p- block elements

General electronic configuration: $ns^2 np^{1-6}$

Position in periodic table: Group 13 - 18. (extreme right)

GROUP- 13:

Group 13 elements

Property	B	Al	Ga	In	Tl
Atomic no.	5	13	31	49	81
Atomic mass	10.81	26.98	69.72	114.82	204.38
Electronic configuration	[He] $2s^2 2p^1$	[Ne] $3s^2 3p^1$	[Ar] $3d^{10} 4s^2 4p^1$	[Kr] $4d^{10} 5s^2 5p^1$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$

Except B, all elements of group 13 are metals. The most abundant element in the Earth's crust is Al.

Except B, all other elements in the group show +1 oxidation state, which becomes most stable down the group due to inert pair effect.

Chemical Property :-

① Thermal stability of group 13 element

hydrides of the type MH_3 decreases down the group M. AlH_3 is a solid & has Al–H–Al bridge polymerisation.

2. Except Boron, all metals exhibit a well defined aqueous chemistry in their tripositive state.

3. Group 13 elements react with halogen to give binary halides except Tl (III) hydrid

- The fluorides are ionic & have hig M.P. Chlorides, bromides & iodides, are essentially covalent compounds with low M.P. & all the trihalides are strong Lewis acids.

BF_3, $AlCl_3$ → Lewis acid.

④ All the elements form oxides & hydroxides of the type M_2O_3 & $M(OH)_3$, whose basic character increases from Al ⟶ Tl

$Al(OH)_3$ & $Ga(OH)_3$ show amphoteric nature whereas $B(OH)_3$ is acidic.

⑤ Al, Ga, In, & Tl ions form octahedral aqua ions of the type $[M(OH)_6]^{3+}$ in aqueous solns. & many salt like halides, nitrates & sulfates.

⑥ The +I oxidation state gets stabilized in increasing order down from Ga → Tl. (inert pair effect)

Most Al compounds exist in +3 oxidation state. But, a few exist in -

+I oxidation state such as AlF, AlCl, AlBr, AlI. (monohalides)

These compounds are only thermodynamically stable at high temperature & low pressures in the singlet ground state.

→ dark red solid

Under cold temp. < 77K, AlCl solid can be kept for periods of long time.

$$Al(l) + HCl(g) \xrightarrow{1200\,K} AlCl(g) + \frac{1}{2} H_2$$

Since MF possess a bond much stronger than its congeners, AlF is synthesized by comproportionation of Al & AlF_3, which are pressed & mixed into pellet.

$$2Al(s) + AlF_3(s) \longrightarrow 3AlF(g)$$

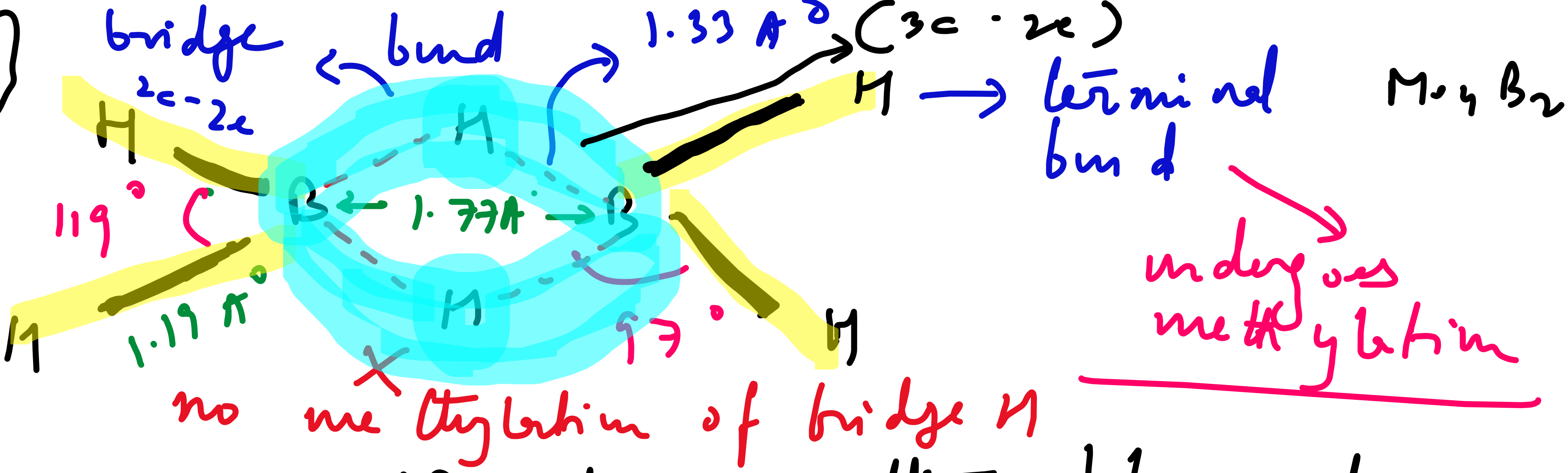
⑦ Due to small size, high ionization energy, & absence of 'd' orbitals. B shows diagonal relationship with Si.

⑧ Lewis acidity decreases in the order

$B > Al > Ga > I$.

⑨ Boron forms a number of hydrides with general formula: B_nH_{n+4} & B_nH_{n+6} also known as boranes; e.g. B_2H_6, B_4H_{10}, B_5H_{11} etc. They contain multicentred bonds like (3c – 2e).

Structure of diborane



Me_4B_2H

Electron diffraction & other physical studies establish the structure of diborane.

1. The two B-atoms are joined by two B-H-B bridges in a plane nearly perpendicular to the plane of terminal B-H bonds.

2. The bridge B - H bonds (133 pm) are somewhat longer than terminal B - H bonds (119 pm)

3. The terminal B - H distance is similar to that expected for a normal covalent bond involving two electrons shared between two atoms.

④ That the two bridge atoms are in a diff. environments are confirmed by Raman spectra & the fact that methylation of diborane proceeds only up to $Me_4B_2H_2$

With a total 12 electrons B_2H_6 is an electron deficient compound.

⑩ Aluminium sulfate forms

p- block elements.

Group - 13.

In Group-13, there is an increasing tendency to form univalent compounds on descending down the group. Compounds with Ga(I), In(I) & Tl(I) are known. With Ga(I) & In(I) the +I oxidation state is less stable then +III state. However, the stability of lower oxidation state increases on descending down the group. Tl(I) thallous compounds are more stable than Tl(III) compounds.

The strength of the bonds in MX_3 compounds decreases down the group.

$GaCl_3$ = 242 (mean bond energy)

$InCl_3$ = 206 "

$TlCl_3$ = 153 "

The inert pair effect is not the explanation of why monovalency occurs in Group 13. It merely describes what happens i.e. 2 electrons do not participate in bonding because of energy factors.

Inert pair effect is not only restricted to <u>Group-13</u>:

- Group 14 : Sn^{2+} & Pb^{2+}
- Group 15 ; Sb^{3+} & Bi^{3+}

Pg. 389.
J.D. Lee'
Sudarshan
Guha!

Lower oxidation state becomes more stable descending down the group. Sn^{2+} is a reducing agent but Pb^{2+} is stable & similarly, Sb^{3+} is a reducing agent but Bi^{3+} is stable. When the s electron remains paired, the oxidation state is typically two lower than usual oxidation state for the group:

s block: Group 1 & 2 only shows group valency. Groups in the f-block shows variable valency.

Size: The ionic radii of M^{3+} decrease down the group, though not in a regular way:

M^{3+}	(Å)
B	0.27
Al	0.535
Ga	0.620
In	0.800

Tl — 0.885 Å.

14 f-block elements

d block contraction - Lanthanide contraction.

Preparation of B:

1. Boron from borax / colemanite :

Step I: Preparation of B_2O_3

$$Na_2B_4O_7 + HCl/H_2SO_4 \longrightarrow NaX + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3$$

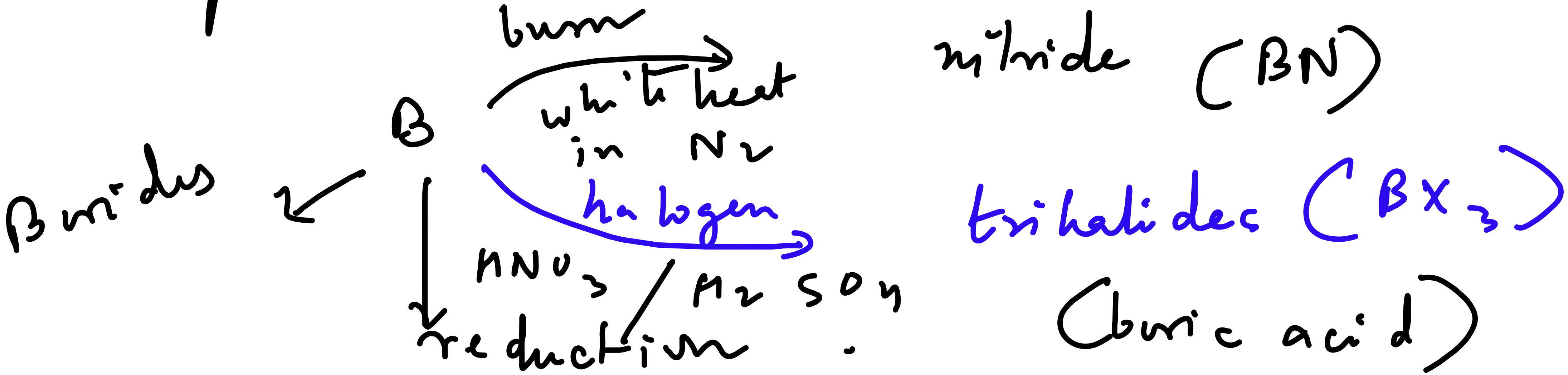
$$H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O.$$

Step II :

$$B_2O_3 + Na/K/Mg/Al \longrightarrow B + Na_2O/K_2O/MgO/Al_2O_3$$

Reactions of B :

Pure crystalline B is very unreactive. However, if it is attacked at high temperature by strong oxidizing agent such as conc. HNO_3, conc. H_2SO_4, or Na_2O_2. Finely divided amorphous B is however, more reactive.



