

NITROGEN FAMILY

PREPARATION OF N₂

$\text{NH}_4\text{NO}_2 \xrightarrow{\text{Heating}} \text{N}_2 + 2\text{H}_2\text{O}$
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heating}} \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
 $\text{Ba(N}_3)_2 \xrightarrow{\text{Heating}} \text{N}_2 + \text{Ba}$

PROPERTIES OF N₂

$\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$
 $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C}$
 NITROLIME

OXIDES OF NITROGEN

NO $\text{N}=\text{O}$ THERMALLY STABLE *2 (NEUTRAL GAS)
 N₂O $\text{N} \equiv \text{N}^+-\text{O}^-$ +1 (NEUTRAL GAS)
 NO₂ $\text{O}=\text{N}-\text{O}^\bullet$ +3 (ACIDIC BROWN GAS)
 N₂O₃ $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$ +4 (ACIDIC BLUE SOLID)
 N₂O₄ $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$ +4 (ACIDIC COLOURLESS GAS)
 N₂O₅ $\text{O}=\text{N}-\text{O}-\text{N}=\text{O}$ +5 (ACIDIC COLOURLESS GAS)

OXIDES OF NITROGEN

$\text{N}_2\text{O} \xrightarrow{\Delta} \text{N}_2 + \text{O}_2$
 NO BROWN RING TEST
 $\text{N}_2\text{O}_3 \xrightarrow{\Delta} \text{NO} + \text{N}_2\text{O}_4$
 $\text{NO}_2 \xrightarrow{\Delta} \text{Pb(NO}_3)_2$
 $\text{N}_2\text{O}_4 \xrightarrow{\text{low T, high P}} 2\text{NO}_2(\text{g})$
 $\text{N}_2\text{O}_5 \xrightarrow{\Delta} \text{P}_4\text{O}_{10} + \text{HNO}_3$

OXOACIDS OF NITROGEN

COMMERCIAL PREPARATIONS
 OSTWALD'S PROCESS
 $\text{NH}_3 + \text{O}_2 \xrightarrow{\text{Pt}} \text{NO}$
 $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2$
 $\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$

REACTION WITH NON METALS
 $\text{I}_2 + \text{HNO}_3 \rightarrow \text{HIO}_3 + \text{NO}_2$
 $\text{P}_4 + \text{HNO}_3 \rightarrow \text{H}_3\text{PO}_4 + \text{NO}_2$
 $\text{S}/\text{SO}_2 + \text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + \text{NO}_2$
 $\text{C} + \text{HNO}_3 \rightarrow \text{CO}_2 + \text{NO}_2$

REACTION WITH METALS

$\text{Zn} + \text{dil. HNO}_3 \rightarrow \text{Zn(NO}_3)_2 + \text{N}_2\text{O}$
 $\text{Cu} + \text{dil. HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + \text{NO}$
 $\text{Zn} + \text{Conc. HNO}_3 \rightarrow \text{Zn(NO}_3)_2 + \text{NO}_2$

AMMONIA

COMMERCIAL PREPARATIONS
 HABER'S PROCESS
 $\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe catalyst, Mo (Promoter)}} 2\text{NH}_3$

REACTIONS
 $\text{CuSO}_4 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow [\text{Cu(NH}_3)_4]\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$

OXOACIDS OF PHOSPHORUS

PHOSPHORUS TYPE
 - Hypo phosphorous acid (H_3PO_2)
 $\text{P}-\text{H} \rightarrow 2$
 $\text{P}-\text{OH} \rightarrow 1$
 Basicity=1
 - Orthophosphorous acid (H_3PO_3)
 $\text{P}-\text{H} \rightarrow 1$
 $\text{P}-\text{OH} \rightarrow 2$
 Basicity=2

PHOSPHORIC TYPE

- Pyrophosphorous acid ($\text{H}_4\text{P}_2\text{O}_5$)
 $\text{P}-\text{H} \rightarrow 2$
 $\text{P}-\text{OH} \rightarrow 2$
 Basicity=2
 - Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$)
 $\text{P}-\text{OH} \rightarrow 4$
 Basicity=4
 - Orthophosphoric acid (H_3PO_4)
 $\text{P}-\text{OH} \rightarrow 3$
 Basicity=3
 - Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$)
 $\text{P}-\text{OH} \rightarrow 4$
 Basicity=4

META PHOSPHORIC

- cyclo metaphosphoric (HPO_3)
 $\text{P}-\text{O}-\text{P} \text{ Bond} = 3$
 $\text{P}-\text{OH} \rightarrow 3$
 Basicity=3

OXIDES OF PHOSPHORUS

P_4O_6 $\text{P}-\text{O}-\text{P} = 6$
 $\text{P}-\text{O} = 12$
 P_4O_{10} $\text{P}-\text{O}-\text{P} = 6$
 $\text{P}-\text{O} = 16$

HALIDES OF PHOSPHORUS

1) PCl_3	2) PCl_5
Preparation $\text{P}_4 + 3\text{SOCl}_2 \rightarrow \text{PCl}_3 + \text{SO}_2 + \text{S}_2\text{Cl}_2$ (white) (thionyl chloride)	Preparation $\text{P}_4 + 5\text{SOCl}_2 \rightarrow \text{PCl}_5 + \text{SO}_2 + \text{S}_2\text{Cl}_2$ (white) (sulphuryl chloride)
Properties PCl_3 $\frac{5-3}{2} = 1 \rightarrow (3,1)$ Shape: Pyramidal	Properties PCl_5 $\frac{5-5}{2} = 0 \rightarrow (5,0)$

In PCl_5 gaseous & liquid phase exist as trigonal bipyramidal
 In solid phase, it exist as ionic crystal
 $\text{PCl}_5 \rightarrow [\text{PCl}_4]^+[\text{Cl}]^-$

PH₃, phospheni

• Holmes signal ($\text{Ca}_3\text{P}_2 + \text{CaC}_2$)
 • $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2$ (Flammable)

PHOSPHOROUS & ITS ALLOTROPES

1. White phosphorous

- Translucent white waxy solid
 - Poisonous & show chemiluminescence
 - Soluble in CS_2 but insoluble in H_2O
 - Occurs in discrete units
 - Highly reactive due to angle strain
 - Fumes in air due to formation of P_4O_{10}
 - In basic medium, it disproportionate to form PH_3 & NaH_2PO_2
 $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$

2. Red phosphorous

- Grey lustre
 - Insoluble in water and CS_2
 - Non poisonous
 - No chemiluminescence
 - Obtained by heating white P at 573 K
 - Occurs as polymer. So it is less reactive

3. Black phosphorous

α - black phosphorous
 - Prepared by heating Red P at 803 K
 β - black phosphorous
 - Prepared by heating white P at 473 K

CHEMICAL PROPERTIES

Hydrides

Bond Angle
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
Basicity
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 (Reducing nature/ ability to act as RA)
Acidity
 $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$
 (Due to large size of Bi, it can easily release H^+)

Thermal stability/ Bond dissociation energy
 $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$
 (Bi can easily release H^+ and hence have low thermal stability)

BP
 $\text{NH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$
 (As molecular mass $\uparrow \rightarrow$ BP \uparrow)

MP
 $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$
 (due to similar size of N and H, NH_3 has high M.P)

Oxides

- Generally it forms oxides of the type A_2O_3 and A_2O_5
 - Acidic character increases with increase in oxidation number
 $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{NO}_2 < \text{N}_2\text{O}_4 < \text{N}_2\text{O}_5$
 - In a group thermal stability of oxides decreases down the group
 $\text{N}_2\text{O}_5 > \text{P}_2\text{O}_5 > \text{As}_2\text{O}_5 > \text{Sb}_2\text{O}_5 > \text{Bi}_2\text{O}_5$

Nature of Oxides

N_2O_5 } Acidic
 P_2O_5 }
 As_2O_5 } Amphoteric
 Sb_2O_5 }
 Bi_2O_5 } Basic

p-BLOCK ELEMENTS

OXYGEN FAMILY

PHYSICAL PROPERTIES

Electron affinity
 $\text{S} > \text{Se} > \text{Te} > \text{Po} > \text{O}$

CHEMICAL PROPERTIES

Hydrides
Bond Angle
 $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
Thermal Stability
 $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$
Acidic Character
 $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$
Reducing Power
 $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$
B.P
 $\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$

OXOACIDS OF SULPHUR

1) Thionous type

i) Dithionous acid $\text{H}_2\text{S}_2\text{O}_4$ (+3)
 $\text{HO}-\text{S}(=\text{O})_2-\text{OH}$
 ii) Dithionic acid $\text{H}_2\text{S}_2\text{O}_5$ (+5)
 $\text{HO}-\text{S}(=\text{O})_2-\text{SO}_3\text{H}$
 iii) Polythionic acid $\text{H}_2\text{S}_4\text{O}_6$ (+5,0)
 $\text{HO}-\text{S}(=\text{O})_2-\text{SO}_2-\text{SO}_2-\text{SO}_3\text{H}$
 iv) Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$ (+6,-2)
 $\text{HO}-\text{S}(=\text{O})_2-\text{SH}$

2) Sulphurous type

i) Sulphurous acid H_2SO_3
 ii) Sulphuric acid H_2SO_4
 iii) Pyrosulphuric acid $\text{H}_2\text{S}_2\text{O}_7$ (Oleum)

3) Peroxo type

i) Peroxomono sulphuric acid $\text{H}_2\text{S}_2\text{O}_8$ (Caro's acid)
 $\text{HO}-\text{SO}_2-\text{O}-\text{SO}_2-\text{OH}$
 ii) Peroxo disulphuric acid $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid)
 $\text{HO}-\text{SO}_2-\text{O}-\text{SO}_2-\text{SO}_3\text{H}$

H_2SO_4

Preparation
 $\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$
 $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3$
 $\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$
 $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$ (98%)

Properties
 $3\text{S} + 2\text{H}_2\text{SO}_4 \rightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$
 $\text{Cu} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
 $\text{C} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}$

SO_2

Properties
 - Act as reducing agent (in aqueous medium)
 $\text{SO}_2(\text{aq}) + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{NO} + \text{H}_2\text{SO}_4$
 - Act as oxidizing agent in the presence of
 $\text{SO}_2 + \text{CO} \rightarrow \text{S} + \text{CO}_2$
 $\text{SO}_2 + \text{Fe} \rightarrow \text{FeS} + \text{FeO}$

Uses:

1. Act as a bleaching agent due to the formation of nascent atomic hydrogen in H_2O

SO_3

Properties
 $\text{SO}_3 \rightarrow 6/2 = 3(3,0) \rightarrow$ bent shape (120°)
 100% oleum/sulphan \rightarrow liquid SO_3

ALLOTROPES OF SULPHUR

1) Rhombic Sulphur [α]
 - Exist in room temperature
 - Soluble in CS_2 but insoluble in H_2O
 - Yellow in colour
 - Exist below 369 K
 2) Monoclinic Sulphur [β]
 - Soluble in CS_2
 - Obtained by melting rhombic sulphur above 369 K

Transition Temperature:
 369 K, at which both monoclinic & sulphur exist. Above this temperature monoclinic exist, below this temperature rhombic sulphur exist.

At elevated temperature (1000K) S_2 is dominant species and is paramagnetic like O_2 (Vapour) state partly exist as S_8 molecule which has two unpaired electrons in π orbitals like O_2

PHYSICAL PROPERTIES

Electron affinity/EGE
 $\text{Cl} > \text{F} > \text{Br} > \text{I}$
 Oxidation State
 - F shows only (-1) O.S. in its compounds
 - All other shows -ve & +ve O.S
 Bond dissociation energy
 $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$
 Bond dissociation energy of F_2 is lower than that of Cl_2 & Br_2 due to its inter electronic repulsion

CHEMICAL PROPERTIES

1) Oxidising Power:
 - F is the strongest oxidizing agent
 $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (OA)
 F_2 displaces Cl_2 , Br_2 & I_2
 Cl_2 displaces Br_2 and I_2
 $\text{Br}_2 + 2\text{KI} \rightarrow 2\text{KBr} + \text{I}_2$
 $\text{I}_2 + \text{KBr} \rightarrow$ No reaction

2) With H_2O :
 $\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{O}_2$ (Release O_2 from H_2O , good oxidizing agent)
 $\text{Cl}_2/\text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$
 $\text{HBr} + \text{HOBr}$
 $\text{I}_2 + \text{H}_2\text{O} \rightarrow$ No reaction

3) With H_2 : **Hydrides**
 Acidic Character
 $\rightarrow \text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 Reducing Power
 $\rightarrow \text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 Thermal Stability
 $\rightarrow \text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
 BP $\rightarrow \text{HF} > \text{HI} > \text{HBr} > \text{HCl}$

COMPOUNDS OF CHLORINE

1) Cl_2
 Preparation: Commercial
 Deacon's Process
 $\text{HCl} + 1/2\text{O}_2 \xrightarrow{723\text{K}} \text{H}_2\text{O} + 1/2\text{Cl}_2$

Properties
 - Greenish yellow coloured gas
 $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$
 greenish yellow colourless
 - With NH_3
 $\text{NH}_3 + \text{Cl}_2 \rightarrow \text{NH}_4\text{Cl} + \text{N}_2$ (excess)
 $\text{NH}_3 + \text{Cl}_2 \rightarrow \text{NCl}_3 + \text{HCl}$ (excess)
 - With Alkali
 $\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$ (Cold & dilute)
 $\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl}_3 + \text{NaCl} + \text{H}_2\text{O}$ (Cold & Conc.)
 $\text{Ca(OH)}_2 + \text{Cl}_2 \rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2 + 2\text{H}_2\text{O}$ (calcium hypochlorite)
 $\text{Ca(OCl)}_2 + \text{CaCl}_2 \rightarrow$ Bleaching powder

uses
 - Powerful bleaching agent due to oxidizing property
 - Bleaching powder
 $\rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2$
 - Preparation of poisonous gas
 1) Tear gas $\rightarrow \text{CCl}_3\text{NO}_2$
 2) Phosgene $\rightarrow \text{COCl}_2$
 3) Mustard gas
 $\rightarrow \text{Cl}-(\text{CH}_2)_2-\text{S}-(\text{CH}_2)_2-\text{Cl}$

NOBLE GASES

All these, except Radon & Oganesson occur in the atmosphere.

Physical properties

- Atomic radii $\rightarrow \uparrow$ down the group
 $\rightarrow \text{IE} \rightarrow \downarrow$ down the group
 - He is having maximum ionisation energy of all known substances
 - Ne is having high positive value of electron gain enthalpy
 $\rightarrow \text{B.P.} \rightarrow \uparrow$ down the group
 - He is having lowest B.P among all known substance (4.2K)

COMPOUNDS OF Xe

Xenon Fluoro compounds
Preparation:
 $\text{Xe(g)} + \text{F}_2(\text{g}) \xrightarrow{673\text{K}, 1\text{bar}} \text{XeF}_2(\text{s})$ (Xenon in excess)
 $\text{Xe(g)} + 2\text{F}_2(\text{g}) \xrightarrow{673\text{K}, 1\text{bar}} \text{XeF}_4(\text{s})$ [1:5 ratio]
 $\text{Xe(g)} + 3\text{F}_2(\text{g}) \xrightarrow{573\text{K}, 60-70\text{bar}} \text{XeF}_6(\text{s})$ [1:20 ratio]
 $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$

Structure
 $\text{XeF}_2 \rightarrow \frac{8-2}{2} = 3 \rightarrow$ linear
 $\text{XeF}_4 \rightarrow \frac{8-4}{2} = 2 \rightarrow$ square planar
 $\text{XeF}_6 \rightarrow \frac{8-6}{2} = 1 \rightarrow$ Distorted Octahedral

Properties and uses
 ClF_3 & $\text{BrF}_3 \rightarrow$ Uranium enrichment for fluorinating (U^{235})
 $\text{ICl} \rightarrow$ Exist in 2 polymeric form α & β
 - Inter halogens are very reactive than halogens (except F_2)

INTERHALOGEN COMPOUNDS

Types: $\text{XX}' \rightarrow \text{ICl}, \text{BrF}$
 $\text{XX}_3 \rightarrow \text{ClF}_3, \text{BrF}_3$
 $\text{XX}_2 \rightarrow \text{BrF}_2$
 $\text{XX}'_2 \rightarrow \text{IF}_2, \text{ClF}_2$

Properties
 - Powerful bleaching agent due to oxidizing property
 - Bleaching powder
 $\rightarrow \text{Ca(OCl)}_2 + \text{CaCl}_2$
 - Preparation of poisonous gas
 1) Tear gas $\rightarrow \text{CCl}_3\text{NO}_2$
 2) Phosgene $\rightarrow \text{COCl}_2$
 3) Mustard gas
 $\rightarrow \text{Cl}-(\text{CH}_2)_2-\text{S}-(\text{CH}_2)_2-\text{Cl}$