

Group 15 (Nitrogen Family)

* Physical properties

* chemical properties

* Chemistry of Nitrogen \Rightarrow N_2 , NH_3 , oxides of nitrogen & oxy acids of nitrogen (HNO_3)

* Chemistry of Phosphorous \Rightarrow allotropes, oxides, oxy acids & halides of P.

Physical properties. General EC: $nS^2 nP^3$ (extremely stable)

Electron configuration & Metallic & Nonmetallic character

	Atomic no	EC	Inner core.
Metal	N 7	[He] $2S^2 2P^3$	Noble gas
	P 15	[Ne] $3S^2 3P^3$	
Metalloids	As 33	[Ar] $3d^{10} 4S^2 4P^3$	Pseudo noble gas
	Sb 51	[Kr] $4d^{10} 5S^2 5P^3$	
Metal — Bi	83	[Xe] $4F^{14} 5d^{10} 6S^2 6P^3$	$d^{10} + F^{14} \rightarrow Ns^2$

on going down the group metallic character of elements increases.

Bi \Rightarrow Last stable non-radioactive element

2] Nature & Allotropy

N_2 is a colourless, diatomic gas & does not show Allotropy

Remaining all element (P, As, Sb, Bi) are solids and shows allotropy

P₄ - soft solid

Allotropes: white, Red & Black

Phosphorous

N≡N \Rightarrow Due to very strong triple bond in N₂ it is an inert gas.

Bond Strength: N-N < P-P

N has less tendency to undergo catenation.

Atomic size

On moving down the group atomic size increases

N < P < As < Sb < Bi

(In pm) 70 110 121 141 148



Variation is less due to Lanthanide Contraction.

Ionization enthalpy

On moving down the group IE \downarrow due to increase in atomic size.

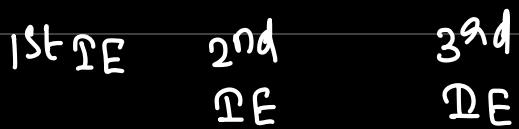
IE: N > P > As > Sb > Bi

* Group 15 elements 1st ionisation enthalpy is higher as compared to Group 16

IE: Group 15 (ns² np³) > Group 16 (ns² np⁴)

* For Group 15 elements:

$$\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$$



Electronegativity

On going down the group EN \downarrow es



3 2.1 2 1.9 1.9

Density

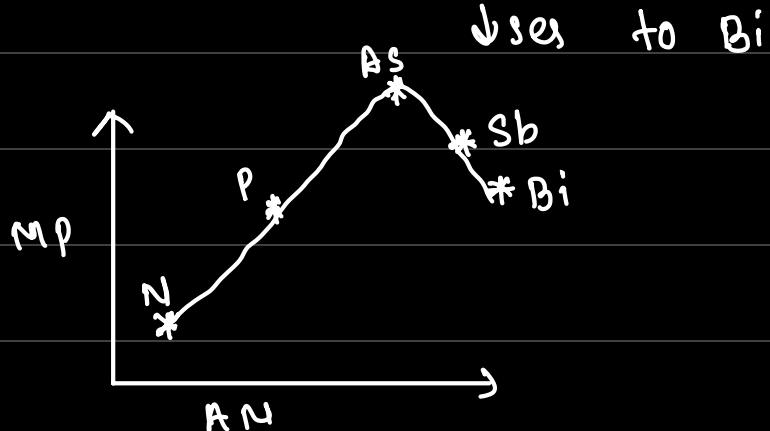
Density increases down the group.



Melting point and Boiling point

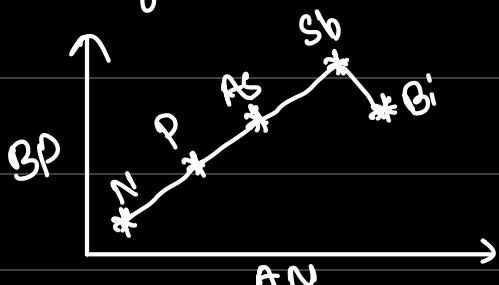
Melting point: MP \uparrow es from N to As then

\downarrow es to Bi



highest MP

Boiling point: BP \uparrow es from N to Sb then \downarrow es to Bi



highest BP

Chemical properties

Oxidation number

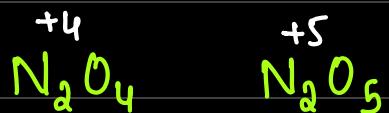
Most common oxidation state of group 15 elements.

: +5, +3, -3

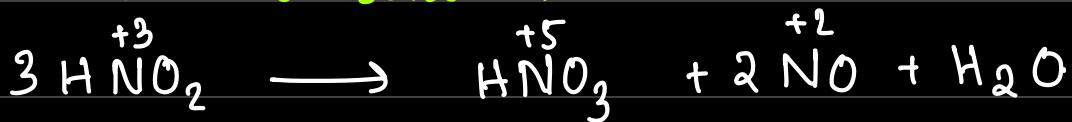
* tendency to show -3 oxidation state decreases down the group due to ↑ size & ↑ metallic character. Bi rarely shows -3 oxidation state.

tendency to show -3 OS : N > P > As > Sb > Bi

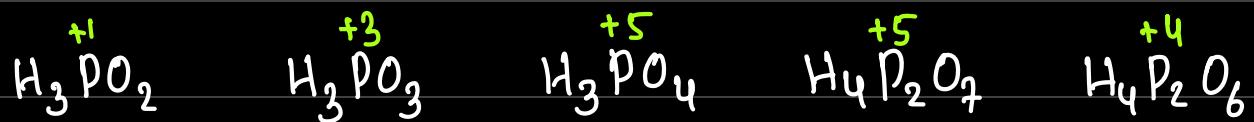
* N also shows +1, +2 & +4 OS.



