



p-BLOCK

15 and 16 Group

for JEE-MAIN

One Shot

By VJ Sir

1:30 PM Today

Apni Kaksha

A

P-block Element

NITROGEN FAMILY

GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

Occurrence :

Nitrogen : Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs as sodium nitrate, NaNO_3 (called Chile saltpetre) and potassium nitrate (Indian saltpetre).

Phosphorus :

(i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family, $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaX}_2$ ($\text{X} = \text{F}, \text{Cl}$ or OH) (e.g., fluorapatite $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaF}_2$) and also found as chlorapatite $\text{Ca}_9(\text{PO}_4)_6 \cdot \text{CaCl}_2$.

(ii) Arsenic , antimony and bismuth are found mainly as sulphide minerals.

Electronic Configuration :

The valence shell electronic configuration of these elements is ns^2np^3 .

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Atomic and Ionic Radii :

Covalent radius : N < P < As < Sb < Bi

Ionisation Enthalpy :

N > P > As > Sb > Bi (IE1 values)

Electronegativity :

N > P > As > Sb = Bi

Metallic Character



N < P < As < Sb < Bi

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Physical Properties :

- (i) All the elements of this group are **polyatomic**. Dinitrogen is a diatomic gas while all others are solids.
- N₂ P_γ As_γ
- (ii) Metallic character increases down the group.
- (iii) The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.
- (iv) Except nitrogen all the elements show **allotropy**.
- P → exists in three allotropic form as white, red and black

As, Sb → exist as yellow and grey

Bi → exist as α , β , γ , δ allotropic form

Catenation

The group 15 elements also show catenation property but to much smaller extent than carbon.

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For example hydrazine (H_2NNH_2) has two N atoms bonded together HN_3 has three N atoms.



- Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in comparison to carbon is their low dissociation enthalpies.

<u>C – C</u>	<u>353.3 kJ/mole</u>	$C-C > P-P > N-N > As-As$
<u>N – N</u>	<u>160.8 kJ/ mole</u>	
<u>P – P</u>	<u>201.6 kJ/ mole</u>	
<u>As – As</u>	<u>147.4 kJ/ mole</u>	

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Chemical Properties :

Oxidation states and trends in chemical reactivity

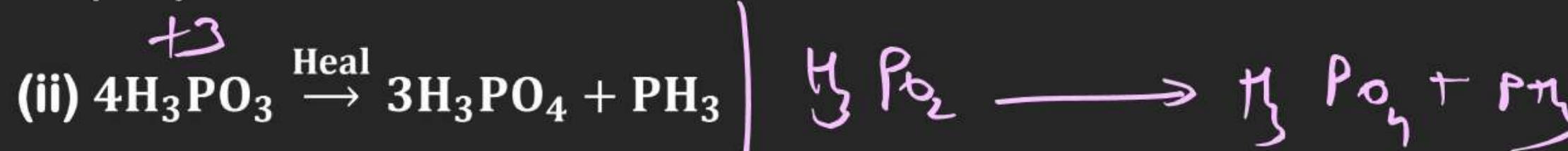
- (i) The common oxidation states of these elements are -3 , $+3$ and $+5$. $\text{Bi}^{+5} + 2e^- \rightarrow \text{Bi}^{+3}$
(O.A)
- (ii) The tendency to exhibit -3 oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in $+3$ oxidation state.
- (iii) The stability of $+5$ oxidation state decreases down the group. The only well characterised Bi(V) compound is BiF_5 .
- (iv) The stability of $+5$ oxidation state decreases and that of $+3$ state increases (due to inert pair effect) down the group.
- (v) Nitrogen exhibits $+1$, $+2$, $+4$ oxidation states also when it reacts with oxygen. Phosphorus also shows $+1$ and $+4$ oxidation states in some oxoacids.

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(vi) In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,



(vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.

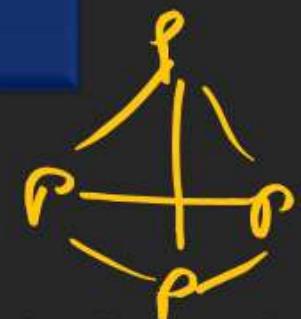


(viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

(ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.

(x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding 6 (covalency) and hence, expand their covalency as in PF_6^- .

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Anomalous properties of nitrogen

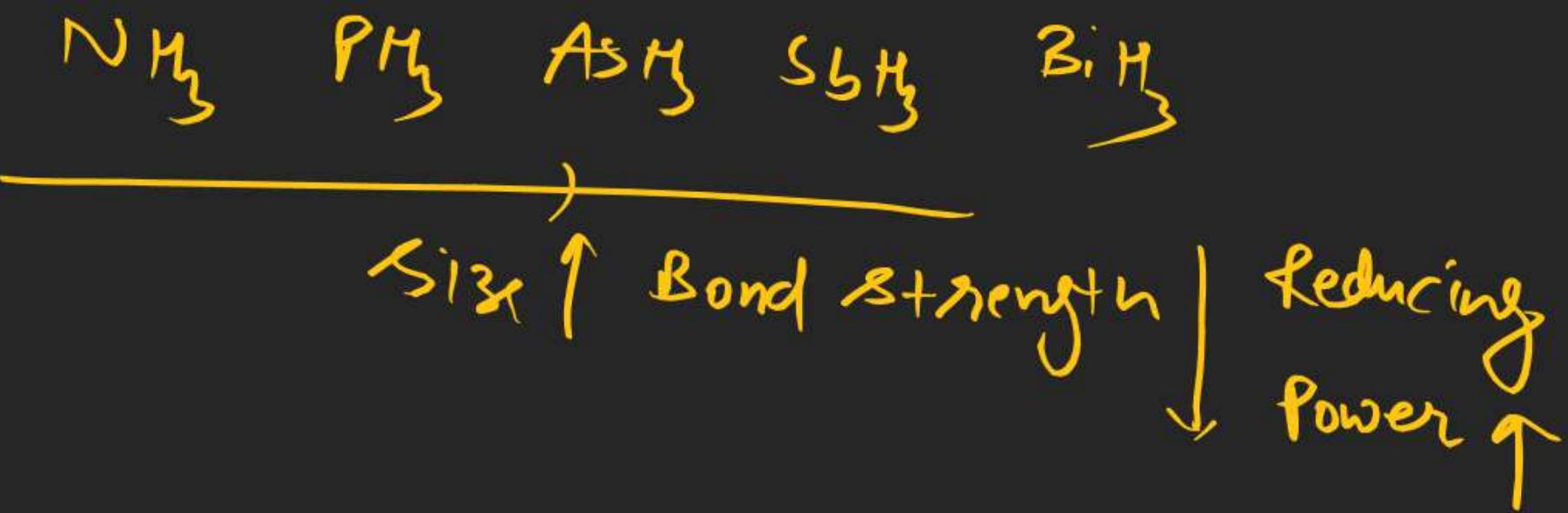
- (i) Nitrogen has unique ability to form $p_{\pi} - p_{\pi}$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).
- (ii) Heavier elements of this group do not form pp-pp bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.
- (iii) Nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms.

 $\boxed{N \equiv N} \times \boxed{P \equiv P} \rightarrow 3P_{\pi} - 3P_{\pi}$ sideways overlapping does not exist
- (iv) Phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state.

Reactivity towards hydrogen:



Reactivity of Hydrogen



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(ii) **Reactivity towards oxygen:** All these elements form two types of oxides: E_2O_3 and E_2O_5 . Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony does not exist. The oxides of bismuth are amphoteric and those of bismuth predominantly basic.

does not exist

Reactivity towards halogens: These elements react to form two series of halides:

EX_3 and EX_5 . In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

NF_3 } stable

NCI_5

NBr_3

explosive

(iv) **Reactivity towards metals:** All these elements react with metals to form their binary compounds exhibiting -3 oxidation state, such as, Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Ni_3

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DINITROGEN

Preparation :

(a) Commercial preparation :

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air.

Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

(b) Laboratory preparation :

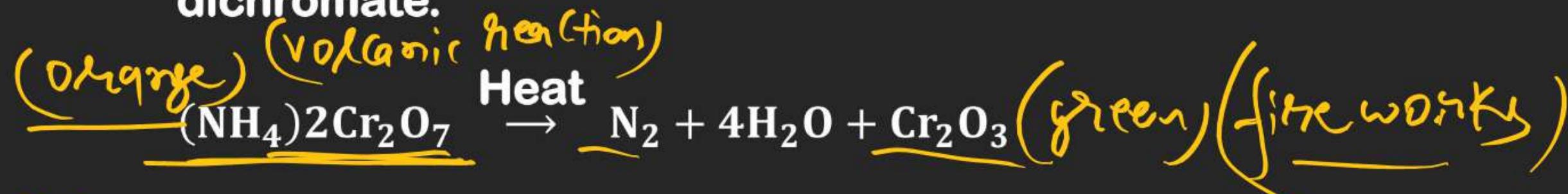
(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.



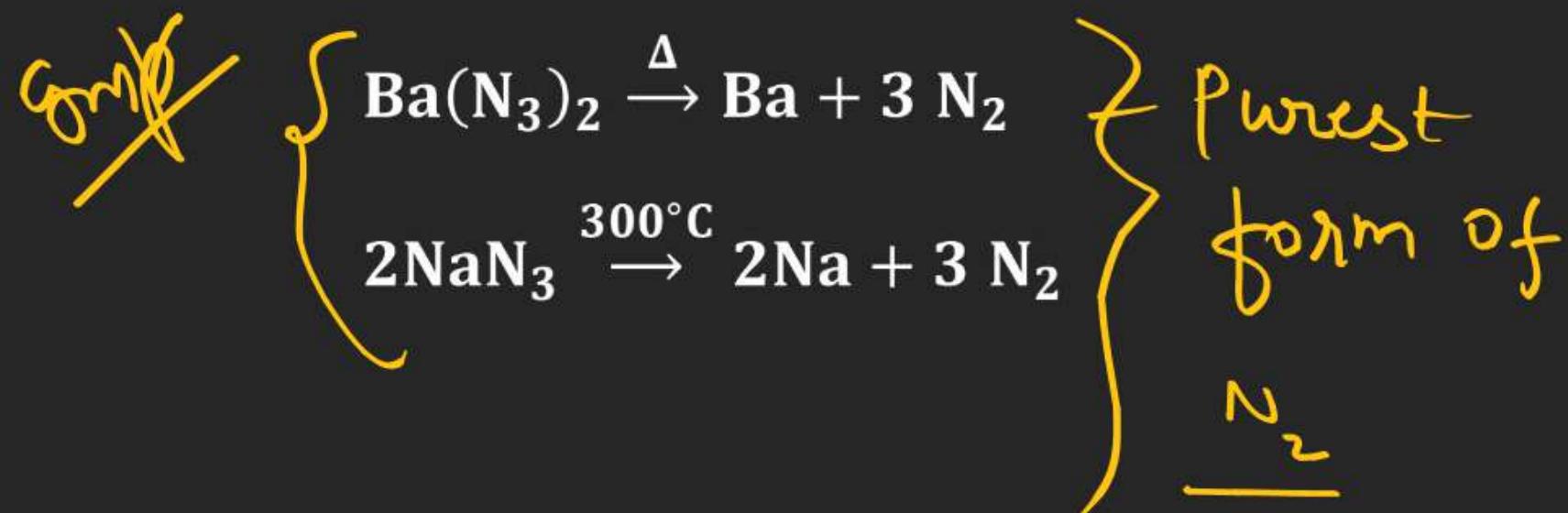
Small amounts of NO and HNO₃ are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

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- (ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.



