)$	
h)	**Types of cement** 1) Portland cement 2) Pozzolanic cement 3) Natural cement 4) High alumina cement 5) Super sulphate cement 6) Quick setting cement	½ mark each for any four
1B	**Attempt any two**	**8**
a)	**Water Gas (continuous process):** Raw materials: Steam, coal, oxygen Reactions: $C + O_2 \longrightarrow CO_2$ $C + H_2O \longrightarrow CO + H_2$	2
	Process description: This process was invented in 1940 by Germans. This process is based on use of tonnage or low purity grade oxygen made by air separation procedure. The correct ratio of steam, oxygen and coal is added to the reactor to yield a self-sustaining reaction of approximately zero heat release. Subsequent innovations allow for ash content >30% so Indian coal can be used	2

<table>
<tr><td></td><td>in this process</td><td></td></tr>
<tr><td>b)</td><td>**Diaphragm cell**

</td><td>4</td></tr>
<tr><td>c)</td><td>**Hardening of cement:** Hardening is a process of crystallization. Crystals form (after a certain length of time which is known as the initial set time) and interlock with each other. Concrete is completely fluid before the cement sets, and then progressively hardens. The cement and water mixture that has crystallized in this way encloses the aggregate particles and produces a dense material.
The term **Setting** is used to describe the stiffening of the cement paste. Setting of cement refers to changes of cement paste from a fluid to rigid state. Setting differs from Hardening of cement.</td><td>2
2</td></tr>
<tr><td>**2**</td><td>**Attempt any two**</td><td>**16**</td></tr>
<tr><td>a)</td><td>**Ammonia**
Raw Material:
Synthesis gas, Air
Reaction :
$N_2+3H_2=2NH_3$</td><td>1</td></tr>
</table>

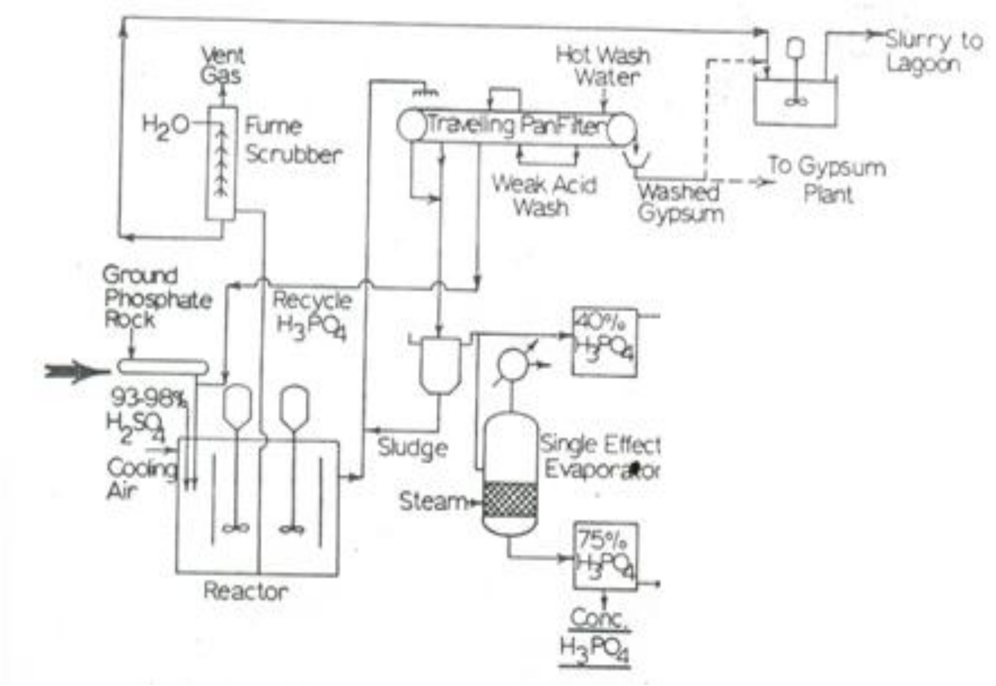
	Process Ammonia synthesis gas is compressed to the operating pressure. It is send through a filter to remove compression oil and additionally through a high temperature guard converter to convert carbon monoxide, carbon dioxide to methane and remove traces of water vap, hydrogen sulfide. This is done 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.	4
		3

b)

Phosphoric acid

Reaction:

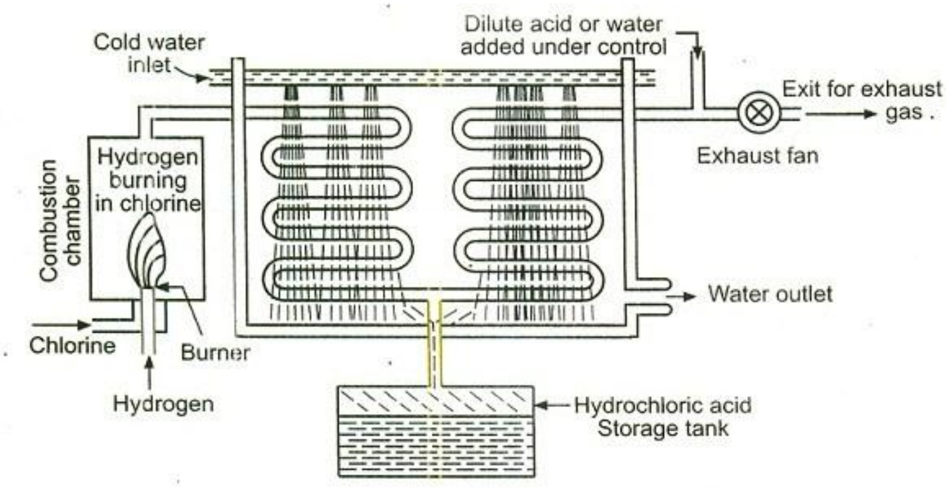
$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4.2H_2O)$ 2



3

Process:

Phosphate rock is ground and fed to chute where a recycle stream of weak phosphoric acid washes into reaction tank. Strong sulfuric acid is fed to the reactor. Around 98% conversion takes in 4-6 hours. Heat of reaction is controlled by using cooling air. Gypsum –Acid slurry is fed to travelling pan filter where 40% acid is removed and cake is washed with water. Filtrate is return to the reactor. The gypsum obtained is dried and send for paint or cement manufacturing. Dilute acid obtained can be concentrated in single effect evaporator.

		3
c)	**Synthesis process for HCl** 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. $$H_2 + Cl_2 \longrightarrow 2\ HCl$$  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 The gas is passed through a cooler cooled by water spray and then through absorber through which water flows down in controlled quantities.	1 4 3

	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. An exhaust fan on the extreme right pumps out the waste gases which escape in the atmosphere.	
3	**Attempt any four**	**16**
a)	Yellow phosphorous kept under water Because when exposed to air it ignites spontaneously. **Yellow to Red phosphorous** Yellow phosphorus is converted into red phosphorous in covered retorts containing a reflux condenser to retain any evolved phosphorous vapors. The vessel is gradually heated and the contents melt and slowly change to red phosphorus. This mass is solidified when approximately 70% has been converted. Heat control is required as reaction is exothermic.	1 3
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.	4
c)	**Difference between wet process and electric furnace process:**	1 mark

Wet Process	Electric furnace process
1. High grade phosphate rock is used	Low grade phosphate rock is used
2. Cost of plant is low	Cost of plant is high
3. Comparatively low pure acid is obtained	Highly pure acid can be obtained
4. This process doesn't get affected by rate of electricity	This process is economical in those places where electricity is quite cheap
5. Phosphate rock is finely ground and prepulped in the mixing tank with cooled recycled H3PO4 from the slurry cooler	Phosphate rock ground and sized. Rock and sand mixed with coke, sintered and introduced into electric furnace
6. Reaction temperature is comparatively low	Reaction temperature is high

each for any 4

d) **Cell notation for diaphragm cell** 2

Anode Cathode

$\uparrow Cl_2, C \mid NaCl\,(aq) \qquad NaOH\,(aq) \mid Fe, H_2 \uparrow$

Cell reaction :