* N with oxidation state +1 to +4 tends to disproportionate in acid solution.



* P can also show +1 & +4 OS in some of its oxy acids.



all intermediate OS tends to dis proportionate in to +5 & -3 in both acid & alkali solution.

* tendency to show +3 OS rises down the group due to inert pair effect.

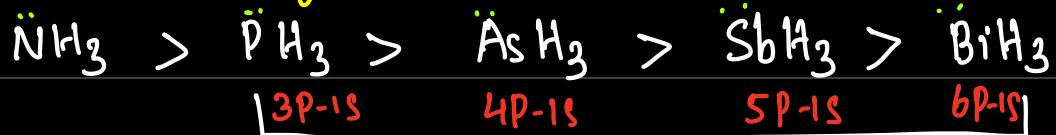
2) Reactivity towards Hydrogen

All elements readily combines with Hydrogen to form hydride of the type MH_3



* thermal stability of hydrides decreases down the group due to \downarrow se in bond strength M-H (i.e., Bond dissociation energy of M-H \downarrow es down the group).

thermal stability order:



\Downarrow \Downarrow
 SP^3 Do not undergo hybridisation, pure hybridisation. P orbitals directly overlap with 1s orbitals of H. having a range of BA $90 - 93^\circ$

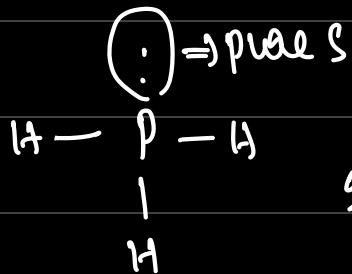
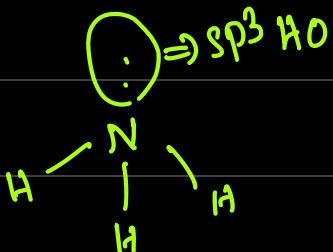
* Reducing character of Hydrides rises down the group.



very mild
RA

(strongest RA)

*



% S character \propto EN

Basicity of Hydrides \downarrow goes down the group.



* NH_3 shows Hydrogen bonding in solid as well as in liquid state, so its MP & BP are comparatively higher.

BP & MP \uparrow goes down the group



* Bond length: N-H < P-H < As-H < Sb-H < Bi-H

Bond angle: $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

107.8 93.6 91.8 91.3

$\Delta_f H^\circ$ (kJ/mol)	NH_3	$<$	PH_3	$<$	AsH_3	$<$	SbH_3	$<$	BiH_3
	-46.1		13.4		66.4		145.1		278

\downarrow
endothemic

endothemic

Bond dissociation : $\Delta H_{\text{dissociation}}$ goes down the group.

$\Rightarrow \text{NH}_3$ exists but NH_5 does not exist (due to absence of d orbitals in N)

$\Rightarrow \text{PH}_3$ exists but PH_5 does not exist. (H is not sufficiently electronegative to bring excitation of π to d orbitals)

3) Reactivity towards oxygen

All these elements forms two types of oxide
on directly combining with $O_2 \Rightarrow M_2O_3$ & M_2O_5

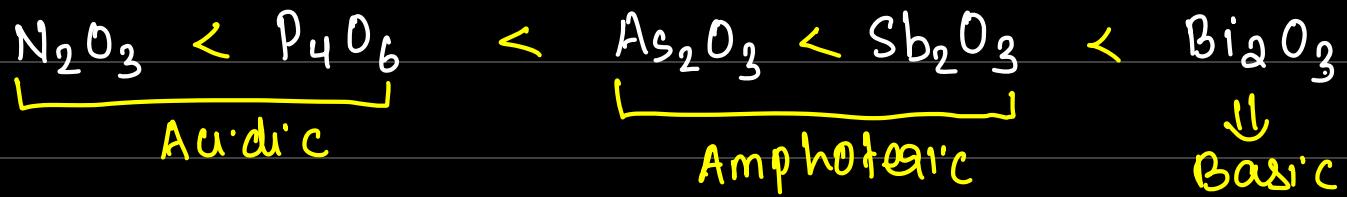


oxides of N : N_2O NO N_2O_3 N_2O_4 N_2O_5

P : Ру 06 Ру 010

(dimer of P_2O_3) (dimer of P_2O_5)

* Basic character of oxides goes down the group.



* Stability of +5 OS oxides decreases down the group
(linear pair effect)

M^{+3} OS is less acidic than M^{+5} .

N_2O_5 is more acidic than N_2O_3 .

4) Reactivity with Halogens

All elements combines directly with X_2 to form two types of halides MX_3 & MX_5
(except N & Bi)

MX_5 does not exist (N can not show covalency
more than 4 due to absence of d orbitals)

Bi does not show stable +5 OS due to inert pair effect.



* Penta halides more covalent than trihalides.

* In trihalides except BiF_3 everything are covalent
 $BiF_3 \Rightarrow$ has ionic character.

* In trihalides of nitrogen, only NF_3 is stable.

5) Reactivity towards metal

All these elements can react with metal to form their binary compounds exhibiting -3 OS.

e.g. :



Compounds of Nitrogen.

Air contains around 78% by volume of N₂ gas.

* N₂ is produced commercially by the liquefaction and fractional distillation of air.