Note : Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.



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(Trimendously explosive)

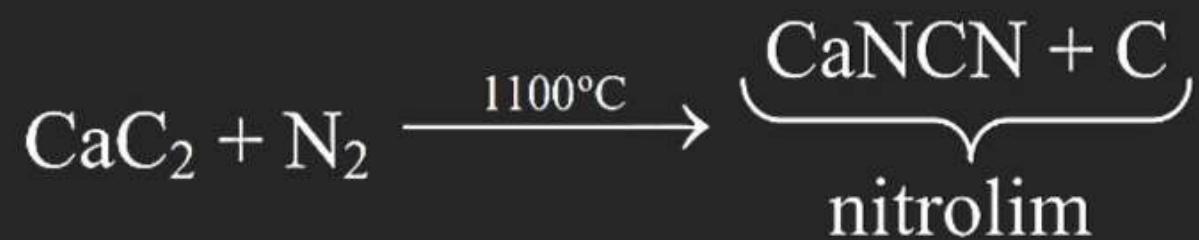
Physical properties :

- (i) ~~★~~ Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.
- (ii) Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N .
- (iii) It has a very low solubility in water (23.2 cm³ per litre of water at 273 K and 1 bar pressure)
- (iv) ~~★~~ Dinotrogen has low freezing and boiling points.

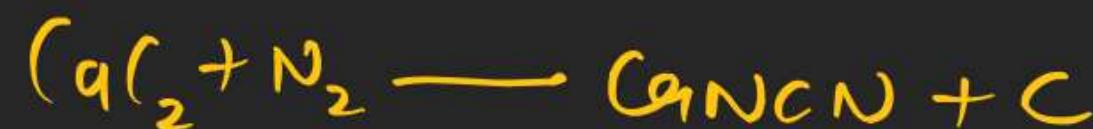
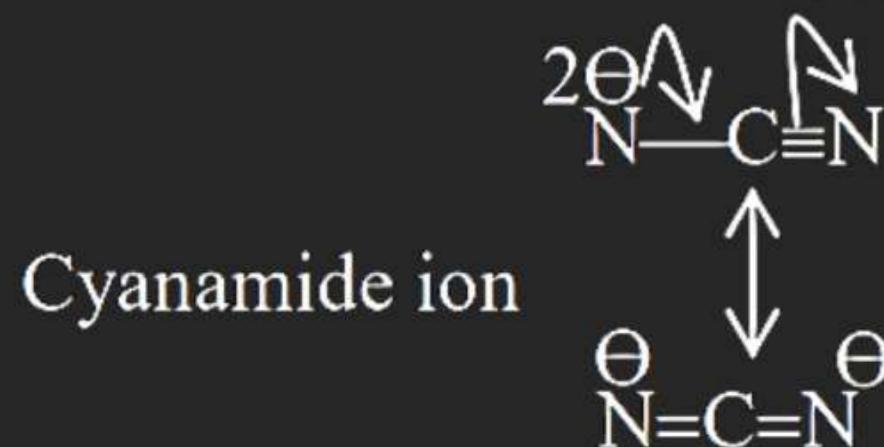
Chemical properties

Reaction with metal : At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

P-block Element

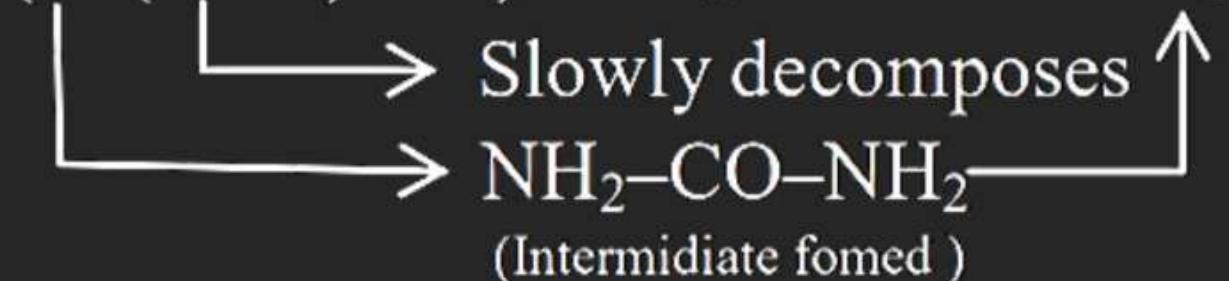
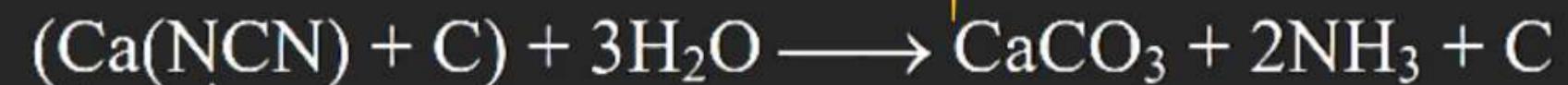


It is a very good fertiliser.



Calcium
cyanamide

nitrolim



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Ques. Why dinitrogen is inert at room temperature ?

Ans. Dinitrogen is inert at room temperature because of the high bond enthalpy of $\text{N}\equiv\text{N}$ bond. Reactivity, however, increases rapidly with rise in temperature.

TYPES OF NITRIDE

Salt like or ionic : Li_3N , Na_3N , $\text{K}_3\text{N}(?)$, Ca_3N_2 , Mg_3N_2 , Be_3N_2

Covalent : AlN , BN , Si_3N_4 , Ge_3N_4 , Sn_3N_4

Interstitial : $\underbrace{\text{M} = \text{Sc}, \text{Ti}, \text{Zr}, \text{Hf}, \text{La}}_{\text{HCP or FCC}}$

AMMONIA

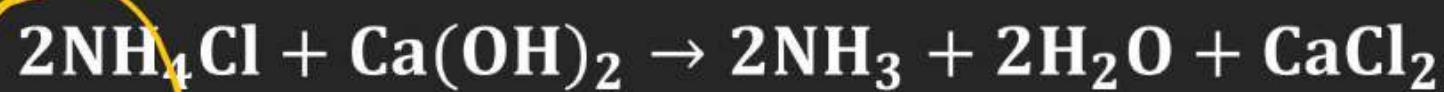
Preparation :

- (i) **Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.**

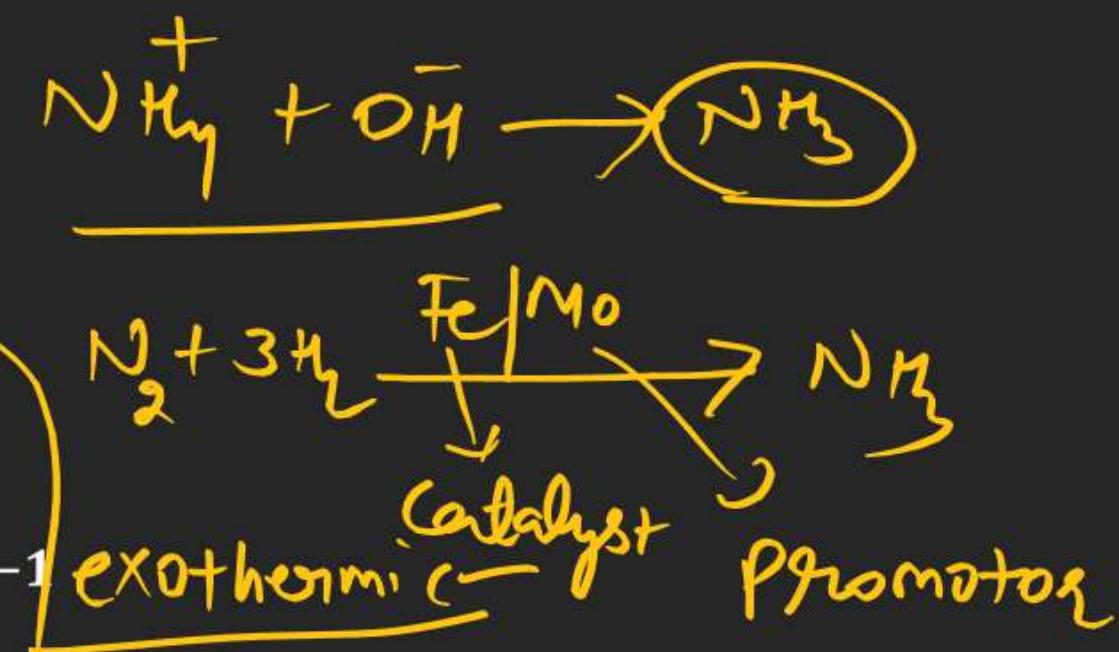
P-block Element



(ii) **Small scale preparation By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.**