	Reaction	Comment
1.	$4B + 3O_2 \rightarrow 2B_2O_3$	At high temperature
2.	$2B + 3S \rightarrow B_2S_3$	" 1200° C
3.	$2B + N_2 \rightarrow BN$	" very high temp.
4.	$2B + 3F_2 \rightarrow 2BF_3$	" high temp.
5.	$2B + 3Cl_2 \rightarrow 2BCl_3$	" " "
6.	$2B + 3I_2 \rightarrow 2BI_3$	
7.	$2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$	When fused with alkali
8.	$2B + 2NH_3 \rightarrow 2BN + 3H_2$	At very high temp.
9.	$B + M \rightarrow M_xB_y$	Many metals form borides (Group 1)

Boric acid or orthoboric acid H_3BO_3 or $B(OH)_3$

Preparation :

1. $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$

(Treatment of borax with dil. HCl)

2. From the mineral colemanite by passing SO_2 through a mixture of powdered mineral in boiling H_2O

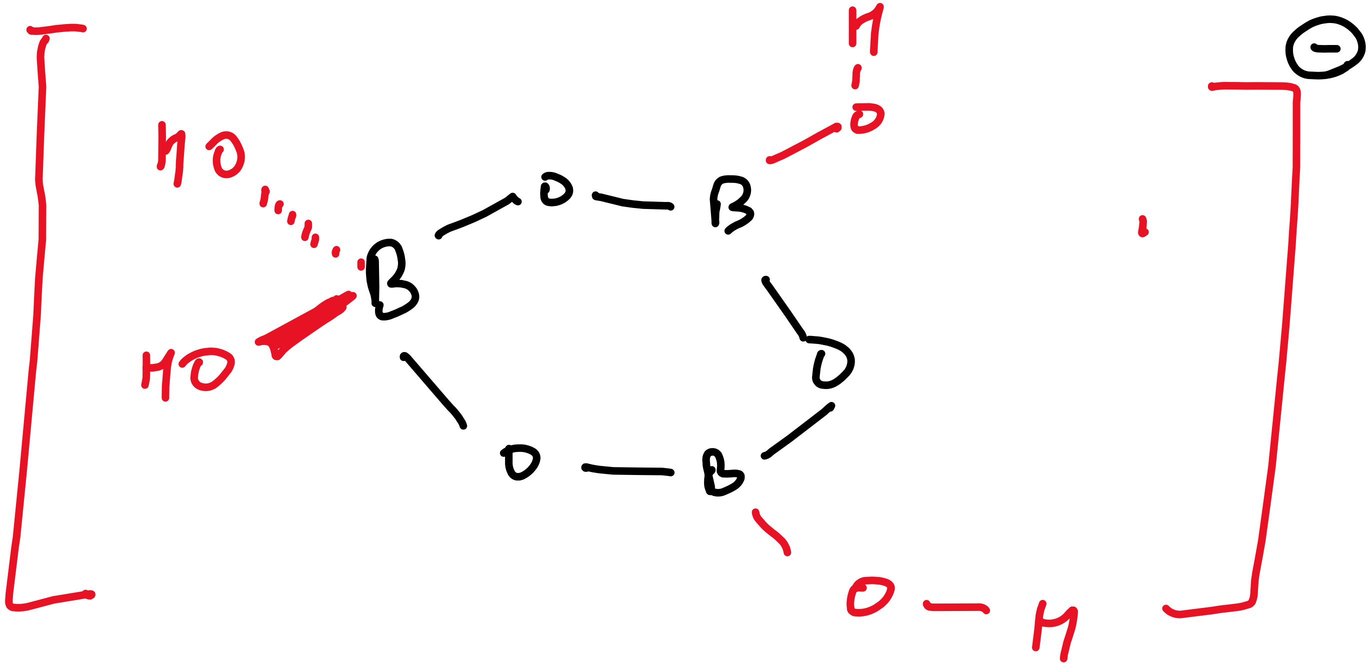
$$Ca_2B_6H_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Property :

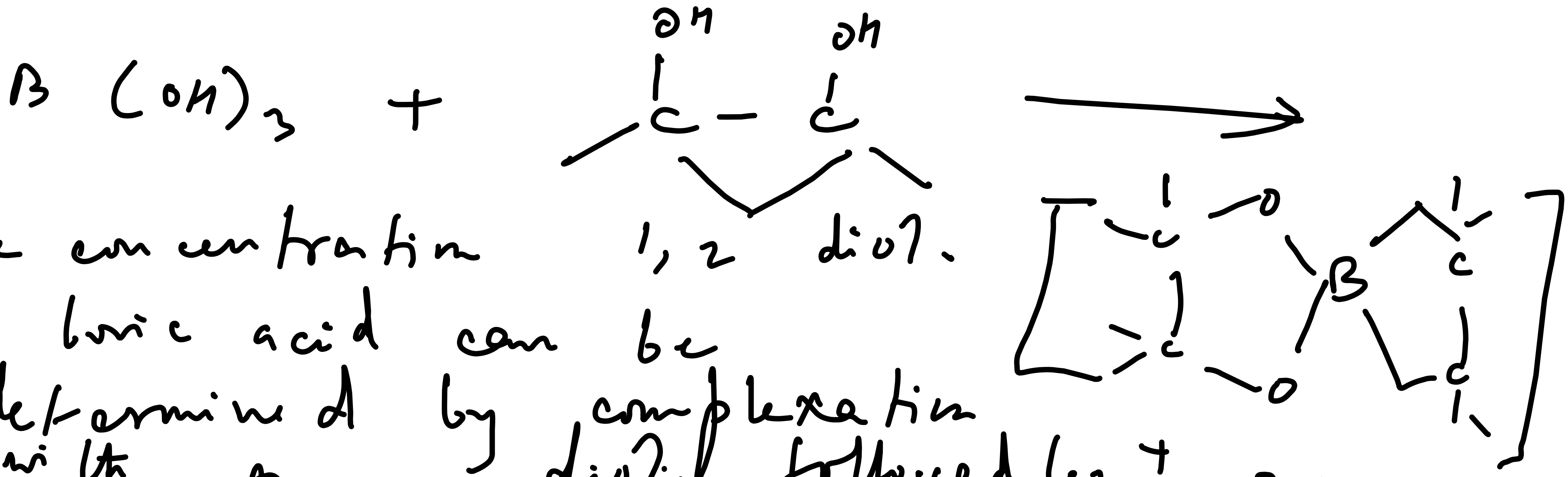
1. It is a very weak monobasic acid; Does not act as a proton donor but behaves as a L.A.

$$H_3BO_3 + H_2O \longrightarrow [B(OH)_4]^- + H^{\oplus}$$

$B(OH)_4^{\ominus}$ ion occurs in many borate type minerals, but most borates have complex structures such as the ring anion.



Boric acids & borates form very stable complexes with 1, 2 diols.