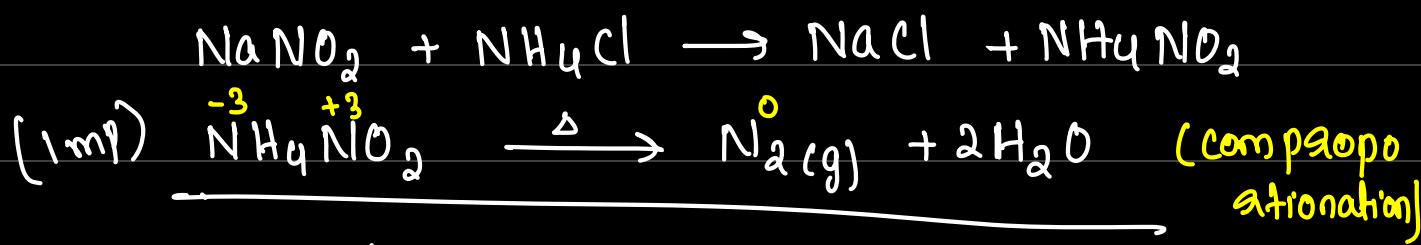
Liquid N₂ (BP = 77.2 K) distills out first leaving behind liquid O₂ (BP = 90 K)

Laboratory method.

treating aqueous solution of ammonium chloride with sodium nitrite.



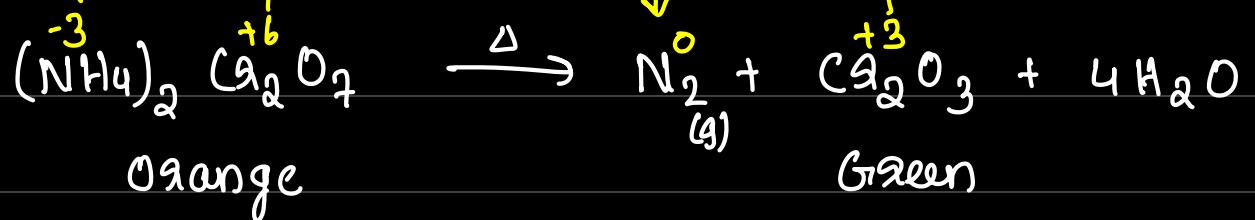
⇒ this reaction occurs in two step.



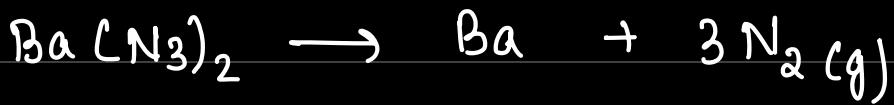
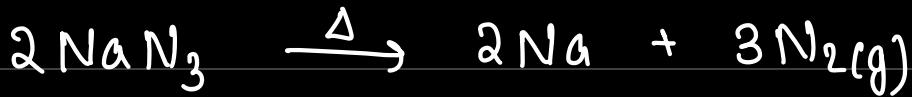
* By heating Ammonium dichromate

oxidation

reduction.



* Very purest of N_2 is obtained by heating sodium or Barium Azide.



Properties of N_2

* N_2 is colourless, odourless, tasteless and Non toxic gas

* It has low solubility in water.

* It has Low Freezing point & Boiling point.

* N_2 is inert at room temperature, due to high bond enthalpy of $\text{N} \equiv \text{N}$

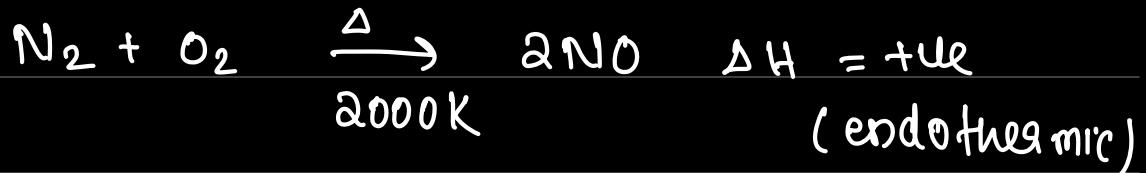
* At higher temperature, N_2 directly combines with metals and nonmetals to form Ionic nitride & covalent nitrides respectively.



Diagonal relation
shp.



Exothermic



Uses of N₂

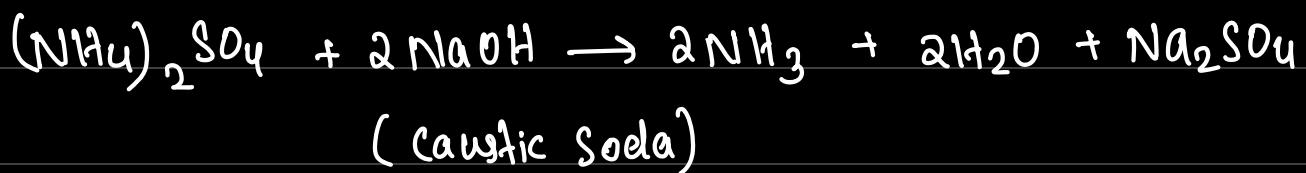
- * Used for manufacture of NH₃ & other industrial chemicals containing nitrogen (e.g. calcium cyanamide etc.)
- * It is used to provide inert atmosphere in industrial processes, where presence of O₂ or air is avoided.
- * Liquid N₂ is used as a refrigerant to preserve biological materials, food items etc.

Ammonia (NH₃)

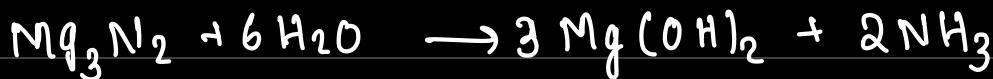
Preparation

Laboratory method.

