MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION

SUMMER 2013 EXAMINATION

Model Answer

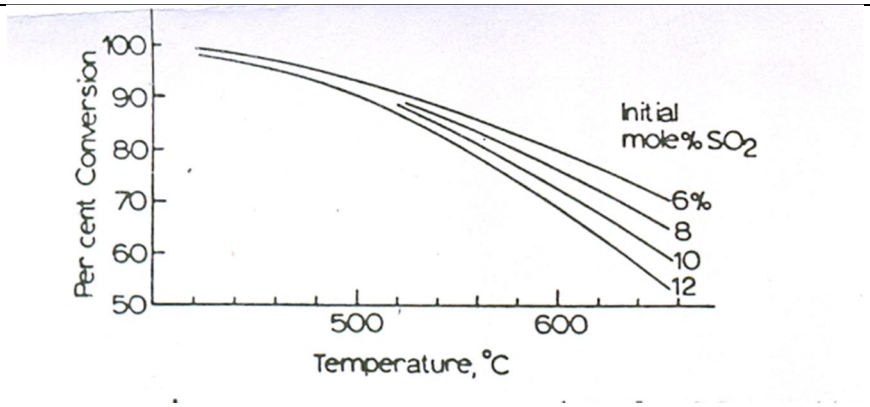
Subject & code : TIC(12079)

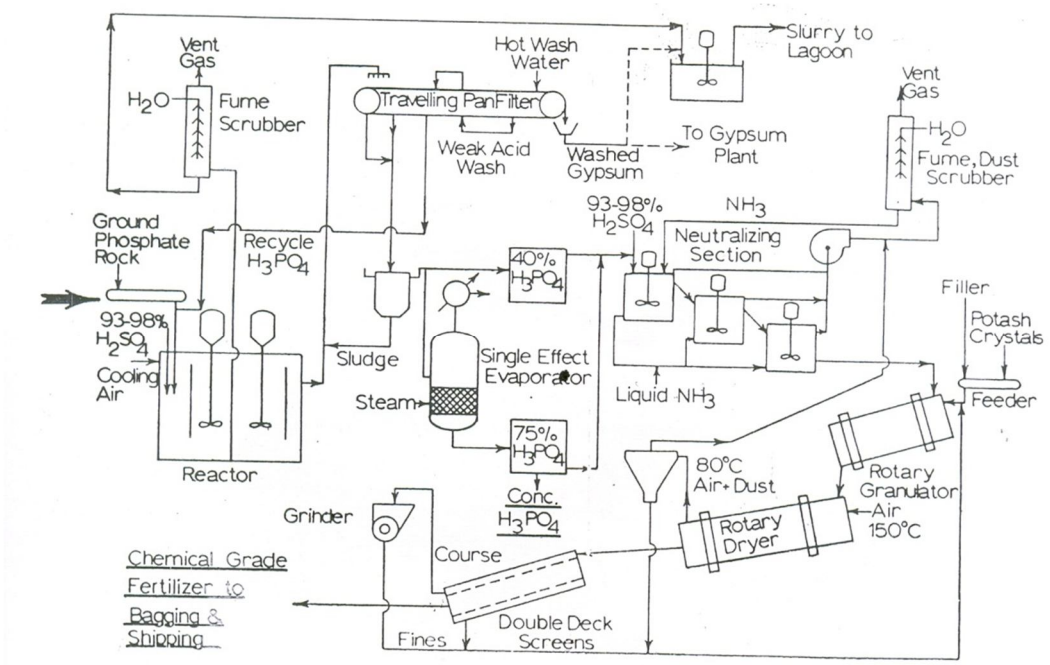
Important instructions to examiners :

1. The answers should be examined by keywords 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 given more importance.
4. While assessing figures, examiner may give credit for principal components indicated in a 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 answer and model answer.
6. In case of some questions credit may be given by judgment of relevant answer based on candidates understanding.

