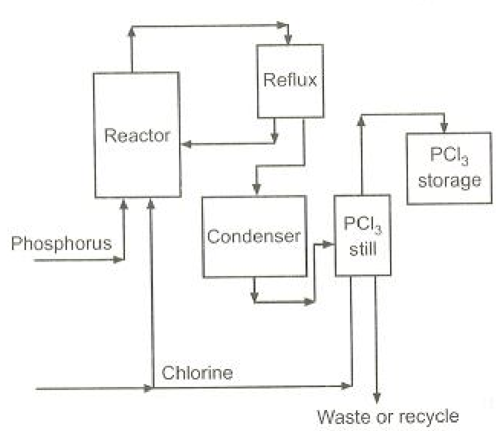
SUMMER-14 EXAMINATION

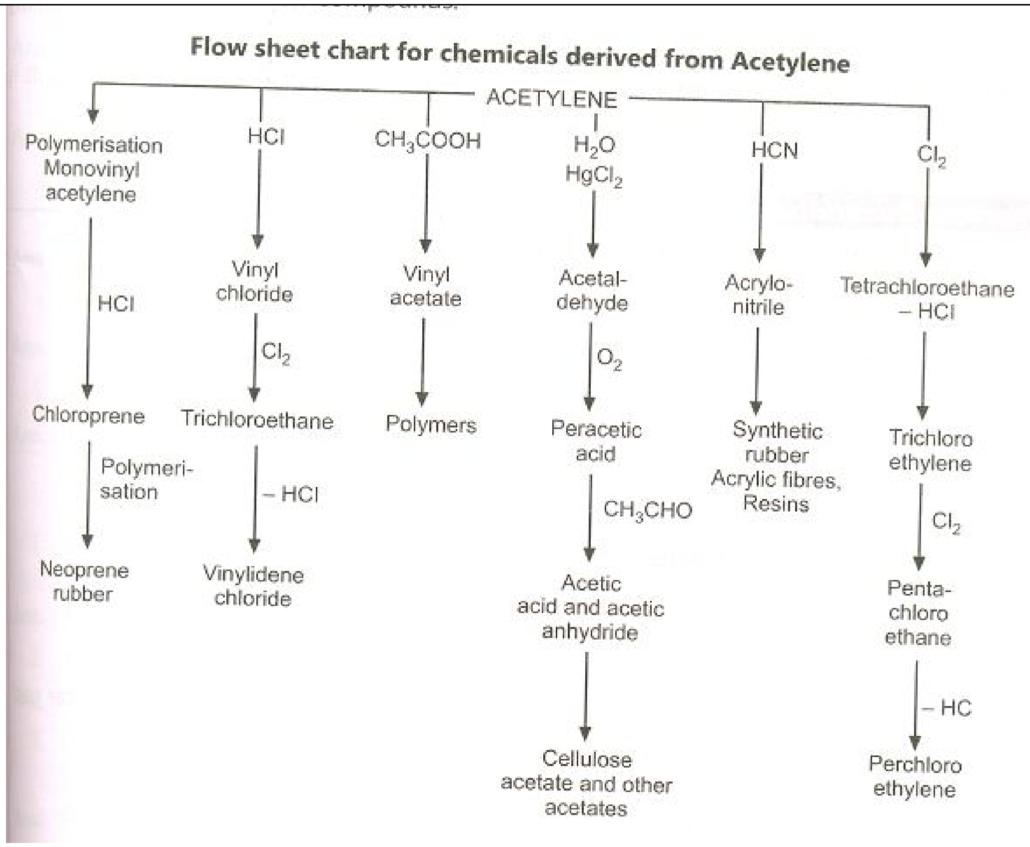
Model Answer

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 on equivalent concept.