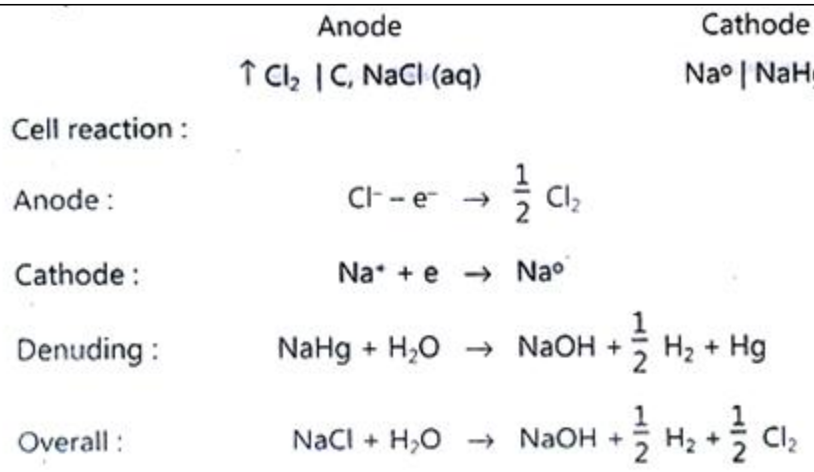
Anode : $Cl^- - e^- \rightarrow \frac{1}{2} Cl_2$

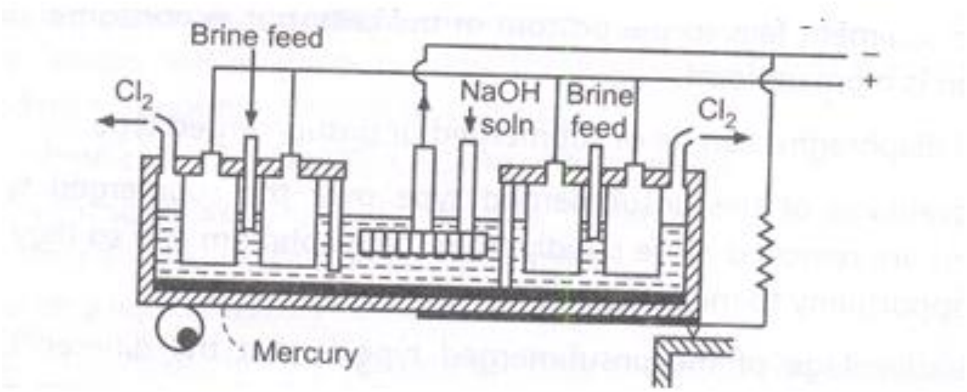
Cathode : $Na^+ + H_2O + e \rightarrow Na^+ + OH^- + \frac{1}{2} H_2$

Overall : $NaCl + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + \frac{1}{2} Cl_2$

Cell notation for mercury cell

2

	 Anode Cathode $\uparrow Cl_2$ | C, NaCl (aq) Na° | NaHg Cell reaction : Anode : $Cl^- - e^- \rightarrow \frac{1}{2} Cl_2$ Cathode : $Na^+ + e \rightarrow Na^o$ Denuding : $NaHg + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + Hg$ Overall : $NaCl + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + \frac{1}{2} Cl_2$	
e)	**Ammonisation tower**: Ammonia is absorbed in ammoniation tower in purified brine. Some amount of CO_2 is also absorbed here. **Carbonating tower:** In the second step, ammoniated brine is allowed to trickle down a carbonating tower known as solvay tower. This tower is also fitted with baffle plates. Here brine is mixed with carbon dioxide gas, produced by heating lime stone in a separate chamber called "kiln".The baffle plates ensure the flow of solution and breaks up carbon dioxide into small bubbles to produce good conditions for reaction.	2 2
f)	**Mercury Cell**	2

	 The cell contains a large angular trough with a layer of mercury at the bottom and divided into two compartments in the SLATE PARTITION not touching the bottom. Thus Hg in one compartment can flow into the other but any solution in one compartment cannot flow into other. The left hand compartment is fitted with graphite anode dipping in brine whereas the right hand compartment is fitted with iron cathodes dipping in dilute NaOH solution. Hg acts as an intermediate electrode by induction, cathode,being on the left-hand side anode on the right. The cell is kept rocking with the help of an eccentric wheel. On passing electric current , chlorine is liberated at the anode in the left hand compartment & is led out through an exit at the top. Solution ts liberated at mercury cathode & forms an amalgam with it. Sodium amalgam passes into right hand compartment due to the rocking motion & reacts with water there to form NaOH & H2 which is allowed to escape through the exit at the top. Caustic soda is removed periodically & water added. The conc. Solution is evaporated to get fused caustic soda.	2
4	**Attempt any four**	**16**