Q.No.	Answer	Mark	Total Mark
1.A-a	Ammonia is used for the production of 1. Urea 2. Nitric acid 3. Ammonium nitrate 4. In fermentation process 5. Refrigerant (any two may be not mentioned in list)	1+1	2
1.A-b	1. Removal of impurities in phosphate rock 2. Fumes and dust formation during granulation	1+1	2
1.A-c	$4HF+SiO_2 \longrightarrow SiF_4+2H_2O$ $3SiF_4+2H_2O \longrightarrow 2H_2SiF_6+SiO_2$ $H_2SiF_6+2NaCl \longrightarrow Na_2SiF_6+2HCl$	1+1	2

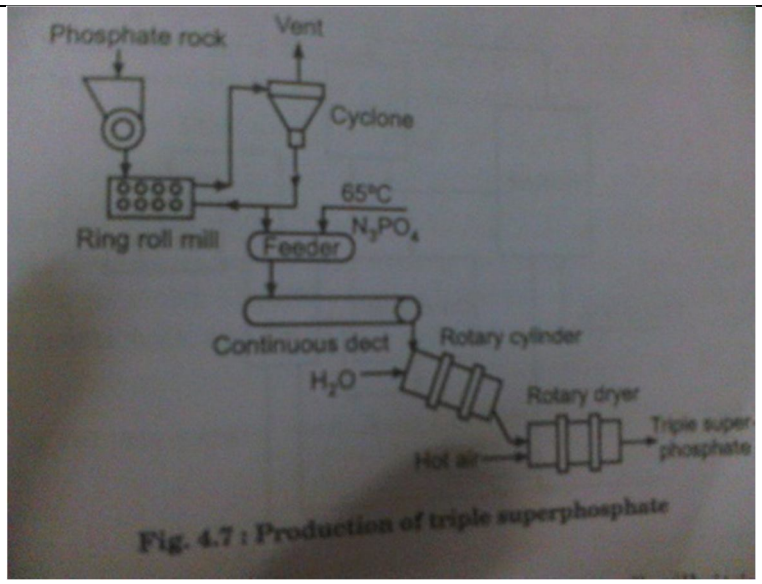
1.A-d	$Cl_2\uparrow$ | C NaCl (anode) Na^o | NaHg (cathode)	2	2
1.A-e	$NH_3 + H2O = NH_4^+ + OH^-$ $CO2 + OH^- = HCO3^-$ $NaCl + NH_4^+ + HCO_3^- = NH_4Cl + NaHCO_3$ $2NaHCO_3 = Na_2CO3 + CO_2 + H_2O$	2	2
1.A-f	Acetylene is used for manufacturing of 1) Neoprene (rubber) 2)Vinyl Chloride 3) Vinyl acetate 4) perchloroethylene 5) cutting and welding of metals	2	2
1.A-g	$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$	2	2
1.A-h	$CaSO_4 \cdot 2H_2O$	2	2
1.A-i	Clay, Limestone, Gypsum	2	2
1.A-j	Silicon and Carbon	2	2
1.A-k	Mixed fertilizers gives better crop yield in low cost.	2	2
1.A-l	$NH_2CONHCONH_2$ It reduces crop yield.	2	2
2 a	As temperature increases equilibrium conversion get reduces according to Le Chatelier's principle. Multistage catalytic converts are having highly exothermic reaction. Fig shows relation of temp vs conversion.	2+6	8