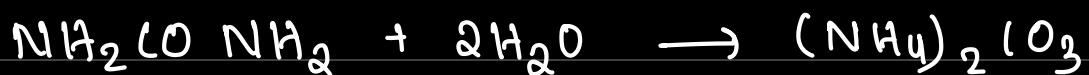
- * By action of Any base on NH₄⁺ salt.



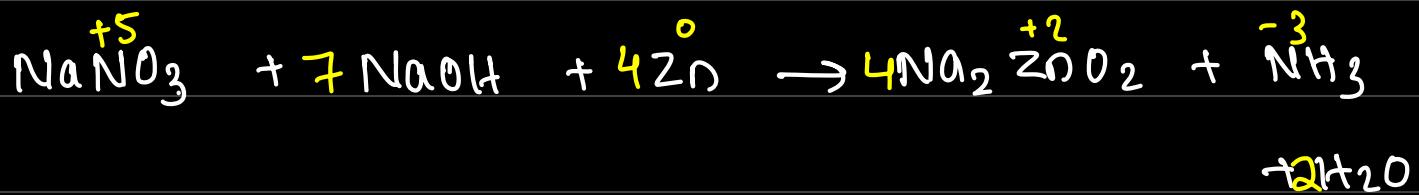
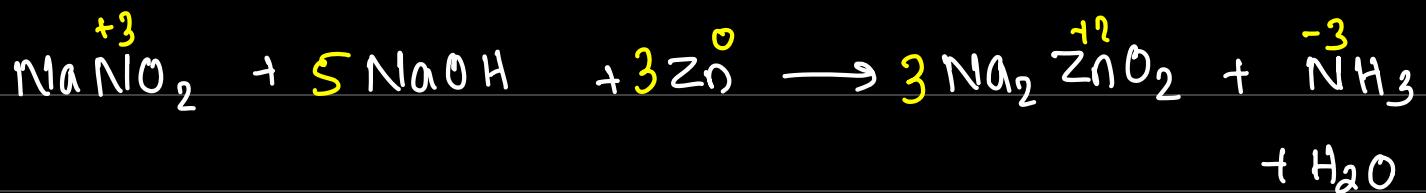
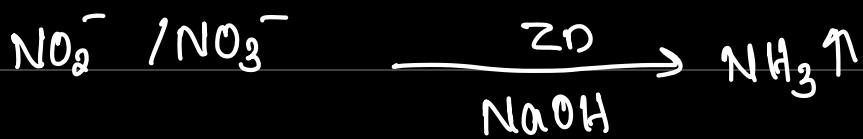
- * By hydrolysis of Nitrides.



* By hydrolysis of urea.



Quantitative estimation of ammonia



Industrial method - Haber's process.



for better yield of NH_3

* High P (200 atm)

* low temp (500°C) \Rightarrow min temp required.

* catalyst - iron oxide with a small amount of K_2O & Al_2O_3 .

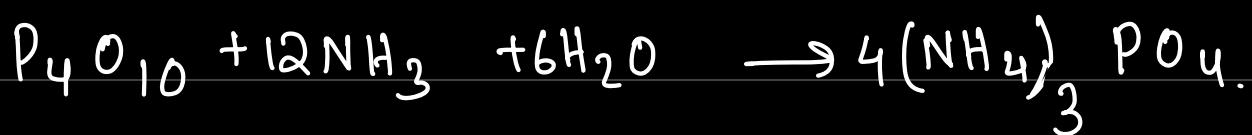
② * By Hydrolysis of cyanamide

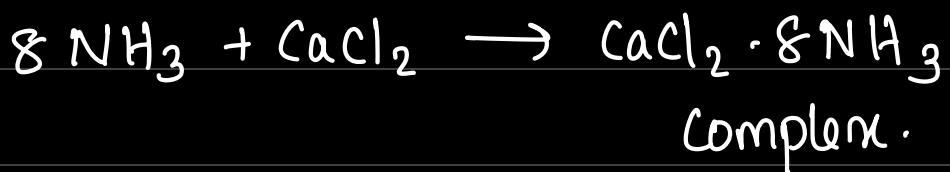


Drying of moist NH_3



Dehydrating agent \uparrow conc. H_2SO_4 , P_4O_{10} , anhydrous $CaCl_2$
can not be used for drying moist NH_3





* Quick lime (CaO) is used for drying of NH_3 .



Properties of NH_3

* It is a colourless gas pungent smell.

* Its freezing & boiling point are 198.4 239.7 K respectively.

Because in solid & liquid state it can show H bonding.

* It is soluble in water to significant extent in aqueous solution, it is basic in nature.



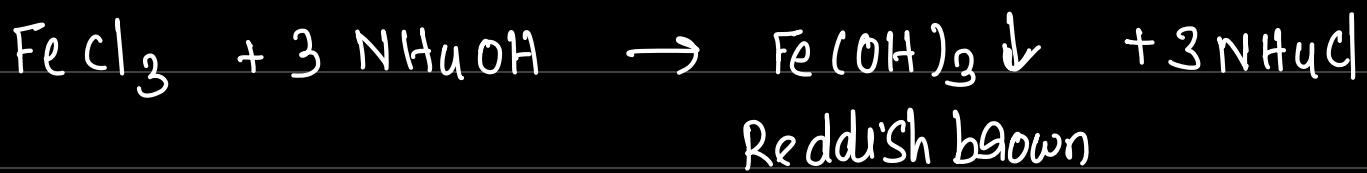
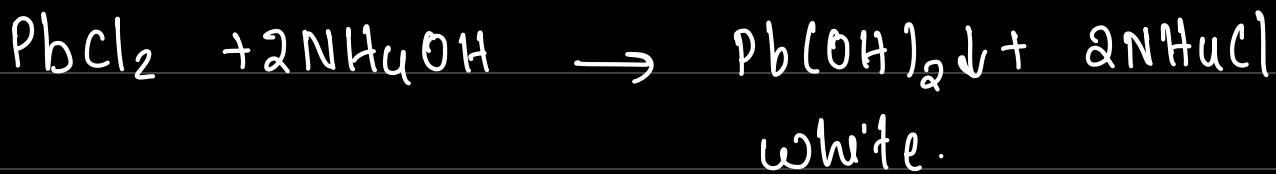
It's A weak Lewis base as well as Brønsted base.