a)	**Manufacturing Process of caustic soda and chlorine** Purified saturated brine is heated and electrolyzed in a diaphragm cell. The cell operating at 45-55% decomposition efficiency, discharges 10-12% solution of caustic soda with about equal concentration of NaCl. Multiple effect evaporator concentrates the cell liquor to 50% NaOH solution The opted salt is separated, centrifuged, washed, then slurried with treated brine. Salt saturator overflow is 50% caustic soda product. This further brine is again treated the mercury cell and the yield from this section is 70% of caustic soda. Chlorine is collected, dried, compressed and cooled upto-30^{o}C and collected as liquid chlorine	4
b)	**Phosphorous trichloride** is prepared by direct reunion of phosphorus and chlorine, the reaction being exothermic and spontaneous. $P_4 + 6Cl_2 \longrightarrow 4 PCl_3$ 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. It is analyzed for elemental phosphorus. Based on this analysis, additional chlorine is introduced to remove traces of unreacted phosphorus. **Phosphorus pentachloride** Phosphorus pentachloride is prepared in two stages. 1) Preparation of phosphorous trichloride 2) Chlorination of Phosphorus trichloride. Phosphorous trichloride is prepared by direct reunion of phosphorus and chlorine, the reaction being exothermic and spontaneous. $P_4 + 6Cl_2 \longrightarrow 4 PCl_3$ 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	2 2

still for distillation and finally for storage.

It is analyzed for elemental phosphorus. Based on this analysis, additional chlorine is introduced to remove traces of unreacted phosphorus.

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.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

c) **Single and triple super phospahte**

2

Parameter	**Single Superphospahte**	**Triple Superphosphate**
Raw material	Phosphate rock, sulfuric acid	Phosphate rock, phosphoric acid
Uses	Fertiliser	Fertiliser
Process	It requires 24 hours storgae	It can directly granulated after reaction.

Single super phosphate

$$[Ca_3(PO_4)_2]_3CaF_2 + 7H_2SO_4 = 3CaH_4(PO_4)_2 7CaSO_4 + 2HF$$

2

Triple super phosphate

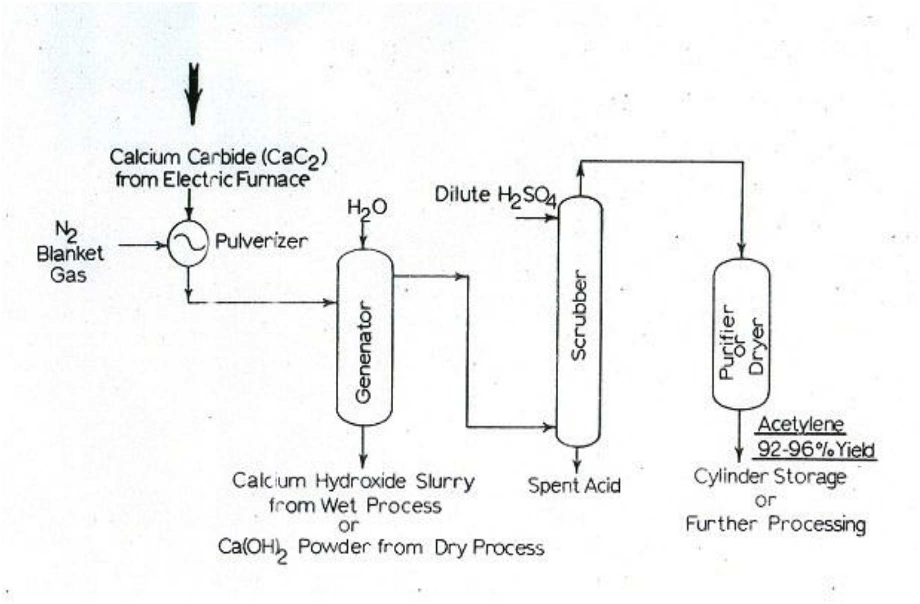
$$CaF_2.3Ca_3(PO_4)_2 + 14H_3PO_4 = 10Ca(H_2PO_4)_2 + 2HF$$

d) **Uses of Chlorine(any 2)**

2

1. Pulp and Paper
2. PVC
3. Chlorinated paraffin wax
4. Pesticides and insecticides
5. Water treatment
6. Rayon grade wood pulp