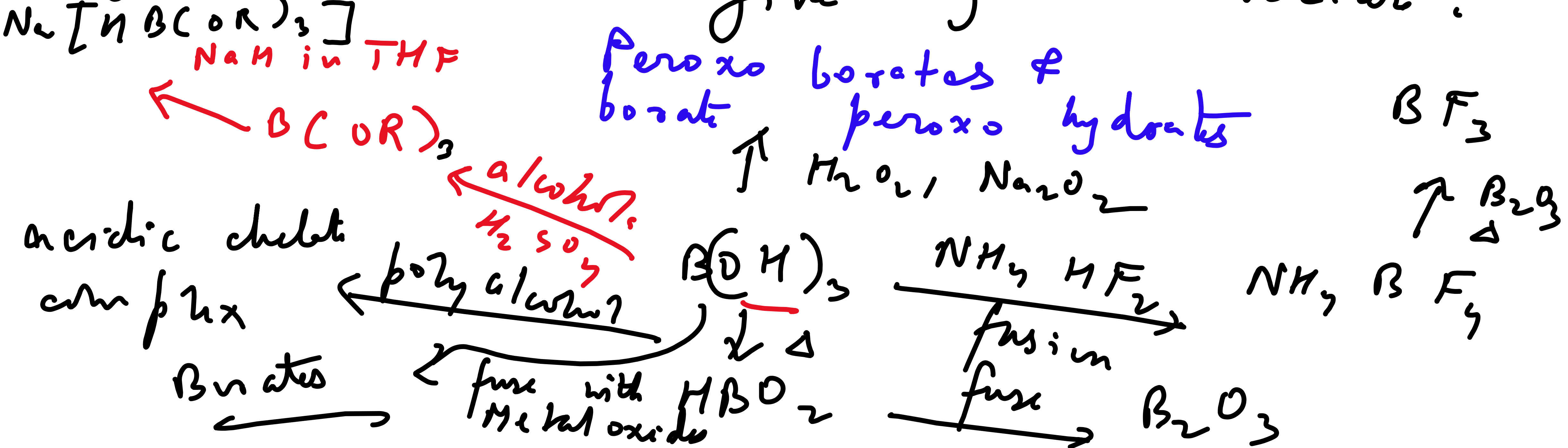
The concentration of boric acid can be determined by complexation with a diol, followed by NaOH titration.

Boric acid is used as —

fuse = melt with intense heat

1. Preservative for food
2. Mild antiseptic for eye wash.
3. For preparation of glaze & enamels in pottery

In boric acid, BO_3^{3-} units are joined by H-bonds to give layered structure.



Boron nitride :

Routes of preparation.

1. $2B + N_2 \xrightarrow{1000°C} 2BN$
2. $Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$

Properties :

1. It resembles graphite in its crystalline structure, mechanical & lubricating properties
2. Can withstand high temp. upto 3000°C.

iii)

$2BN + 3H_2O \cdot HCl \xrightarrow{HCl} B_2O_3 + 2NH_3$

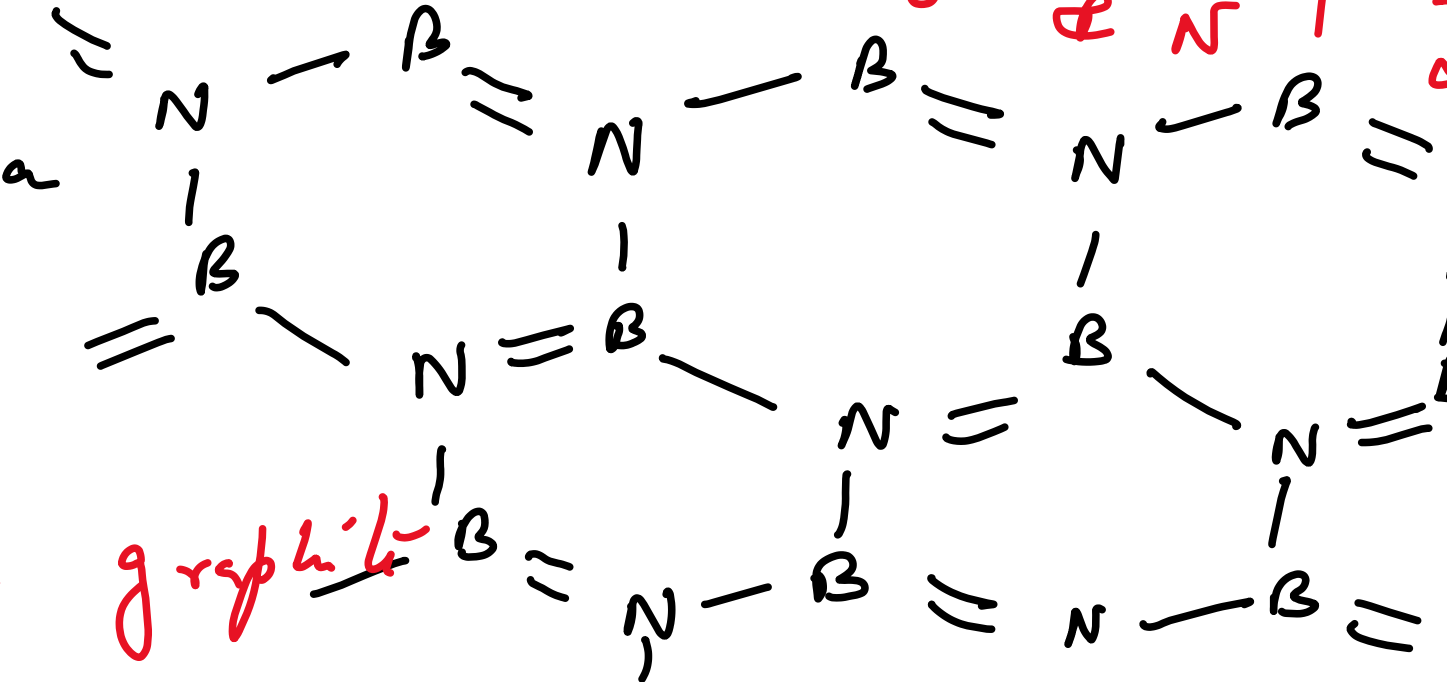
iv) $BN + 4HF \longrightarrow NH_4BF$.

v) $3BN + 3KOH + 3H_2O \longrightarrow K_3B_3O_6 + NH_3$

Structure :

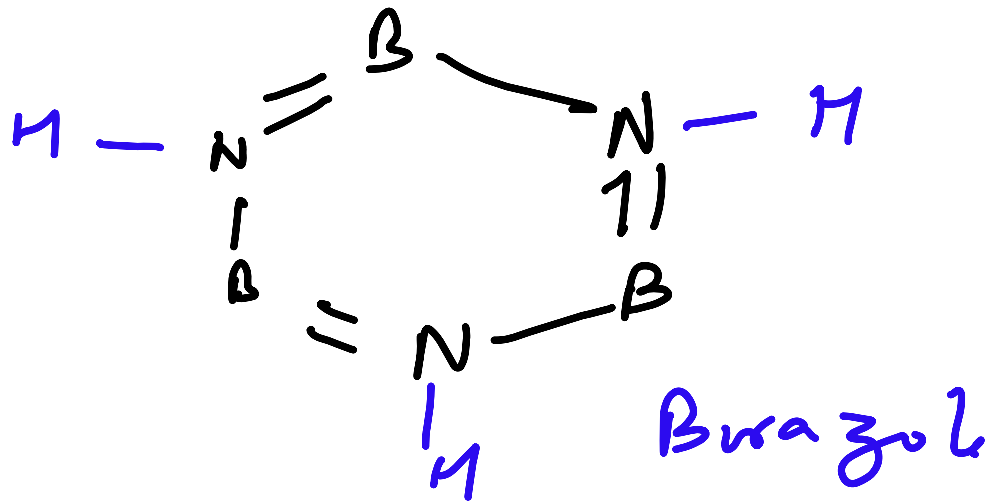
BN_3 has a layered lattice structure

hexagonal arrangement of B & N atom.

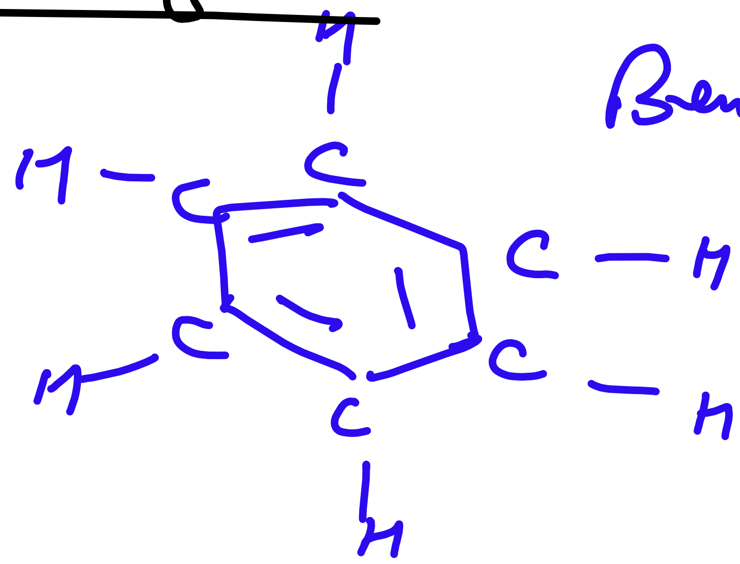


Inorganic graphite

Borazole : $B_3N_3H_6$ has a flat, hexagonal ring structure containing $-BH=$ & $-NH=$ groups alternatively. Therefore its structure is analogous to that of C_6H_6 & is, therefore, called as inorganic benzene.



Borazole.



Benzene

Group- 15 (Revision)

Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb), Bismuth (Bi)

Nitrogen = 78% of air.

↙ diatomic gas.

Minerals of nitrogen ; Chile saltpetre

$NaNO_3$ → white colored salt. Also called as Peru saltpeter. Large deposits of $NaNO_3$ are found in the Atacama desert in Chile & Peru.