so, it can react with acid & form salt

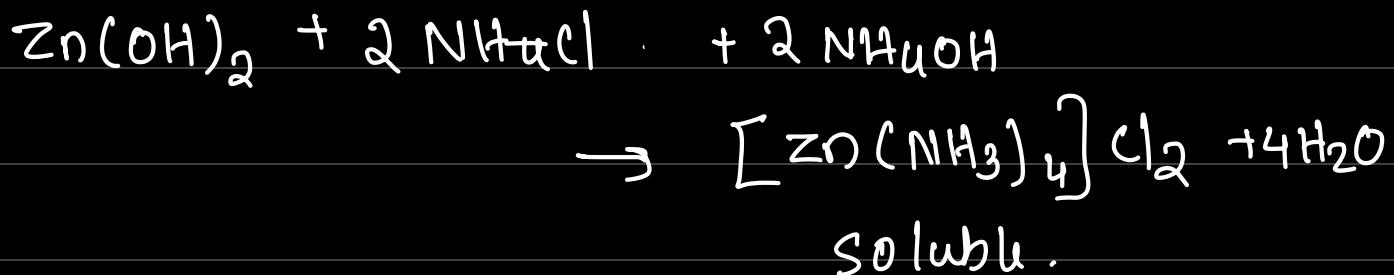
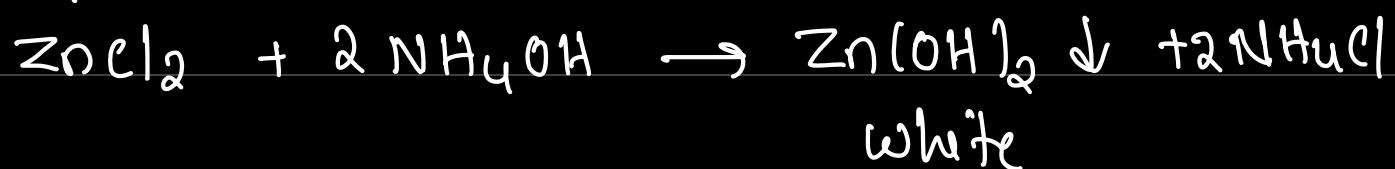


Reaction of NH_3 with Salt

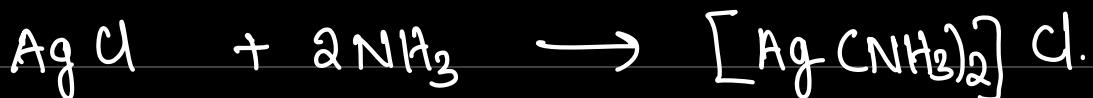
* It can react with salts & produce insoluble hydroxide.



* On reaction with Zn it can form soluble complex.



* NH₃ can form complex



Heating effect of Ammonium salts

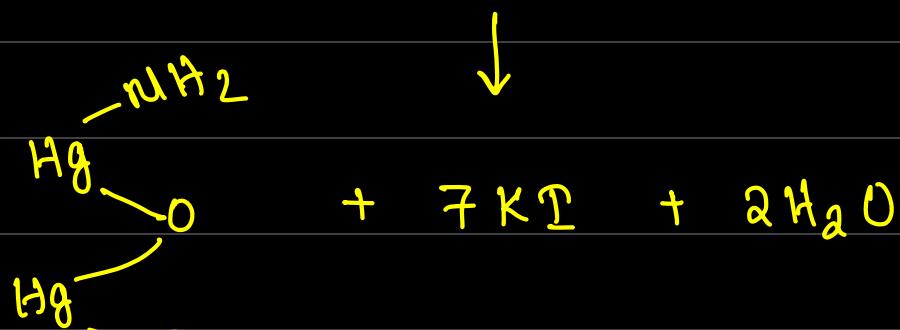
Generally Ammonium Salts on heating gives NH₃ gas.





Test for NH_3

When NH_3 gas is passed through an alkaline solution of Negle's reagent $[K_2[HgI_4]]$, Brown precipitate of Brown colour is obtained.



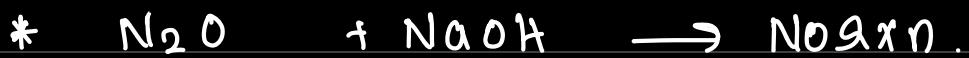
Todide of millon's base

Uses of NH_3

* Used as a refrigerant liquid.

* For manufacturing of fertilizers.

- * As a starting material for preparation of HNO_3 by Ostwald's process
- * Used as a laboratory reagent.



Neutral



Neutral



Oxyacids of Nitrogen



Nitric acid (HNO_3)

Laboratory Method

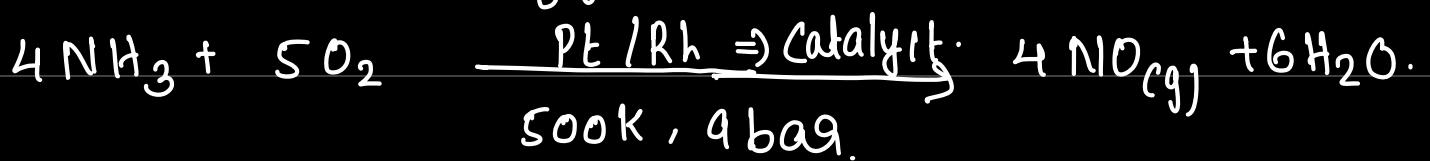


Industrial Method

On large scale HNO_3 is prepared by Ostwald's

process.