Uses of HCl (any 2)

	1.HCl is widely used in the petroleum, 2.Used in chemical industry, 3.Used in food industry 4.Used in metal industry. 5.It increases production of oil wells by increasing permeability of oil-bearing formation. 6.It is also finding use in steel packing in preference to sulfuric acid.	2
e)	**Acetylene PFD**  OR Acetylene from methane and ethane	4

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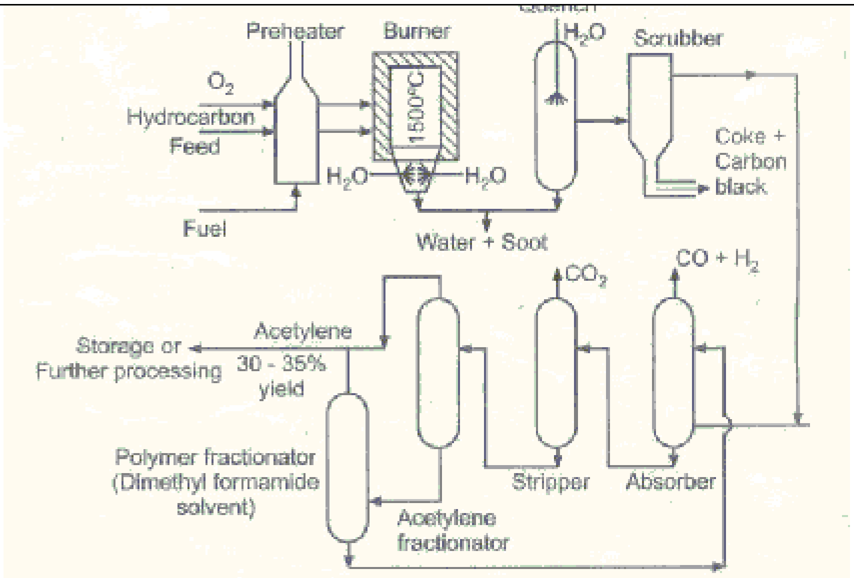
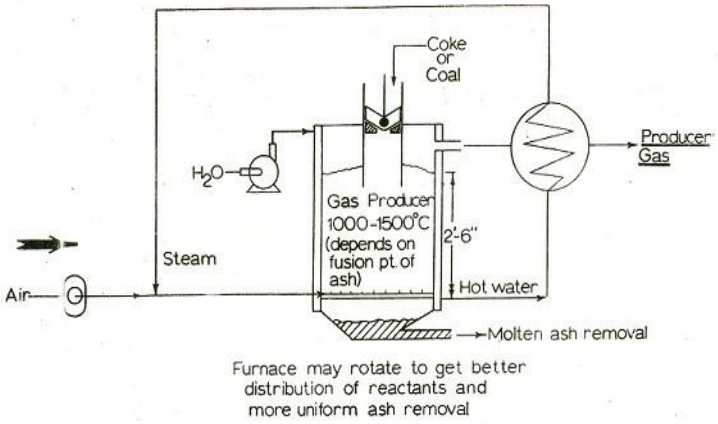
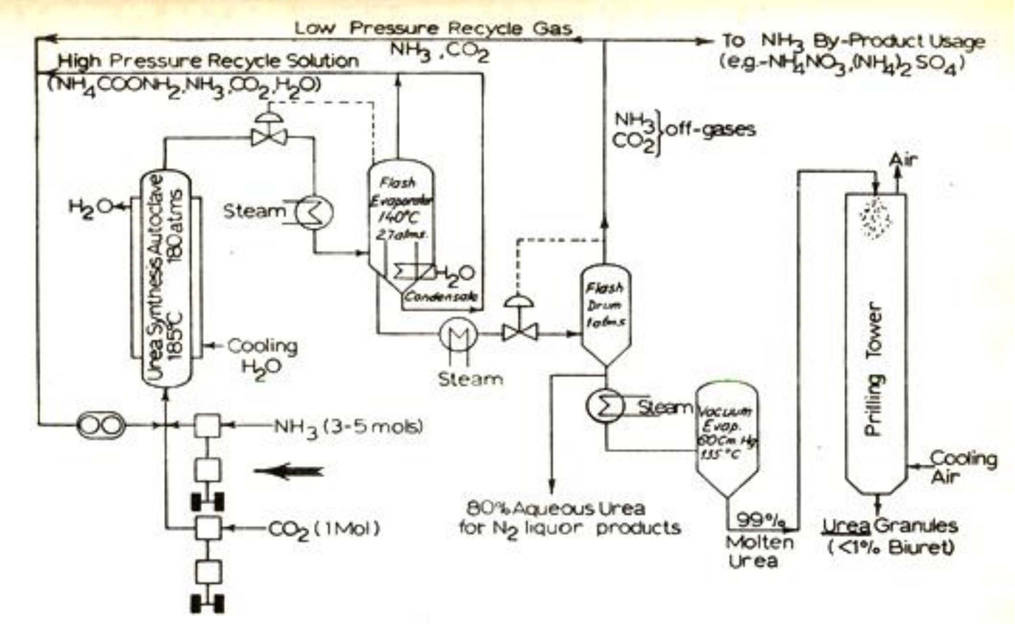
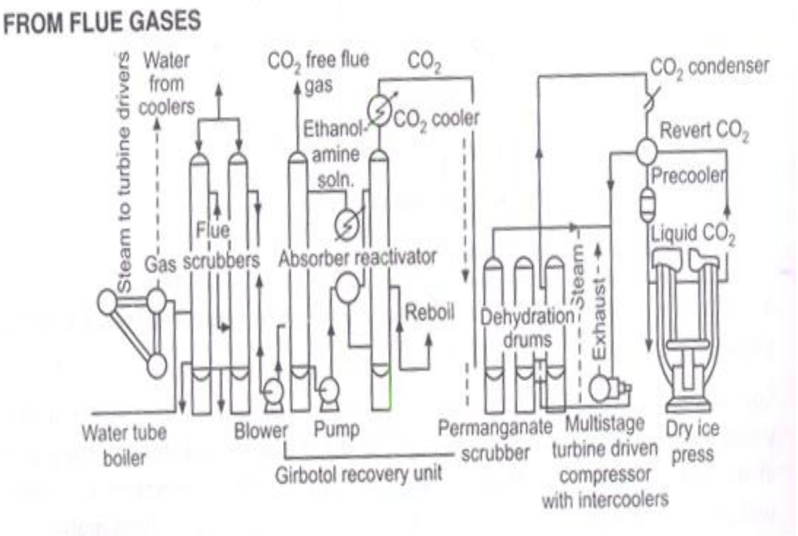
<tr><td></td><td>
</td><td></td></tr>
<tr><td>f)</td><td>**Producer gas**, mixture of flammable gases (principally carbon monoxide and hydrogen) and nonflammable gases (mainly nitrogen and carbon dioxide) made by the partial combustion of carbonaceous substances, usually coal, in an atmosphere of air and steam.