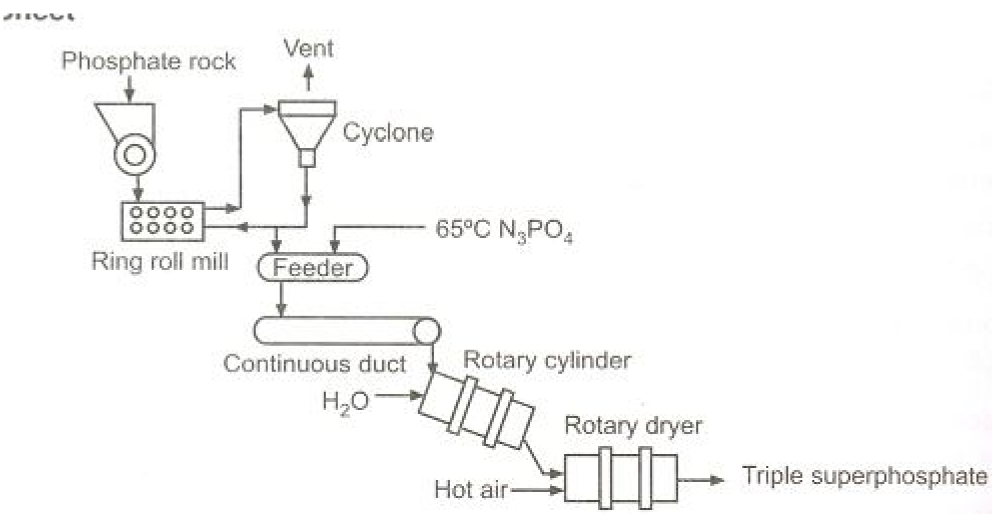
Q No.	Answer	marks	Total marks
1A-a	**Reactions in sulfuric acid manufacturing** $S + O_2 = SO_2$ $SO_2 + ½ O_2 = SO_3$ $SO_3 + H_2O = H_2SO_4$ In actual process SO_3 is not directly absorbed in water to form sulfuric acid but in conc. sulfuric acid to form oleum.	2	2
1A-b	**NaOH from brine** $NaCl + H_2O = NaOH + ½ H_2 + ½ Cl_2$	2	2
1A-c	**Uses of phosphoric acid** 1) Fertilizer production 2) As a food additive 3) As a pH adjuster in cosmetics and skin-care product 4) As a dispersing agent in detergents and leather treatment.	One mark each for any two	2
1A-d	Question is not clear. If SPM means semi permeable membrane, it is not used in diaphragm cell. (If student attempt this question please give him full marks)	2	2
1A-e	**Types of cement** 1) Portland cement 2) Pozzolanic cement 3) Natural cement 4) High alumina cement 5) Super sulphate cement 6) Quick setting cement	Any four (half mark each)	2
1A-f	**10-20-30 fertilizer**	2	2

	Nitrogen, Phosphorus and Potassium are the 3 most abundant ingredients listed on every fertilizer label. They are always in this order, N-P-K. 10-20-30 means 10% available nitrogen, 20% available phosphorous and 30% available potassium.		
1A-g	**Properties of sulfuric acid** • Molecular weight: 98 • Melting point 10.5 ^oC • Boiling point 340^oC with decomposition • Completely miscible with water with large heat of solution • Formation of oleum with SO_3	Any four (half mark each)	2
1A-h	**Uses of ammonia** • For the production of nitric acid • For the production of ammonium nitrate • As a refrigerant • For the production of urea • For the production of ammonium sulphate • For the production of acrylonitrile	Any four (half mark each)	2
1B-a	**Flow sheet for Phosphorous Trichioride Manufacture :** 	3	4

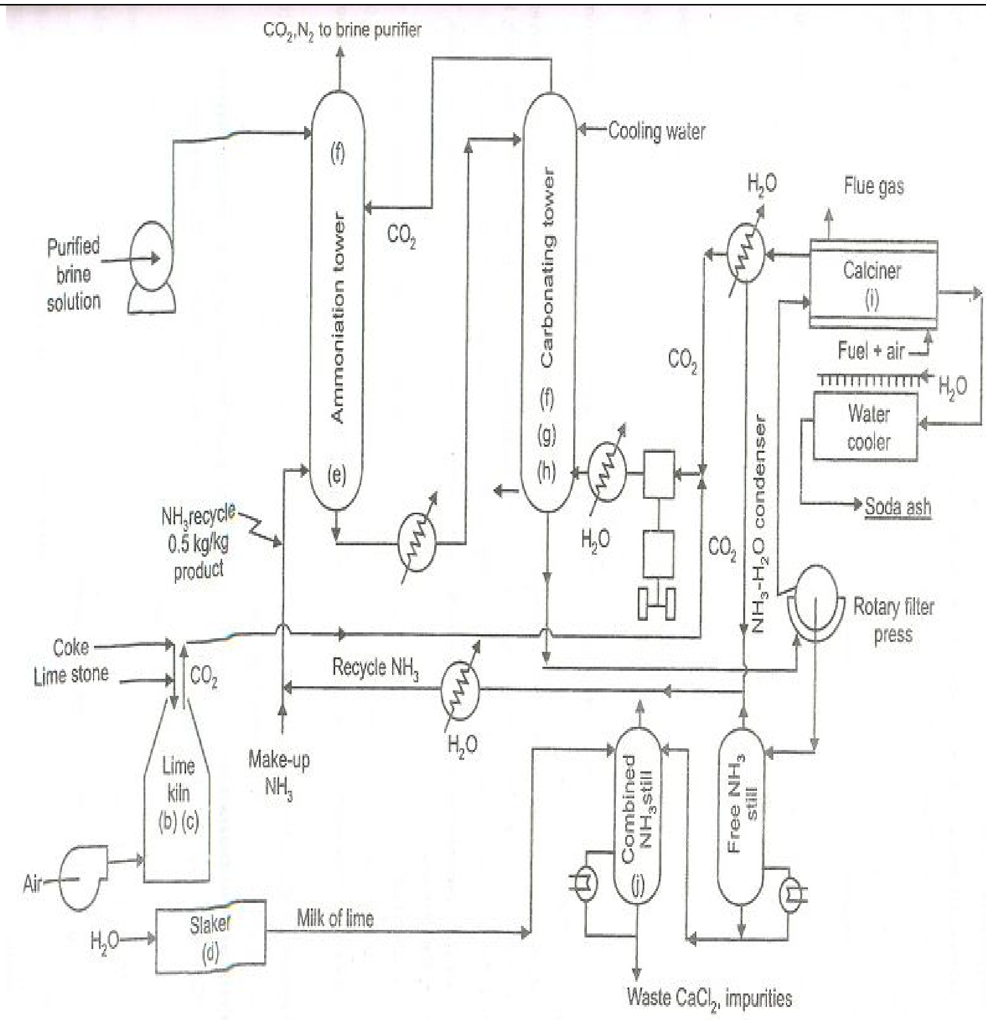
	Reaction : $P_4 + 6Cl_2 = 4PCl_3$	1	
1B-b		4	4
1-B-c	Raw material used for cement **As a source of calcium** • Lime stone • Calcite • Aragonite • Shale **As source of silicon** • Marl	4	4