Step I \Rightarrow Catalytic oxidation of NH_3 by atmospheric oxygen.



Step II \Rightarrow Nitrogen oxide formed combines with O_2 & form NO_2



Nitrogen dioxide is dissolved in water to form HNO_3 .



\Rightarrow aqueous HNO_3 can be concentrated by distillation up to 68% of HNO_3 by mass. & with specific gravity 1.504

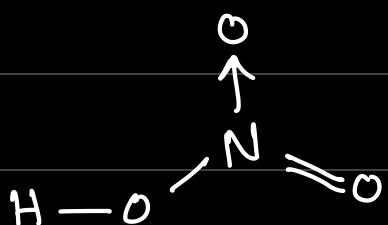
* 98% HNO_3 can be obtained by dehydrating with conc. H_2SO_4 .

Properties of HNO_3

* It is a colourless liquid with $\text{FP} = 231.4\text{K}$

$\text{bp} = 355.6\text{K}$.

* In gaseous state it exist as a planar molecule.



$\text{sp}^2 \Rightarrow$ trigonal planar geometry.

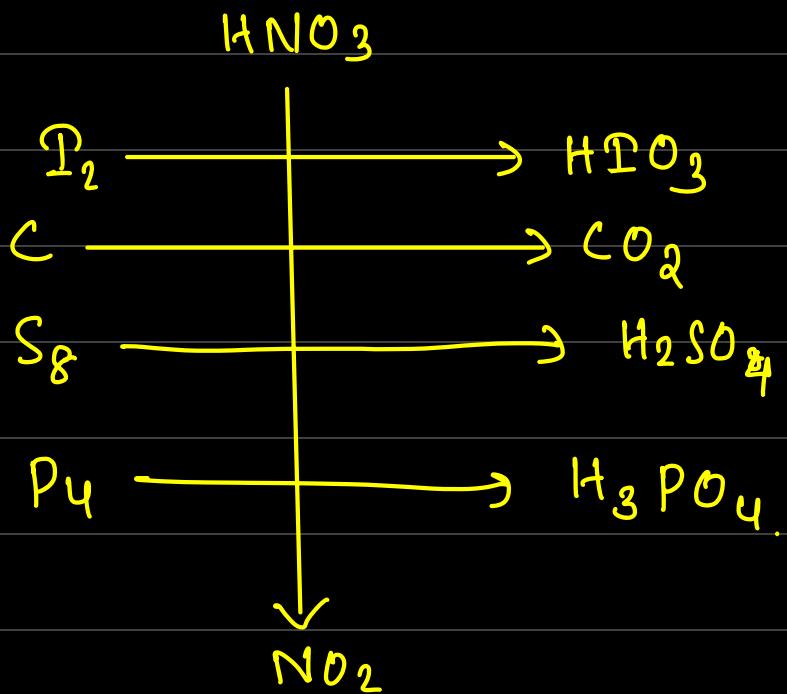
* Aqueous solution of HNO_3 behaves as a strong acid.



* Conc. HNO_3 is a strong oxidising agent & can attack most metals except Au & Pt.

Product of oxidation depends on concentration of the acid, temperature, & the nature of material undergoing oxidation.

HNO_3 on Reaction with Non metals.



* On Reaction with metal Mn, Mg HNO_3 can produce H_2 gas



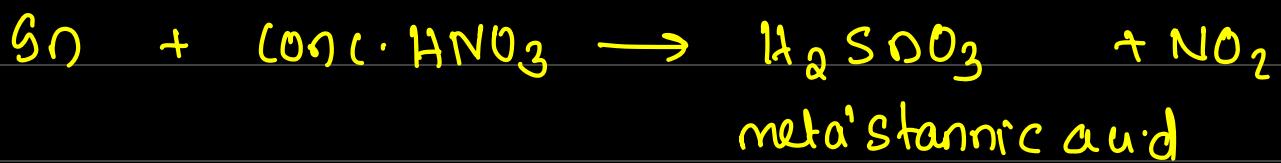
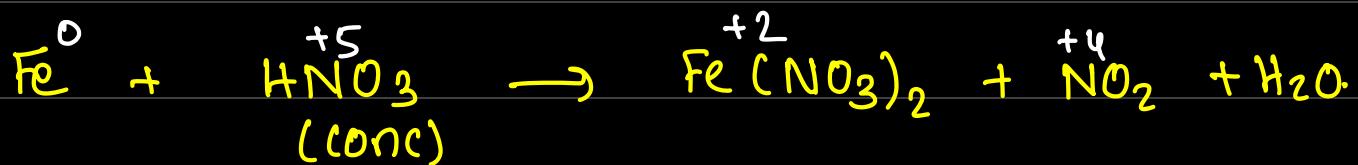
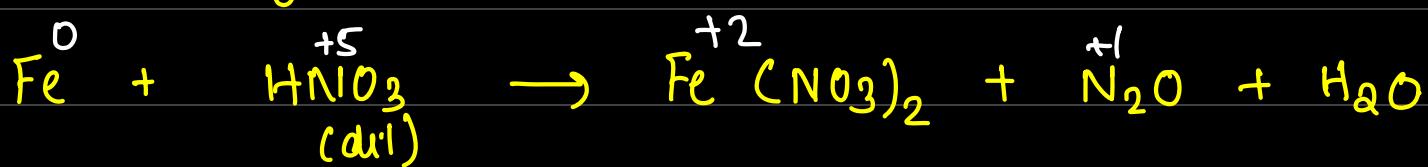
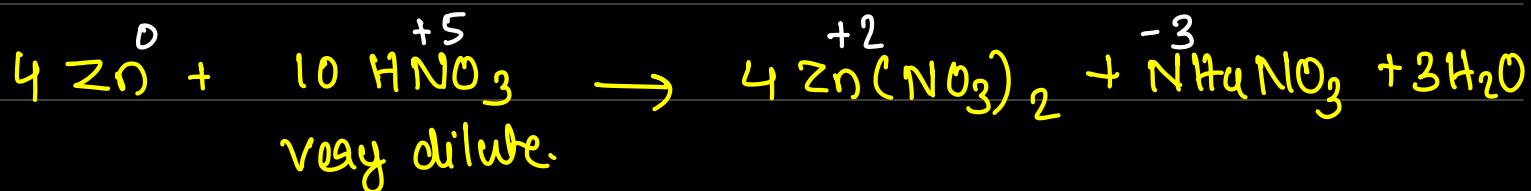