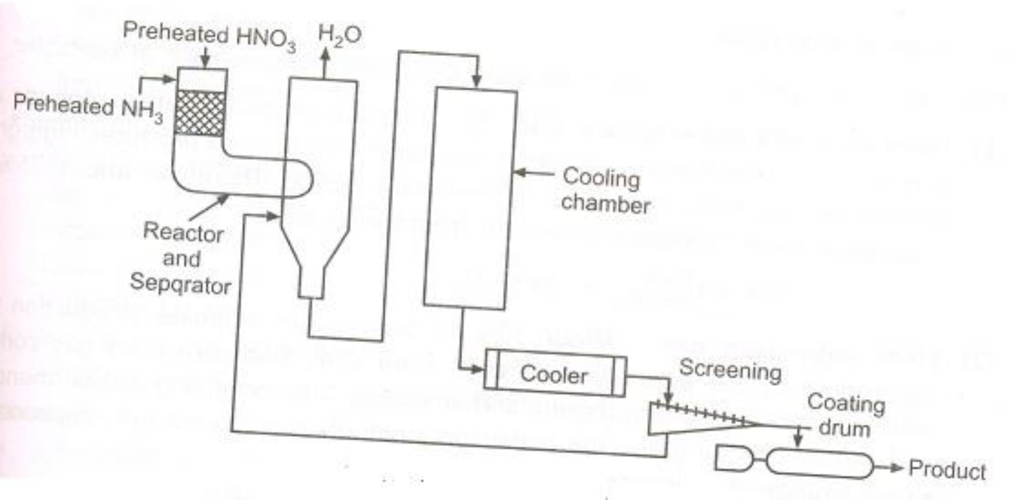


Steam and air mixture injected in the bottom of water cooled jacket steel</td><td>2
2</td></tr>
</table>