Saltpetre : Nitre / Niter
(peter)

i) KNO_3 → Indian saltpetre

ii) $NaNO_3$ (Chil)

iii) $Ca(NO_3)_2$ Lime / wall saltpeter

Proteins, nucleic acids, amino acids → nitrogen is found as a key constituent.

Phosphorus - 11th most abundant element in the Earth's crust.

Fluoroapatite, Chloroapatite, Hydroxyapatite.

Phosphorus → animal & plant matter

PO_4^{3-} group → key constituent of nucleic acids, i.e. D.N.A & R.N.A. 60% of bones & teeth are made out of phosphates

Phosphoproteins → egg yolk, milk, bone marrow.

Arsenic, Antimony, Bismuth → occurs as sulfides. Stibnite, Arsenopyrite, etc.

Group 15 - Pnicogen, (To choke) → Greek word

Electronic configuration : $ns^2 \boxed{np^3} \rightarrow$ half-filled electronic arrangement

N : $[He]\, 2s^2\, 2p^3$

P : $[Ne]\, 3s^2\, 3p^3$

As : $[Ar]\, 3d^{10}\, 4s^2\, 4p^3$

Sb : $[Kr]\, 4d^{10}\, 5s^2\, 5p^3$

Bi $[Xe]\, 4f^{14}\, 5d^{10}\, 6s^2\, 6p^3$

Trend in properties :

1. Atomic radii 2. Ionization energy.
3. Electronegativity 4. Oxidation states.

1. **Atomic radii :** N P As Sb

Moving down the group atomic size/radii increases because another principal energy level / new electronic shell is added to the element.

2. **I.E :** These elements present higher values of I.E as compared to Group 14 elements due to their higher atomic charge, smaller nuclear radii, & stable half-filled electronic setups.

Down the group → I.E. decreases due to progressive increment in nuclear size/atomic radii

3. **Electronegativity**: Same trend as I.E. →
Electronegativity decreases on moving down the group due to increament in atomic radius.

4. **Metallic character** → Increase dow the group.

5. **Melting point**: M.P. increases from N → As because of the continuous

increment in nuclear size. The low M.P. of N is because of its discrete diatomic particles High M.P. of As is due to its goliath layered structure in which the layers are firmly pressed.

Although nuclear size / atomic size increases moving down from As — Sb, there is a decrease in M.P. Like As, Sb has also layered structure but it has a low M.P. because of the generally free pressing of particles. In case of Bi, the M.P. is even lower because the packing of atoms are loosely held by metallic bonding.

B. P $\longrightarrow$ N $\rightarrow$ Bi $\longrightarrow$ step by step increase. Same trend for density.

Allotropy

All elements in group 15 except Bi exhibits allotropy.

$$\begin{tikzcd}
& \alpha \text{ nitrogen} \\
N \arrow[r] & \text{allotropic forms} \arrow[ur] \arrow[dr] & \\
& \beta \text{ } ''
\end{tikzcd}$$

P $\longrightarrow$ Red P, White P. .. etc.

As $\longrightarrow$ black, grey, yellow.

Sb : Yellow, metallic, & explosive.

Oxidation state :

No. of electrons in valence shell = 5

" " " required to complete octet = 3

$$5 + \boxed{3} = 8$$

Basic negative oxidation state of Group 15 elements = -3

Moving down the group, the tendency to display -3 oxidation state diminishes. This is because of the expansion in nuclear size & metallic character.

Group 15 elements indicate +ve oxidation states of +3 & +5 by developing covalent bonds. Due to inert pair effect, the stability of +5 oxidation state will decrease down the group while that of +3 O.S. increases.

Since N has only s & p orbitals & no d orbitals, N can exhibit a covalency (most extreme) of 4 by sharing its lone pair of electrons to another ion or partic.

P & the rest of the elements can display a covalency of 5 & most extreme covalency of 6. This is because they have d orbitals in their valence shell.

N_2H_4 : Hydrazine $\boxed{\text{O.S.} \; -2}$

$2x + 4 = 0$

$\therefore x = -2$

N_2O (nitrous oxide)

$2x - 2 = 0 \quad \therefore x = 1$

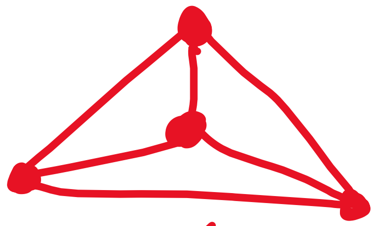
N_2O_3 : $x = +3$

N_2O_5 : $x = +5$

Nitrogen varies from other elements in the group in its properties.

The anomalous behavior of N_2 can be ascribed to its small size, high I.E., high E.N., & non-availability of d orbitals. Nitrogen can easily form $p\pi - p\pi$ bonds with different elements with a small size & hig E.N. for. e.g. C & O.

P, As, Sb exists as tetra atomic particle.



P/As/Sb.

Bi in its elemental state forms metallic bonds. The catenation inclination is less for N when compared with alternate elements of the group. This is on the grounds that there are higher inter electronic repulsions among the lone pair of electrons present on the nitrogen atoms.

Nitrogen $\longrightarrow$ $p\pi - p\pi$ bonds.

$\cancel{\longrightarrow}$ $d\pi - p\pi$

no vacant d orbital.

Phosphorus can frame $d\pi - p\pi$ bonds.

Eg. Triethyl phosphate.

Phosphorus oxo chloride.

Chemical Reactivity :

Hydrides: The elements of Group 15 form volatile hydrides of formula MH_3 which are all poisonous & foul smelling.

On descending the group from $NH_3 \to BiH_3$

1) Hydrides become increasingly difficult to prepare ;
2) Their stability decreases
3) Reducing ability decreases
4) Ease of H replacement by another grp decreases
5) Electron donating ability decreases

Hydride formation ⟶

$N_2 + 3H_2 \longrightarrow 2NH_3$

$P_4 + 6H_2 \longrightarrow 4PH_3$

$4Sb + 6H_2 \longrightarrow 4SbH_3$

$As_4 + 6H_2 \longrightarrow 4AsH_3$

} inertness of hydrides decreases from $NH_3 \rightarrow Bi$;

As the central atom gets bigger in size, the $\boxed{M}-H$ bond gets weaker.

central element

$NH_4NO_3 \xrightarrow{\Delta}$?

Problem:

decompose rapidly on heating.

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

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

$\overset{+III}{NH_4}\overset{+V}{NO_3} \xrightarrow{\Delta}$? $\overset{+I}{N_2O} + 2H_2O$

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta}$? $\overset{0}{N_2} + 4H_2O + Cr_2O_3$

$\overset{+III}{NH_4}\overset{+III}{NO_2} \xrightarrow{\Delta}$? $\overset{0}{N_2} + 2H_2O$

If the anion is not particularly oxidizing e.g. Cl^-, CO_3^{2-}, SO_4^{2-}, then ammonia is evolved.

If the anion is more oxidizing, then NH_4^+ is oxidized to N_2 or N_2O

Group - 15

Preparation of NH_3 : (Laboratory method)

1. $NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$

NH3 is prepared in the laboratory by heating an ammonium salt with NaOH.

2. Haber Bosch process. 1931 → high pressu reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \Delta$$

Nobel Prize 1918

This Reaction is reversible. Le Chatelier's principle suggests that high pressure & low temperature are required to drive the reaction to the right, & thus form, NH_3.

If this reaction is performed at low temp., a higher percentage conversion to NH_3 is possible, but the reaction is slow in reaching equilibrium, necessitating involvemen of a catalyst.

Typical condition: 200 atm pressure, 380 - 450°C temp. & a catalyst of promoted iron. It is more economic to use a higher temperature, so that equilibrium will be reached much faster.

Catalyst Prep.

$\underbrace{Fe_3O_4 + KOH \text{ (fusion)}}$ refractory material MgO, SiO_2, Al_2O_3

— — — — — — — — ..

⟶ Broken into small lumps & put into ammonia converter where Fe_3O_4 is reduce to give small crystals of iron in a refractory matrix. This is active catalyst.

3. $\boxed{CaNCN} + 3H_2O \longrightarrow 2NH_3 + CaCO_3$

Calcium cyanamide
(fertilizer)

Ammonium salts:

$$2NH_4NO_3 \xrightarrow{\Delta} 2N_2 + O_2 + 4H_2O$$

can cause explosion

mixed with

$CaCO_3$ & $(NH_4)_2SO_4$ to make it safe.

$$NH_4NO_3 \xrightarrow[280^\circ C]{\Delta} N_2O + 2H_2O.$$

Preparation of $(NH_4)_2SO_4$:

used as fertilizer

$(NH_4)_2SO_4$ is made by passing NH_3 & CO_2 gases into a slurry of $CaSO_4$ in water (i.e. slurry of gypsum)

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + CaSO_4 \longrightarrow CaCO_3 + (NH_4)_2SO_4$$

$(NH_4)_2HPO_4$ & $(NH_4)_2H_2PO_4$ → used as fertilizer. Also used for fireproofing wood, papers & textiles.

Phosphine : PH_3

PH_3 vs NH_3 → Which one is a stronger base?

