



SUMMER-16 EXAMINATION
Model Answer

Subject code : (17314)

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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.



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Q No.	Answer	marks	Total marks
Q1 A	Attempt any six		12
a)	Catalyst used for sulfuric acid production <ul style="list-style-type: none">• Platinum• Vanadium pentoxide	1 mark each	2
b)	Oleum or fuming sulfuric acid , is a solution of various compositions of sulfur trioxide in sulfuric acid.	2	2
c)	Reactions in sulfuric acid manufacturing $S + O_2 = SO_2$ $SO_2 + \frac{1}{2} O_2 = SO_3$ $SO_3 + H_2O = H_2SO_4$	2	2
d)	Properties of sulfuric acid <ul style="list-style-type: none">• Molecular weight: 98• Melting point 10.5 °C• Boiling point 340°C with decomposition• Completely miscible with water with large heat of solution• Formation of oleum with SO₃ Uses of sulfuric acid Production of phosphoric acid, Fertiliser, petroleum refining, concentration of nitric acid.	½ each for any two uses and propertie s	2
e)	Catalyst for ammonia production Iron promoted with K ₂ O, CaO, SiO ₂ , and Al ₂ O ₃	2	2
f)	Cell notation for diaphragm cell		2



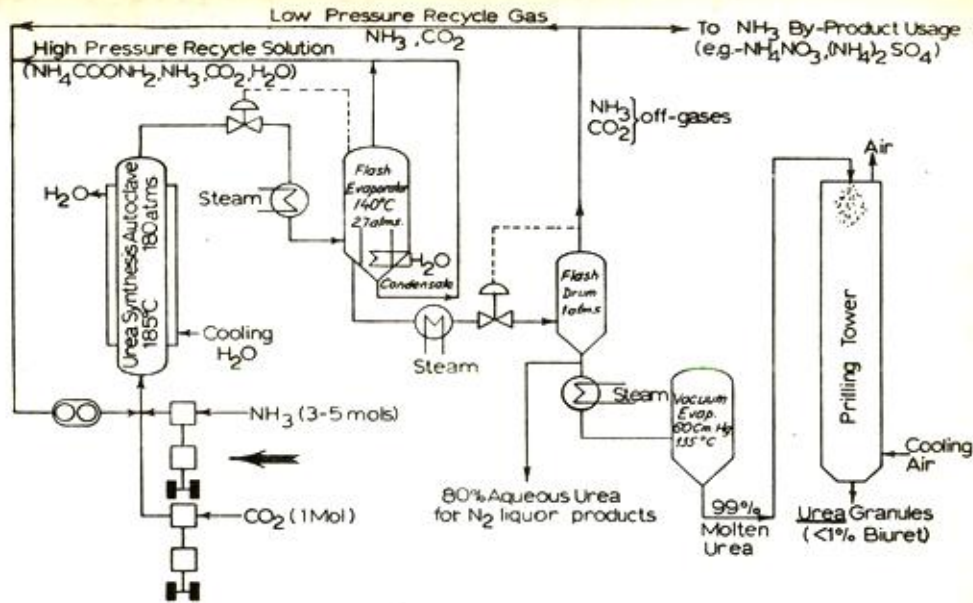
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c)	<p>Cement</p> <p>Cement is generic name for powdered material which initially have plastic flow when mixed with water but form a solid structure in several hours with varying degree of strength and binding properties which continue to improve with age.</p> <p>Portland Cement</p> <table border="1" data-bbox="188 695 1094 1304"> <thead> <tr> <th>Compound</th> <th>Formula</th> <th>Shorthand form</th> </tr> </thead> <tbody> <tr> <td>Tricalcium aluminate</td> <td>$\text{Ca}_3\text{Al}_2\text{O}_6$</td> <td>$\text{C}_3\text{A}$</td> </tr> <tr> <td>Tetracalcium aluminoferrite</td> <td>$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$</td> <td>$\text{C}_4\text{AF}$</td> </tr> <tr> <td>Belite or dicalcium silicate</td> <td>Ca_2SiO_5</td> <td>C_2S</td> </tr> <tr> <td>Alite or tricalcium silicate</td> <td>Ca_3SiO_4</td> <td>C_3S</td> </tr> <tr> <td>Sodium oxide</td> <td>Na_2O</td> <td>N</td> </tr> <tr> <td>Potassium oxide</td> <td>K_2O</td> <td>K</td> </tr> <tr> <td>Gypsum</td> <td>$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$</td> <td>$\text{CSH}_2$</td> </tr> </tbody> </table>	Compound	Formula	Shorthand form	Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$	C_3A	Tetracalcium aluminoferrite	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	C_4AF	Belite or dicalcium silicate	Ca_2SiO_5	C_2S	Alite or tricalcium silicate	Ca_3SiO_4	C_3S	Sodium oxide	Na_2O	N	Potassium oxide	K_2O	K	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CSH_2	2	4
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Q 2	Attempt any two		16																								
a)	<p>Urea by Montecatini Process:</p> <p>Chemical reaction:</p> <p>i) CO_2(carbon dioxide) + 2NH_3 (ammonia) \rightarrow $\text{NH}_4.\text{COO}.\text{NH}_2$ (ammonium carbamate)</p> <p>ii) $\text{NH}_4.\text{COO}.\text{NH}_2$ (ammonium carbamate) \rightarrow $\text{NH}_2.\text{CO}.\text{NH}_2$ (urea) + H_2O</p> <p>iii) Undesirable side reaction :</p> <p>$\text{NH}_2.\text{CO}.\text{NH}_2$ (urea) \rightarrow $\text{NH}_2.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2$ (biuret) + NH_3</p> <p>Flow diagram :</p>	Reaction-1 Diagram-4 Process-3	8																								