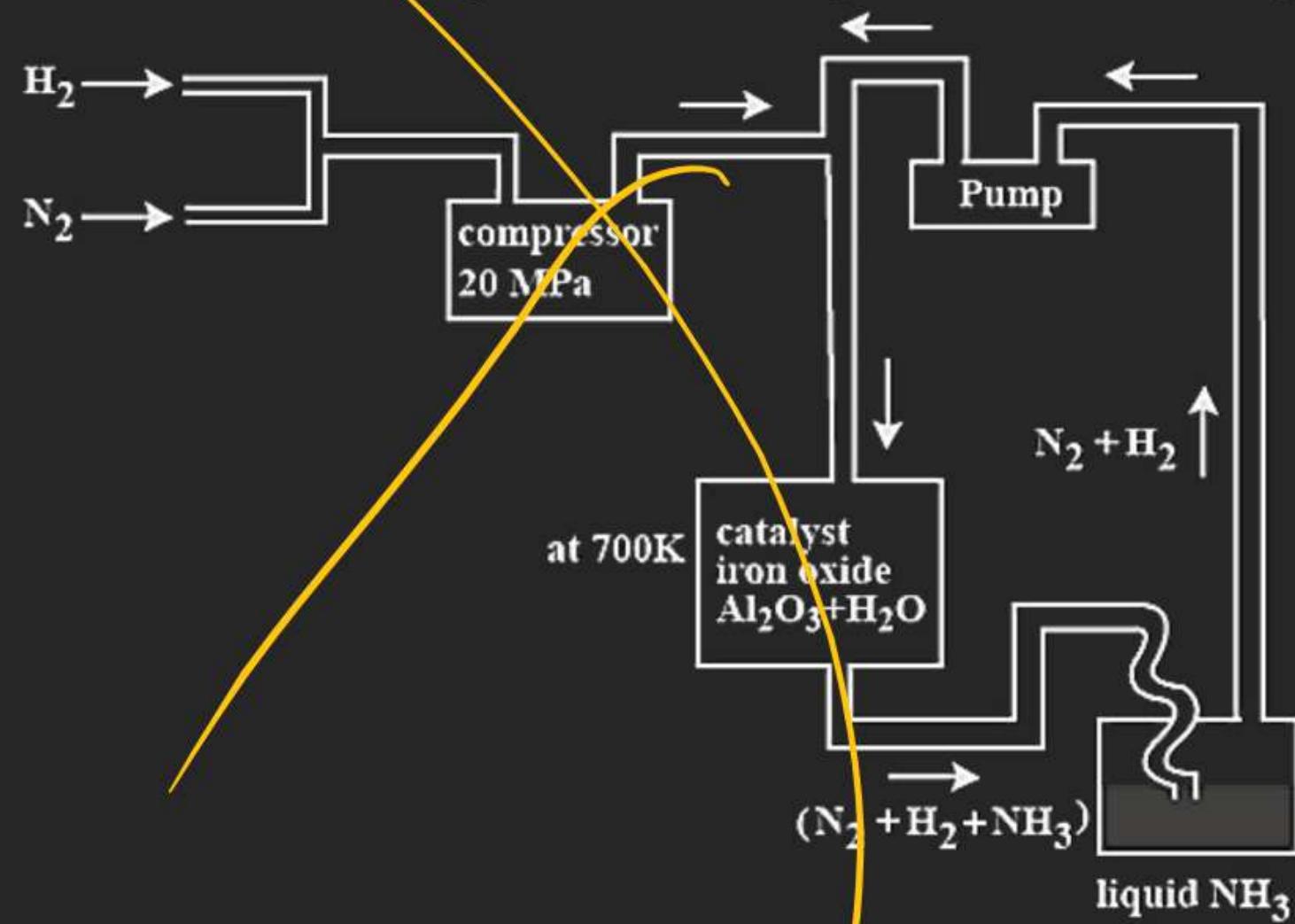
(iii) **Large scale manufacturing (Haber's Process)**



- ❖ According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.
- ❖ The optimum conditions for the production of ammonia are a pressure of $200 \times 10^5 \text{ Pa}$ (about 200 atm), a temperature of $\sim 700 \text{ K}$.

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- ❖ Use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.
- ❖ The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Manufacturing of Ammonia

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Other preparation :

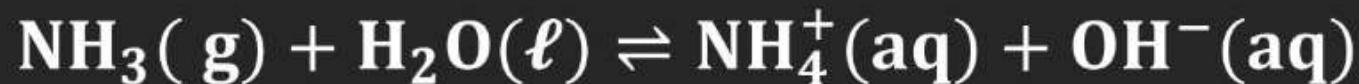
- (i) ~~Nitrate or nitrite reduction : $\text{NO}_3^-/\text{NO}_2^- + \text{Zn or Al} + \text{NaOH} \rightarrow \text{NH}_3 + [\text{Zn}(\text{OH})_4]^{2-}$ or $[\text{Al}(\text{OH})_4]^-$~~
- (ii) ~~Metal nitride hydrolysis : $\text{N}^{3-} + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 \uparrow + 3\text{OH}^-$~~

Properties :

- (i) Ammonia is a colourless gas with a pungent odour.
- (ii) Its freezing and boiling points are 198.4 and 239.7 K respectively.
- (iii) In the solid and liquid states, it is associated through hydrogen bonds.
- (iv) Ammonia gas is highly soluble in water.

Basic character :

Its aqueous solution is weakly basic due to the formation of OH^- ions.



It forms ammonium salts with acids, e.g., NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, etc.

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Note - 2 : Hydrolysis and Ammonolysis occurs is a same way.



Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

Uses :

- (i) Ammonia is used to produce various nitrogenous fertilisers.
- (ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.
- (iii) Liquid ammonia is also used as a refrigerant.

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laughing gas

$\text{NO}, \text{N}_2\text{O}$

Oxides of Nitrogen

Oxides of Nitrogen

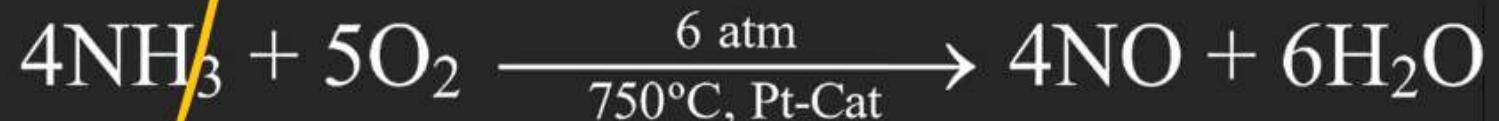
Name	Formula	Oxidation state of nitrogen	Common Methods of Preparation	Physical Appearance and Chemical nature
Dinitrogen oxide [Nitrogen oxide]	N_2O	+1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{ K}} 2\text{N}_2\text{O}_3$	Blue solid, acidic Blue liquid (-30°C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{ K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	Brown gas. Acidic
Nitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} \text{N}_2\text{O}_4$	Colourless solid / liquid, acidic
Nitrogen pentaoxide [Nitrogen (V) oxide]	N_2O_5	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	Colourless solid, acidic

Preparations:**1. N₂O**

(dil. & cold)

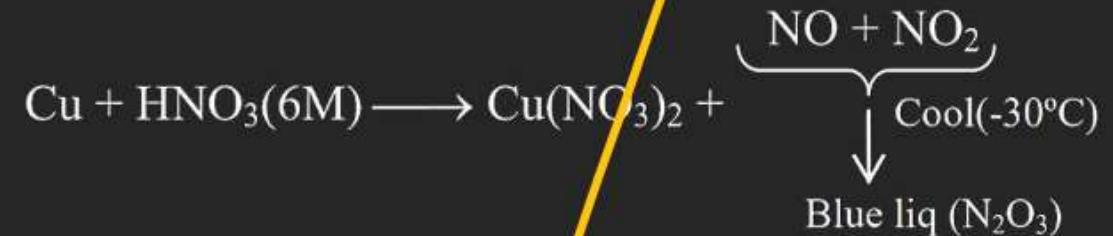
2. NO

hot

**(iii) Oswald process-Restricted oxidation of NH₃. Industrial process.**

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3. N_2O_3

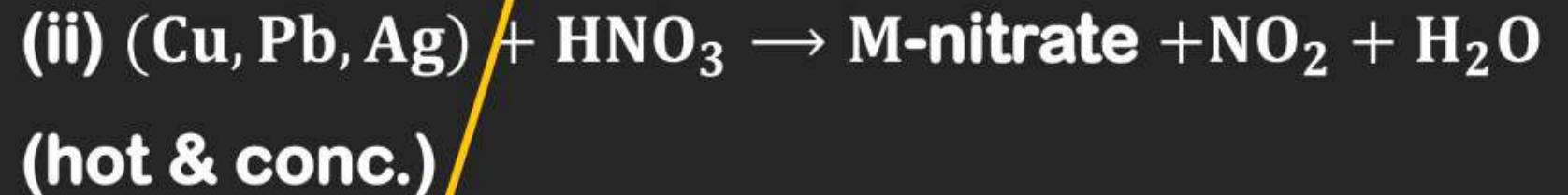


(ii)

4. NO_2



$\text{M} = \text{Pb, Cu, Ba, Ca}$



N_2O_5

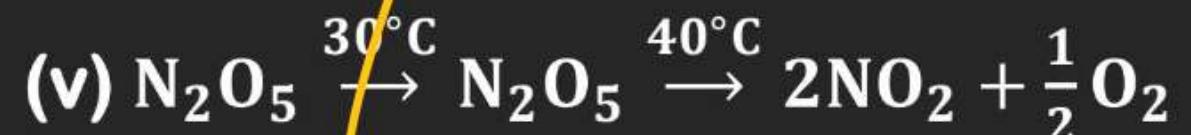


Properties:**(I) Decomposition Behaviour**

(Blue liq.) at (-30°C)



(white solid) Brown gas at (-11°C)



P-block Element

Colourless	yellow
Solid	liq.

(II) Reaction with H₂O & NaOH



(i) N₂O : Fairly soluble in water and produces neutral solution

(ii) NO : Sparingly soluble in water and produces neutral soln.