	• Clay • Sand • Husk • Slag **As a source of aluminum** • Fly ash • Shale **As a source of iron** • Clay • Blast furnace slag		
2-a	The Haber process is the production of ammonia from a reaction between nitrogen and hydrogen, because of an iron substitute. This process is known for the commercial synthesis of ammonia. There is great abundance of nitrogen in the air when it is combined with hydrogen under extreme pressure and high temperature. This process is a great example of chemical equilibrium. **Le Chatelier's Principle** The Haber process incorporates Le Chatlier's Principle, which is a good example of equilibrium principles. Uses of Le Chatlier's Principle are reversible reactions and reversible reactions involving gases. Chemical equilibrium is when a reaction has no tendency to change the quantity of the products and reactants, so the reaction can go both ways. • Increasing the pressure and decreasing the temperature results in the higher yield of ammonia by causing a move of the reaction to the right. • Because there are more molecules on the left side than the right side, when the pressure is increased, the system adapts to the change by	6	8

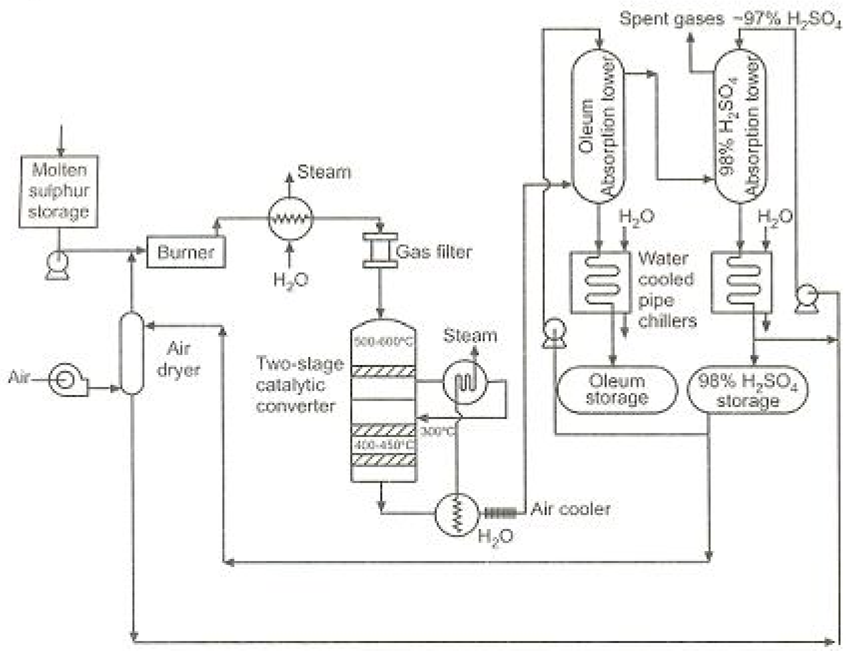
	moving the molecules left to right to decrease the overall pressure. • For temperature, it moves from right to left when the temperature drops is because of the process being exothermic, where heat is released. N_2 (g) + $3H_2$ (g) ↔ $2NH_3$ (g) • If the volume is decreased here, it has the same result as when the pressure is decreased. • If the pressure is increased, in this equation, it will move right because there are fewer gas molecules are produced going to the right then the backwards one. When you increase the pressure so that the least amount of molecules will be formed, there won't be an increase in collisions. However, if more gas molecules are formed, there will be an increase in collisions, thus moving the way that will produce the least amount of molecules. **Catalyst** A catalyst is used to speed up a reaction by lowering the activation energy. So, in this reaction, the iron catalyst is used to lower the activation energy so that the N_2 and H_2 can be easier to break down.	2	
2-b	**Triple super phosphate** $[Ca_3(PO_4)_2]_3.CaF_2 + 14H_3PO_4 \longrightarrow 10CaH_4(PO_4)_2 + 2HF$ The phosphate rock is ground in a jaw crusher. In a ring roll mill, it is sized by a sieve of 100 mesh. Then it is mixed with 50 to 54% phosphoric acid at about 65 to 70 ^{O}C. This mixture is run on a continuous belt where reaction takes place for about 15 mins. The process may also be run in a manner similar to that for	2 2	8