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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 carbamate, water and unreacted NH_3 and CO_2 results.

This liquid effluent is let down to 27 atm 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.

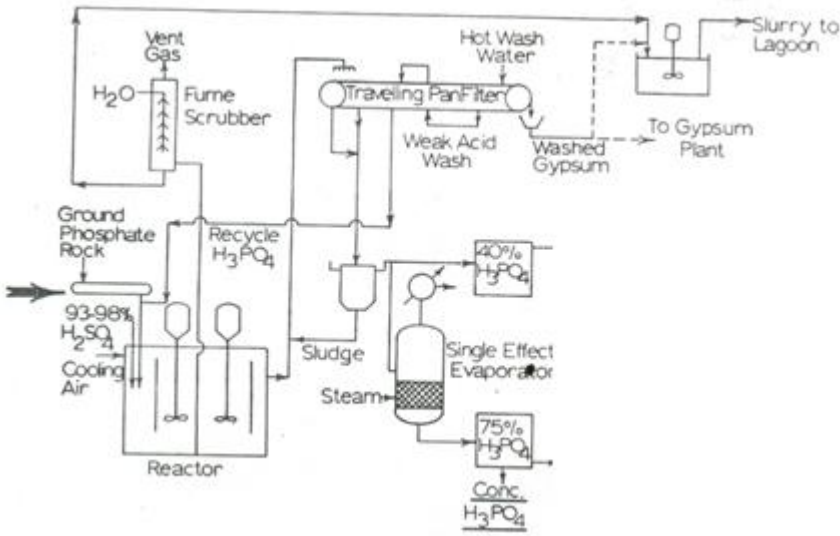
The 80% aqueous urea solution can be used as it is or sent to a vacuum evaporator to obtain molten urea containing less than 1% water. The molten



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	<p>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.</p>		
<p>2-b</p>	<p>Phosphoric acid Reaction: $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} = 2\text{H}_3\text{PO}_4 + 3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$</p>  <p>1Process: 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.</p>	<p>2</p> <p>3</p>	<p>8</p>



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	<p>Properties MW =60 MP = 44.1°C BP = 280 °C Stored under water due to reaction with oxygen.</p>	2	
b)	<p>Electro thermal process: A mineral phosphate with sand and coke is charged in the electric furnace. It is heated upto 1400 to 1500 °C. Initially at 1150°C, SiO₂ displace more volatile P₂O₅ from calcium phosphate. P₂O₅ is then reducing to phosphorous by coke at 1500°C. following reaction takes place $\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 \rightarrow 3\text{CaSiO}_3 + \text{P}_2\text{O}_5$$2\text{P}_2\text{O}_5 + 10\text{C} \rightarrow \text{P}_4 + 10\text{CO}$ CaSiO₃ 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.</p>	Rection-1 Process-3	4
c)	<p>Phosphorous trichloride is prepared by direct reunion of phosphorus and chlorine, the reaction being exothermic and spontaneous. $\text{P}_4 + 6\text{Cl}_2 \longrightarrow 4 \text{PCl}_3$ Liquid phosphorous and chlorine gas are fed in reactor. PCl₃ 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.</p>	2	4