* Metals which are placed above hydrogen in electrochemical series

Fe & Zn react with very dil. $\text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$

dil. $\text{HNO}_3 \rightarrow \text{N}_2\text{O}$

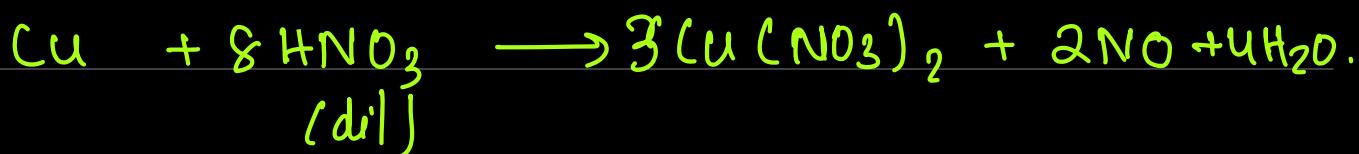
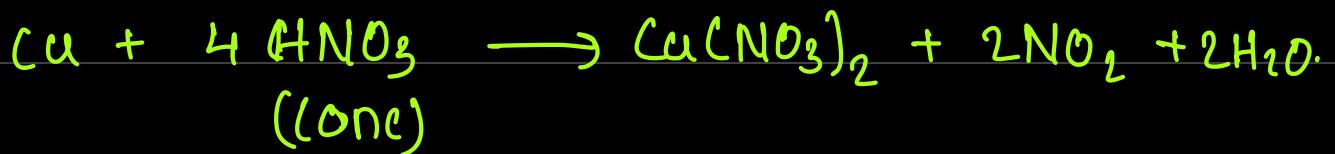
conc. $\text{HNO}_3 \rightarrow \text{NO}_2$



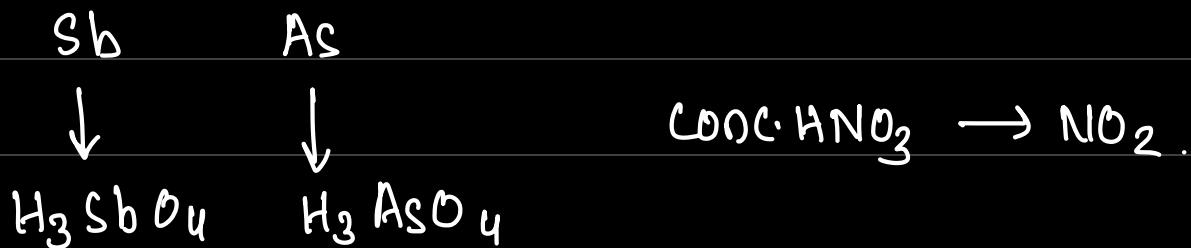
* Be, Fe, Co, Ni, Ca, Al these metals become passive with conc. HNO_3 due to twin layers of oxide on their surface.

* Metals placed below H in electrochemical series.

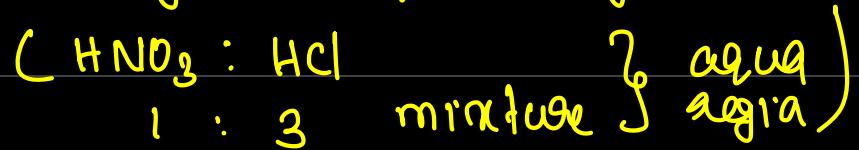
Cu, Ag, Hg, Pb



* On reaction of HNO_3 with metalloid.



* Au & Pt dissolves only in aqua regia

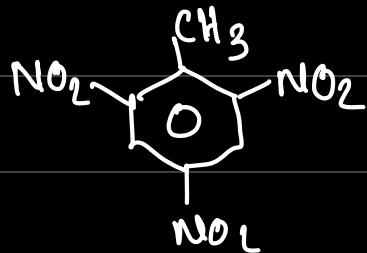


Use

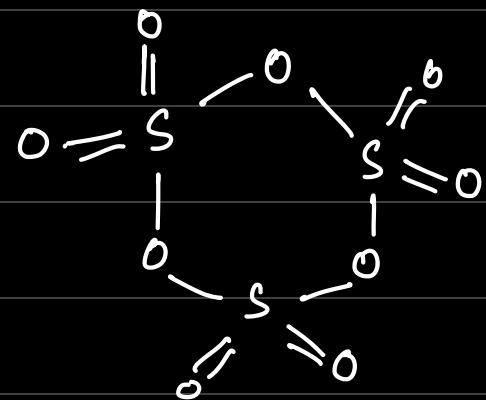
⇒ Manufacture of NaNO_3 for fertilizers, other nitrates & for explosives

TNT

tannic acid toluene



* It is used as an oxidiser in rocket fuel.



Oxygen Family [Group 16]

Physical Properties

Electronic Configuration, Metallic & Non metallic character.

General EC: $ns^2 np^4$

Atomic no

EC

Inner core

Nonmetal	O	8	$[He] 2s^2 2p^4$	Inert gas
	S	16	$[Ne] 3s^2 3p^4$	

Metalloids	Se	34	$[Ar] 3d^{10} 4s^2 4p^4$	Pseudo inert
	Te	52	$[Kr] 4d^{10} 5s^2 5p^4$	gag

Metal. $\leftarrow P_0$ 84 $[Xe] 4f^{14} 5d^{10} 6s^2 6p^4$ \rightarrow

$$\Downarrow t_{1/2} = 13.8 \text{ days.}$$

Radioactive. $[Z \geq 84 \text{ all are radioactive}]$

On moving down the group metallic character increases.

Atomic Size / Ionic Size (E^{2-})

Atomic size or Ionic size \uparrow es down the group because of \uparrow se in no. of shells.

$$\text{AS/PS: } \text{O} < \text{S} < \text{Se} < \text{Te}$$

Tonisation enthalpy.

Tonisation enthalpy \downarrow es down the group due to \uparrow se in atomic size.

$$\text{DE: } \text{O} > \text{S} > \text{Se} > \text{Te} \quad \text{1st DE}$$

Group 15 $>$ Group 16.

Melting point & Boiling point

MP & BP \uparrow es down the group.

$$\text{MP: } \text{O} < \text{S} < \text{Se} < \text{Po} < \text{Te}$$

$$\text{BP: } \text{O} < \text{S} < \text{Se} < \text{Po} < \text{Te}.$$

Density

Density \uparrow es down the group

$$\text{O} < \text{S} < \text{Se} < \text{Te}.$$

Electronegativity

EN \downarrow es down the group.

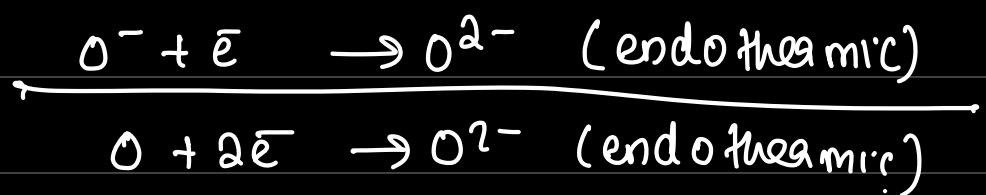
$$\text{EN: } \text{O} > \text{S} > \text{Se} > \text{Te.} > \text{Po}$$

$$3.5 \quad 2.58 \quad 2.55 \quad 2.01 \quad 1.76$$

Electro gain enthalpy

$\Delta_{\text{eg}}H$ \downarrow es down the group.





$$\Delta_{eg}^H : S > Se > Te > Po > O$$

due to small size of oxygen & inter electron repulsion, O has least Δ_{eg}^H

Catenation

S can show catenation.

chemical properties

Oxidation State

Elements Group 16 GEC: $nS^2 nP^4$

max OS = +6

min OS = -2

stability of -2 oxidation state goes down the group due to increased atomic size & increased metallic character.

stability: $O^{2-} > S^{2-}$

* except O, all other elements can show +2, +4 & +6 OS, \Rightarrow +4 & +6 are most common OS.

S, Se, Te \Rightarrow shows +4, +6 OS with O & F-

* stability of +6 OS goes & +4 OS goes on going down the group due to inert pair effect.

Reaction with O₂

all elements (except O) can form oxides of the type EO₂ & EO₃

Both types of oxides are acidic in nature & on dissolving in water it forms oxy acids



Acidic nature : SO₂ < SO₃

* on going down the group Acidic nature of oxides decreases.

Reaction with Hydrogen

All elements of Group 16 forms hydrides of the type H₂E.



↓

It has extensive H bond

1 H₂O: can form 4 H bond

H₂O ⇒ Liquid

H₂S, H₂Se, H₂Te ⇒ Gases.

MP/BP : H₂S < H₂Se < H₂Te < H₂O

Highest.

ΔH_f :	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te.
(KJ/mol)	-286	-20	73	100
exothermic.			endothermic	

Bond length : H₂O < H₂S < H₂Se < H₂Te.
in H₂E

Bond angle : H₂O > H₂S > H₂Se > H₂Te
104.5 q₂ q₁ 90.

\downarrow
SP³ Not undergone hybridization
Hybridized

* thermal stability ↓ goes down the group
H₂O > H₂S > H₂Se > H₂Te.

* Reducing nature.

Reducing nature of hydrides ↑ goes down the group.



It can only undergo oxidation

* Reaction with Halogens.

elements of group 16 (except O) can form a number of halide EX₆ EX₄ EX₂ [X = F, Cl, Br, I]

* O forms O₂F₂ & OF₂

stability order: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

* Among nona halides, hexafluorides are stable SF_6 , SeF_6 & TeF_6 stable. (sp^3d^2 - octahedral)
exceptionally stable.

* tetra fluorides SF_4 SeF_4 TeF_4
 \downarrow Gas liquid Gas.
 $\text{sp}^3\text{d} \Rightarrow$ seesaw.