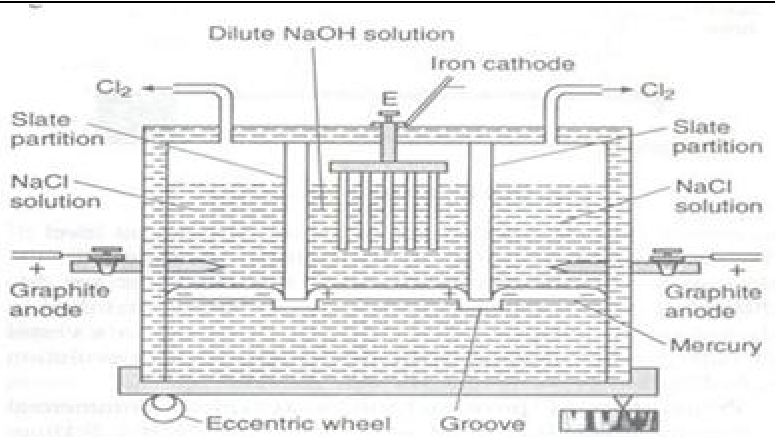
	normal superphosphate, simply following the reaction mass to cure. The product is granulated using a water spray and then dried & screened. The material is packed in plastic bags. 	4	
2-c	**Soda ash** Main reaction is $CaCO_3(s) + 2NaCl\ (aq) = Na_2CO_3 + CaCl_2$	2 marks for reaction 2 marks for discriptio n,4marks for flowsheet	8

	This reaction takes place in a number of steps : (b) $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$; (c) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$; (d) $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_2(aq)$; (e) $NH_{3(g)} + H_2O \rightleftharpoons NH_4^+ + OH^-$; (f) $CO_{2(g)} + OH^- \rightleftharpoons HCO_3^-$ (g) $CO_{2(g)} + H_2O \rightleftharpoons HCO_3^- + H^+$ (h) $Na^+ + Cl^- + NH_4^+ + HCO_3^- \longrightarrow NH_4^+Cl^-_{(aq)} + NaHCO_3\downarrow$ (i) $2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$; (j) $2NH_4Cl_{(aq)} + Ca(OH)_{2(s)} \longrightarrow 2NH_{3(g)} + CaCl_{2(aq)} + 2H_2O_{(l)}$ Initially brine solution is fed to the ammoniation tower followed by carbonating tower. Precipitate formed is filtered through rotary filter and then send to calciner where product soda ash formed. Reactions taking place in various equipments are shown above. Carbon dioxide required foe the process is obtained from calcinations of lime stone. Ammonia used is recovered in the process and reused.	4	