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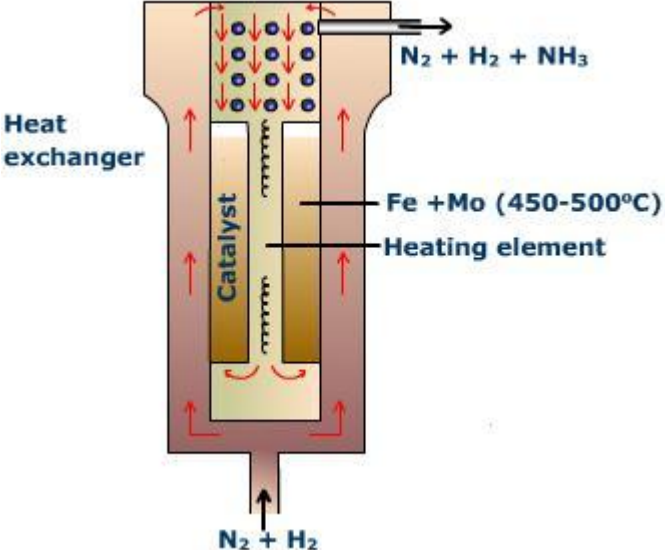
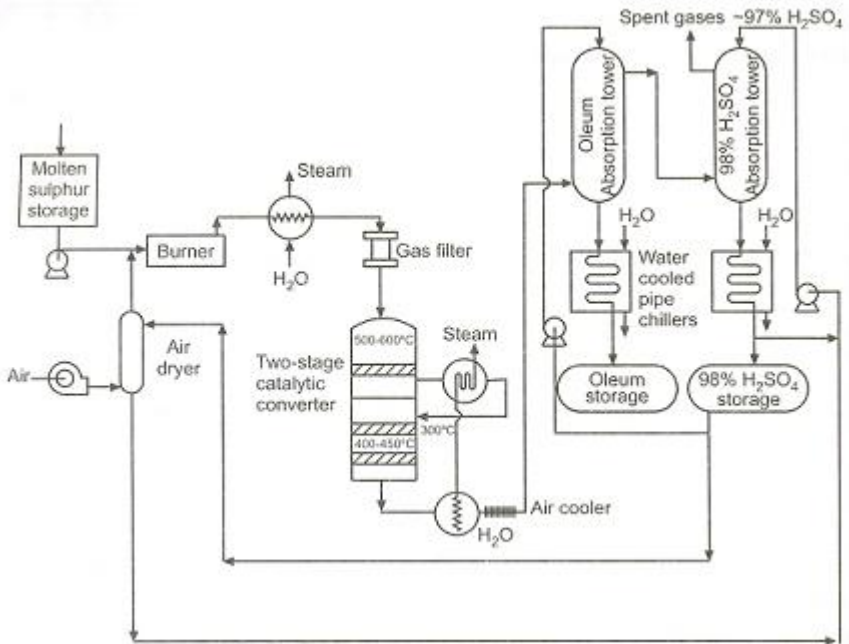
	Uses of Caustic soda (any 2) 1. Textile industry 2. Paper and Pulp 3. Alumina 4. Soap and detergent 5. Dyes	1	
e)	Ammonia converter. The gases enter the converter at the base and pass upward round the chamber containing catalyst Fe + Mo. Then they pass downward through the heat exchanger. The heat exchanger contains several coils of pipe, the mixture of gases get, heated by heat exchange and then passes downwards through the central chamber. It contains heating element. The mixture of gases passes up through the contact chamber containing catalyst. Finally mixture of gases passes out through the coils of pipe of heat exchanger. It gives most of the heat to the fresh gases on their way to contact chamber. The proportion of ammonia in the coming out from converter is about 10 to 20 % and is removed by cooling the mixture.	2	4



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		2	
f)	<p>Sulfuric acid and oleum production</p> 	4	4

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Q 4	Attempt any four		16
a)	<p>Synthesis process:</p> <p>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.</p> <div style="text-align: center;"> $\text{H}_2 + \text{Cl}_2 \longrightarrow 2 \text{HCl}$ </div> <p>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</p> <p>The gas is passed through a cooler cooled by water spray and then through absorber through which water flows down in controlled quantities.</p> <p>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.</p> <p>An exhaust fan on the extreme right pumps out the waste gases which escape in the atmosphere.</p>	2	4
b)	Plaster of Paris , quick-setting gypsum plaster consisting of a fine white	2	4