(iii) N₂O₃: 2HNO₂
Hence it is known as

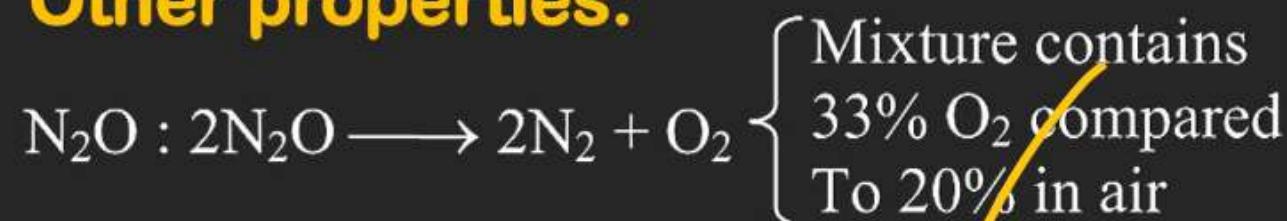
NaNO₂ anhydride of HNO₂ NaNO₂

(iv) NO₂: HNO₂ + HNO₃
called as mixed anhydride NaNO₂ + NaNO₃

(v) N₂O₅: 2HNO₃
called as anhydride of NaNO₃ HNO₃

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Other properties:



Hence it is better supporter for combustion



NOTE: -



(ii) **It supports combustion also for molten sulphur and hot phosphorous.**



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(iii) It is being absorbed by FeSO_4 solution.

(iv) It is having reducing property.



(v) NO shows oxidising property also.



(Used for NH_2OH preparation)

(vi) NO combines with X_2 ($\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{F}_2$) to produce NOX



N_2O_3 : No more properties.

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(1) It is having oxidising property.



P-block Element

(2) Reducing property of NO_2 .



N_2O_5 :

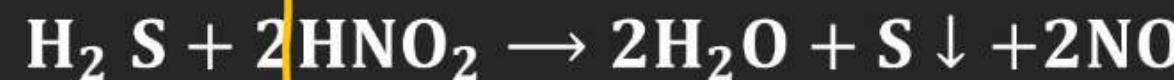


I_2O_5 is used for the estimation of CO

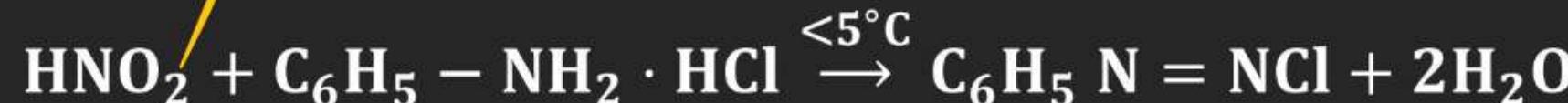


This like proves that N_2O_5 is consisting of ion pair of NO_2^+ & NO_3^-

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(b) Reducing property : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.



Benzene diazonium chloride

P-block Element

NITRIC ACID

Imp.

It was named **aqua fortis** (means strong water) by alchemists.

Preparation :

Laboratory Method : By heating KNO_3 or NaNO_3 and concentrated H_2SO_4 in a glass retort.



Large scale preparation (Ostwald's process) :

(i) This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.



(ii) Nitric oxide thus formed combines with oxygen giving NO_2 .



(iii) Nitrogen dioxide so formed, dissolves in water to give HNO_3 .





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NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4 .

Birkel and Eyde Process or arc process



Properties

Physical properties

(i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(ii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into NO_2 .

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The yellow or brown colour of the acid can be removed by warming it to 60 – 80°C and bubbling dry air through it.

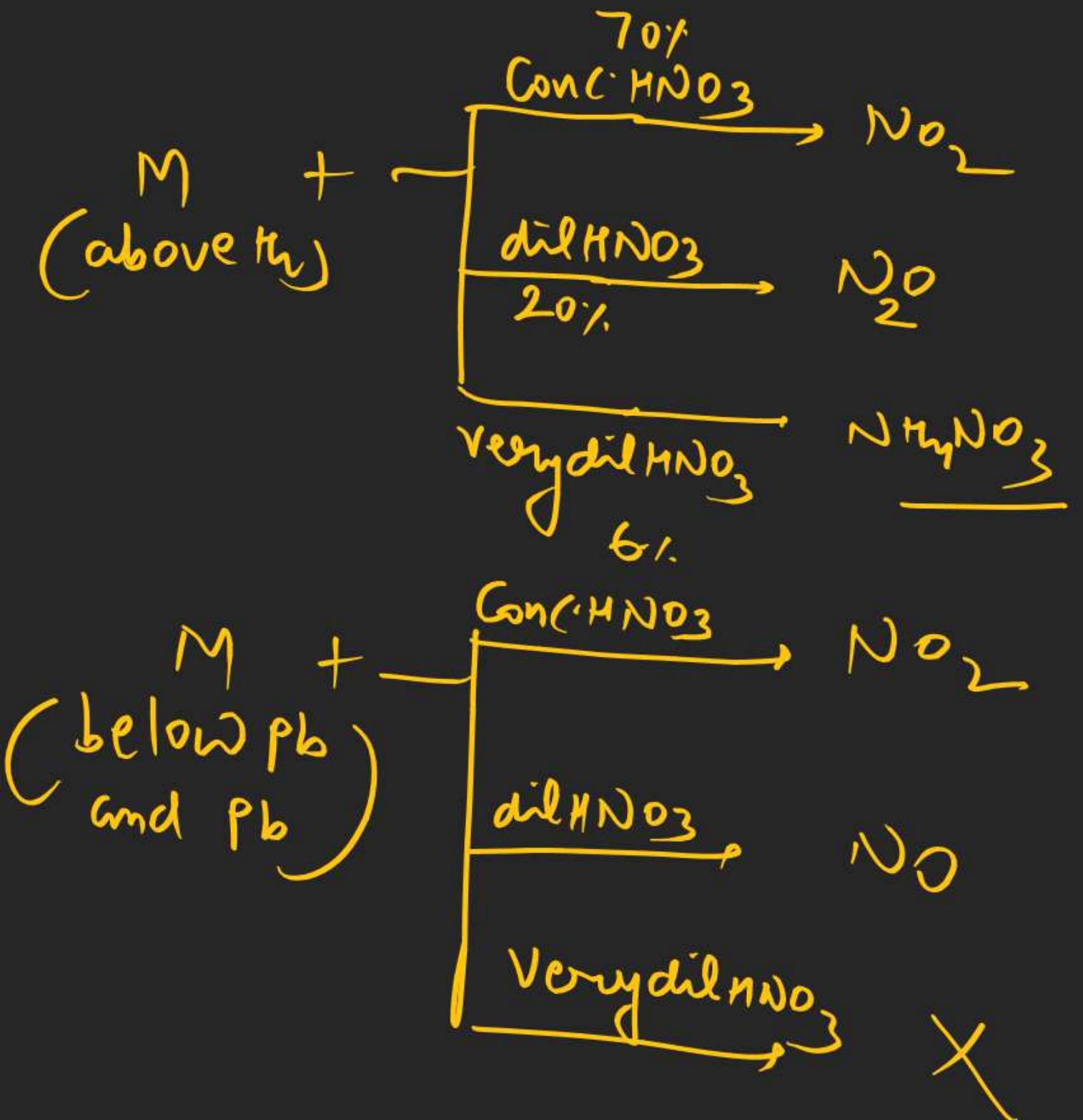
Chemical properties

Acidic character in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



Oxidising nature: Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.





Li

K

Cu

Ni

Mg

Al

Mn

Zn

Cr

Fe

Cd

Co

Ni

Sn

Pb

Hg

Ag

Tl

monmetal
or
Metalloide + Conc HNO_3 — ic form of oxyacid + NO_2



As



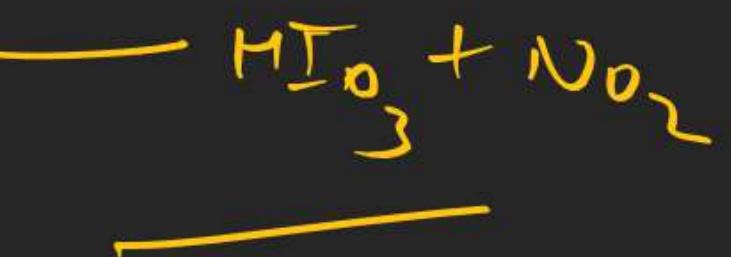
P



S



X_2



Note

Highest O.S = ic acid

except Halogen

+ 5 O.S \Rightarrow ic acid

HIO_3
Iodide
acid

HIO_4
Iodide acid

P-block Element

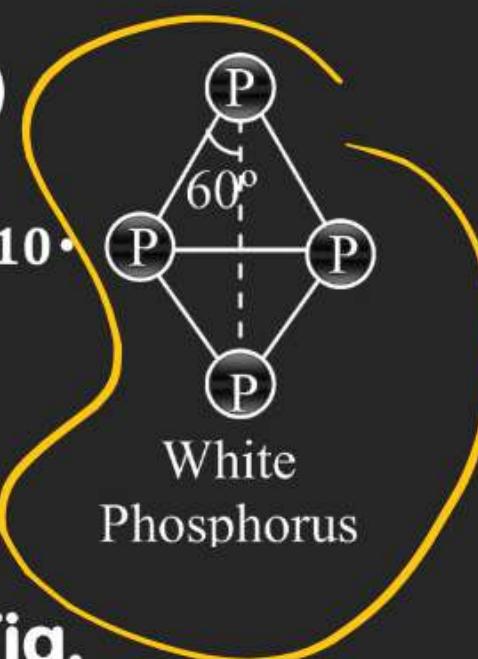
ALLOTROPIC FORMS OF PHOSPHORUS

Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus dissolves in boiling NaOH solution in an inert atmosphere giving PH_3 .



(Sodium hypophosphate)

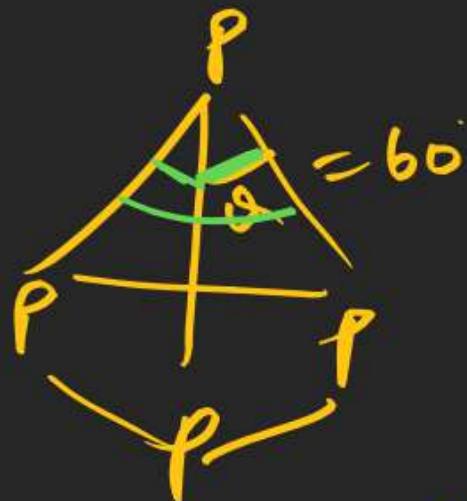
It readily catches fire in air to give dense white fumes of P_4O_{10} .



It consists of discrete tetrahedral P_4 molecule as shown in Fig.

Red phosphorus : It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig.