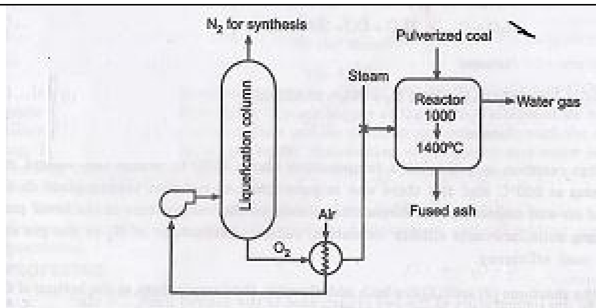


CO2,N2 to brine purifier
Cooling water
Purified brine solution
Ammoniation tower
Carbonating tower
CO2
(f)
(e)
(f)
(g)
(h)
H2O
Flue gas
Calciner
(i)
Fuel + air
H2O
Water cooler
Soda ash
NH3-H2O condenser
NH3 recycle 0.5 kg/kg product
H2O
CO2
Rotary filter press
Coke
Lime stone
Recycle NH3
Lime kiln
(b) (c)
Make-up NH3
H2O
Combined NH3 still
(j)
Free NH3 still
Air
H2O
Slaker
(d)
Milk of lime
Waste CaCl2, impurities

3-a	Contact process  	4	4
3-b	Uses of PCl_3- To prepare phosphorus oxychloride, pesticide, intermediates, phosphate & phosphite esters and salts, surfactants, organic acyl alkyl chlorides	1 mark for 1 use(any 4)	4
3-c	**Reactions in nitric acid manufacturing** 1) $4\ NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ 2) $4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$ 3) $2NO + O_2 \rightleftharpoons 2NO_2$ 4) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$	1 mark for each	4
3-d	**Mercury Cell** :	4	4



3-e	**Manufacturing of Gypsum** Gypsum rock is mined, crushed, dried and ground to a fine powder. The powder is "calcined" to drive off the remaining chemically combined water. This produces a product commonly called "plaster of Paris" or "stucco." The calcined gypsum is mixed with water and other ingredients to form a slurry which is fed between two continuous rolls of paper. As the paper slurry sandwich moves down the conveyor line, the gypsum rehydrates and returns to its original rock state. The board is cut to the desired length and dried further before shipping	4	4
3-f	**Water gas by continuous process** Reactions- $C + O_2 \rightarrow CO_2$ $C + H_2O \rightarrow CO + H_2$	2	4

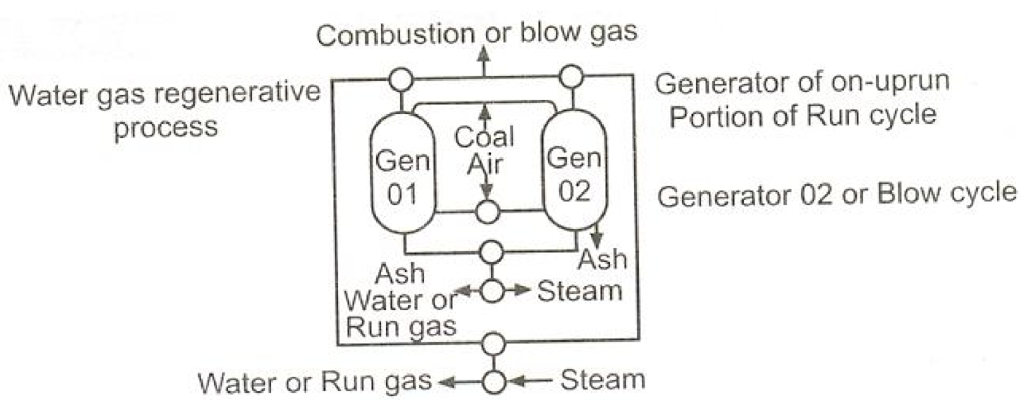


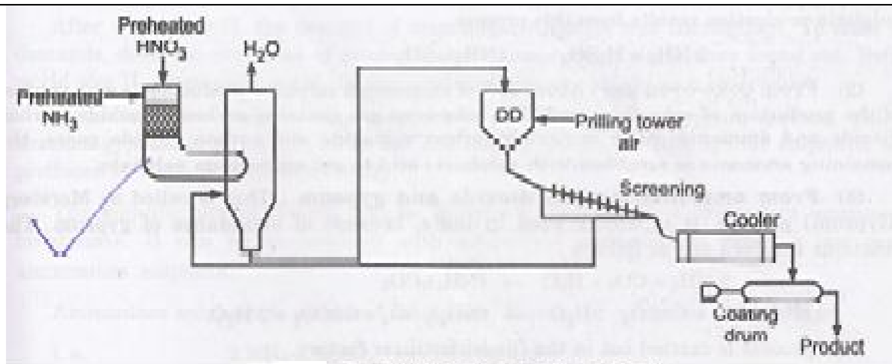
Process Description- Nitrogen is separated from air by liquefaction process. The correct ratio of steam oxygen and coal is added to reactor to yield water gas as shown in the above flow dig. As continuous supply of all reactants are taking place at temperature of 1000 to 1400 ^{o}C product is formed and fused ash is removed continuously. — 2