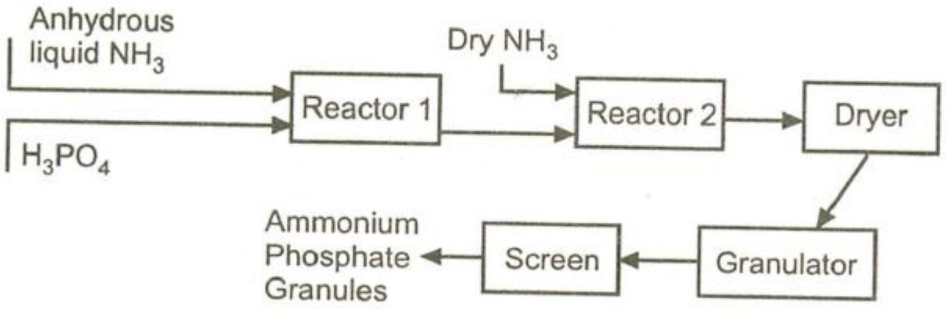
	furnace equipped with rotating grate to remove fusible ash as shown in figure. Solid fuel is added from hopper valve on the top. Producer gas is cooled by passing through waste heat boiler.	
5	**Attempt any two**	**16**
a)	**Urea by Montecatini Process:** Chemical reaction: i) CO_2(carbon dioxide) + $2NH_3$ (ammonia) → $NH_4.COO.NH_2$ (ammonium carbamate) ii) $NH_4.COO.NH_2$ (ammonium carbamate) → $NH_2.CO.NH_2$ (urea) + H_2O iii) Undesirable side reaction : $NH_2.CO.NH_2$ (urea) → $NH_2.CO.NH.CO.NH_2$ (biuret) + NH_3 Flow diagram :  Process description : Ammonia and carbon dioxide are compressed separately and added to the high	Rection -1 Diagram-4 Process -3

	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)	**Manufacturing of CO_2 by flue gas: Process description**: Fflue gases result from burning carbonaceous material are cooled, purified and washed by passing through two water scrubbers contain Na_2Co_3. $(Na_2Co_3 + CO_2 + H_2O \rightarrow 2NaHCO_3)$	4

	 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.	4
c)	**Ammonium Nitrate** **Reaction:** $NH_3 + HNO_3 \text{----}\rightarrow NH_4NO_3 \quad \Delta H= -20\text{ kcal}$ **Process description** – In the Stengel process, vapours of ammonia & nitric acid are mixed in a stainless steel reactor. The reaction is exothermic & hence heat is given out. The mixture of steam & molten ammonium nitrate is fed to cyclone type separator. The molten mass is solidified on the water cooled stainless steel belts .Then material is passed to a grinder where is the material is crushed dried and ground to flake size then, ammonium nitrate flakes are	2 3

	coated with clay.  	3
6	**Attempt any four**	**16**
a)	**Acetylene from CaC_2** Raw materials: lime stone, coke, water Chemical reactions: $CaO + 3C \rightarrow CaC_2 + CO$ $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + CH{\equiv}CH$ $CaCO_3 \longrightarrow CaO + CO_2$ $2CO + O_2 \rightarrow 2\,CO_2$ Process Description: Calcium carbide is produced by heating lime and coke in an electric furnace at 2100 ˚C . Molten CaC_2 is solidified and cooled and ground under nitrogen In the wet process the pulverized carbide is fed through a gas tight hopper to a C2H2 generator in which the quality of water used is sufficient to discharge $Ca(OH)_2$. The carbide is fed to water at a measured rate until exhausted. Calcium hydroxide slurry containing 90% water is discharged. The gas is passes through a scrubber to remove impurities like NH_3, sulphides, phosgene	1 1 2