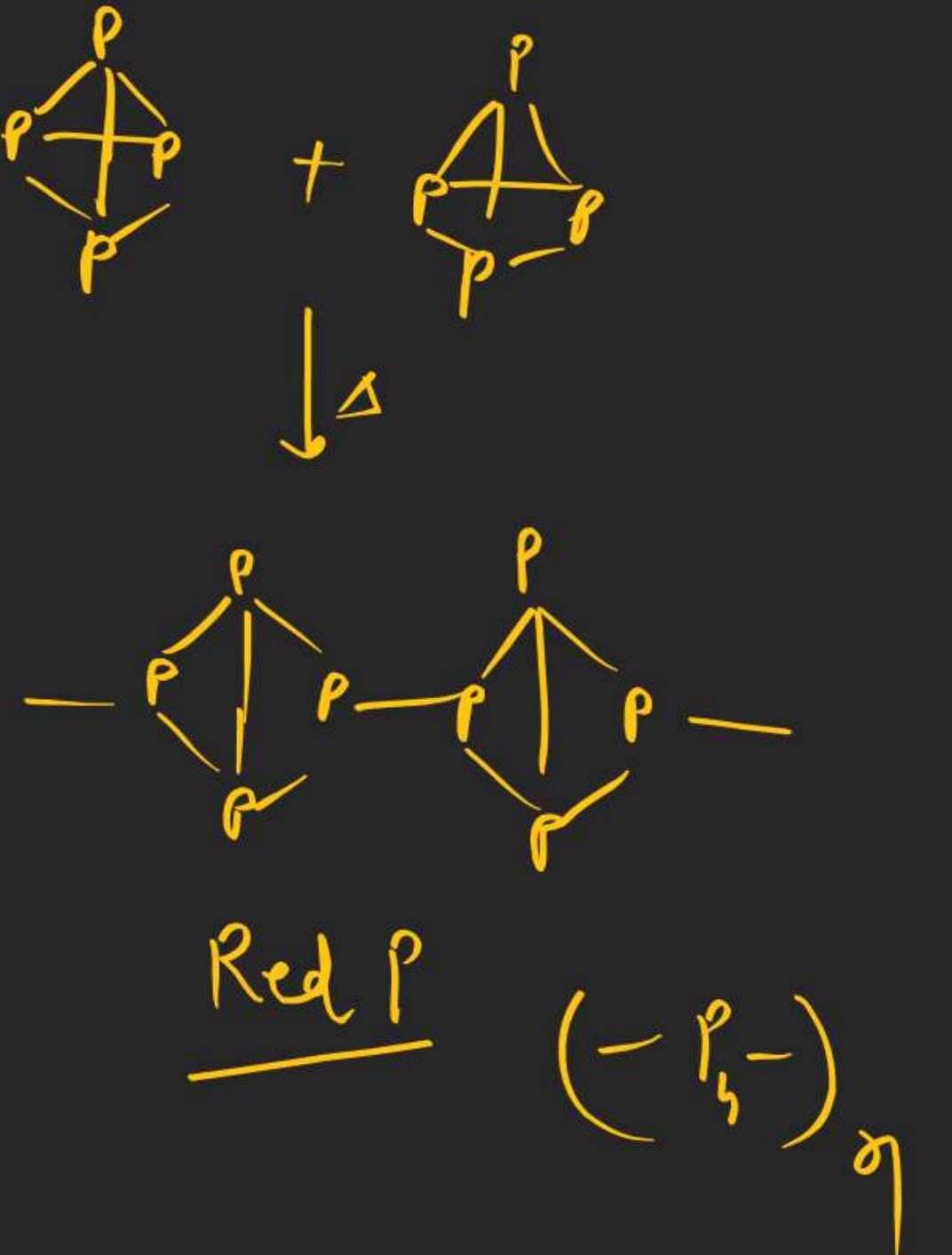
White



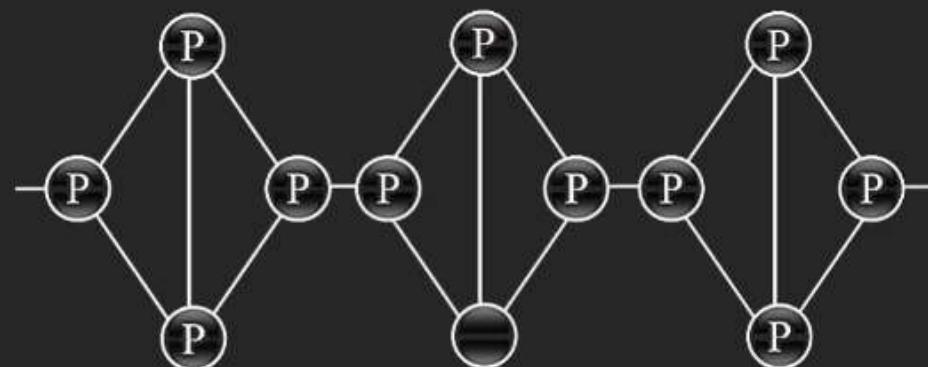
$$P - \hat{P} - P = 12$$

$$P - P_{\text{face}} = 4$$

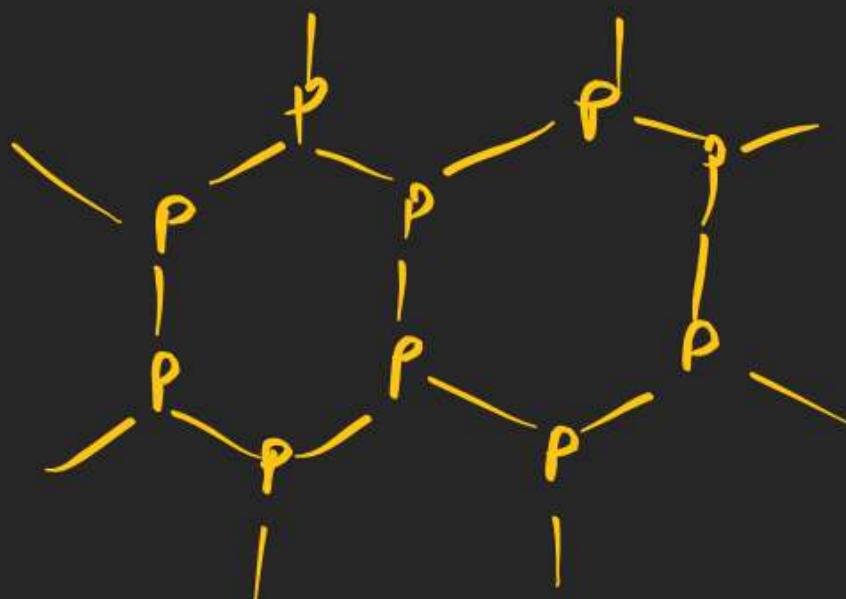
$$P - P_{\text{side}} = 6$$



P-block Element



Red Phosphorus



Black phosphorus :

- (i) It has two forms α -black phosphorus and β -black phosphorus.
- (ii) α -Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K.
- (iii) It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- (iv) It does not oxidise in air. β -Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.
- (v) It does not burn in air upto 673 K.

P-block Element

Comparison between White and Red Phosphorus

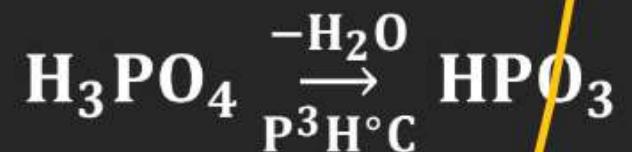
Property	White phosphorus	Red phosphorus
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure. Attains yellow colour On standing.	Red.
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	Insoluble.
Solubility in CS_2	Soluble	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable
Phosphorescence	Glows in dark	Does not glow in dark.
Molecular formula	P_4	Complex polymer.

P-block Element

Preparation of white 'P'



(Coke) **White 'P'**



meta phosphoric acid



Coke **white 'P'**

P-block Element

Reactions of 'P'



Reaction with hot metal —



or



or



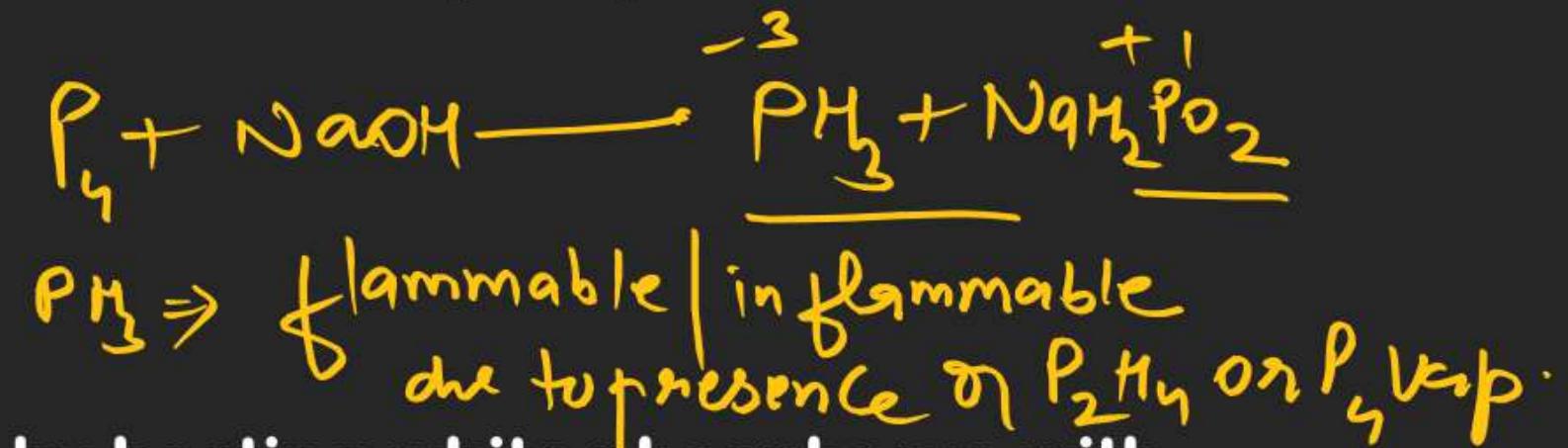
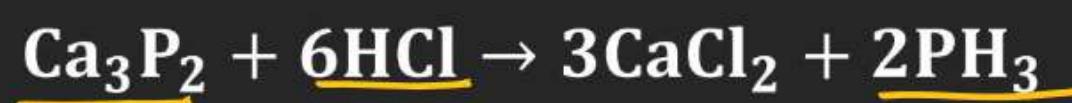
P-block Element

Gmp PHOSPHINE

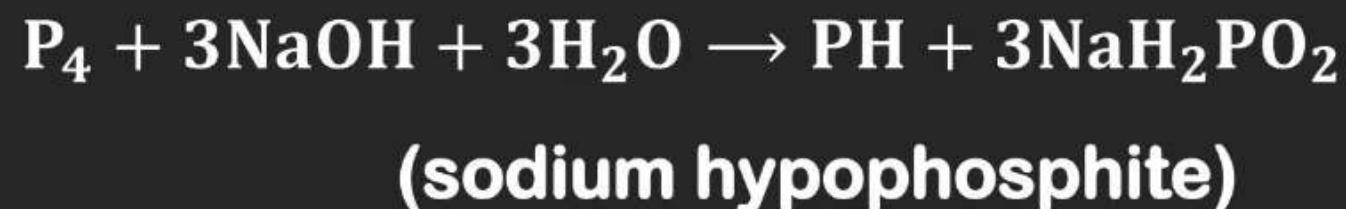
Preparation

(i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute

HCl.