OR

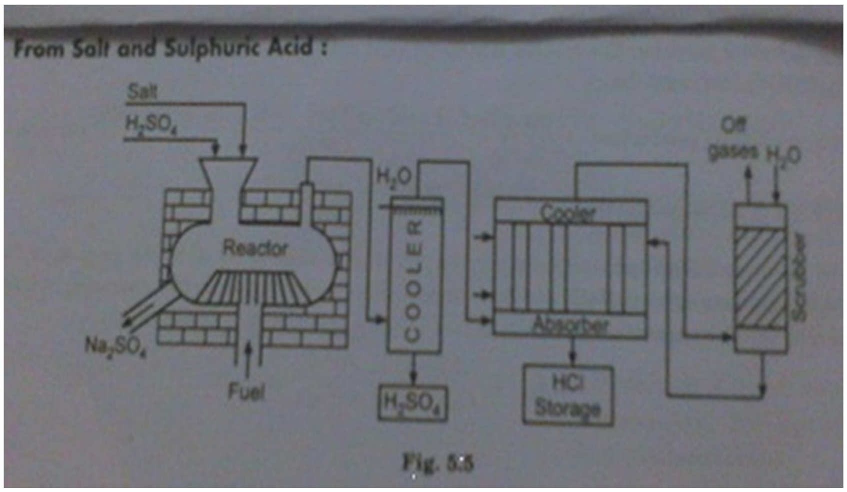
By regenerative process

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.

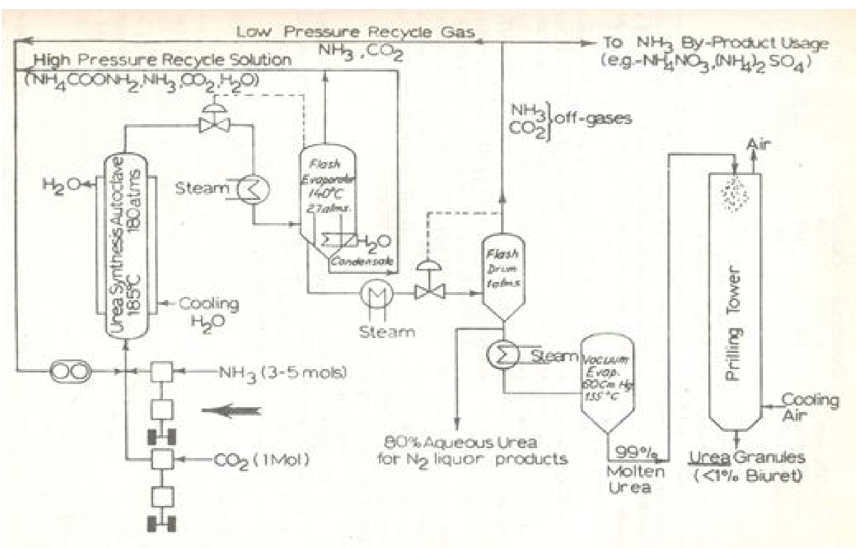


4-a	 **: Production of ammonium nitrate** Process description – In the Stengel process, vapours of ammonia & nitric acid are mixed in a stainless steel reactor. The reaction is exothermic & hence heat is given out. The mixture of steam & molten ammonium nitrate is fed to cyclone type separator. The molten 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 coated with clay.	2 2	4
4-b	Raw materials for sulfuric acid production • Sulphur • air	2 mark for each	4
4-c	Air is liquefied by linde's & claude's process **Principle of linde's process-** When a gas under pressure is allowed to expand suddenly through a small orifice into region of low pressure, it falls in temperature. During expansion work is not done against external pressure but against internal attraction forces between molecules.	1 1.5	4

	Uses of Oxygen- High purity oxygen is used for Welding & cutting metals , medicinal purposes Low purity oxygen is used for blast furnace operations and industrial oxidation process. **Uses of Nitrogen –** It is used for mfg. of nitrogen compounds It is used for refrigerative cooling in transportation industry.	1.5	
4-d	**Process Description:** Nacl + $H_2SO_4 \longrightarrow NaHSO_4 + HCl$ $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$ Both reactions involves the displacement of volatile acid from salt . The equilibrium can be displaced in desired direction by choice of condition .The high temp. process is superior to vaccum for this purpose . To promate reaction rate it is desirable to have temp sufficiently high to keep at least one of the reacting component in liquid condition. Calculated quantity of common salt & conc. Acid is heated in a pan of salt cake. HCl produced as a result of reaction 1 passes out through exit at top . Sodium bisulphate (Called salt cake) obtainted is removed from pan & mixed with more common salt & heated strongly in a muffle to produced more HCl. HCl thus produced by both reaction is passed in absorption tower from bottom where water is sprayed from top . Aqueous HCl is obtained from bottom of the tower (HCl gas is absorbed in water) . This reacycled through absorption tower to get higher conc. of acid	2	4