NH_3 is more basic than PH_3 due to smaller size of N compared to P, more polar bonds, & its greater ability to donate orbital. Due to smaller atomic size the density of l. p. electrons on N in NH_3 is longer than P in PH_3.

PH_3 is a colorless & extremely toxic gas. Highly reactive. PH_3 is less soluble in water & more soluble CS_2 & other organic solvents.

Chemical reactions :

1. $PH_3 + HBr \longrightarrow PH_4Br$ (phosphonium compounds with acids)

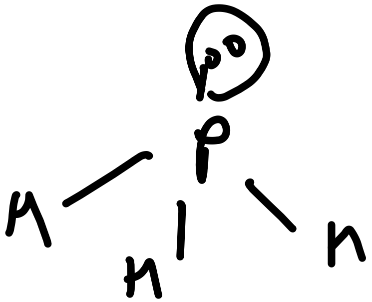
(weekly basic)

2. Addition compounds.

$SnCl_4 \cdot 2PH_3$ $CuCl_2 \cdot 2PH_3$ $AlCl_3 \cdot 2PH_3$

3. NH_3 & PH_3 can be absorbed by bleaching powder.

$$PH_3 + 3Ca(OCl)Cl + 3H_2O \longrightarrow PCl_3 + 3HCl + 3Ca(OH)_2$$



$$NH_3 + 3Ca(OCl)Cl \cancel{\longrightarrow} NCl_3 + 3HCl + 3Ca(OH)_2$$

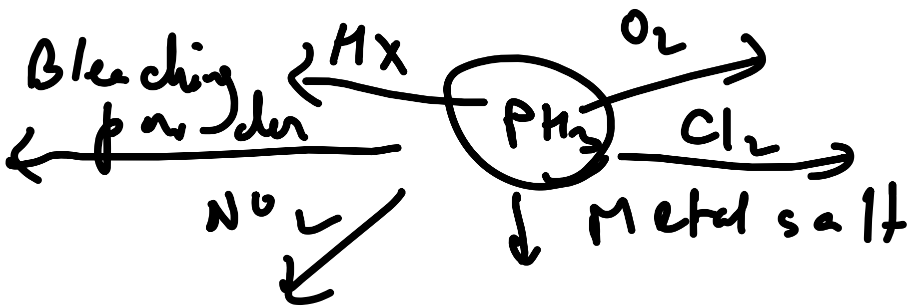
$$NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$$

4. $$PH_3 + O_2 \xrightarrow{150^\circ c} H_3PO_4 + H_2O$$

$$PH_3 + Cl_2 \longrightarrow PCl_3 + 3H_2O$$

$$PH_3 + 2NO_2 \xrightarrow[\text{spark}]{\text{electric}} N_2 + H_3PO_4$$

Phosphides



a) $2PH_3 + 3CuSO_4 \rightarrow Cu_3P_2 + 3H_2SO_4$

$2PH_3 + 3HgCl_2 \rightarrow Hg_3P_2 + 6HCl$

b) $PH_3 + 6AgNO_3 \rightarrow \underbrace{[Ag_3P \cdot 3AgNO_3]\downarrow}_{\text{yellow ppt}} + 3HNO_3$

$Ag_3P \cdot 3AgNO_3 + 3H_2O \rightarrow \underbrace{3Ag\downarrow}_{\text{black ppt}} + 3HNO_3 + H_3PO_3$

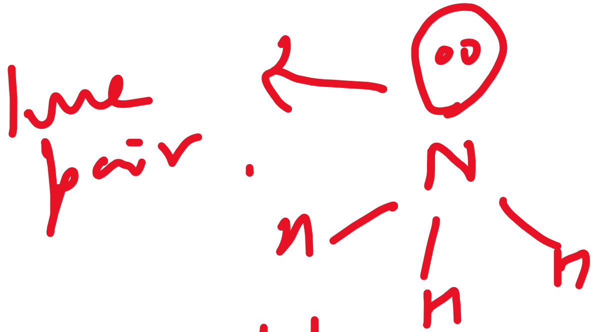
Preparation of PH_3 :-

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

Phosphine is formed by hydrolysing metal phosphides, such as Na_3P or Ca_3P_2 with H_2O, or by hydrolysing white P with NaOH soln.

Structure of hydrides :-

Ammonia (NH_3)   Shape – Pyramidal



Regular tetrahedral shape slightly distorted.

Bond angle : 107° 48'

PH_3 , AsH_3 , SbH_3 → similar expectation.

In practice, the bond pairs of electrons are much further away from the central atom than they are in NH_3. Thus, the lone pair causes even greater distortion in PH_3, AsH_3 & SbH_3. The bond angle decreases from 107° 48' in N to 91° 18' in SbH_3.

PH_3 : 93° 36'

$As-H_3$: 91° 48'

These suggests that orbitals used for bonding are close to f orbitals.

M.P. & B.P of hydrides increase from $PH_3 \longrightarrow SbH_3$.

Hydrazine (Rocket fuel)

Manufacture: (Raschig process)

Step I : $NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$

(chloramine) (fast)

Step II $2NH_3 + NH_2Cl \longrightarrow NH_2{-}NH_2 + NH_4Cl$ (slow)

Side reaction $N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$.

Inorder to prevent the side reaction, the reaction is carried out in distilled H_2O rather than tap water because heavy metal ions present in tap water may catalyze the side reaction, resulting in transformation of N_2H_4 to N_2.

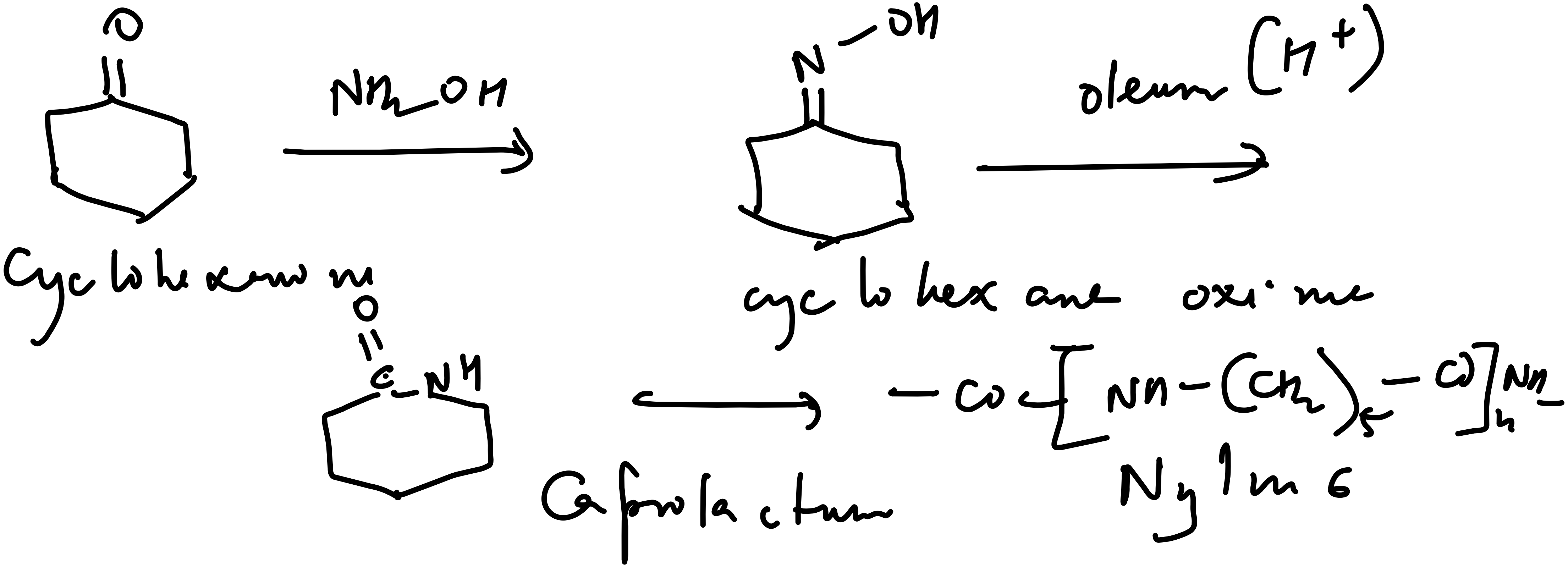
Hydroxyl amine NH_2OH

Hydroxyl amine is manufactured by reducing nitrites or from nitromethane.