(ii) Laboratory preparation it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2 .

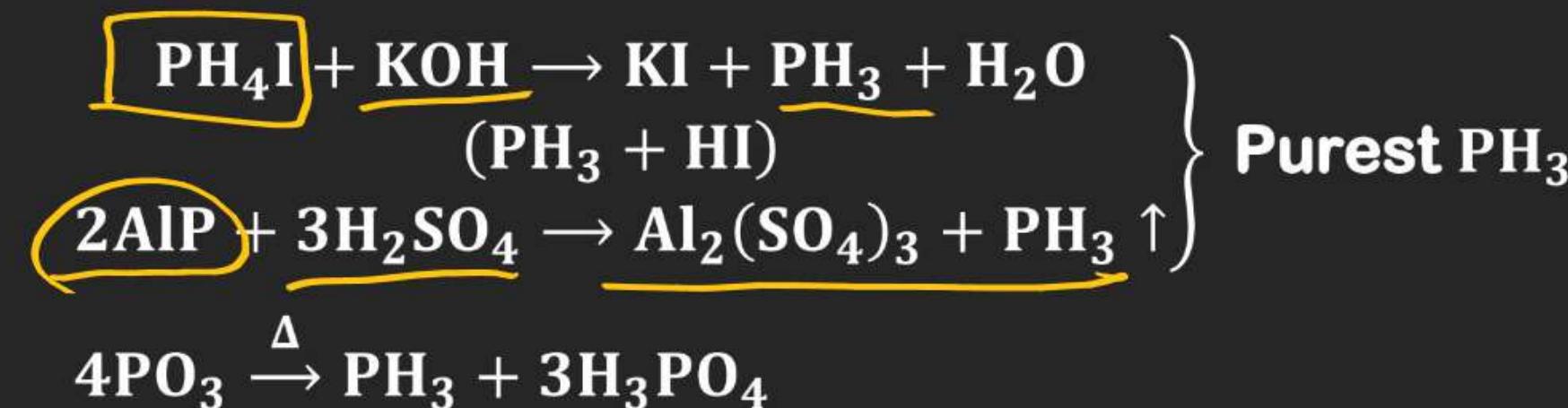


Pure \rightarrow Inflammable

Pure PH_3 is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

P-block Element

Other preparation



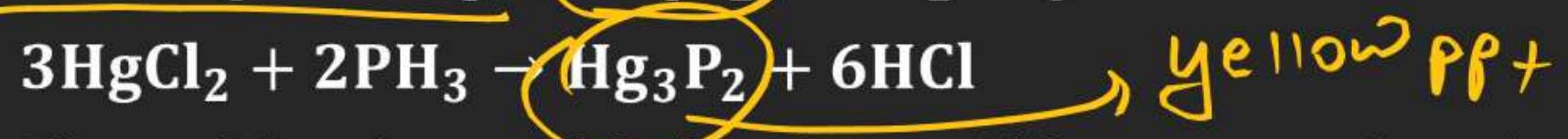
Physical Properties :

- ★ (i) It is a colourless gas with rotten fish smell and is highly poisonous.
- ★ (ii) It explodes in contact with traces of oxidising agents like HNO_3 , Cl_2 and Br_2 vapours.
- (iii) It is slightly soluble in water but soluble in CS_2 . The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2 .

P-block Element

Chemical Properties :

(i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.



Black

yellow ppt

Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,



P-block Element



Black ppt.



white/colourless solid

**which is used for making
fire-proof cotton fabrics**

Note :

Like NH_3 , PH_3 also can form addition product.



PH_3 can be absorbed by Ca(OCl)Cl .



P-block Element

Uses :

- (i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- (ii) It is also used in smoke screens.

PHOSPHORUS HALIDES

Phosphorus forms two types of halides, PX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and PX_5 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$).

PHOSPHORUS TRICHLORIDE

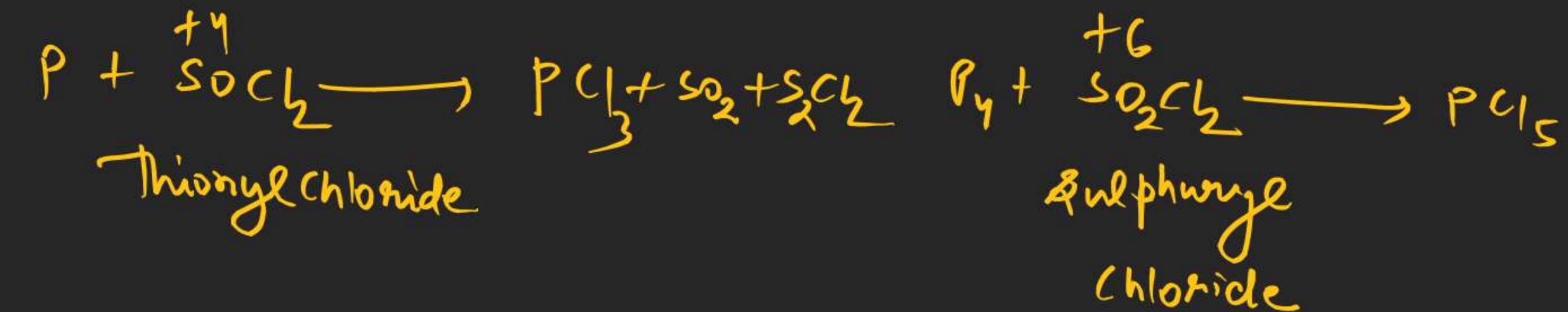
Preparation

- (i) By passing dry chlorine over heated white phosphorus.



- (ii) By the action of thionyl chloride with white phosphorus.





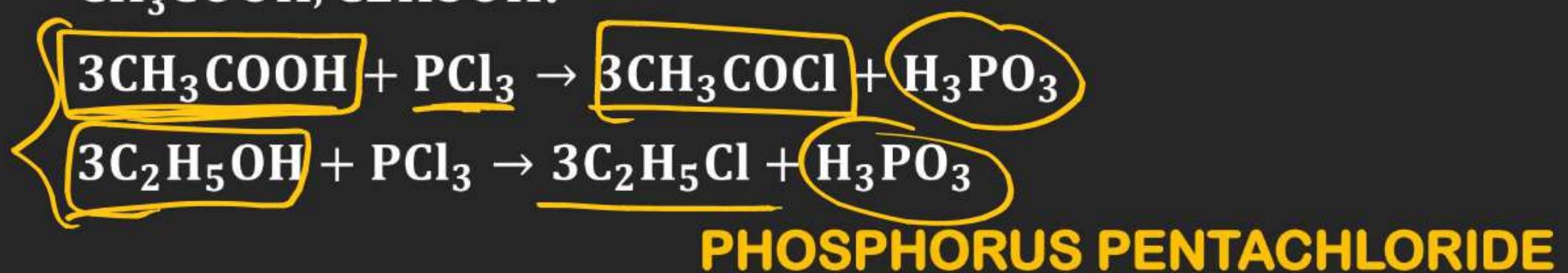
P-block Element

Properties

- (i) It is a colourless oily liquid
- (ii) Hydrolyses in the presence of moisture.



- (iii) It reacts with organic compounds containing $-\text{OH}$ group such as



Preparation

- (i) By the reaction of white phosphorus with excess of dry chlorine.



- (ii) By the action of SO_2Cl_2 on phosphorus.



P-block Element

Properties :

(i) PCl_5 is a yellowish white powder

(ii) It hydrolysis in moist air to POCl_3 and finally gets converted to phosphoric acid.