	and finally through a purifier containing iron oxide and alumina or silica gel. The temperature in the gas generator is kept below 90˚C and a pressure of 2 atm. In a dry process equal weights of the quantities H_2O and CaC_2 are used in the generator to eliminate waste disposal problem of lime slurry. The heat of reaction is largely dissipated by water vaporization leaving by product lime in dry state. The dry process is more dangerous because of the temperature control in the generator. Acetylene polymerizes at 250˚C and above and decomposes violently at 650˚C . Hence temperature is maintained below 150˚C and 30 cm of water pressure.	
b)	**Rotary Kiln** Cement kilns are used for the pyroprocessing stage of manufacture of Portland and other types of hydraulic cement, in which calcium carbonate reacts with silica-bearing minerals to form a mixture of calcium silicates. The kiln is the heart of the plant – what an entire cement plant is dimensioned around, and where most of the final chemical reactions take place. **Pollution control in cement plant** The cement manufacturing process generates lot of dust, which is captured and recycled to the process. The sources of dust emission include clinker cooler, crushers, grinders and material-handling equipments.Several mechanical equipments are used in cement manufacturing plant to control / collect dust. These are 1. Dust collector - A dust collector (bag house) is a typically low strength enclosure that separates dust from a gas stream by passing the gas through a media filter. The dust is collected on either the inside or the	2 2

	outside of the filter. 2. Cyclone - Dust laden gas enters the chamber from a tangential direction at the outer wall of the device, forming a vortex as it swirls within the chamber. The larger articulates, because of their greater inertia, move outward and are forced against the chamber wall.Cyclones are typically used as pre-cleaners and are followed by more efficient air-cleaning equipment such as electrostatic precipitators and bag houses. 3. Electrostatic Precipitator - In an electrostatic precipitator, particles suspended in the air stream are given an electric charge as they enter the unit and are then removed by the influence of an electric field.	
c)	**Ammonium Phosphate** 	4
d)	**LINDES PROCESS:** 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. During expansion work is not done against external pressure but against	1

<table>
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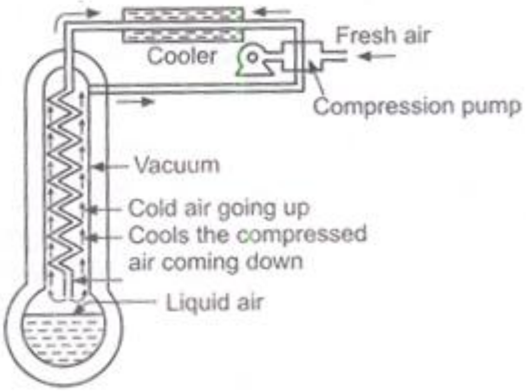
<td>internal attraction force between the molecules.
Flow diagram:


Process description:
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 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.</td>
<td>2
1</td>
</tr>
<tr>
<td>e)</td>
<td>Difference between yellow and red phosphorous
<table>
<tr><th>Yellow phosphorus</th><th>Red phosphorus</th></tr>
<tr><td>Melting point = 44.1 ^{o}C</td><td>Melting point = 593 ^{o}C</td></tr>
<tr><td>Ignite spontaneously in air</td><td>Higher resistance to oxidation</td></tr>
<tr><td>Highly toxic</td><td>Comparatively Less toxic</td></tr>
<tr><td>Lesser denser</td><td>Higher Denser</td></tr>
</table>
</td>
<td>One mark each for any four</td>
</tr>
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	Used for the production of P_2O_5 and phosphoric acid	Used in safety matches, tracer bullets, incendiary devices, pesticides, pyrotechnic devices

f)	**Mixed fertiliser** typically refers to a fertiliser containing two or more of the elements of nitrogen, phosphorus and potassium (NPK) which are essential for promoting plant growth and high crop yields. They are obtained by thoroughly mixing the ingredients either manually or mechanically.NPK mixture fertilisers are formulated and recommended by agricultural scientists to enhance the output of crops by giving it specific and exclusive blend of plant nutrients. They are slow releasing by nature and remain in the field for a long time. They are tailor made as per the soil and are crop specific. Mixed fertilisers are important because: • Use of mixed fertilisers results in reduction of labour costs as applying a mixture consumes lesser time as compared to applying the components separately. • Micro nutrients which help in increasing soil organic matter content are applied in small amounts to the soil. They can be incorporated in fertiliser mixtures. This facilitates uniform soil application of plant nutrients. • If a proper mixture suits a particular soil type and crop, the use of a fertiliser mixture leads to balanced manuring. It results in higher crop yield. • Being in granulated form, mixtures have a better physical condition and hence their application is easier. • Residual acidity of of fertilisers can be controlled by using neutralisers	4

	in the mixture.	