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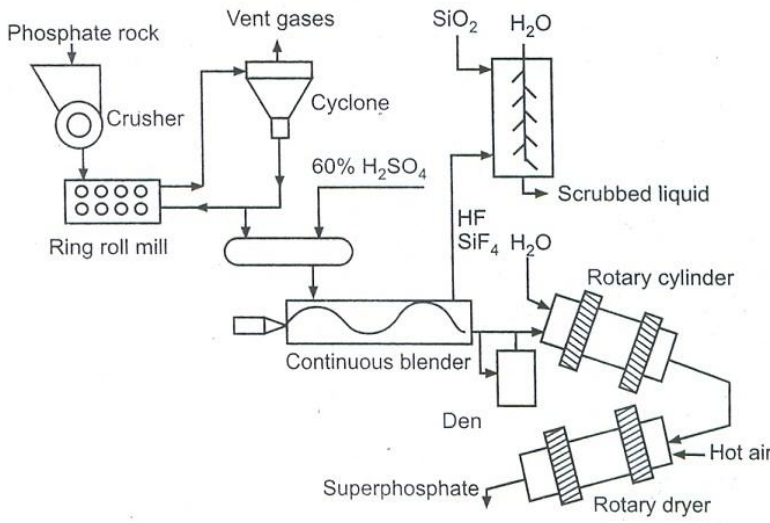
	<p>powder (calcium sulfate hemihydrate), which hardens when moistened and allowed to dry. Known since ancient times, plaster of paris is so called because of its preparation from the abundant gypsum found near Paris.</p> <p>Uses:</p> <p>passive fire protection, as fireproofing products</p> <p>Insulation</p> <p>Filler in fertilizer</p> <p>Decorative purpose</p>	2	
c)	<p>Single super phosphate</p> <p>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.</p> <p>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 multi stage conventional scrubbers & venturi Scrubbers. The material gets cured in a few days time.</p> <p>Reaction</p> $[\text{Ca}_3(\text{PO}_4)_2]_3\text{CaF}_2 + 7\text{H}_2\text{SO}_4 = 3\text{CaH}_4(\text{PO}_4)_2 + 7\text{CaSO}_4 + 2\text{HF}$	2	4



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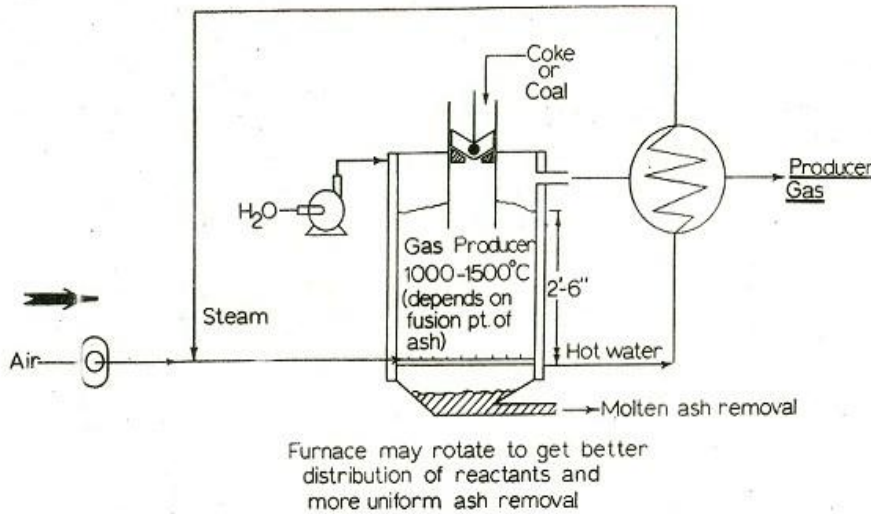
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		2	
d)	<p>Fertilizer is any organic or inorganic material of natural or synthetic origin (other than liming materials) that is added to soil to supply one or more plant nutrients essential to the growth of plants. Mined inorganic fertilizers have been used for many centuries, whereas chemically synthesized inorganic fertilizers were only widely developed during the industrial revolution.</p> <p>Inorganic fertilizers</p> <ol style="list-style-type: none">1. Nitrogen fertilizer : Urea, Ammonium nitrate, Ammonium sulphate, Ammonium phosphate2. Phosphorous fertilizer: Single superphosphate, Triple super phosphate3. Potassium fertilizer : Potassium chloride, Potassium sulphate	2 2	4
e)	<p>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.</p> <p>Steam and air mixture injected in the bottom of water cooled jacket steel</p>	2	4



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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.