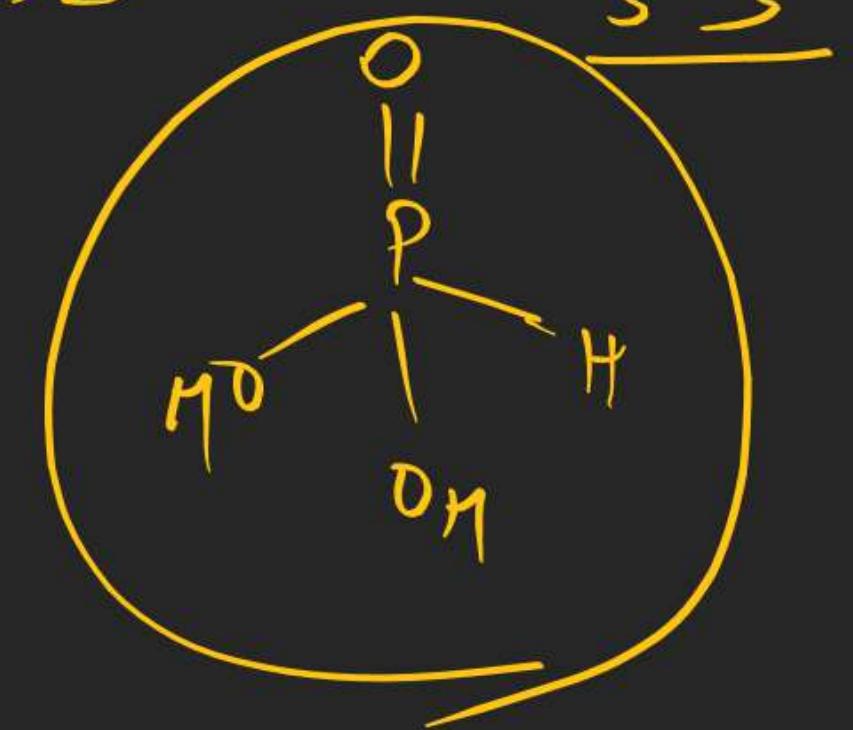
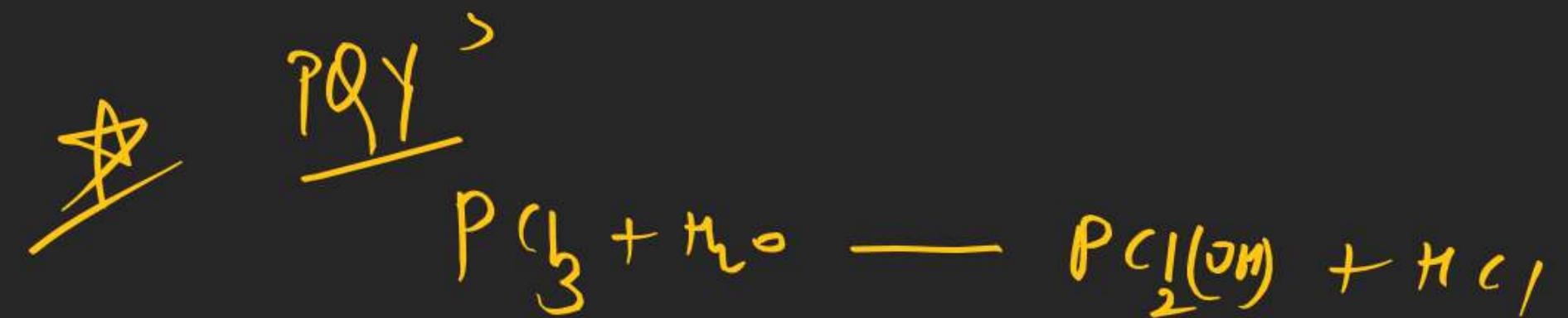


(iii) When heated, it sublimes but decomposes on stronger heating.



(iv) It reacts with organic compounds containing $-\text{OH}$ group converting them to chloro derivatives.





P-block Element

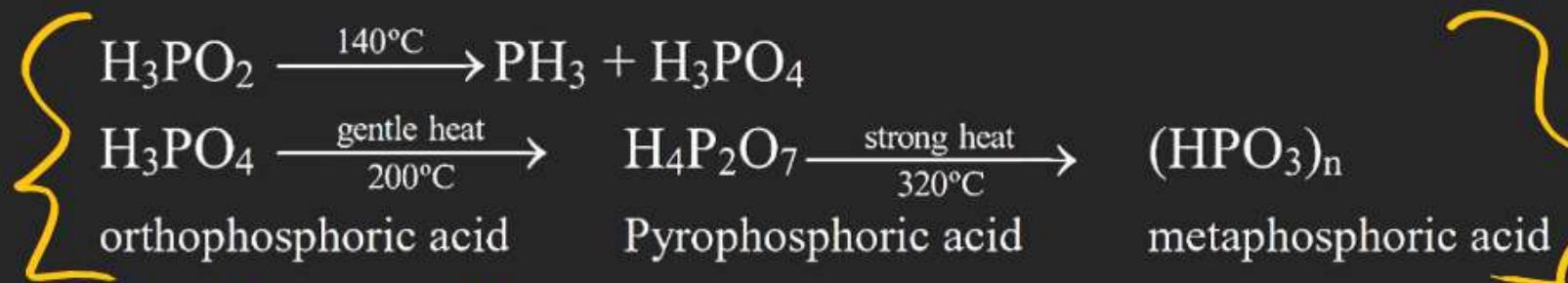
Oxoacids of Phosphorus

Name	Formula	Oxidation State of Phosphorus	Characteristic Bonds and their number	Preparation
Hypophosphorus (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	White P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$\text{P}_2\text{O}_3 + \text{H}_2\text{O}$
Pyrophosphorous	$\text{H}_4\text{P}_2\text{O}_5$	+3	Two P – OH Two P – H Two P = O	$\text{PCl}_3 + \text{H}_3\text{PO}_3$
Hypophosphoric	$\text{H}_4\text{P}_2\text{O}_6$	+4	Four P – OH Two P = O One P – OH	Red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = P	$\text{P}_4\text{O}_{10} + \text{H}_2\text{O}$
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$	+5	Four P – OH Two P = H One P – O – P	Heat phosphoric acid
Metaphosphoric	$(\text{HPO}_3)_n$	+5	Three P – OH Three P = O Three P – O – P	Phosphorous acid $+\text{Br}_2$, heat in a sealed tube



P-block Element

Heating Effect :



Graham salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten NaPO_3 . Graham's salt is soluble in water. These solutions give precipitates with metal ions such as Pb^{2+} and Ag^+ but not with Ca^{2+} and Mg^{2+} .

Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.



Sodium trimetaphosphate

(Graham's salt) (glass)

P-block Element

Elemental State

Oxygen exist as diatomic molecular gas in this case there is $p\pi - p\pi$ overlap thus two O atoms form double bond $O = O$. The intermolecular forces in O_2 are weak VB forces. $\therefore O_2$ exist as gas . On the other hand, other elements of family do not form stable $p\pi - p\pi$ bonds and do not exist as M_2 molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg.



Catenation

In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.



(Poly oxides)



(Polysulphides or polysulphones)



P-block Element

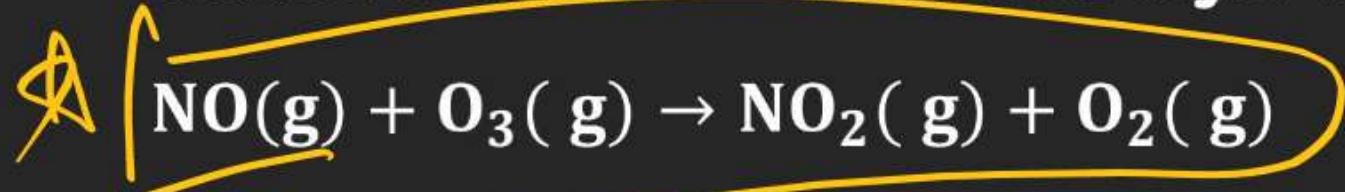
Neutral oxide: There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N₂O.

OZONE

Ozone is an allotropic form of oxygen.

Threats to ozone layer

(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.



(ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

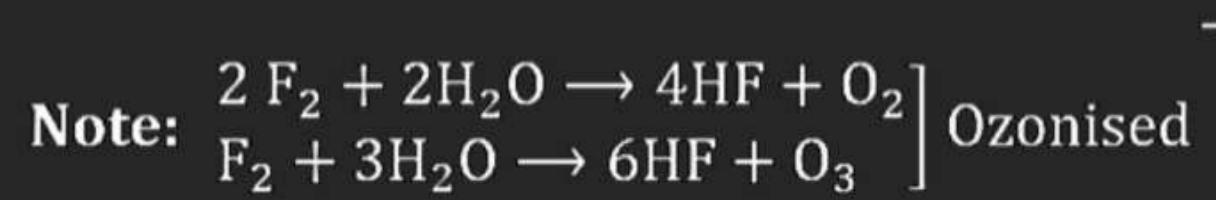
P-block Element

Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.



Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.



Is separated by passing into spiral tube cooled by liq. Oxygen air. Ozone condenses at -112.4°C . [b.p. of $\text{O}_2 - 183^\circ\text{C}$; b.p. of liq. Air is -190°C]

P-block Element

Properties

- (i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- (ii) It is diamagnetic gas.
- (iii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

Toxic effect :

- (a) Toxic enough (more toxic than KCN). Its intense blue colour is due to the absorption of red light.
- (b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Oxidizing properties

It is one of best oxidising agent, in acid solution, its standard reduction potential value is 2.07 V.
 $O_3 + 2H^+ + 2e \rightarrow O_2 + H_2O \quad E^\circ = +2.07 \text{ V}$

It is next to F₂. [above 2.07 V, only F₂, F₂O are there]

P-block Element

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.



(i) Metal Sulphides to Sulphates.

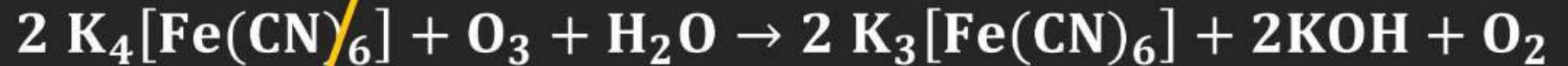
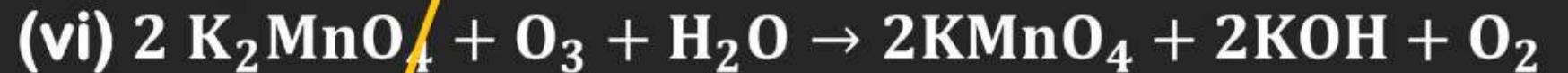
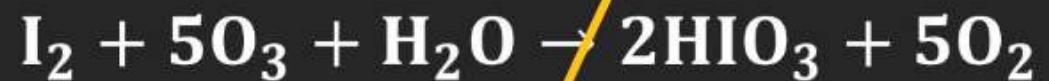


P-block Element

(iv) **Moist S, P, As + O₃ ⇒**



(v) **Moist I₂ → HIO₃ whereas dry iodine → I₄O₉ (yellow)**



P-block Element



Brown



P-block Element



In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O -atom.



Uses :

(i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

P-block Element

Uses : (i) As a rocket propellant:



(ii) In detection of Cr^{+3} , Ti^{+4} etc.



Yellow or orange

Pertitanic acid

ALLOTROPIRIC FORMS OF SULPHUR

α – sulphur \rightleftharpoons β – sulphur

~~$\geq 369\text{ K}$~~

~~369 K~~

At 369 K both the forms are stable. This temperature is called transition temperature.

P-block Element

Rhombic sulphur (α -sulphur)

- (i) This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06 .
- (ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2 .
- (iii) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.
- (iv) It is readily soluble in CS_2 .

