



## Phosphorus

Qr. What are the Ores of phosphorus how is phosphorus extracted by modern method.

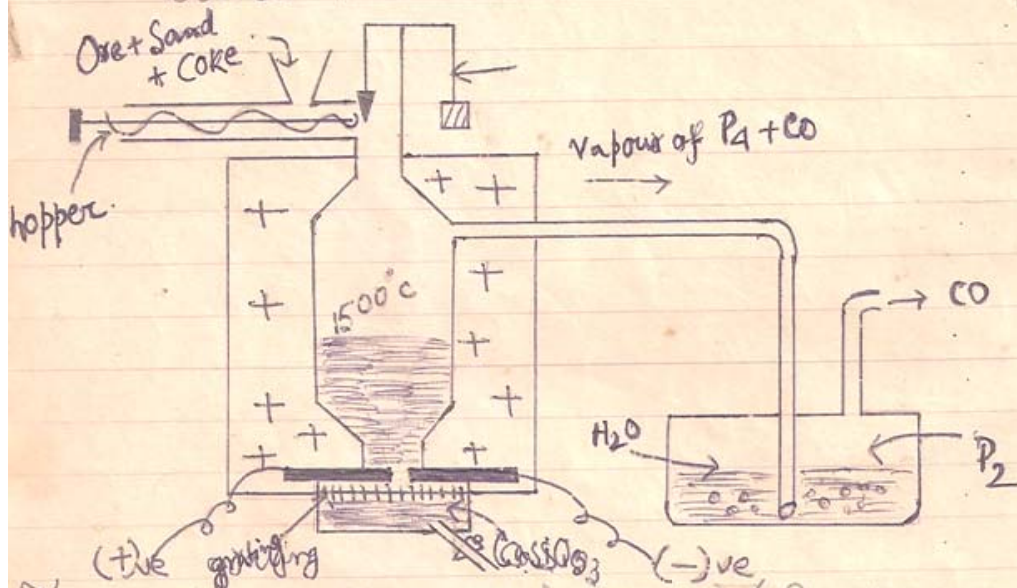
Convert White phosphorus to Red phosphorus:

and vice versa. Discuss the reaction with

①  $\text{HNO}_3$  ②  $\text{NaOH}$  ③  $\text{O}_2$  ④  $\text{I}_2$  mention the uses.

Ores of Phosphorus:- (i) Phosphorite  $\text{Ca}_3(\text{PO}_4)_2$   
(ii) Chlorapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$   
(iii) Fluorapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$   
(iv) Vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

Other source 'Bone ash' is also a source of  $\text{P}_4$ .

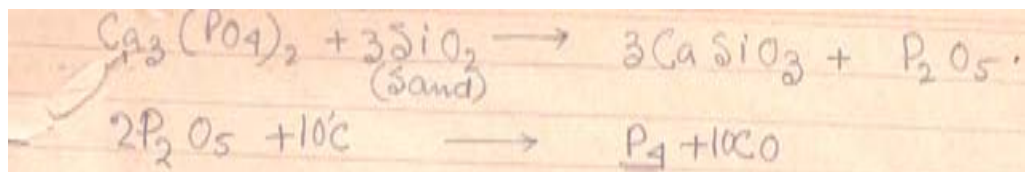


The modern electrical process:- / Readman, Parkar, Robinson process.

Theory: When a mixture of Phosphorite (main ore), Sand and coke is heated at about  $1500^\circ\text{C}$  we get vapour of  $\text{P}_4$  and  $\text{CO}$  gas which being passed through water gives white ~~white~~ phosphorus and  $\text{CO}$  is obtained as byproduct.



## Phosphorus



**Procedure:** The mixture is fed through a hopper via an warm conveyor into an electric furnace heated to a high temperature by means of electric current, using graphite electrodes. As  $1500^\circ\text{C}$  temp<sup>r</sup> is needed the furnace is made of fire bricks as shown in the diagram.

According to the above reaction we get the vapour of Phosphorus and CO gas which escape through an outlet at the top in to water to get solid phosphorus in water.

Slag,  $\text{CaSiO}_3$  thus formed is tapped out at the bottom.

**Purification:** Expected impurities are Sand and Carbon particles so this sample is melted with water in a m beaker (M.P of Phosphorus is  $44^\circ\text{C}$ ) then it is filtered through canvas or thin cloth to remove Sand and Carbon. -

To remove impurities like S it is heated with  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  to oxidised the impurity. Phosphorus collects at the bottom is cast into sticks it is kept always in water.