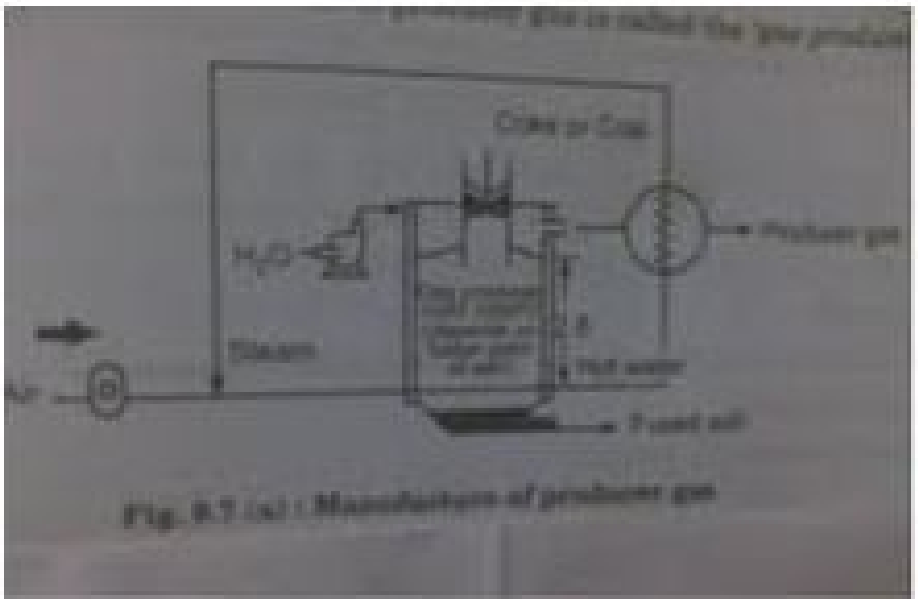
			
2 b	1. Temperature: Urea production rate increases as temperature increases up to 180°C and then fall sharply. 2. Pressure: Urea production rate increases as temperature increases. Pressure maintained is 180 atm. 3. Formation of biuret: Formation of biuret is not desirable in urea. It forms when two urea molecules combine with each other. It can be avoided by keeping urea solution temperature just above melting point before sending to prilling tower. $2NH_2.CO.NH_2 = NH_2.CO.NH.CO.NH_2 + NH$ 4. Prilling tower: Urea as fertilizer must be in uniform in size to use in farm. Molten mass of urea is taken to a tower where it is sprayed through nozzle from top. Air is send from the bottom. The uniform size granules obtained is called prills and tower is called as prilling tower.	2X4	8
2.c	Reaction: $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4.2H_2O)$ 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	2+2+4	8

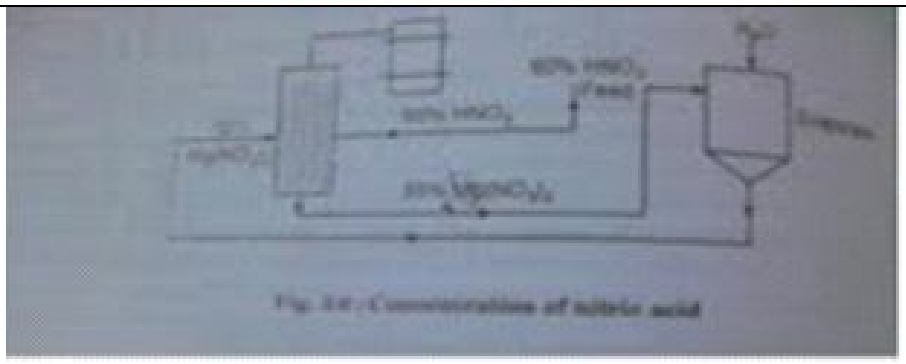
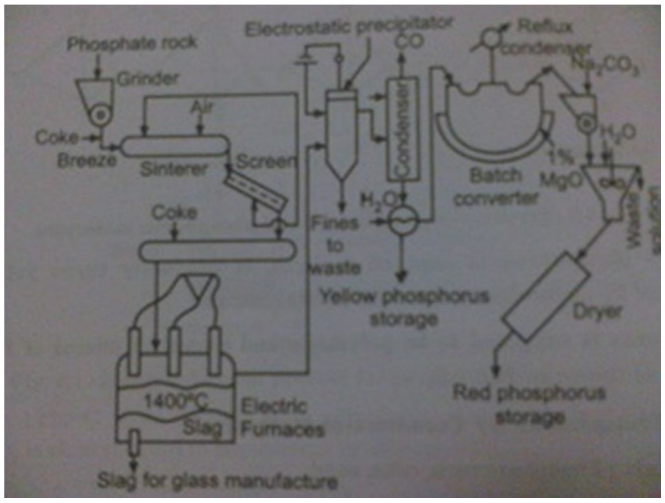
	reactor. The gypsum obtained is dried and send for paint or cement manufacturing. Dilute acid obtained can be concentrated in single effect evaporator.  		
3.a	Process Description: $Nacl + H_2SO_4 \xrightarrow{400^0C} NaHSO_4 + HCl$ $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$ Both reactions involves 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 promote 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) obtained 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	1 3	4