2

f) **CO₂ by 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 CO₂ 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

4

4

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	tank		
Q5	Attempt any two		16
a)	<p>Solvay process</p> <p>The overall reaction can be regarded as between calcium carbonate and sodium chloride:</p> $\text{CaCO}_3 + 2\text{NaCl} \longrightarrow \text{CaCl}_2 + \text{Na}_2\text{CO}_3$ <p>However, calcium carbonate is too insoluble to react with a solution of salt. Instead the product is obtained by a series of seven stages.</p> <p>The process is known as the ammonia-soda process or the Solvay process, named after the Belgian industrial chemist who patented it in 1861. The various stages of the Solvay process are interlinked as can be seen from the diagram and description below.</p>	Reaction-2 Diagram-3 Process-3	8



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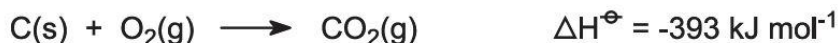
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(1) Ammoniation of brine

Ammonia gas is absorbed in concentrated brine to give a solution containing both sodium chloride and ammonia. $\text{Na}^+(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{NH}_4^+(\text{aq})$, $\text{OH}^-(\text{aq})$ ions and $\text{NH}_3(\text{aq})$ are present.

(2) Formation of calcium oxide and carbon dioxide

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



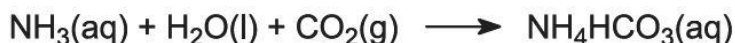
The heat of combustion raises the temperature of the kiln and the limestone decomposes:



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:



The solution now contains ions $\text{Na}^+(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{NH}_4^+(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$. Of the four substances which could be formed by different

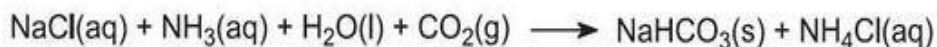


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combinations of these ions, sodium hydrogencarbonate (NaHCO_3) is the least soluble. It precipitates as a solid in the lower part of the tower, which is cooled. The net process is:



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 hydrogencarbonate

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:



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.

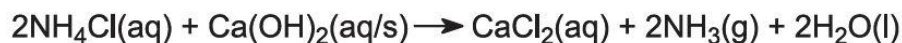
(6) Formation of calcium hydroxide

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:



(7) Regeneration of ammonia

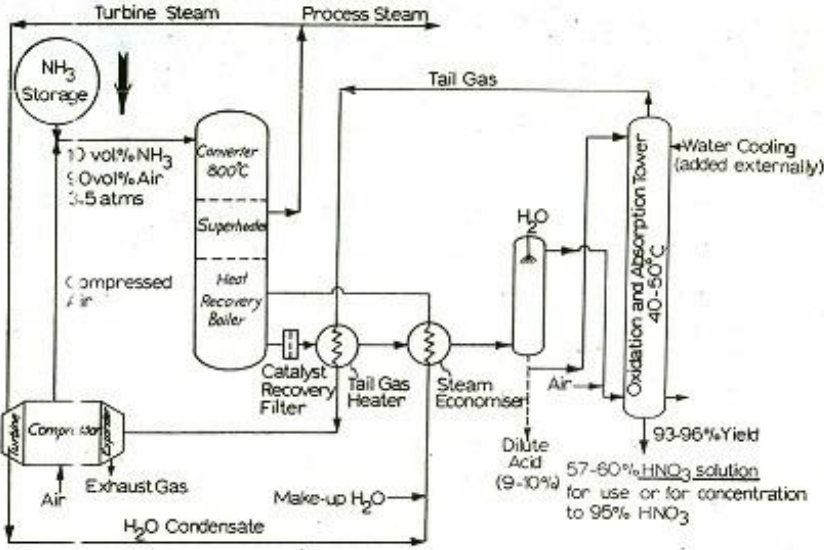
This calcium hydroxide suspension is mixed with the ammonium chloride solution left from step (4) and heated:



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	<p>The ammonia is thus recovered, and sent back to step (1). Calcium chloride is the only by-product of the whole process.</p> <p>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)</p>		
<p>b)</p>	<p>Nitric Acid Production</p> <p>Raw material Ammonia, air, water</p> <p>Reaction</p> $4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O}$ $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$  <p>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 be utilized to run turbine by producing steam and gas expander. Both are connected to the compressor. Hence compressor does not require external</p>	<p>Reaction-2</p> <p>Diagram-3</p> <p>Process-3</p>	<p>8</p>