		02	
4-e	**Comparision between wet & dry process** • In the wet process high grade phosphate rock used whereas dry process low grade phosphate rock is used. • Highly pure acid can be obtained by dry process as compares with acid obtained in the wet process. • Dry process is more economical in those places where electricity is quite cheap. • Gypsum , a product of wet process is a useful material .whereas the by product of dry process slag, carbon di-oxide and phosphorus are partially used.	01 mark for each point	4
4-f	**Comparison between dry &wet process** Dry process- 1) Cheaper 2) Accurate control of raw materials is not possible. 3) Raw materials are mixed in dry condition 4) the dry process is used for the mfg. of cement when the raw material is either cement rock or blast furnace slag.	1 mark for each point	4

	Wet process- 1) Costlier 2) Accurate control of raw materials possible. 3) Raw materials are mixed with water. 4) This process is used for any raw materials.		
5-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 iii) Undesirable side reaction : $NH_2.CO.NH_2$ (urea) → $NH_2.CO.NH.CO.NH_2$ (biuret) + NH_3 Flow diagram :	(Reaction 4 marks and PFD 4 marks)	8



5-b	**Processes for hydrogen manufacturing are** 1) Lane's process 2) Bosch process 3) Steam reforming 4) Partial oxidation	(Process list 2 marks) (Any process description 6 marks)	8

	Lane's process Where hydrogen was commonly produced with the single retort like the Messerschmitt and the Bamag type, Lane introduced the multiple retort type. In the Lane generator water gas was used to heat the retorts up to 600-800 °C after which water gas-air was used in the retorts. In the steam-iron process the iron oxidizes and has to be replaced with fresh metal, in the Lane hydrogen producer the iron is reduced with water gas back to its metallic condition, after which the process restarts. The chemical reactions are $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$ $Fe_3O_4 + 4CO \text{ (or } H_2) \rightarrow 3Fe + 4CO_2 \text{ (or } H_2O)$ The net chemical reaction is: $CO + H_2O \rightarrow CO_2 + H_2$ **Bosch Process** The first stage in this method involves passing steam over red-hot coke (carbon) at a temperature of about 1200°C to form a mixture of hydrogen and carbon monoxide gas known as water gas. (steam) $H_2O(g)$ + (coke) $C(s) \rightarrow CO(g) + H_2(g)$ (water gas) The second stage involves mixing excess steam with the water gas in the presence of a catalyst at 450°C to form carbon dioxide and hydrogen gas. $CO(g) + H_2(g) + H_2O(g) \leftrightarrow CO_2(g) + 2H_2(g)$ The catalyst used for this reaction could be chromium oxide or iron oxide. Also, the reaction is reversible so that the equillibrium must be made to shift to the		

right if the intension is to produce more of the products. The high temperature, use of catalyst and increase in the concentration of the reactants will aid the production of more of the products.

The carbon dioxide in the product must be removed in order to obtain the hydrogen. Methods used to remove the carbon dioxide are:

1. Dissolving the mixture in water under pressure of 30 atm or
2. Passing the mixture through caustic soda solution or other solvents that absorbs carbon dioxide.

Reforming process

Fossil fuels are the dominant source of industrial hydrogen. Hydrogen can be generated from natural gas with approximately 80% efficiency, or from other hydrocarbons to a varying degree of efficiency. Specifically, bulk hydrogen is usually produced by the steam reforming of methane or natural gas. At high temperatures (700–1100 °C), steam (H_2O) reacts with methane (CH_4) in an endothermic reaction to yield syngas

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

In a second stage, additional hydrogen is generated through the lower-temperature, exothermic, water gas shift reaction, performed at about 360 °C:

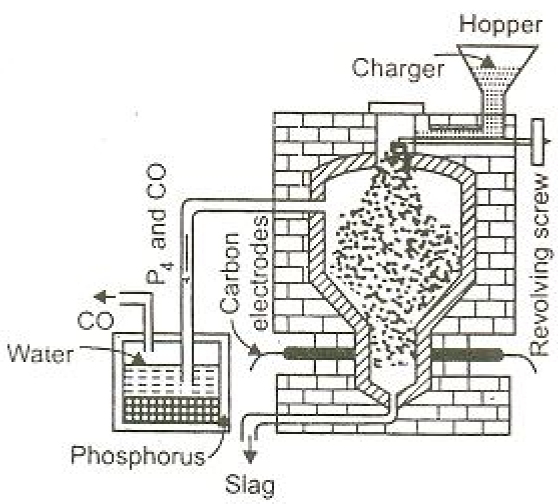
$$CO + H_2O \rightarrow CO_2 + H_2$$

Essentially, the oxygen (O) atom is stripped from the additional water (steam) to oxidize CO to CO_2. This oxidation also provides energy to maintain the reaction. Additional heat required to drive the process is generally supplied by