a) $NH_4NO_2 + NH_4HSO_3 + SO_2 + 2H_2O \longrightarrow$

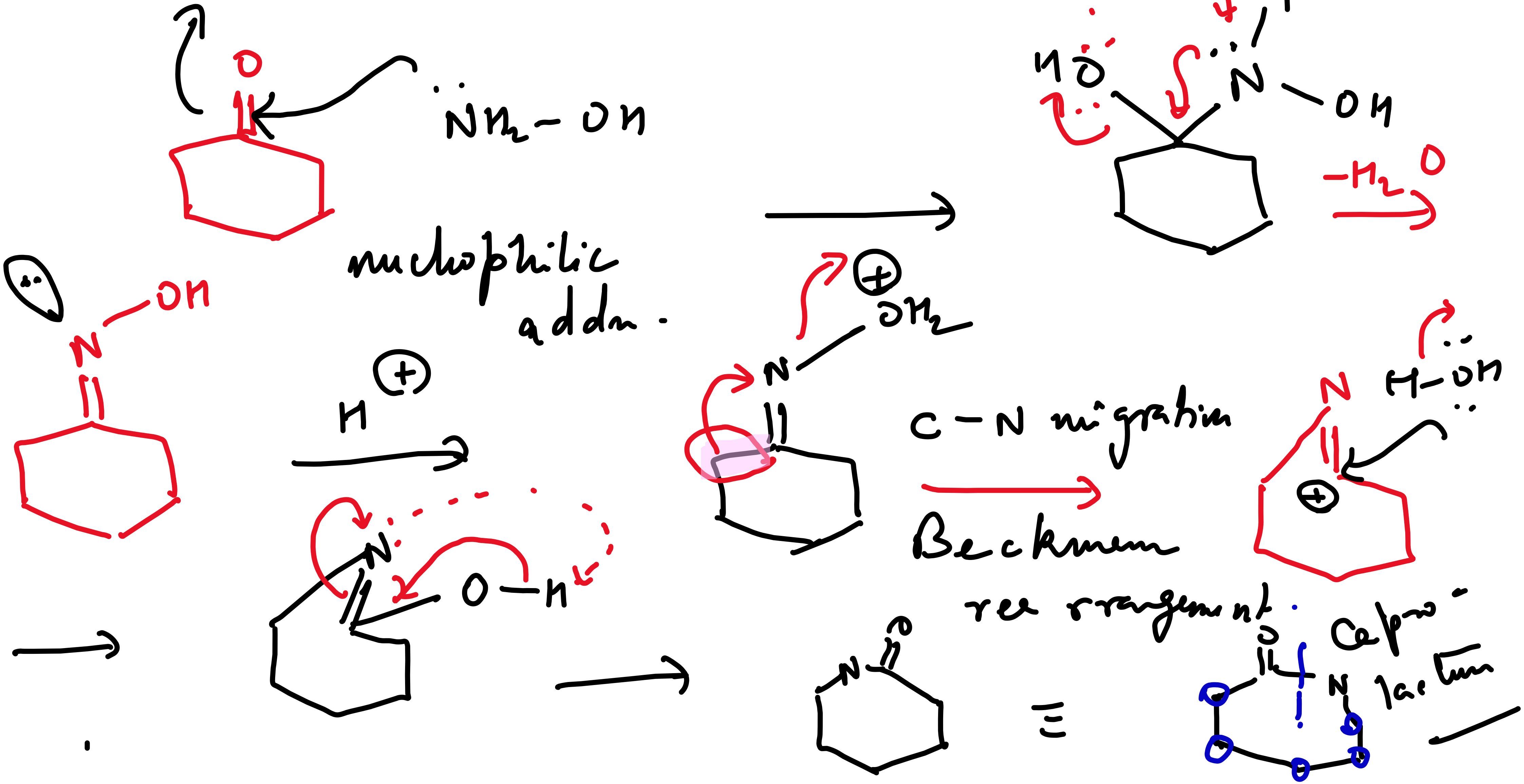
$[NH_3OH]^{\oplus} HSO_4^{\ominus} + (NH_4)_2SO_4$

b) $CH_3NO_2 + H_2SO_4 \longrightarrow [NH_3OH]^{\oplus} HSO_4^{\ominus} + CO.$



$-CO-[NH-(CH_2)_5-CO]_n NH-$

Beckman Rearrangement:



Azide : $-N_3$

Preparation of NaN_3

$N_2O + NaNH_2 \rightarrow NaN_3 + H_2O$

Passing nitrous oxide gas into fused sodamide at 190 °C. under anhydrous condn.

$H_2O + NaNH_2 \rightarrow NH_3 + NaOH$.

HN_3 (hydrazoic acid)
↓ highly poisnous.

$2HN_3 \rightarrow H_2 + 3N_2$.

Covalent azides are used as detonators & explosives.

Ionic azide are usually more stable.

$N_2O + NaNH_2 \longrightarrow NaN_3 + \cancel{H_2O}$

$\cancel{H_2O} + NaNH_2 \longrightarrow NH_3 + NaOH$

$N_2O + 2NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH.$

Cyanamide Process -

$CaC_2 + N_2 \xrightarrow{1100^\circ C} \underbrace{CaNCN + C}_{\text{nitrolim}}$

$CaNCN + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$

used as fertilizer

NPK fertilizer

Plant fertilizers

contains 3 main ingredients :

1. N in a combined form (e.g. NH_4NO_3, or urea) to facilitate plant growth, particularly leaves. Since N is an essential constituent of amino acids & proteins, it is crucial for making new cells.

2. P → essential for root growth.

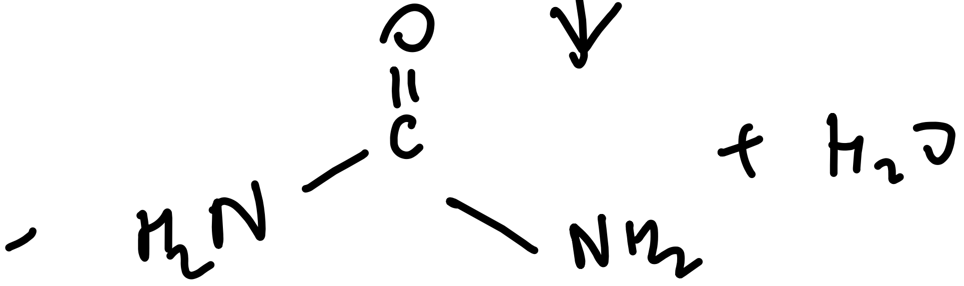
Superphosphate / Triple superphosphate

made from fluoroapatite $[3Ca_3(PO_4)_2 \cdot CaF_2]$

3 K in ⟷ flowering → K_2SO_4.

Urea : $2NH_3 + CO_2 \xrightarrow[\text{high pressure}]{180-200^\circ C} H_2NCOONH_4$

$$\downarrow \Delta$$



$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$

Phosphate fertilizer

$[3(Ca_3(PO_4)_2)CaF_2] + 7H_2SO_4$

$\downarrow$

$\underbrace{3\,Ca(H_2PO_4)_2 + 7CaSO_4}_{\text{super phosphate}} + 2HF$

$Ca(H_2PO_4)_3$ Triple superphosphate

Group - 15

Q. Bismuth is not able to form oxides in + 5 oxidation state - Explain.

Ans: Due to inert pair effect Bi is unable to form oxides in + 5 oxidation state.

Oxides formed from elements when in higher oxidation state are more acidic than that of lower oxidation state.

∴ N_2O_3 vs. N_2O_5 -

Acidic strength increases from $\overset{+3}{N_2O_3} \longrightarrow \overset{+5}{N_2O_5}$

$N_2O_5 > N_2O_3$

Reactivity towards halogen :

All elements of Group 15 forms trihalides or pentahalide.

$2P + 3Cl_2 \longrightarrow 2PCl_3$ (trihalide)

$2P + 5Cl_2 \longrightarrow 2PCl_5$ (pentahalide)

NF_3, PF_3, AsF_3, SbF_3, BiF_3 → all are trihalides.

Nitrogen does not from pentahalides due to the non-availability of d orbitals in their valence shell.

Reaction with metals:

E = group 1 element

Each element of group 15 react with metals to form binary compounds, (M_3E_2) demonstrating −3 oxidation state.

Eg. $3\,Ca + N_2 \longrightarrow Ca_3\overset{-3}{N_2}$ (nitride)

$+2 \times 3 + 2x = 0$

$\Rightarrow 2x + 6 = 0 \Rightarrow x = -3$

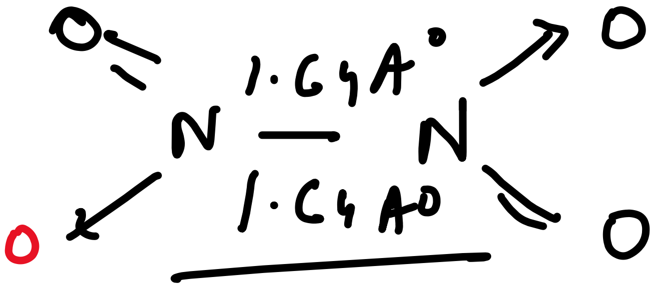
$6\,Ca + P_2 \longrightarrow 2\,Ca_3P_2$

calcium phosphide.

$6Zn + 4Sb \longrightarrow 2Zn_3Sb_2$ Zinc antimonide

$6Mg + 4Bi \longrightarrow 2Mg_3Bi_2$ magnesium bismuthide

Structure of NO_2 / N_2O_4



long bond

$\angle O-N-O = 132^\circ$

O – N bond length – 1.20 A°

strong oxidizing agent.