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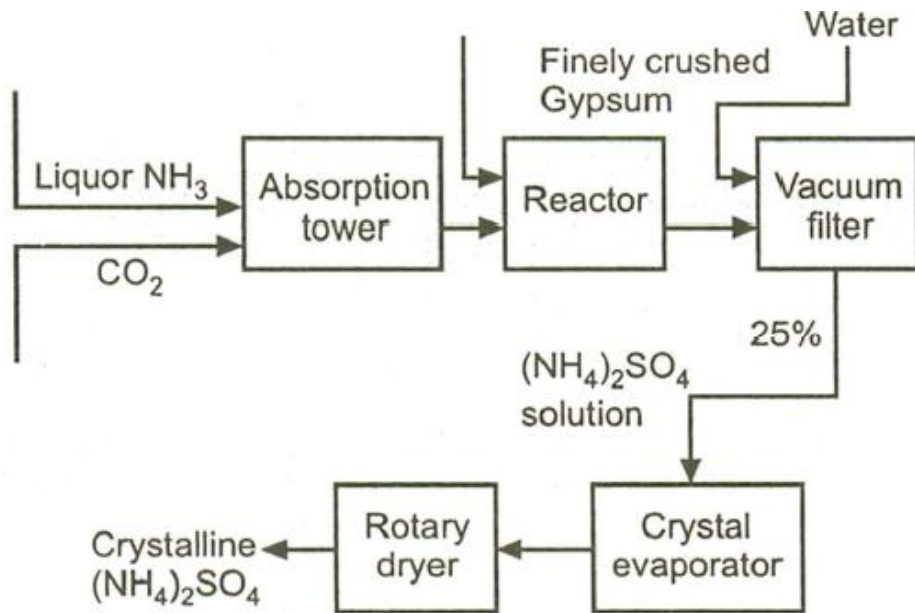
	<p>liquid oxygen. a part of the air gets liquefied and collects. the condensation is 50% N₂,50%O₂ .the gas which escape condensation passes downwards through side tubes surrounded by liquid oxygen and condenses. The condensation being 99% N₂ and 1% O₂</p> <p>The condensed liquid is pumped to the top of fractionating column, while the bottom liq. Is pumped to a level slightly above the fractionating column, where it meets an upward current of gases. the liq is wormed up a little as it comes down and loses a volatile constituents more and more. i.e. N₂ bye evaporation and gets gradually richer in O₂ . similarly up going gases loses more and more O₂ by condensation due to cooling and gets richer in N₂.by the time gases rich the top, it is 99% pure N₂ which escape to the exit provided. Liq O₂ evaporate as it cools the air and escape to the exit indicated</p>	3	
Q6	Attempt any four		16
a)	<p>Acetylene from CaC₂ Raw materials: lime stone, coke, water</p> <p>Chemical reactions:</p> $\begin{aligned} \text{CaO} + 3\text{C} &\rightarrow \text{CaC}_2 + \text{CO} \\ \text{CaC}_2 + \text{H}_2\text{O} &\rightarrow \text{Ca(OH)}_2 + \text{CH}\equiv\text{CH} \\ \text{CaCO}_3 &\rightarrow \text{CaO} + \text{CO}_2 \\ 2\text{CO} + \text{O}_2 &\rightarrow 2\text{CO}_2 \end{aligned}$ <p>Process Description: Calcium carbide is produced by heating lime and coke in an electric furnace at 2100 °C . Molten CaC₂ is solidified and cooled and ground under nitrogen</p> <p>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.</p> <p>Calcium hydroxide slurry containing 90% water is discharged. The gas is passes through a scrubber to remove impurities like NH₃, sulphides, phosgene</p>	<p>Mark should be given for any method</p> <p>1</p> <p>3</p>	4



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	<p>$(\text{NH}_4)_2\text{CO}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3 + 2\text{H}_2\text{O}$</p>  <pre>graph LR; NH3[Liquor NH3] --> AT[Absorption tower]; CO2[CO2] --> AT; AT --> R[Reactor]; FG[Finely crushed Gypsum] --> R; R --> VF[Vacuum filter]; W[Water] --> VF; VF --> CE[Crystal evaporator]; S["25% (NH4)2SO4 solution"] --> CE; CE --> RD[Rotary dryer]; RD --> CS["Crystalline (NH4)2SO4"]</pre>		
d)	<p>Ammonium Nitrate</p> <p>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.</p>	2	4