	burning some portion of the methane. **Process:** he desulfurized hydrocarbon feed is mixed with superheated process steam in accordance with the steam/carbon relationship necessary for the reforming process. After that, this gas mixture is heated up and then distributed on the catalyst-filled reformer tubes. The gas mixture flows from top to bottom through tubes arranged in vertical rows. While flowing through the tubes heated from the outside, the hydrocarbon/steam mixture reacts, forming hydrogen and carbon monoxide. To minimize the methane content in the synthesis gas while simultaneously maximizing the H2 yield and preventing the formation of elemental carbon and keeping it from getting deposited on the catalyst, the reformer is operated with a higher steam/carbon relationship than theoretically necessary.. The burners for the firing are arranged on the ceiling of the firing area between the tube rows and fire vertically downward. The residual gas from the pressure swing adsorption unit as well as heating gas from battery limits is used as fuel gas. The flue gas is then cooled down in a convection zone, generating steam.		
5-c	**Electrolysis:** - Electrolysis is the passage of a direct electric current through an ionic substance that is either molten or dissolved in a suitable solvent, resulting in chemical reactions at the electrodes and separation of materials. The main components required to achieve electrolysis are : • An electrolyte : a substance containing free ions which are the carriers of electric current in the electrolyte. If the ions are not mobile, as in a solid salt then electrolysis cannot occur. • A direct current (DC) supply : provides the energy necessary to create or discharge the ions in the electrolyte. Electric current is carried by	4	8

	electrons in the external circuit. • Two electrodes : an electrical conductor which provides the physical interface between the electrical circuit providing the energy and the electrolyte Electrodes of metal, graphite and semiconductor material are widely used. Choice of suitable electrode depends on chemical reactivity between the electrode and electrolyte and the cost of manufacture. **Calcination: - Calcination** (also referred to as **calcining**) 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 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 $CaCO_3 \rightarrow CaO + CO_2(g)$	4	
6-a	**Fertilizer** is any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to soil to supply one or more plant nutrients essential to the growth of plants. Mined inorganic fertilizers have been used for many centuries, whereas chemically synthesized inorganic fertilizers were only widely developed during the industrial revolution. After independence India was importing food grains from other countries due to growing population and low of yield from agriculture. After setting up synthetic fertilizer plant by government of India, crop production is increased. In present situation India is not only producing sufficient grains for our population but	4	4

	also exporting it. If we will eliminate chemical fertilizer from our agriculture then agricultural production will drop immediately and people will not have sufficient food for them		
6-b	<table><tr><th>Yellow phosphorus</th><th>Red phosphorus</th></tr><tr><td>Melting point = 44.1 ^oC</td><td>Melting point = 593 ^oC</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><tr><td>Used for the production of P_2O_5 and phosphoric acid</td><td>Used in safety matches, tracer bullets, incendiary devices, pesticides, pyrotechnic devices</td></tr></table>	One mark each for any four	4
6-c	**Uses of hydrogen** • For the production of ammonia • For the production of inorganic acids • As a fuel in rocket • As a coolant in generator • For the hydrogenation of vegetable oil • For enhancement of plasma welding • It is used as automobile fuels	One mark each for any four	4
6-d	**Direct fertilizers:-** These are the nutrient elements in form their compounds which are directly assimilated by plants. e.g. phosphetic fertilizer, nitrogeneous fertilizer	1.5	4

	Indirect fertilizers:- The substances which are introduced into soil mainly to improve its chemical and biological properties are called as indirect fertilizers. e.g. lime stone **Mixed fertilizer: -** The fertilizers prepared by mechanically mixing together number of direct fertilizer. e.g 10-26-26 (N-P-K)	1.5 1	
6-e	**Furnace used in production of Phosphorous**:  : Electro-thermal process for preparation of phosphorus	4	4
6-f	**Sources of Carbon dioxide** • Flue gas • Fermentation • Calcination of lime stone • Ethylene oxide production • Hydrogen production by steam reforming **Uses of Carbon dioxide** • For the production of – Urea , methanol, sodium carbonate	2 2	4

	• As a dry ice • In fire extinguisher • In beverages • To enhance oil recovery • As a refrigerent		