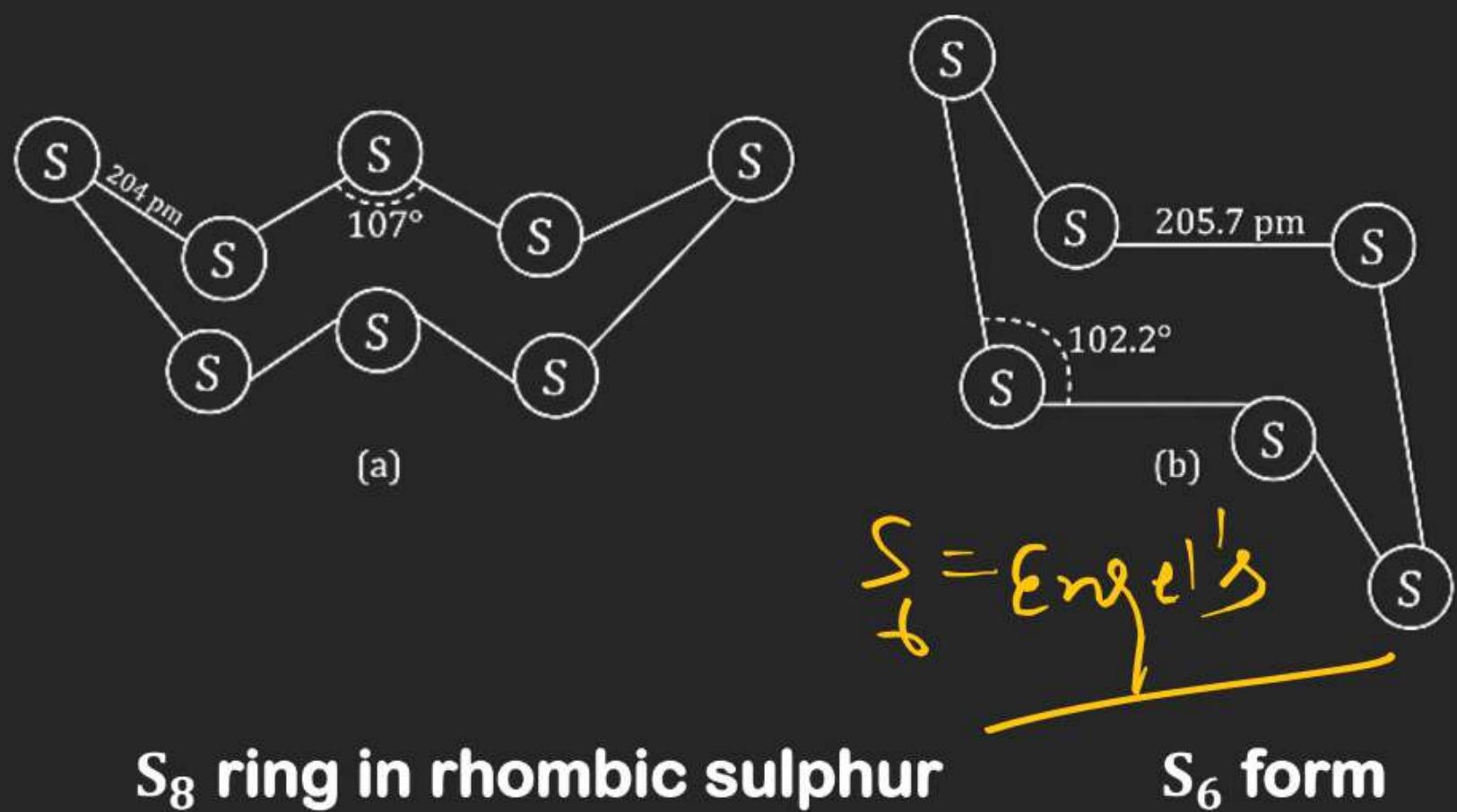
Monoclinic sulphur (β -sulphur)

- (i) Its m.p. is 393 K and specific gravity 1.98.
- (ii) It is soluble in CS_2 .

Structure of α and β sulphur

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape.

P-block Element



Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last two decades. In cyclo- S_6 , the ring adopts the chair form. At elevated temperatures (~ 1000 K), S_2 is the dominant species and is paramagnetic like O_2 .

P-block Element

SULPHURIC ACID

Industrial Manufacturing (Contact process)

Steps involved :

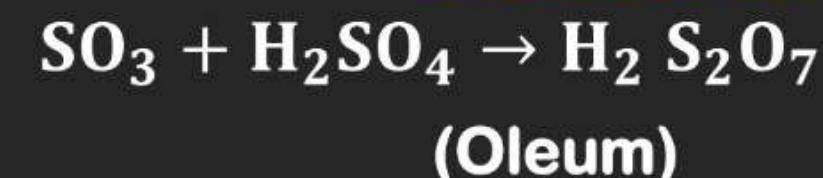
- (i) Burning of sulphur or sulphide ores in air to generate SO_2 .
- (ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5):

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

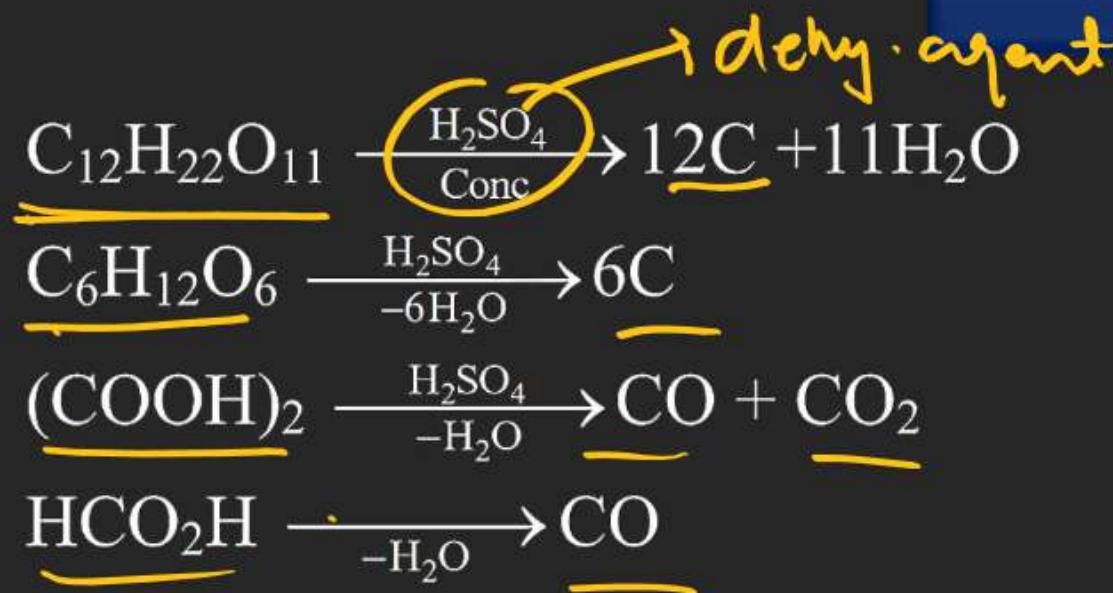


The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume.

- (iii) The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration.



P-block Element

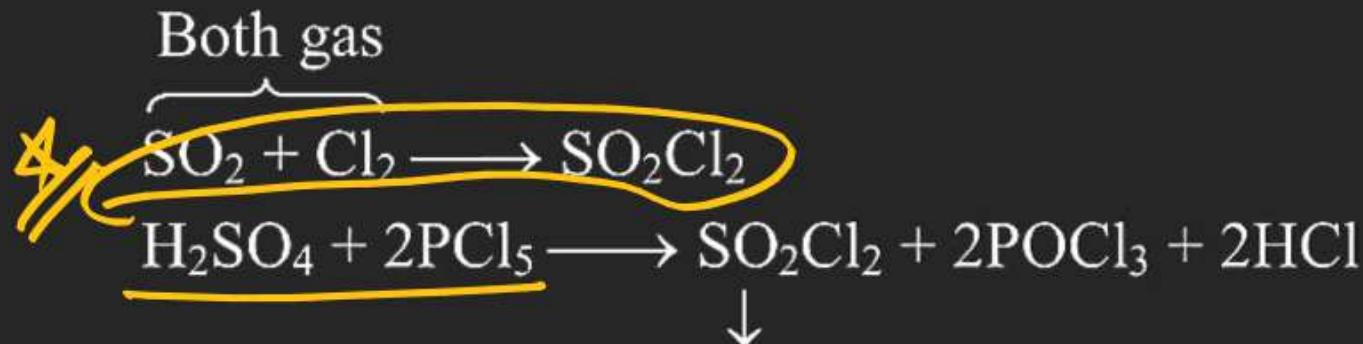


(3) Oxidizing Nature :

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids.



H_2SO_4 & SO_3 :



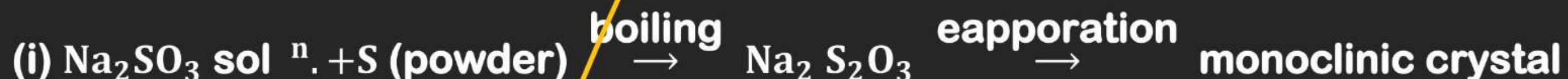
Uses: good chlorinating agent

- (i) petroleum refining
- (ii) manufacture of pigments, paints and dyestuff intermediates
- (iii) detergent industry
- (iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising)
- (v) storage batteries
- (vi) in the manufacture of nitrocellulose products and
- (vii) as a laboratory reagent.

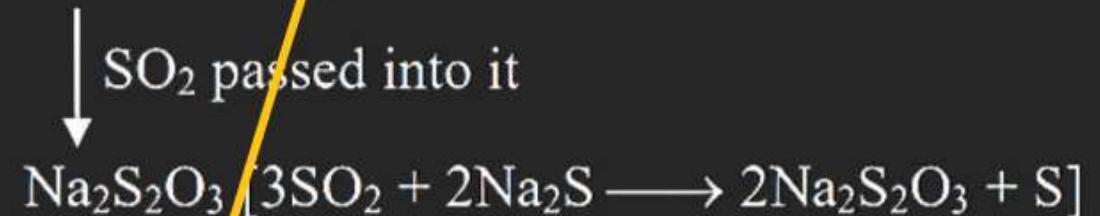
P-block Element

SODIUM THIOSULPHATE

Prepn:



(ii) Salt cake Coke



Props:

