GROUP 15 Section - 4

The elements of group 15 have $ns^2 np^3$ as their valence shell electronic configuration. They can complete their octets in two different ways :

(a) Electron Transfer : The atoms of the elements of this group may accept three electrons from more metallic elements to form triply charged negative ions such as nitride, N^{3-} ion and phosphide, P^{3-} ion and thereby attain noble gas configuration. Only small atoms can form highly charged negative ions because of their greater electronegativities. Obviously nitrogen with greater electronegativity and smaller size, has a stronger tendency to form N^{3-} ion as compared to phosphrous to form P^{3-}. The other members of the family show little tendency to form triply charged negative ions and this tendency decreases down the group because of increase of size and decrease of electronegativity.

The elements of this group also exhibit oxidation states of +3 and +5 and these ions are generally not known because their ionization enthalpy will be very high. As we go down the group, the stability of +3 oxidation state increases while that of +5 decreases.

(b) Electron Sharing : Since the atoms of these elements contain three unpaired p-electrons so these can pair with unpaired p-electrons in another atom or atoms to form three covalent bonds, e.g. , NH_3, PH_3, AsH_3, BiH_3.

Hydrides :

Stability order	:	$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
Basicity	:	$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
H - E - H bond angle	:	$NH_3 > PH_3 > AsH_3 > SbH_3$
Boiling point	:	$SbH_3 > NH_3 > AsH_3 > PH_3$
Reducing character	:	$BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$

The bond angle in PH_3, As H_3 and SbH_3 is close to 92° which suggests the orbitals used for bonding are close to pure p-orbitals.

Oxides :

Oxides with higher oxidation state are more acidic :

$$\underbrace{\overset{\mathrm{I}}{N_2O} < \overset{\mathrm{II}}{NO}}_{\text{neutral}} < \underbrace{\overset{\mathrm{III}}{N_2O_3} < \overset{\mathrm{IV}}{NO_2} < \overset{\mathrm{V}}{N_2O_5}}_{\text{acidic}}$$

Moreover, acidity decreases down the group :

$$\underbrace{N_2O_3 > P_4O_6}_{\text{acidic}} > \underbrace{As_4O_6 > Sb_4O_6}_{\text{Amphoteric}} > \underbrace{Bi_2O_3}_{\text{basic}}$$

Halides : NX_3 are unstable except NF_3.

Ammonia forms NCl_3, $NBr_3.6NH_3$ and $NI_3.6NH_3$ (used as explosives) with Cl_2, Br_2 and I_2 respectively. NCl_3 was formerly used to bleach flour to make white bread but it was banned when it was suspected that this bread sent dogs mad !!

Penta halides are more covalent than trihalides because higher oxidation state leads to high polarising power.

Nitrogen and its Compounds :

Nitrogen is present in air to the extent of 78.06 % by volume. N_2 is colourless, tasteless, odorless and diamagnetic. It is lighter than air, sparingly soluble in water and a non-supporter of combustion.

Preparation :

1. In laboratory, nitrogen samples are obtained by warming ammonium nitrite or by oxidising ammonia by bromine water, sodium hypochlorite (NaOCl) or CuO

$$\underset{\text{Nitrite}}{NH_4Cl + NaNO_2} \xrightarrow{\Delta} \underset{\text{Unstable}}{NH_4NO_2} + NaCl$$

$$NH_4NO_2 \xrightarrow{\text{Warm}} N_2 + H_2O$$

$$NH_3 + CuO \longrightarrow N_2 + Cu + H_2O$$

$$+ NaOCl \longrightarrow N_2 + NaCl + H_2O$$

$$+ Br_2 \longrightarrow N_2 + NH_4Br.$$

2. Small quantities of very pure N_2 is obtained by carefully warming sodium azide, barium azide etc.

$$NaN_3 \xrightarrow{300°C} N_2 + Na$$

3. Heating ammonium salts with more oxidizing anion

$$(Cr_2O_7^{2-}, NO_2^-, NO_3^-, ClO_4^-)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O \;;$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

Chemical Properties :

(i) It is used to prepare NO in the 'Birkeland and Eyde process'.

$$N_2 + O_2 \xrightarrow[3500°C]{\text{Electric arc}} 2NO$$

(ii) It is used to prepare ammonia by 'Haber's Process'.

$$N_2 + H_2 \xrightarrow[\substack{500°C \\ 250\text{ atm}}]{Fe/Mo} NH_3$$

(iii) Reaction with metals :

$$\left.\begin{array}{l} N_2 + Mg \longrightarrow Mg_3N_2 \\ \quad + Al \longrightarrow Al\,N \\ \quad + Li \longrightarrow Li\,N \end{array}\right\} \xrightarrow{H_2O} NH_3\uparrow + \text{Metal hydroxide}$$

[a] Ammonia NH_3

Ammonia is a colourless gas having characteristic pungent smell. It is quite poisonous and brings tears in eyes. NH_3 is highly soluble in water due to extensive hydrogen bonding.

$$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Preparation :

1. In laboratory : $\underset{\text{ammonium salt}}{NH_4Cl} + NaOH \longrightarrow NaCl + NH_3 + H_2O$

NH_3 produced is dried with quick lime CaO. Note that it cannot be dried with H_2SO_4, $CaCl_2$ or P_4O_{10} as they react with the gas instead of drying it.

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
$$+ CaCl_2 \longrightarrow CaCl_2 \,.\, 8NH_3$$
$$+ P_4O_{10} \longrightarrow (NH_4)_3PO_4$$

2. Haber - Bosch Process :

$$N_2 + H_2 \underset{\substack{\text{high pressure (200 atm)} \\ \text{low temp. (500°C)}}}{\overset{\text{Finely divided Fe + Mo}}{\rightleftharpoons}} NH_3 \uparrow \qquad \Delta H^{\ominus} = -46.1 \text{kJ/mol}$$

3. NH_3 is prepared by the Cynamide process :

$$CaO + C \xrightarrow{1000°C} CaC_2 + CO\uparrow$$
$$CaC_2 \xrightarrow{+N_2} \underset{\text{Calcium cynamide}}{CaNCN + C}$$
$$CaNCN \xrightarrow{+H_2O} NH_3\uparrow + CaCO_3$$

4. Serpeck's Process :

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO \;;\; AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \uparrow$$

Chemical Properties :

1. Ammonia is a non supporter of combustion but burns in oxygen with a pale yellow flame if continuous heat is supplied.

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 3H_2O$$

Also, it undergoes catalytic oxidation.

$$4NH_3 + 5O_2 \xrightarrow[800°C]{\text{Pt gauze}} 4NO + 6H_2O$$

2. Formation of complex ions used in qualitative analysis :

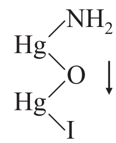
$$\underset{\text{excess}}{NH_4OH} + \underset{\text{white}}{AgCl} \longrightarrow \underset{\text{colourless}}{Ag(NH_3)_2Cl} + H_2O$$

$$+ CuSO_4 \longrightarrow \underset{\text{Blue}}{Cu(OH)_2} \downarrow + (NH_4)_2SO_4 \;;\; 4NH_3 + CuSO_4 \longrightarrow \underset{\text{Deep Blue}}{[Cu(NH_3)_4]SO_4}$$

$$+ ZnSO_4 \longrightarrow \underset{\text{white}}{Zn(OH)_2} \downarrow$$

3. Reaction with Nessler's Reagent is used as a test to detect ammonia :

$$\underset{\text{Red}}{HgCl_2 + KI \longrightarrow KCl + HgI_2} \xrightarrow{+KI} \underset{\text{Nessler's reagent}}{K_2HgI_4} \xrightarrow{+KOH + NH_3} H_2O + KI +$$



Red-Brown Precipitate

[Iodide of Million's base]

4. Reaction with chlorine :

$NH_3(\text{excess}) + Cl_2 \longrightarrow \underset{\text{white fumes}}{NH_4Cl} + N_2$. This is also used as a test to detect NH_3.

$$NH_3 + Cl_2\ (\text{excess}) \longrightarrow NCl_3 + HCl$$

[b] Ammonium Salt $(NH_4)_xB$:

All ammonium salts are very soluble in water. They are usually slightly acidic and decompose readily on heating producing NH_3, N_2 or N_2O.

➤ If the anion (B^{x-}) is not particularly oxidising (eg. Cl^-, CO_3^{2-} or SO_4^{2-}) then ammonia is evolved.

$$NH_4Cl \xrightarrow{\Delta} NH_3 + HCl$$

$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

➤ If the anion (B^{x-}) is more oxidising (e.g. NO_2^-, NO_3^-, ClO_4^-, $Cr_2O_7^{2-}$) then NH_4^+ is oxidised to N_2 or N_2O.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

$$\underset{\text{Orange}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} N_2 + 4H_2O + \underset{\text{Green}}{Cr_2O_3}$$

[c] Oxides of Nitrogen :

1. Nitrous oxide N_2O [Laughing gas] :

It is colourless, non-combustible gas with a sweetish odour and taste. It is a neutral oxide, and is dimagnetic.

$$:\overset{-}{\underset{..}{N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow N \equiv \overset{+}{N} - O^-$$

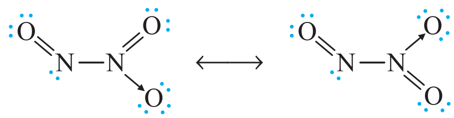
2. Nitric oxide NO/N_2O_2 :

It is a colourless, neutral gas which is paramagnetic due to the presence of odd electrons. It is sparingly soluble in water. It is the most stable oxide of nitrogen.

$$:N \overset{\cdot\cdot\cdot}{=\!=} O: \ ; \ :\dot{N} = \ddot{O}:$$

3. Dinitrogen Trioxide N_2O_3 :

It exists only in solid state at low temperature which is pale blue in colour. N_2O_3 is an acidic anhydride of nitrous acid (HNO_2). It is diamagnetic.

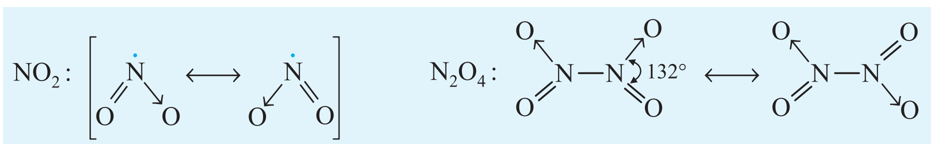


4. Nitrogen Dioxide NO_2 :

It is a reddish brown gas and exists at the room temperature. Being an odd electron molecule it is paramagnetic and dimerises into N_2O_4 at low temperature. It is acidic and mixed anhydride of nitrous acid and nitric acid.

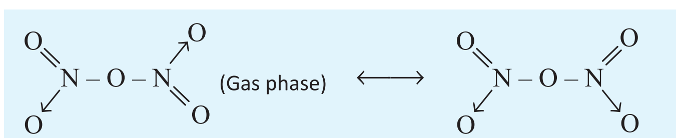
$$\underset{\text{solid colourless}}{N_2O_4} \xrightarrow{10°C} \underset{\text{solid yellow}}{N_2O_4} \xrightarrow{20°C} \underset{\text{vapour Reddish Brown}}{N_2O_4} \xrightarrow{140°C} \underset{\text{Dark Brown}}{2NO_2} \xrightarrow{620°C} \underset{\text{Colour less}}{2NO} + O_2$$

Structure :



5. Dinitrogen Pentoxide N_2O_5 :

It is a colourless crystalline solid which sublimes readily and is acidic.

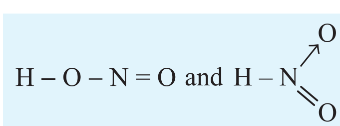


The solid form consists of ($NO_2^+ + NO_3^-$) which is ionic and called as nitronium nitrate while in solution it is covalent.

[d] Oxoacids of Nitrogen :

Nitrous acid HNO_2 :

Nitrous acid is unstable except in dilute aqueous solution. It is considered to be a tautomeric mixture of two forms :



Preparation :

1. It is easily made by acidifying a solution of a nitrite

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + \underset{\text{filtered off}}{BaSO_4 \downarrow}$$

2. Dissolving nitrous anhydride(N_2O_3) in water ofcourse forms nitrous acid :

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

Oxidising Properties :

NO_2^- ion is a weak oxidising agent and gets reduced to NO which forms a red complex with haemoglobin and improves the look of meat.

$$NO_2^- + Fe^{2+} + 2H^+ \longrightarrow Fe^{3+} + NO + H_2O$$

$$2NO_2^- + 2I^- + 4H^+ \longrightarrow I_2 + 2NO + 2H_2O$$

However it is oxidised by $KMnO_4$, Cl_2 forming NO_3^- (but to NO_2 by H_2SO_4) :

$$HNO_2 + Cl_2 + H_2O \longrightarrow HNO_3 + 2HCl$$

$$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

$$2HNO_2 + H_2SO_4 \longrightarrow SO_2 + 2NO_2 + 2H_2O$$

Reactions with Amines :

$$HNO_2 + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{unstable}}{[NH_4NO_2]} \longrightarrow N_2 + 2H_2O$$

$$HNO_2 + \underset{1^\circ\text{ amine}}{EtNH_2} \longrightarrow EtOH + N_2 + H_2O$$

Secondary and tertiary aliphatic amines form nitrosamines with nitrites :

$$HNO_2 + \underset{2^\circ\text{ amine}}{Et_2NH} \longrightarrow Et_2 - N = O + H_2O$$

$$HNO_2 + \underset{3^\circ\text{ amine}}{Et_3N} \longrightarrow [Et_3NH][NO_2] \xrightarrow{\Delta} Et_2 - N - N = O + EtOH$$

Nitrites are used to make diazo compounds used in azo dyes :

$$\underset{\text{aniline}}{PhNH_2} + HNO_2 \longrightarrow \underset{\text{Benzenediazonium chloride}}{Ph - N = \overset{+}{N}Cl^- } + 2H_2O$$

Other Reactions :

On standing HNO_2 decomposes into NO and NO_2 :

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

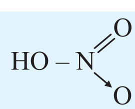
While on boiling it disproportionates :

$$3H\overset{III}{N}O_2 \xrightarrow{\Delta} H\overset{V}{N}O_3 + 2\overset{II}{N}O \uparrow + H_2O$$

Nitric acid HNO_3 :

Also called as Aqua fortis, it is colourless fuming liquid with a pungent smell. Yellow colour occurs on standing due to decomposition into NO_2.

$$HNO_3 \xrightarrow{\text{Light}} \underset{\text{Brown}}{NO_2} + O_2 + H_2O$$



Preparation :

1. In laboratory :

$$\underset{\text{nitrates}}{2NaNO_3} + \underset{\text{conc.}}{H_2SO_4} \xrightarrow[\text{glass retort}]{\text{distilling in}} Na_2SO_4 + 2HNO_3 \uparrow$$

HNO_3 vapours are then condensed in a water cooled receiver.

2. Birkeland and Eyde Process :

$$\underset{\text{Dry air free from } CO_2,\, H_2}{N_2 + O_2} \xrightarrow[3000°C]{\text{Electric arc}} 2NO \xrightarrow{+O_2} 2NO_2 \xrightarrow{+H_2O} HNO_3 + HNO_2 \xrightarrow{\Delta} NO + H_2O + HNO_3$$

3. Ostwald Process :

Step (*a*) : $4NH_3(g) + 5O_2 \xrightarrow[300°C]{\text{Pt gauze}} 4NO + 6H_2O$ (Catalytic Oxidation)

Step (*b*) : $4NO \underset{50°C}{\overset{2O_2}{\rightleftharpoons}} 4NO_2 \xrightarrow{+2H_2O + O_2} \underset{(60\%)}{4HNO_3} \xrightarrow{\text{distillation}} \underset{\substack{(68\%) \\ \text{azeotrope}}}{4HNO_3}$

Due to the formation of azeotrope, HNO_3 cannot be further concentrated by distillation and other methods are used like dehydrating using sulphuric acid vapours.

$$\underset{68\%}{HNO_3} \xrightarrow[H_2SO_4]{\text{dehydration with}} \underset{98\%}{HNO_3}\text{ (conc.)}$$

Oxidising Properties :

$\overset{V}{N}O_3^-$ is a very powerful oxidising agent in acidic solution. Cu, Ag which are insoluble in HCl dissolve in HNO_3. Concentrated HNO_3 forms NO_2 with a reducing agent although Fe, Co, Al, Ni, Cr and B are rendered passive by concentrated HNO_3 due to the formation of a protective oxide layer (like Fe_3O_4 with iron).

Dilute HNO_3 forms NO with a poor reducing agent (Cu, Hg) ; N_2O with a good reducing agent in hot conditions and $\overset{-3}{N}H_4\overset{+5}{N}O_3$ with a good reducing agent in cold conditions.

$$\left.\begin{array}{l} \underset{\text{conc.}}{HNO_3} + Fe \longrightarrow Fe_3O_4 + NO_2 \text{ (Rendered passive)} \\ \underset{\text{dil}}{HNO_3} + Fe \xrightarrow{\text{Hot}} \overset{III}{Fe}(NO_3)_3 + N_2O \\ \underset{\text{dil}}{HNO_3} + Fe \xrightarrow{\text{Cold}} \overset{II}{Fe}(NO_3)_2 + NH_4NO_3 \end{array}\right] \text{with Fe}$$

$$\left.\begin{array}{l} \underset{\text{conc.}}{HNO_3} + Hg \longrightarrow \overset{II}{Hg}(NO_3)_2 + NO_2 \\ \underset{\text{dil}}{HNO_3} + Hg \longrightarrow \overset{I}{Hg_2}(NO_3)_2 + NO \end{array}\right] \text{with Hg}$$

$$\underset{\text{conc.}}{HNO_3} + Sn \longrightarrow H_2SnO_3 + NO_2$$

$$\underset{\text{dil. hot}}{HNO_3} + Sn \xrightarrow{\text{Hot}} H_2SnO_3 + N_2O$$

$$\underset{\text{dil. cold}}{HNO_3} + Sn \xrightarrow{\text{Cold}} Sn(NO_3)_2 + NH_4NO_3$$

with Sn

Some reactions with non-metals are :

$$\underset{\text{dil. or conc.}}{HNO_3} + N_2 \longrightarrow \text{no reaction}$$

$$\underset{\text{conc.}}{HNO_3} + P_4 \longrightarrow H_3PO_4 + NO_2$$

$$\underset{\text{dil.}}{HNO_3} + P_4 \xrightarrow{\text{Hot}} H_3PO_4 + NO$$

$$\underset{\text{dil.}}{HNO_3} + P_4 \xrightarrow{\text{Cold}} H_3PO_3 + NO$$

with P_4

$$\underset{\text{conc.}}{HNO_3} + As \longrightarrow H_3AsO_4 + NO_2$$

$$\underset{\text{dil.}}{HNO_3} + As \xrightarrow{\text{Hot}} H_3AsO_4 + NO$$

$$\underset{\text{dil.}}{HNO_3} + As \xrightarrow{\text{Cold}} H_3AsO_3 + NO$$

with As

- Only Mg and Mn react with 2% dil. HNO_3.

  $$HNO_3\ (\text{dil.}2\ \%) + Mg\ (\text{or } Mn) \longrightarrow Mg(NO_3)_2 + H_2\uparrow$$

- Solution of 75% HCl and 25% HNO_3 is called Aqua Regia which contains $NO^+\ Cl^-$ ions. Aqua Regia is capable of dissolving Gold and Platinum by forming soluble $HAuCl_4$ and H_2PtCl_6 respectively.

Other Oxoacids :

HOONO	Pernitrous acid
H_2NO_2	Hydronitrous acid
HNO_4	Pernitric acid
$H_2N_2O_2$	Hyponitrous acid

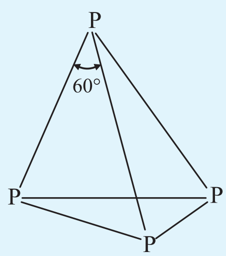
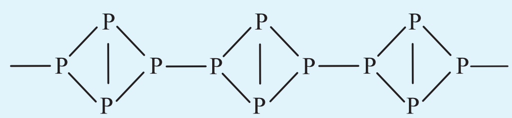
Remember that N_2O is NOT an anhydride of Hyponitrous acid ($H_2N_2O_2$)

Phosphorous and its Compounds :

Allotropy :

It exists in many allotropic forms, the important ones being white, red and black phosphorous

$$\text{White P} \xrightarrow[\text{inert atmosphere for several days}]{300°C} \text{Red P} \xrightarrow{\Delta} \underset{\text{thermodynamically most stable allotrope}}{\text{Black P}}$$

White Phosphorus	Red Phosphorous
It is a white, waxy and highly toxic solid. It glows in dark (*Chemiluminescence* / *Phosphorescence*)	It is non poisonous and does not show phosphoresence
It is unstable due to angular strain and spontaneously reacts with O_2 and catches fire. $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$ Thus it is stored in water in which it is insoluble (white phosphorous is soluble in CS_2).	It is stable in air and not stored in water. It is insoluble in organic solvents.
 Tetrahedral	

Only white phosphorous reacts with caustic alkalies to undergoes a disproportionation reaction.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3\uparrow}$$

Uses :

Red phosphorus is used in Match - Industry and white phosphorus as a rat poison.

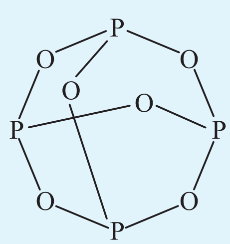
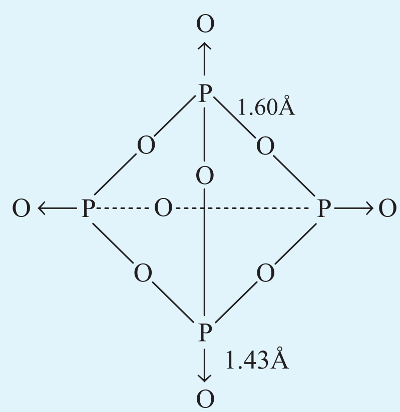
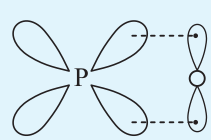
Preparation :

Phosphorous is obtained by the reduction of calcium phosphate with C in an electric furance. Sand (SiO_2) is added to remove the calcium as a fluid slag.

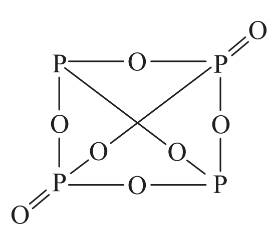
$$Ca_3(PO_4)_2 + SiO_2 \longrightarrow \underset{\text{slag}}{CaSiO_3} + P_4O_{10}$$

$$P_4O_{10} + C \longrightarrow P_4 + CO\uparrow$$

Oxides of Phosphorous

Phosphorous Trioxide [P_2O_3/P_4O_6]	Phosphorous Pentoxide [P_2O_5/P_4O_{10}]
It is also called Phosphorus oxide or Phosphorous anhydride. It is a soft white solid.	It is called Phosphoric oxide or Phosphoric anhydride.
Preparation : $P_4 + \underset{\text{(Limited supply)}}{3O_2} \longrightarrow P_4O_6$ The oxide formed in small amount is removed by filteration through glass wool.	Preparation : $P_4 + \underset{\text{(excess)}}{5O_2} \longrightarrow P_4O_{10}$ $\downarrow$ Collected in form of snowy powder called Flower of Phosphorus $P_4O_6 + O_2 \longrightarrow P_4O_{10}$
P_4O_6 is acidic and hydrolyses in water : $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$	It is used as a drying agent as it absorbs moisture and becomes sticky. It hydrolyses violently in water : $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ as dehydrating agent : $2H_2SO_4 + P_4O_{10} \longrightarrow 2SO_3 + 4HPO_3$ $4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$
Phosphorous trioxide is dimeric and written as P_4O_6  Structure of phosphorus trioxide P_4O_6	 The shorter $P \rightarrow O$ coordinate bond is in fact a 'double bond' different from the usual double bond. A full P orbital on O overlaps side ways with an empty d orbital on p atom forming $p\pi - d\pi$ back bonding or a dative bond 

Other oxides like P_4O_8 and P_4O_9 are intermediate between P_4O_6 and P_4O_{10} and form a mixture of phosphoric acid P(+V) and phosphorous acid P(+III) on hydrolysis.



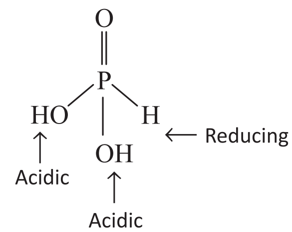
Oxo Acids of Phosphorous

All oxo acids of phosphorus can be categorized into two main acid series namely, phosphorus acid series and phosphoric acid series.

The Phosphorous acid series :

They contain P(+III) and are generally reducing agents due to the presence of P – H bonds which are reducing (as they break down easily to lose H^+).

[I] Orthophosphorous acid H_3PO_3 :



H_3PO_3 is a dibasic acid formed by hydrolysis of P_4O_6 .

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

1. H_3PO_3 forms phosphites on hydrolysis which are very strong reducing agents in basic solutions.

$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \qquad Ka_1 = 1.6 \times 10^{-2}$$

$$H_2PO_3^- \rightleftharpoons H^+ + HPO_3^{2-} \qquad Ka_2 = 7 \times 10^{-7}$$

2. On heating orthophosphorous acid disproportionates :

$$4H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$$

3. It is a moderately strong reducing agent and reduces Ag^+ to Ag, Au^{3+} to Au, Cu^{2+} to Cu and itself gets oxidised to H_3PO_4:

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag\downarrow + 3HNO_3 + H_3PO_4$$

[II] Hypophosphorous Acid H_3PO_2 :

It is prepared by alkaline hydrolysis of (white) phosphorous.

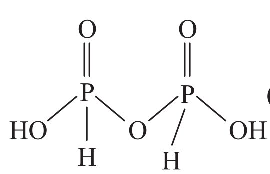
$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3\uparrow + \underset{\text{Hypophosphite Ion}}{3H_2PO_2^-}$$

It is a monobasic acid and a very strong reducing agent.

$$4Ag^+ + H_3PO_2 + 2H_2O \longrightarrow 4Ag + H_3PO_4 + 4H^+$$

[III] Pyrophosphorous Acid $H_4P_2O_5$:

$H_3PO_3 + PCl_3 \longrightarrow$



$(H_4P_2O_5)$

Dibasic

While reaction with PCl_5 is : $H_3PO_3 + 3PCl_5 \longrightarrow \underset{\text{Trichloride}}{PCl_3} + \underset{\text{Oxychloride}}{3POCl_3} + 3HCl$

The Phosphoric Acid Series :

They usually contain P(+V) and have oxidising properties. The simplest phosphoric acid is orthophosphoric acid.

[I] Orthophosphoric acid H_3PO_4 :

Preparation :

1. It is formed by hydrolysis of phosphorous pentaoxide (P_2O_5 or P_4O_{10}).
2. In laboratory $\underset{\text{conc.}}{P_4 + 20\,HNO_3} \xrightarrow[\text{Catalyst}]{I_2} 4H_3PO_4 + 20NO_2 + 4H_2O$
3. Impure H_3PO_4 is prepared in large amounts by '*Wet Process*'.

$$\underset{\text{Phosphate Rock}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

$CaSO_4$ is hydrated to gypsum $CaSO_4.2\,H_2O$ and filtered off. H_3PO_4 thus produced is used to make fertilizers.

Properties :

1. H_3PO_4 is hydrogen bonded in aqueous solution and thus the 'concentrated acid' is syrupy and viscous.
2. It forms meta phosphates on heating:

$$H_3PO_4 \xrightarrow{220°} \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[Br_2]{320°C} \underset{\text{metaphosphoric acid}}{(HPO_3)_n}$$

$(Na\,PO_3)_n$ or sodium metaphosphate is called Graham's salt or Calgon (Commercial name). It is soluble in water and precipitates Pb^{2+} , Ag^+ but not Ca^{2+}, Mg^{2+}. Thus it is used for softening water.

3. It forms 3 series of salts :

(a) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $\quad Ka_1 = 7.5 \times 10^{-3}$

Dihydrogen phosphates are slightly acidic in water.

(b) $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ $\quad Ka_2 = 6.2 \times 10^{-8}$

Monohydrogen phosphates are slightly basic in water.

(c) $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ $\quad Ka_3 = 1 \times 10^{-12}$

Normal phosphates are appreciably basic in water.

4 Phosphates are estimated quantitatively by adding a solution containing NH_4OH solution of the phosphate and Mg^{2+}. Magnesium ammonium phosphate precipitated is ignited and weighed as $Mg_2P_2O_7$.

$$2NH_4^+ + 2Mg^{2+} + 2PO_4^{3-} \longrightarrow 2MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

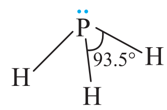
[II] Hypophosphoric acid $H_4P_2O_6$:

It contains P(+ IV) and is prepared by hydrolysis and oxidation of red phosphorous by NaOCl.

On hydrolysis it forms both H_3PO_3 and H_3PO_4

Phosphine [PH_3]

It is a colourless, extremely toxic gas which smells of garlic or rotten fish. It is highly reactive and not very soluble in water. It's aqueous solutions are neutral.



The H – P – H bond angle is 93.5° which suggests the presence of almost pure p orbitals.

Preparation :

It can be formed by hydrolysing metal phosphides or hydrolysing white phosphorous in basic media.

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 \uparrow + 3Ca(OH)_2$$

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 \uparrow + 3NaH_2PO_2 \quad \text{(disproportionation)}$$

The second method also produces small amounts of highly inflammable P_2H_4. Thus PH_3 is removed in the following manner:

$$PH_3 + HI \longrightarrow \underset{\text{Phosphonium Iodide}}{PH_4I} \xrightarrow{+\,KOH} KI + H_2O + \underset{\text{(Pure)}}{PH_3 \uparrow}$$

Properties :

1. PH_3 is stable in air but catches fire at 150°C.

$$PH_3 + 2O_2 \xrightarrow{150°C} H_3PO_4$$

2. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2.

$$2PH_3 + 16HNO_3 \longrightarrow P_2O_5 + 16NO_2 + 11H_2O$$

3. Solution of PH_3 in water decomposes in presence of light giving red phosphorous and H_2.

4. Formation of metallic phosphides :

$$3CuSO_4 + 2PH_3 \longrightarrow \underset{\text{Black}}{Cu_3P_2 \downarrow} + 3H_2SO_4$$

$$3AgNO_3 + PH_3 \longrightarrow \underset{\text{Black}}{Ag_3P \downarrow} + 3HNO_3$$

5. Phosphine is weakly basic and forms phosphonium salts with anhydrous acids while NH_3 readily forms NH_4X in aqueous solutions of the acids.

$$PH_3 + HX \longrightarrow PH_4X \quad (X = Cl, Br, I)$$

Uses :

It is used for making '*Holme's signals*'. Containers containing CaC_2 and Ca_3P_2 are pierced and thrown in sea when gases evolved, burn and serve as a signal.

Halides :

1. PCl_3 is a colourless oily liquid and is widely used in organic chemistry while PCl_5 is a yellowish white powder.

$$\underset{\text{White}}{P_4} + \underset{\text{Dry}}{6Cl_2} \xrightarrow{\Delta} 4PCl_3$$

$$P_4 + \underset{\substack{\text{Thionyl}\\\text{Chloride}}}{8SOCl_2} \longrightarrow 4PCl_3 + 4SO_2$$

$$\underset{\text{White}}{P_4} + \underset{\text{Dry, excess}}{10Cl_2} \longrightarrow 4PCl_5$$

$$P_4 + \underset{\substack{\text{Sulphuryl}\\\text{Chloride}}}{10SO_2Cl_2} \longrightarrow 4PCl_5 + 10SO_2$$

$$PCl_3 + Cl_2 (\text{or } S_2Cl_2) \longrightarrow PCl_5$$

2. PCl_3 fumes in moisture.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 \uparrow + 3HCl \uparrow$$

While, $$PCl_5 + \underset{\text{Moist Air}}{H_2O} \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl.$$

3. In liquid and gaseous state PCl_5 is trigonal bipyramidal. While in solid state it is ionic and hence conducts electricity

$$2PCl_5 \rightleftharpoons \underset{\text{Tetrahedral}}{[PCl_4]^+} + \underset{\text{Octahedral}}{[PCl_6]^-}$$

4. PF_5 forms an unusual trigonal bipyramid where axial and equatorial bonds interchange their positions in short time. This is called pseudo rotation.

IN-CHAPTER EXERCISE - C

1. *Give balanced equations involved :*

(a) effect of heat on

(i) $NaNO_3$ **(ii)** NH_4NO_3 **(iii)** *Mixture of* NH_4Cl *and* $NaNO_2$

(b) *effect of water on*

(i) Li_3N **(ii)** AlN **(iii)** NCl_3

(iv) NO_2 **(v)** PCl_3 **(vi)** PCl_5

(c) *preparation of*

(i) *nitric oxide from nitric acid* **(ii)** NH_3 *commercially*

(iii) HNO_3 *commercially*

2. *Give reasons for the following :*

(i) NF_3 is not hydrolysed but NCl_3 is readily hydrolysed.

(ii) Ammonia has a higher boiling point than phosphine.

(iii) Concentrated nitric acid turns yellow in sunlight.

(iv) $(CH_3)_3N$ is pyramidal in shape while $(SiH_3)_3N$ is planar.

(v) PF_5 is known but NF_5 is not

(vi) NH_3 gas is dried by CaO and not by P_2O_5 and H_2SO_4.

(vii) H_3PO_3 is a dibasic acid

3. *Identify the unknown compounds A, B, C, . . . in the following reactions :*

(a) $P + \text{conc. } HNO_3 \longrightarrow A + B$

(b) $PCl_5 + SO_2 \longrightarrow A + B$

$PCl_5 + P_4O_{10} \longrightarrow B$

A is a colourless fuming liquid which on reaction with P_4 gives $SO_2(g)$ and C.

(c) $NH_3 + O_2 \xrightarrow{Pt} A(g) \xrightarrow{O_2} B \text{ (brown fumes)} \xrightarrow{H_2O} \underbrace{C + D}_{\text{(oxo acids)}}$

$C + I^- \longrightarrow E \text{ (violet vapours)}$

(d) $\text{Colourless salt } (A) + NaOH \xrightarrow{\Delta} B\,(g) + C \text{ (alkaline solution)}$

$B + HCl \longrightarrow \text{white fumes.}$

$A \longrightarrow \underbrace{D(g) + E(l)}_{\text{both triatomic}}$

(e) $\xrightarrow{NaOH,\,\Delta} C \xleftarrow{H_2O} A \xleftarrow{Al,\,\Delta} E(g) \xleftarrow{\Delta} A \text{ or } B$ E is used as an anaesthetic.

(f) $A + P_4 \longrightarrow P_4O_{10} + B \xrightarrow[\text{electric arc}]{+O_2} C \xrightarrow{+O_2} D \text{ (brown fumes)} \xrightarrow{+H_2O} F \xrightarrow{P_4O_{10}} G$

$C + D \xrightarrow{cool} E \text{ (blue)}$

A, B, C, D, E, F are all compounds of nitrogen while A, B, C and D are gases.

4. *Give structural formula for the following :*

(a) H_3PO_3 **(b)** H_3PO_2 **(c)** $H_4P_2O_5$ **(d)** H_3PO_4

(e) $H_4P_2O_6$ **(f)** $H_4P_2O_7$ **(g)** P_4O_{10}

5. **(a)** Reaction of phosphoric acid with $Ca_3(PO_4)_2$ yields a fertilizer "triple phosphate". Represent the same through balanced chemical equation.

(b) Give reason(s) why elemental nitrogen exists as a diatomic molecules while elemental phosphorus is a tetratomic molecule.

6. Ammonia gas can be dried by :

(A) conc. H_2SO_4 **(B)** P_2O_5 **(C)** $CaCl_2$ **(D)** quick lime

7. Which of the following is incorrect ?

(A) NO is heavier than O_2 **(B)** The formula of heavy water is D_2O

(C) N_2 diffuses faster than O_2 through an orifice **(D)** NH_3 can be used as a refrigerant

8. *Which of the following oxides is a coloured gas ?*

(A) N_2O **(B)** NO **(C)** N_2O_4 **(D)** NO_2

9. *The bonds present in* N_2O_5 are :

(A) *only ionic* **(B)** *covalent and coordinate*

(C) *only covalent* **(D)** *covalent and ionic*

10. *Among the trihalides of nitrogen, which one is least basic ?*

(A) NF_3 **(B)** NCl_3 **(C)** NBr_3 **(D)** NI_3

11. *The number of P – O – P bonds in cyclic metaphosphoric acid is :*

(A) 0 **(B)** 2 **(C)** 3 **(D)** 4

***12.** For H_3PO_3 *and* H_3PO_4 *the correct choice is :*

(A) H_3PO_3 *is dibasic and reducing* **(B)** H_3PO_3 *is dibasic and non-reducing*

(C) H_3PO_4 *is tribasic and reducing* **(D)** H_3PO_3 *is tribasic and non-reducing*

13. *The reaction of* P_4 *with X leads selectively to* P_4O_6. *Then X is :*

(A) *dry* O_2 **(B)** *a mixture of* O_2 *and* N_2

(C) *moist* O_2 **(D)** O_2 *in the presence of aqueous NaOH*

***14.** *The nitrogen oxide(s) that contain(s) N – N bond(s) is (are) :*

(A) N_2O **(B)** N_2O_3 **(C)** N_2O_4 **(D)** N_2O_5

***15.** *White phosphrous* (P_4) *has :*

(A) *six P - P single bond* **(B)** *Four P - P single bonds*

(C) *Four lone pair of electrons* **(D)** *PPP angle of* 60°

***16.** *Nitrogen (I) oxide is produced by :*

(A) *Thermal decomposition of* NH_4NO_3 **(B)** *disproportionation of* N_2O_4

(C) *Thermal decomposition of* NH_4NO_2 **(D)** *Interaction of hydroxylamine and nitrous acid.*

ANSWERS TO IN-CHAPTER EXERCISES

A	**5.** A	**6.** AD	**7.** BC	**8.** AB	**9.** A					
B	**7.** B	**8.** B	**9.** D	**10.** C	**11.** ABC					
C	**6.** D	**7.** A	**8.** D	**9.** B	**10.** D	**11.** C	**12.** A	**13.** B	**14.** ABC	**15.** ACD	**16.** AD