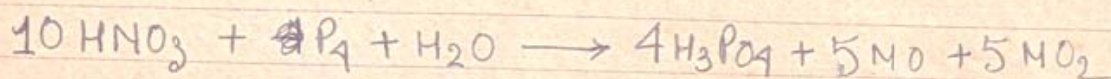
**Physical properties:** It is almost colourless/slightly yellow solid non metal, translucent, wax. like M.P  $44^\circ\text{C}$ . in vapour phase it is  $\text{P}_4$  and at high temp<sup>r</sup> it dissociates into  $\text{P}_2$ . It is highly poisonous insoluble in water soluble in Chloroform, Benzene and  $\text{CS}_2$  (liquid).



# Phosphorus

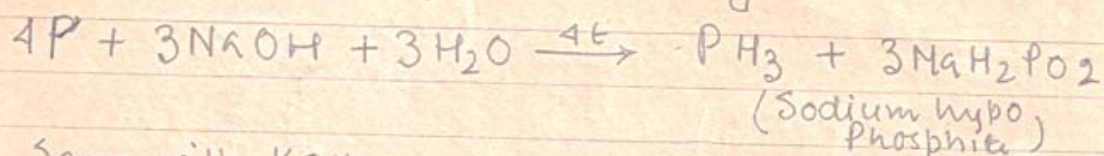


(i) With  $\text{HNO}_3$  :- On heating with Conc.  $\text{HNO}_3$  it gives Ortho phosphoric acid which is commonly known phosphoric acid.



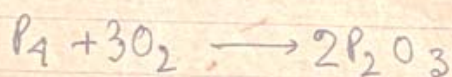
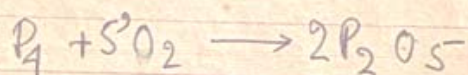
W.H

(ii) With  $\text{NaOH}$  :- When  $\text{P}_4$  is heated with strong  $\text{NaOH}$  sol<sup>n</sup> we get phosphine gas ( $\text{PH}_3$ ).



Same with KOH

(iii) With  $\text{O}_2$  :- When it is burnt in air it mainly gives  $\text{P}_2\text{O}_5$  however with less Oxygen it gives  $\text{P}_2\text{O}_3$ .



mp

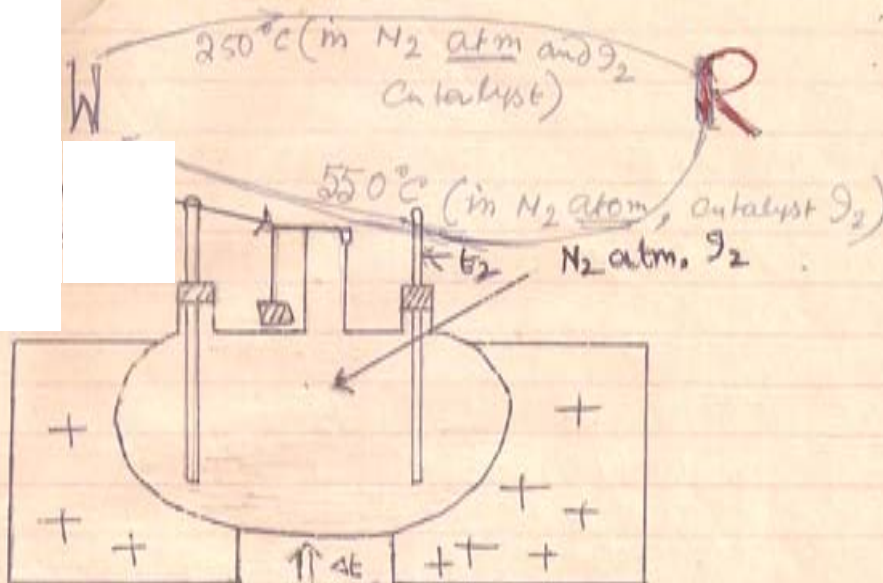
(iv) With  $\text{I}_2$  :- When  $\text{I}_2$  is kept in contact with  $\text{P}_4$  we get  $\text{PI}_3$  which with water/moisture gives





# Phosphorus

Convert White to Red, and vice versa.



(a) When White  $P_4$  is heated at  $250^\circ C$  in an inert atmosphere /  $N_2$  with a little  $O_2$  as a catalyst we get red Phosphorus.

(b) When Red  $P_4$  is heated at  $550^\circ C$  in inert atm and the vapour is suddenly cooled we get white P.

Distinguish white and Red.

Reagent	Red	White
1. Colour	Chocolate colour	almost colourless.
2. Odour	Odourless	Genic smell
3. SP. gravity	2.2	1.8
4. M.P	$500-600^\circ C$	$44^\circ C$
5. With $CS_2$ & $CHCl_3$	Insoluble	Soluble
6. exposed to air	NO Glow, no oxidation	glows and oxidised.
7. Electric current	feeble conductor	bad conductor
8. With $NaOH$ sol <sup>n</sup>	NO action	$PH_3$ is obtained.
9. with $Cl_2$	reacts on heating only.	reacts then and there.





# Phosphorus

Physiological  
action

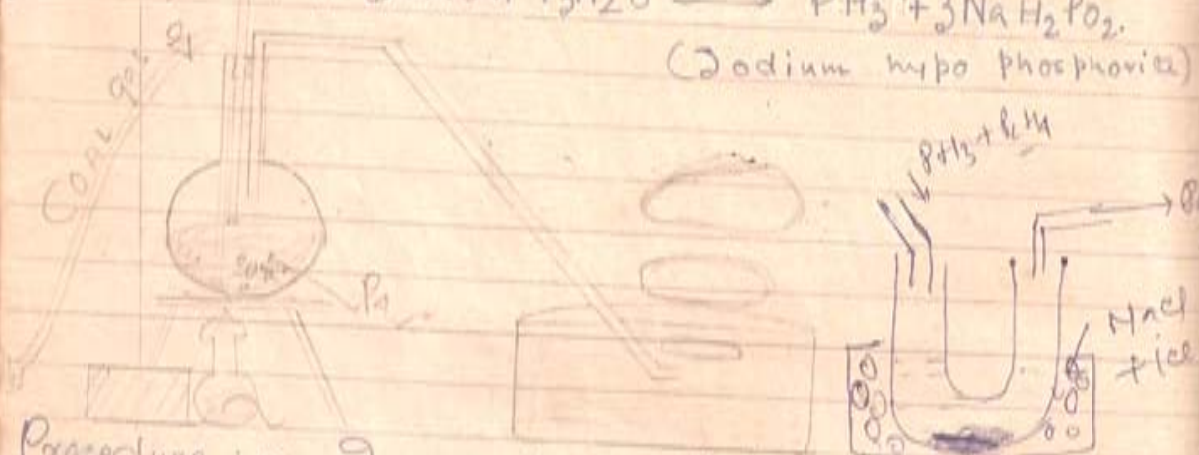
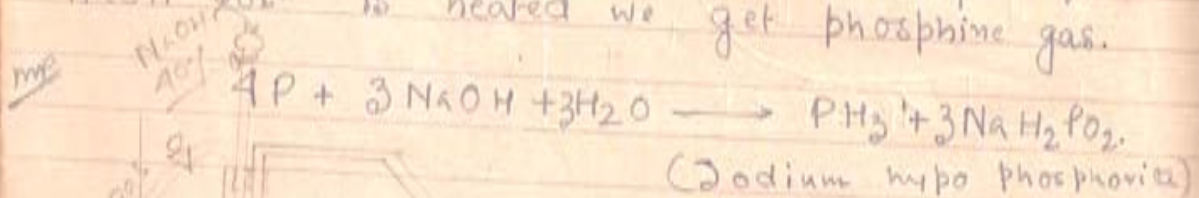
Not poisonous

highly poisonous  
(0.04 gm is fatal dose)

How is Phosphine prepared in the lab. in fairly pure form. Distinguish  $\text{PH}_3$  with  $\text{NH}_3$ . Discuss the properties of phosphine write notes on (i)  $\text{P}_2\text{O}_5$  (ii)  $\text{P}_2\text{O}_5$  (iii) Ortho Phosphoric acid (iv) composition of matchbox. (v)

$\text{PH}_3$ :

Theory: When white Phosphorus and nearly 40%  $\text{NaOH}$  sol<sup>n</sup> is heated we get phosphine gas.



Procedure :- In a round bottom flask about 50 gms of white Phosphorus is taken, fitted with a delivery tube and inlet tube to introduce coal gas to knockout air present inside it. About 40%  $\text{NaOH}$  is added into it through dropping funnel the mixture is gently heated to get  $\text{PH}_3$  gas. The gas is collected by downward displacement of water, however the first two or three gas gers are not accepted as mixed with coal gas then the other gas gers are the specimen (sample) of  $\text{PH}_3$  gas.



## Phosphorus

Precaution: As air comes in contact with  $\text{PH}_3$  it catches fire at once giving flash of light producing voluminous ring of white smoke (of Phosphorus Pentoxide) rising in the air. Therefore the gas is not allowed to escape and the inside atmosphere should be free from air. So coal gas is injected.

Purification: ~ The impurity present is  $\text{P}_2\text{H}_4$  (Phosphorus tetrahydride) So the ensuing gas is passed through a U tube kept immersed in freezing mixture to condense  $\text{P}_2\text{H}_4$  in U tube then it is collected.

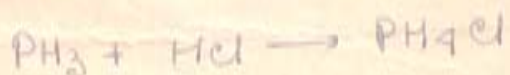
N:B If alcoholic soln of  $\text{NaOH}$  is taken during preparation this  $\text{P}_2\text{H}_4$  is absorbed in alcohol.

Physical properties: Colourless gas, heavier than air, insoluble in water, bad smell, slightly poisonous, it forms  $\text{P}_2\text{O}_5$  in Oxygen

$$2\text{PH}_3 + 4\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$$

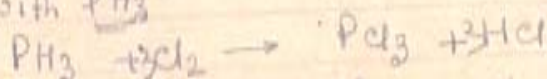
### CHEM

(1) With  $\text{HCl}$   $\rightarrow$  It forms phosphonium chloride  
Similar to  $\text{NH}_4\text{Cl}$



Similarly it reacts with  $\text{HBr}$  and  $\text{HI}$  to give parallel products.

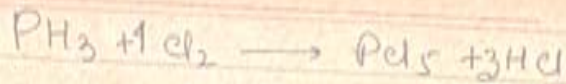
(2) With  $\text{Cl}_2$   $\rightarrow$   $\text{Cl}_2$  gas is ignited. if brought in contact with  $\text{PH}_3$



Also it forms a little  $\text{Pcl}_5$   $\rightarrow$



# Phosphorus



W.H

(3) With  $CuSO_4$  sol<sup>n</sup>: When  $PH_3$  gas is bubbled through  $CuSO_4$  sol<sup>n</sup> we get black ppt of copper phosphide



(4) With  $HgCl_2$ : When  $PH_3$  is passed through  $HgCl_2$  we get black ppt of  $Hg_3P_2$  (Mercuric Phosphide)



Distinction between  $PH_3$  and  $NH_3$ .

Reagent	$NH_3$	$PH_3$
Smell	Pungent Smell.	Rotten fish smell
Density	lighter than air	heavier than air.
Solubility in water.	Highly Soluble in water.	insoluble (slightly)
Basicity	It is basic and forms Ammonium Salt $NH_3 + HX \rightarrow NH_4X$ $X = Cl, Br, I$	It is light basic giving phosphonium salt $PH_3 + HX \rightarrow PH_4X$
Preparation	Prepared by heating $NH_4Cl + NaOH$	Prepared by heating $PH_4Cl$ and $NaOH$
Electric spark.	It gives $N_2 + H_2$	It gives $H_2$ and Red Phosphorus
With $Cl_2$	When $NH_3$ is excess $N_2$ is formed and $NH_3$ is less we get $NCl_3$	It at once burns in $Cl_2$ giving $PCl_3$ & $PCl_5$



## Phosphorus

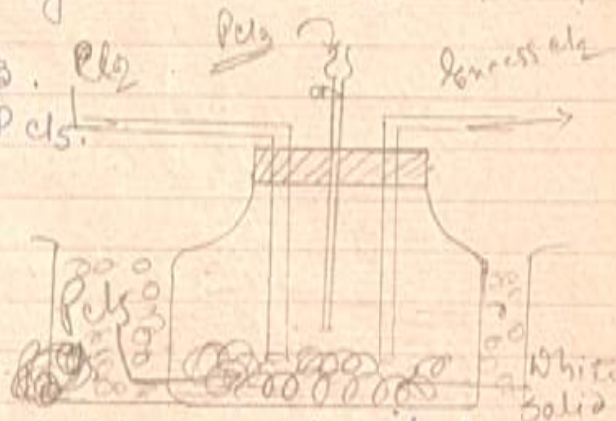
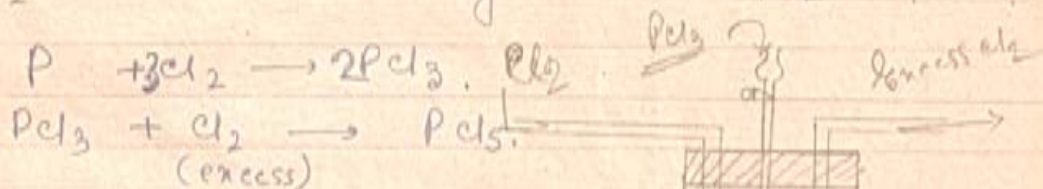
8. Physiological Action

$\text{NH}_3$	Not poisonous.	$\text{PH}_3$	It is poisonous.
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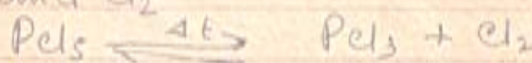
### NOTE (Liquid)

When  $\text{Pcl}_3$  is added with excess of  $\text{cl}_2$  at low temperature we get solid  $\text{P}_2\text{cl}_5$

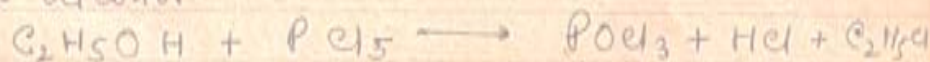
This  $\text{Pcl}_3$  is prepared as a liquid by passing  $\text{cl}_2$  in a controlled way on heated Phosphorus



Properties: It is a white solid. On heating it breaks into  $\text{Pcl}_3$  and  $\text{cl}_2$



With Ethyl alcohol:



Uses: It is highly used in Organic prep<sup>n</sup> and analysis.

(ii)  $\text{P}_2\text{O}_5 \rightarrow$  It is prepared by heating Phosphorus in excess of air/ $\text{O}_2$  free from moisture.

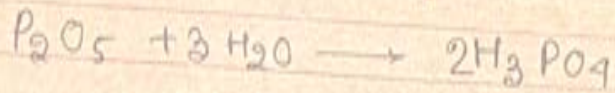






## Phosphorus

$P_2O_5$  is a white solid, hygroscopic. With boiling water it gives Orthophosphoric acid.

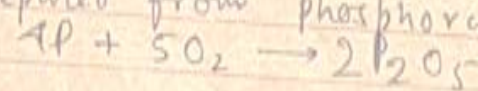
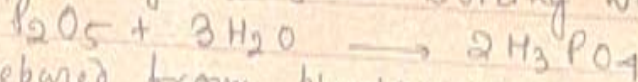


Uses: ① It is highly used for drying gases ② to prepare Phosphoric acid.

3. Phosphoric acid (Orthophosphoric acid) :-

Pre<sup>n</sup>:

① By adding  $P_2O_5$  in boiling water and this  $P_2O_5$  is prepared from phosphorus.

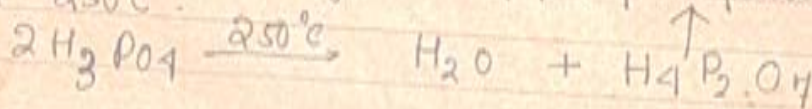


Starting fro  
P<sub>4</sub>

② It is also prepared by heating white  $P_4$  with Conc.  $HNO_3$



Properties: It is colourless syrupy liquid at ordinary temperature. (M.P =  $42^\circ C$ )  
On heating it gives pyro phosphoric acid at  $250^\circ C$ .



However at  $316^\circ$  it gives meta phosphoric acid.



Uses: 1. It is highly used in lab. as a reagent to prepare many more.




# Phosphorus

MICROCOSMIC SALT -  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 24\text{H}_2\text{O}$

$\text{H}^+$   
 $\text{Na}^+$  —  $\text{PO}_4 \cdot 24\text{H}_2\text{O}$   
 $\text{NH}_4^+$

$\text{H}_3\text{PO}_4$   
 $\text{H}^+$   
 $\text{H}^+$  —  $\text{PO}_4$   
 $\text{H}^+$   
Replaces at  
 $\text{H}_2$

MATCH BOX: NOT IN Ise.



Red  $\text{P}_4$ , Antimony Sulphide, glass particles, glue.

$\text{KClO}_3$ ,  $\text{MnO}_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{S}$ ,  $\text{Fe}_2\text{O}_3$ , glue, glass particles.