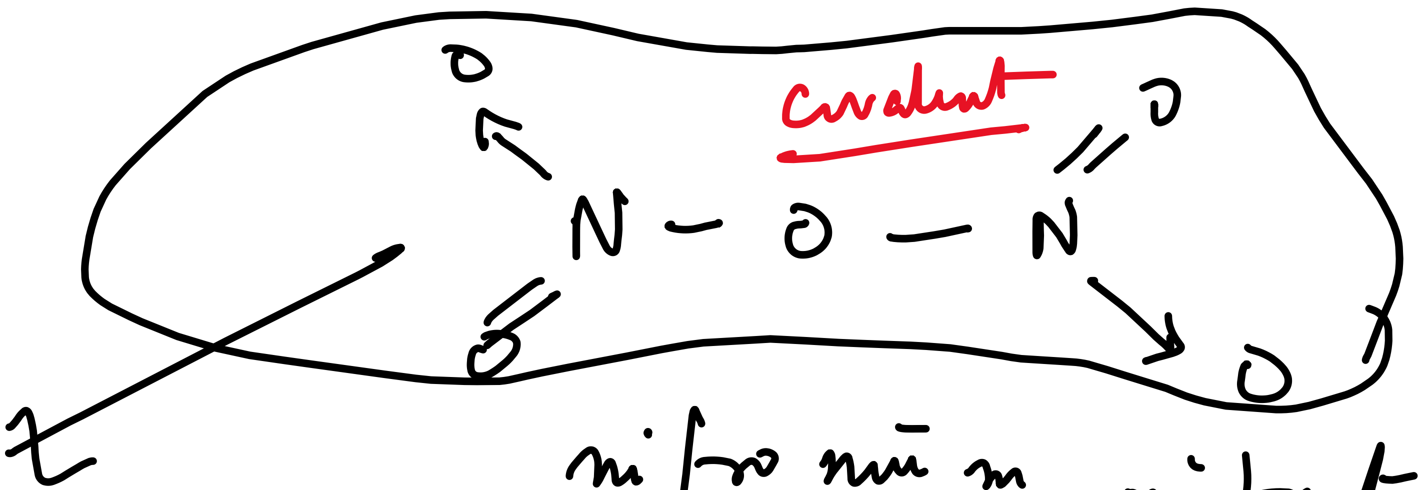
$HCl \rightarrow Cl_2$

$CO \rightarrow CO_2$

$$\overset{+4}{NO_2} + \overset{+2}{CO} \longrightarrow \overset{+2}{NO} + \overset{+4}{CO_2}$$

oxidized.

reduced



nitronium nitrate

Covalent in soln. & gas phase

ionic

N_2O_5 :

$\overset{\oplus}{NO_2}$ $\overset{\ominus}{NO_3}$

(ionic)

Oxoacids of nitrogen: HNO_2, HNO_3.

1. Preparation of HNO_2:

By Acidification of a soln. of nitrite:

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HNO_2$$

2. Group I metal nitrites can be made by heating nitrates:

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$$

$$NaNO_3 + Pb \xrightarrow{\Delta} NaNO_2 + PbO$$

$NaNO_2 \longrightarrow$ Food additive in cured meat, sausage, hot dogs, bacon, & tinned ham.

$NO_2^{\ominus}$ ions inhibit the growth of bacteria, Clostridium botulinum $\rightarrow$ botulism (a particularly unpleasant form of food poisoning)

During cooking of meat, the nitrites may react with amines / & convert into nitrosamines $R_2N-N=O$, which are thought to be carcinogenic.

Nitric acid.

$$4HNO_3 \xrightarrow{\Delta} 4NO_2 + O_2 + 2H_2O$$

Synthesis :

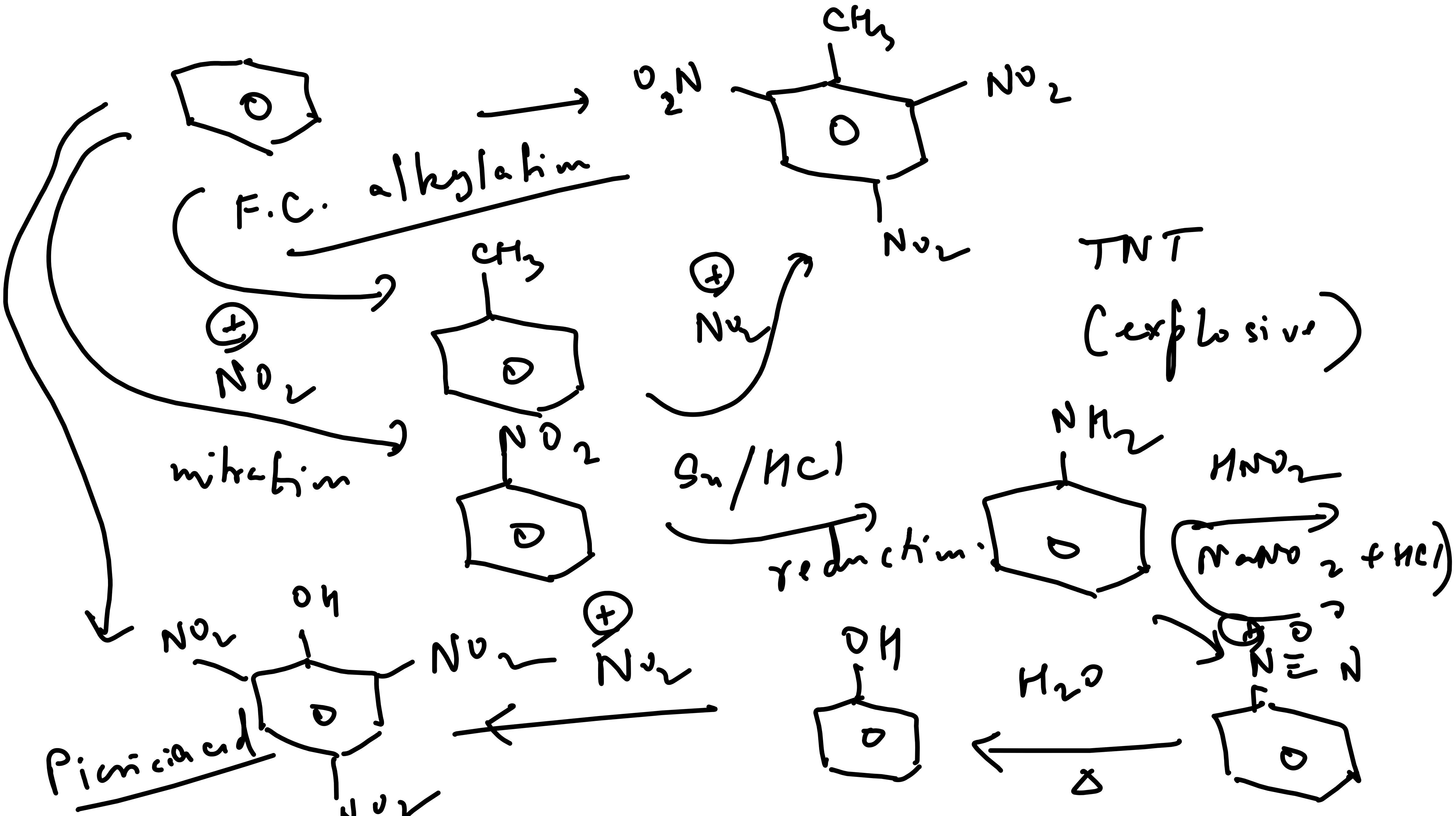
Birkeland - Eyde process

$$N_2 + O_2 \xrightarrow{spark} NO \xrightarrow{+O_2} NO_2 \xrightarrow{H_2O} HNO_3$$

Obsolete

Ostwald :

$$4NH_3 + 5O_2 \xrightarrow[5\ atm,\ 850^\circ C]{Pt/Rh\ catalyst} 4NO(g) + 6H_2O(l)$$


CH3
O2N
NO2
NO2
TNT
(explosive)
F.C. alkylation
CH3
⊕NO2
⊕NO2
nitration
NO2
Sn/HCl
reduction
NH2
HNO2
(NaNO2 + HCl)
⊕ ⊖
N≡N
H2O
Δ
OH
⊕NO2
OH
NO2
NO2
NO2
Picric acid

Reactions of nitric acid

Oxyacids generated are in their highest oxidation state

i) $\overset{0}{S} + 6HNO_3 \longrightarrow H_2\overset{+6}{S}O_4 + 6NO_2 + 2H_2O$

ii) $\overset{0}{P} + 10HNO_3 \longrightarrow 2H_3\overset{+5}{P}O_4 + 10NO_2 + 2H_2O$

iii) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + H_2O$

iv) $Sn + 2HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$

meta stannic acid

metalloids

v) $\overset{0}{As} + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$

$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$.

In case of metals, product depends on concentration of acid & temp.

$$4Zn + \underset{\text{dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + 5H_2O + \overset{+1}{N_2O}$$

$$Zn + \underset{\text{conc.}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + \overset{+4}{NO_2}$$

$$3Cu + \underset{\text{dil.}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

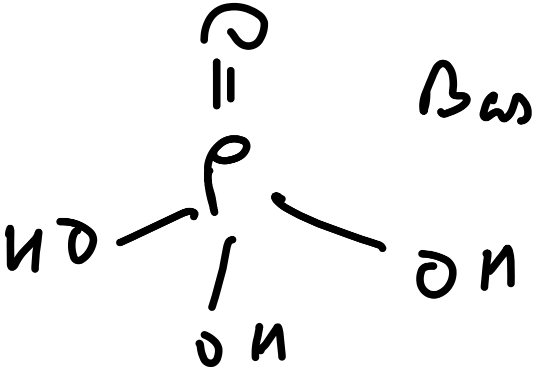
$$Cu + \underset{\text{conc.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Strength of HNO_3	Metal	Main Products
Extremely dilute (2%)	Mg, Mn	Metal nitrate + H_2
Dilute (6%)	Fe, Zn Sn	Metal nitrate + H_2O + NH_4NO_3
Dilute (20%)	Pb, Cu, Ag, Hg	Metal nitrate + NO + H_2O
	Fe, Zn	Metal nitrate + N_2O + H_2O
	Sn	NH_4NO_3 + $Sn(NO_3)_2$
Concentrated	Fe, Sn, Pb, Cu, Ag	Metal nitrate + NO_2 + H_2O
	Sn	H_2SnO_3 + NO_2 + H_2O

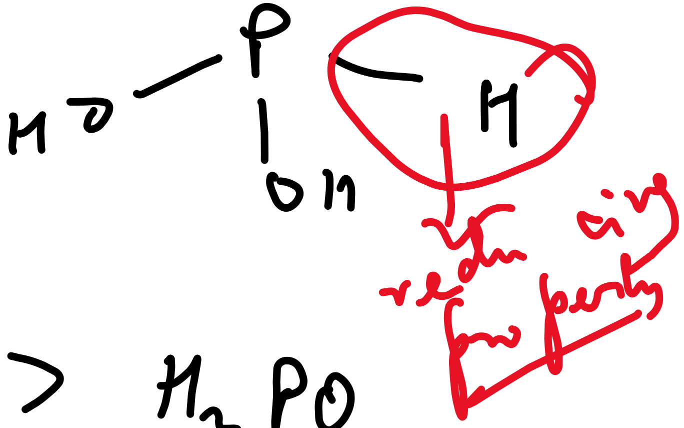
Oxoacids of P :-

Orthophosphoric acid. H_3PO_4

H_3PO_4 vs H_3PO_3 → Basicity ?



Basicity : 3



Basicity : 2

H_3PO_3

pK_{a_1} – 1.3

H_3PO_4

pK_{a_1} – 2.1

Acid strength $H_3PO_2 > H_3PO_3 > H_3PO_4$

Explain the trend.

$$H_3PO_4 \xrightarrow{220^\circ C} ?\ H_4P_2O_7 \xrightarrow[320^\circ C]{\text{strong heat}} ?\ (HPO_3)$$

ortho phosphoric acid

pyrophosphoric acid

$\downarrow$

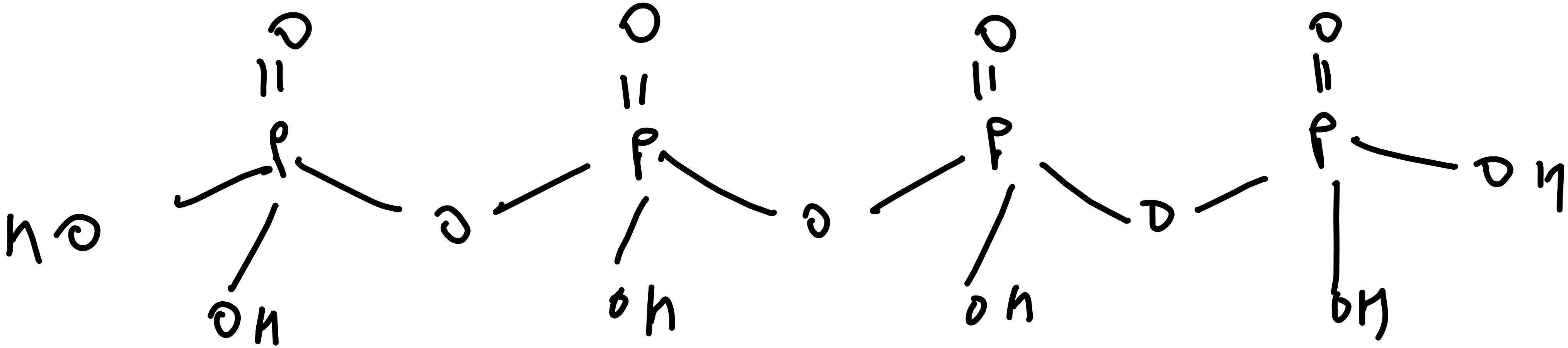
meta phosphoric acid

Pure $H_3PO_4 \longrightarrow ?$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

<u>Polyphosphate</u> : Polymerization of acidic $[PO_4]$ units from isopolyacids.



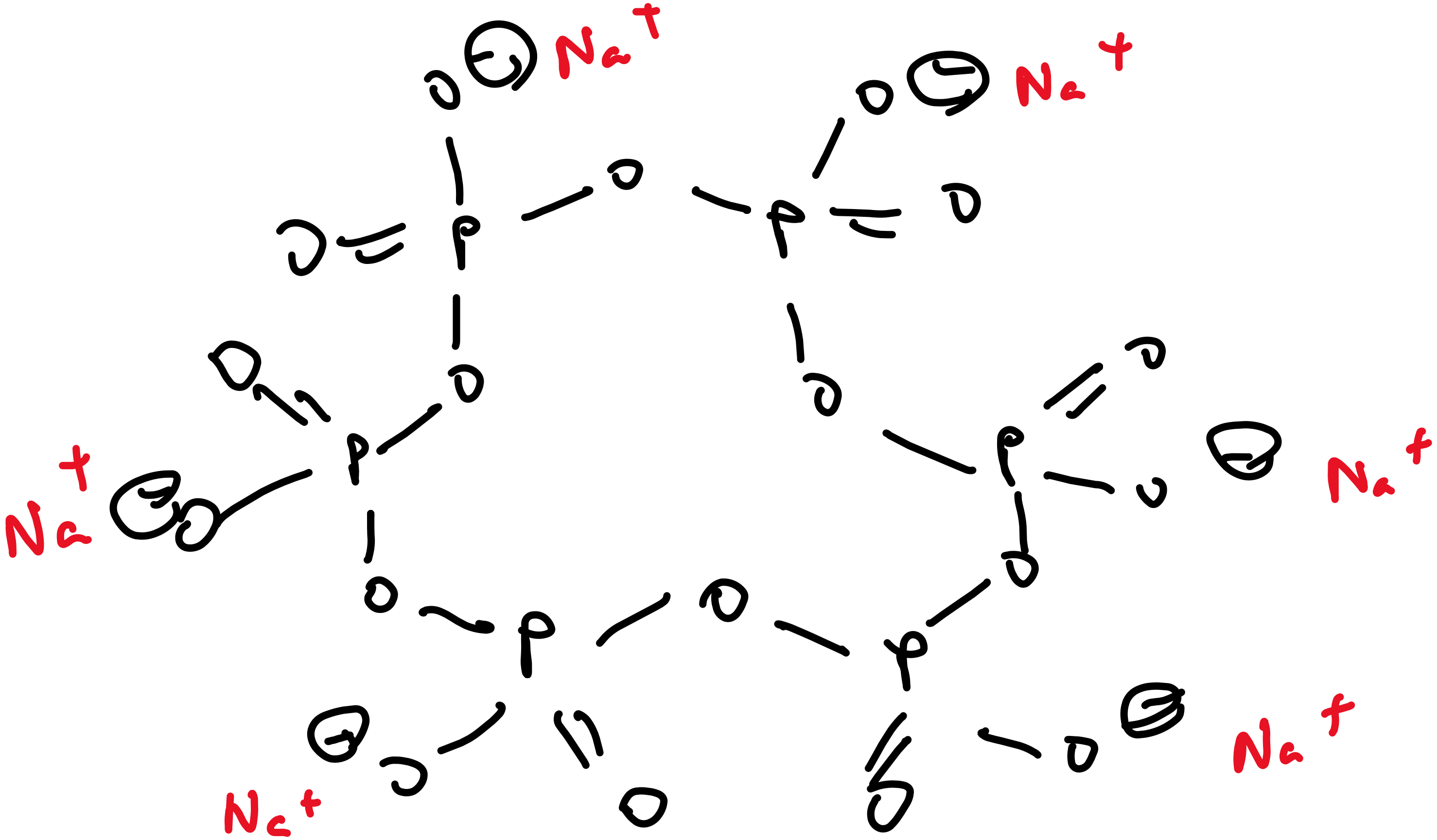
Tetrapolyphosphoric acid

Straight chain compounds.

Graham's salt:

Long chain polyphosphate

Sodium hexametaphosphate $(NaPO_3)_6$



Thickener,
Emulsifier
& Texturizer
used in a
variety of food.

Graham's salt: Calgon:

descaling boiler & pipes ← Water softening: Sequestering agent for Ca^{2+} & Mg^{2+}.