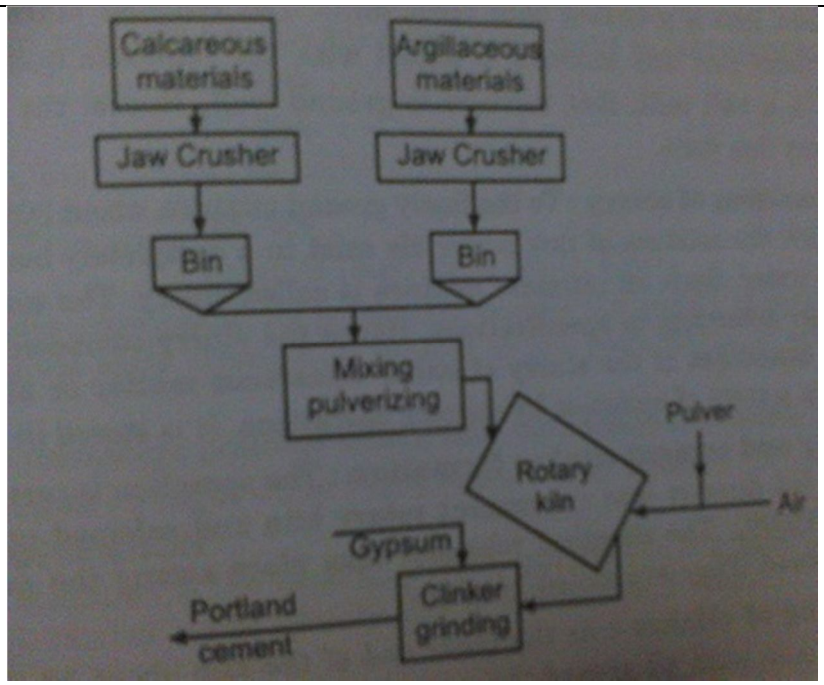
	where water is sprayed from top . Aqueous HCl is obtained from bottom of the tower (HCl gas is absorbed in water) . This recycled through absorption tower to get higher conc. of acid .		
3.b	Theories of 1) The crystallization theory (Le Chatelier's theory): Salt like aluminate &silicate of lime, which are soluble in water in anhydrous state, from insoluble salts when hydrated. Such salts become stable by undergoing two types of reactions – decomposition &combination with water The tricalcium silicate is decomposed in water to a hydrated monocalcium silicate &hydrate of lime $3CaO.SiO_2 + XH_2O \rightarrow CaO.SiO_2.2.5H_2O + 2Cao.H_2O$ Monocalcium silicate crystallizes in the form of needle like crystals which favours interplacement & a large contact surface . The reaction of tricalcium aluminate with water is hydration . $3CaO.SiO_2+XH_2O \longrightarrow 3CaO.Al_2O_3.12H_2O$ The double silicate $2SiO_2(Al_2O_3+Fe_2O_3).3CaO$ of aluminium, and iron is quite inert towards water and merely serves the purpose of assisting the combination of silica and lime by acting as a flux during burning. 2) Selective hydration theory : when water is added is to cement ,C_3A first becomes a solution & these hydrate C_3AH_5 & precipitates it in the form of needle shapes crystals. Gypsum reacts with C_3A & forms calcium sulpho aluminates in the range of $C_3A.3CaSO_4.30H_2O$ $C_3A.3CaSO_4.30H_2O.CaSO_4.12H_2O$. The slow setting C_3SH thus ,decide S the structure of cement.	2 2	4
3.c	The dust escaping cyclone along with preneutriliser are responsible for air pollution.one disadvantage of using nitric acid ais acidulant is that calcium nitrate is formed which is very hygroscopic in nature Therefore calcium nitrate has to be removed refrigeration or converting it to calcium sulphate.	4	4

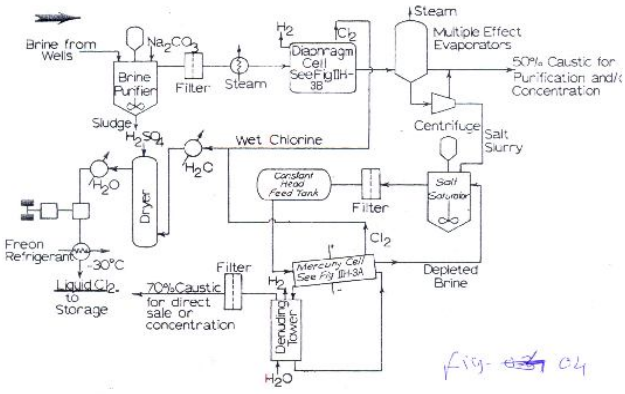
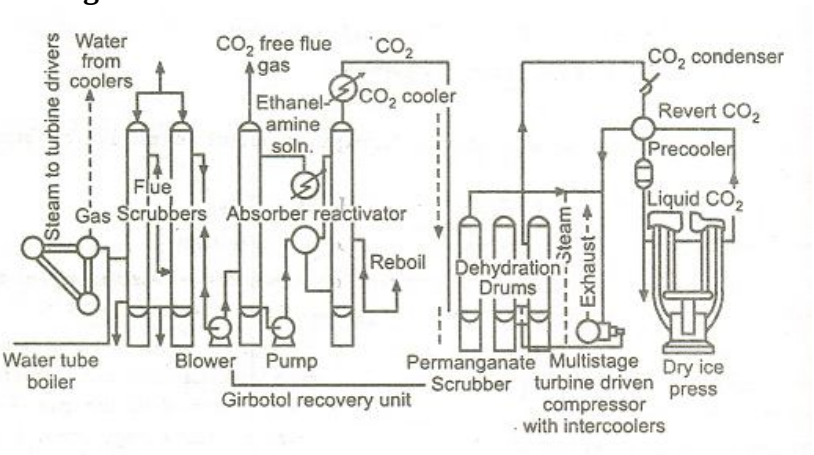
3.d	In the wet process, pulverized carbide is fed through a gas tight hopper to the acetylene generator in which the quantity of water used is sufficient to discharge $Ca(OH)_2$.The carbide is fed to water at a measured rate until exhausted. The calcium hydroxide slurry containing 90% water is discharged. The gas is passed through a scrubber to remove impurities like ammonia, sulfides & finally through a purifier containing iron oxide & alumina. The temp. in gas generator is kept below 90^0C & a pressure of 2 atm. In the dry process, equal weights of quantities H2O & 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 temp control in the generator acetylene polymerizes at 250 ^{0}c & above, & violently at 650 ^{0}C . Hence the temp is maintained below 150^0C & 30cm of water pressure The problems in this method are 1) The choice of lime 2) Consumption of electric power 3) Keeping CaC_2 away from water.	4	4
3.e	Chemical reaction-: $[Ca3(PO4)2]3CaF2+14H_3PO_4 \longrightarrow 10CaH_4(PO_4)_2H_2O$	2	4

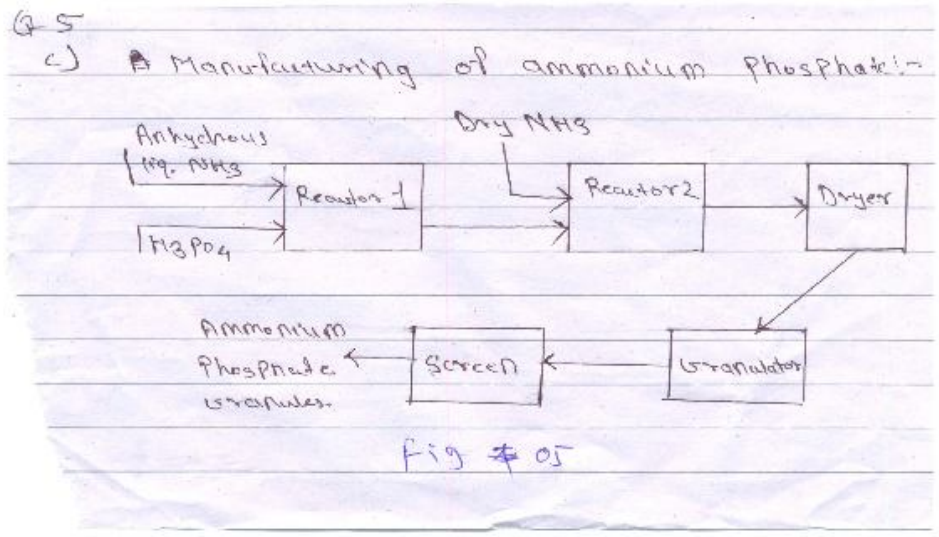
	 Fig. 4.7 : Production of triple superphosphate The phosphate rock is ground in a jaw crusher. In a ring roll mill, it is sized by a sieve of 100 mesh. Then it is mixed with 50to 54% phosphoric acid at about 65 to 70 ^{0}c This mixture is run on a continuous belt where reaction takes place for about 15 mins. the process may also be run in a manner similar to that for 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.	2	
3.f	Reactions-: $C+O_2 \rightarrow CO_2+97000$ Kcal $CO_2 \rightarrow 2CO- 91000$cal $H_2O+C \rightarrow H_2O+CO-30900$cal $2H_2O+C \rightarrow 2H_2+CO_2-20820$cal	2	4

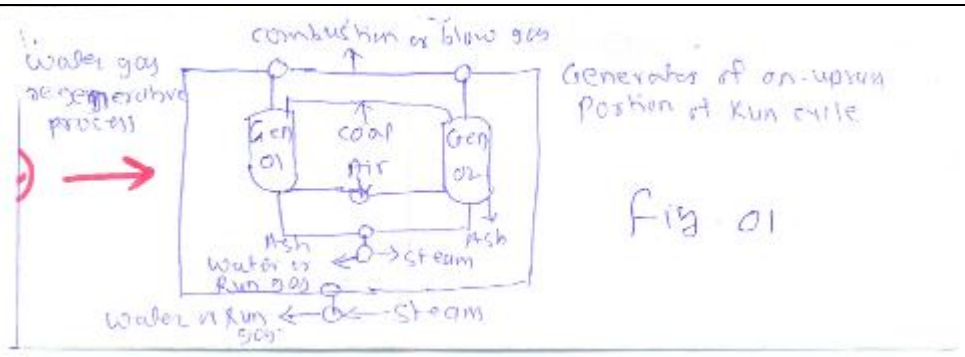
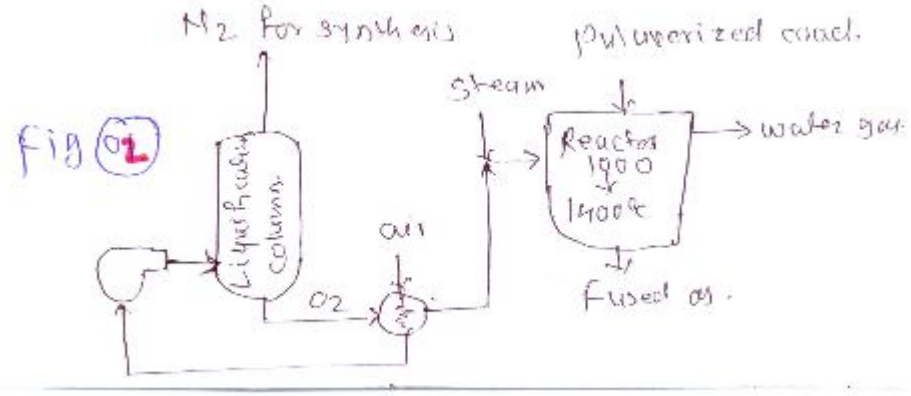
	 Steam and air mixture is injected in the bottom of a water cooled jacketed steel furnace equipped with a rotating grate to remove fusible ash. Solid fuel is added from hopper on top of furnace. The producer gas escapes through the outlet at the top. Furnace may rotate to get /'better distribution of reactants and more uniform ash removal. Producer gas is cooled by passing through a waste heat boiler.	2	
4.a	The first method consists of mixing the 60% nitric acid with strong sulphuric acid. The mixing is carried out in silicon iron or stoneware towers The vapours leaving the tower is 90% nitric acid & the bottom consist of dilute 70-77% sulphuric acid. Another method of concentration of nitric acid is developed in 1958 by Hercules Power company, An aqueous solution containing 79% magnesium nitrate is fed to the middle tower along with dilute nitric acid. The salt solution acts as an extractive distillation agent. So water in nitric acid is removed without azeotropic formation. About 55% magnesium nitrate is removed at the base of tower. After reconcentration to 72%, the magnesium nitrate is recirculated to nitric acidtower. Pure nitric acid of 95% to 98% strength is taken overhead.	4	8

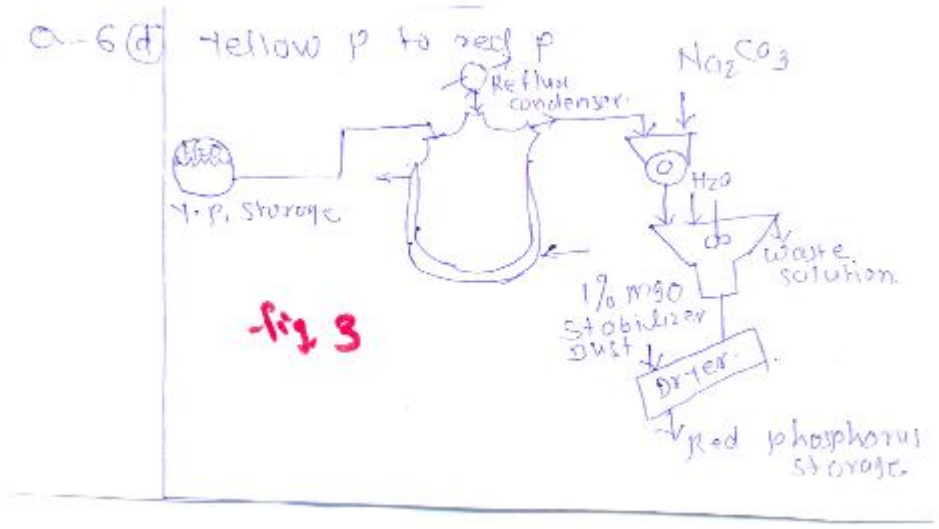
		4	
4.b	Raw materials-: Phosphate rock, coke sand Chemical reactions: 2 Ca3(PO4)2]+10C+6 SiO_2 ⟶ P_4+ 6$CaSiO_3$+10CO  Process Description:- Phosphate rock is ground, mixed with a portion of coke requirement, then sintered into nodules to obtain better electrical resistivity characteristics and to avoid entrainment of fines in the released P_4 and CO vapours . Screening is necessary to maintain size control with the fines recycled to the sintering operation. Coke , breeze sand are mixed in controlled quantities based on phosphate rock analysis The feed charge into the fused section of furnace at 1400-1450 deg. C where reduction takes place. Furnace kept under vacuum by fan & furnace gases move fast to the preceptor to remove dust. And then, yellow phosphorus is collect under water for further processing	1 1 3 3	8

4.c	 Raw materials: i)Calcareous materials: Important calcareous material is limestone. It occurs in variety of forms chalk, metamorphic etc. ii)Argillaceous material: the principle argillaceous material available for making Portland cement are clay, shale, cement rocks, alumina, silica etc. Process Description-: For dry process raw materials are cement rock or blast furnace slag The calcareous & argillaceous. Primarily crushed by jaw or roller crusher then raw material dumped into hugged bins. Then mixed in proper proportion by automatic weighing machine. These mixture is then fed to fine grinding mills, where it pulveriser. This finely powered mixture is fed into rotory kiln, is about 50-80 m long & 3 times in diameter. The kiln is rotated at 1 r.p.m. In the first portion of the kiln , limestone decomposes. alumina and silica combine at about 1400-1500 degree C with lime. The product obtained after sintering is known as clinker. The clinker is removed from the lower end of the kiln &cooled. The clinker is ground with about 2% gypsum.	4 4	8

5.a	 Fig. IIH-2. Electrolytic process for chlorine-caustic soda production. Temperature- 70°C Pressure-93 KPa	6 1 1	8
5.b	• **Manufacturing of CO_2 by using flue gas :** Flue gases results from burning carbaneous material (flue oil, gas coke or natural gas) They are cooled, purified and washed by passing through two wash scrubbers. The scrubbers contain Na_2CO_3 ($Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$) the reaction to left is formed by heating $NaHCO_3$.CO_2 is absorbed in absorber by counter current selective absorption in aqueous solution of ethanolamines, CO2 and steam pass through a "reactivator" then through CO2 cooler to condense steam which returns to the tower as reflux. CO2 now passes through a permanganate scrubber where traces of H2S and amines are removed. It is dried by passing it through dehydration drum. Finally CO2 is condensed cooled in pre cooler and send to liquid CO2 receiver for liquefaction. **Flow diagram** 	4 4	8

5.c	 Anhydrous and dry ammonia and phosphoric acid are charged into the first reactor. About 80% neutralization is done in the first reactor. Further ammonia is added to second reactor. So conversion to the di-ammonium salt is obtained. The reaction is exothermic and hence due to heat of reaction the excess ammonia vapors are given out this are collected at the top of the tank and recharged . this cuts ammonia losses. The slurry obtained in second reactor is allowed to pass to a rotary adiabatic dryer in which moisture is reduced to less than 1%. The bed of dry particles is recycled by moving them through rotating drum granulator. The particles are screamed and dried further white crystalline solid material is obtained.	4 4	8
6.a	• Difference in brine solution used for electrolysis in diaphragm cell and mercury cell: **Diaphragm electrolysis cell** : uses saturated Nacl solution and produces to 10-12% caustic which must be concentrated. Being replaced by membrane cell. **Mercury electrolysis cell** : uses saturated Nacl solution with solid salt makeup, gives 70%caustic solution directly.	2 2	4
6.b	• Two types of process: Regenerative process	2	4

	 The water gas generator is a tower packed with coke and provided with a hoper at the top for adding coke and two inlets near the bottom for blowing steam and air at will. The plant is provided with two generator one operator on blow period which heats carbon and other on the run period where endothermic reaction occurs. During the steam run i.e. when steam is blown water gas is produced. during the air run i.e. the warming up process when air is blown in the products of combustion mostly N_2, CO_2, and CO are allowed to pass into atm. **(OR)** Water gas by continuous process Raw material – steam, coal, oxygen Reaction – $C + O \rightarrow CO_2$ $C + H_2O \rightarrow CO + H_2$  The correct reaction of steam , coal, oxygen is added to reactor to yield water gas .	2	
6.c	• According to Le chateliers principle the formation of sulphur trioxide will be favored by Low temperature High pressure	1X4	4

	Increased concentration of sulphur dioxide or oxygen A use of catalyst for attainment of equilibrium for oxidation of SO_2 to SO_3		
6.d		4	4
6.e	• Cell notation for diaphragm cell $\uparrow cl_2$, clNacl (aq) NaoH(aq)(Fe,H_2) +----------→ - Anode cathode Cell reaction : Anode : $cl^- - e \rightarrow 0.5cl_2$ Cathode : $Na^+ + H_2O + e \rightarrow Na^+ + OH^- + 0.5H_2$ Overall : $Nacl + H_2O \rightarrow NaOH + 0.5H_2 + 0.5cl_2$	4	4
6.f	• Process used for manufacturing of oxygen and nitrogen are: • Lindes process : air free from CO_2 is compressed to about 200 atm pressure and cooled by passing through a pipe surrounded by cold	4	4

		water. This cooled and compressed air is passes through a spiral and escape through a small orifice, when it is cooled by the above effect. This cooled air passes upwards surrounding the spiral pipe. And cools drawn coming air therein. 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 and it is recirculted. **ȧ (OR)** • Claudes process : Air freed from CO_2 is dried. Compressed and passed through a pipe (heat exchanger) surrounded by cold oxygen and nitrogen, where it is cooled. The cooled and compressed air is allowed to do work in an expansion engine where it is further cooled. This cooled air enters the plant through pipe and rises through iron tubes surrounded by liquid oxygen. A part of air gets liquefied and collected. The condensation is 50% N_2 and 50% oxygen. The gas which escape condensation and collects in space passes downward through side tubes surrounded by liquid oxygen. This condenses here and collected. the condensation being 99% N_2 and 1% O_2. Liquid which is collected is pumped to the top of the fractionating columns. while the other liquid is passed to a level slightly above the fractionating columns where it meets an upward current of gases. The liquid is warned up a little as it comes down and loses volatile constituents more and more. i.e. nitrogen by evaporation and gets gradually richer in oxygen.		