NITROGEN FAMILY

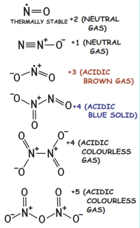
PREPARATION OF N₂

NH_4NO_2
$(NH_4)_2Cr_2O_7$ } Heating
$Ba(N_3)_2$

PROPERTIES OF N_2

$Mg + N_2 \rightarrow Mg_3N_2$
$CaC_2 + N_2 \rightarrow CaCN_2 + C$
NITROLIME

OXIDES OF NITROGEN


NO THERMALLY STABLE +2 (NEUTRAL GAS)
N_2O +1 (NEUTRAL GAS)
NO_2 +3 (ACIDIC BROWN GAS)
N_2O_3 +4 (ACIDIC BLUE SOLID)
N_2O_4 +4 (ACIDIC COLOURLESS GAS)
N_2O_5 +5 (ACIDIC COLOURLESS GAS)

OXIDES OF NITROGEN

N_2O $NH_4NO_3 \xrightarrow{\Delta}$
NO BROWN RING TEST
N_2O_3 $NO + N_2O_4 \rightarrow$
NO_2 $Pb(NO_3)_2 \xrightarrow{\Delta}$
N_2O_4 $2NO_2(g) \xrightarrow[\text{high P}]{\text{low T}}$
N_2O_5 $P_4O_{10} + HNO_3 \rightarrow$

OXYACIDS OF NITROGEN

COMMERCIAL PREPARATIONS
OSTWALD'S PROCESS

$NH_3 + O_2 \xrightarrow{Pt} NO$
$NO + O_2 \rightarrow NO_2$
$NO_2 + H_2O \rightarrow HNO_3$

REACTION WITH NON METALS

$I_2 + HNO_3 \rightarrow HIO_3 + NO_2$
$P_4 + HNO_3 \rightarrow H_3PO_4 + NO_2$
$S/SO_2 + HNO_3 \rightarrow H_2SO_4 + NO_2$
$C + HNO_3 \rightarrow CO_2 + NO_2$

REACTION WITH METALS

$Zn + \text{dil. } HNO_3 \rightarrow Zn(NO_3)_2 + N_2O$
$Cu + \text{dil. } HNO_3 \rightarrow Cu(NO_3)_2 + NO$
$Zn + \text{Conc. } HNO_3 \rightarrow Zn(NO_3)_2 + NO_2$

AMMONIA

COMMERCIAL PREPARATIONS
HABER'S PROCESS

$$N_2 + 3H_2 \xrightarrow{\text{Fe catalyst, Mo (Promoter)}} 2NH_3$$

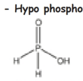
REACTIONS

$CuSO_4 + NH_3 + H_2O \longrightarrow$
$[Cu(NH_3)_4]\ SO_4 + (NH_4)_2SO_4$

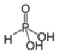
OXOACIDS OF PHOSPHORUS

PHOSPHORUS TYPE

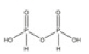
- Hypo phosphorous acid (H_3PO_2)


P-H → 2
P-OH → 1
Basicity=1

- Orthophosphorous acid (H_3PO_3)

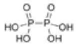

P-H → 1
P-OH → 2
Basicity=2

- Pyrophosphorous acid ($H_4P_2O_5$)

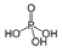

P-H → 2
P-OH → 2
Basicity=2

PHOSPHORIC TYPE

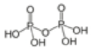
- Hypophosphoric acid ($H_4P_2O_6$)


P-OH → 4
Basicity=4

- Orthophosphoric acid (H_3PO_4)

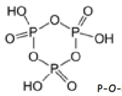

P-OH → 3
Basicity=3

- Pyrophosphoric acid ($H_4P_2O_7$)

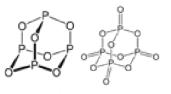

P-OH → 4
Basicity=4

META PHOSPHORIC

- cyclo metaphosphoric $(HPO_3)_3$


P-O-P Bond=3
P-OH → 3
Basicity=3

OXIDES OF PHOSPHORUS


{ P-O-P=6, P-O=12 } { P-O-P=6, P-O=16 }

HALIDES OF PHOSPHORUS

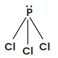
1) PCl_3

Preparation

$P_4 + 2SOCl_2 \rightarrow PCl_3 + SO_2 + S_2Cl_2$
(white) (thionyl chloride)

Properties

$PCl_3 \left[\frac{5+3}{2} = 4 \rightarrow (3,1)\right]$
Shape : Pyramidal



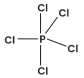
2) PCl_5

Preparation

$P_4 + SO_2Cl_2 \rightarrow PCl_5 + SO_2$
(white) (sulphuryl chloride)

Properties

PCl_5 $\frac{5+5}{2} = 2 \rightarrow (5,0)$



- In PCl_5 gaseous & liquid phase exist as trigonal bipyramidal
- In solid phase, it exist as ionic crystal

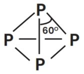
$PCl_5 \rightarrow [PCl_4]^+[PCl_6]^-$

PH_3, phospheni

- Holmes signal $(Ca_3P_2 + CaC_2)$
- $CaC_2 + H_2O \rightarrow C_2H_2$(Flammable)

PHOSPHOROUS & ITS ALLOTROPES

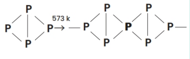
1. White phosphorous


60°

- Translucent white waxy solid
- Poisonous & show chemiluminescence
- Soluble in CS_2 but insoluble in H_2O
- Occurs in descrete 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

$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

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
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Basicity
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(Reducing nature/ ability to act as RA)

Acidity
$BiH_3 > SbH_3 > AsH_3 > PH_3 > NH_3$
(Due to large size of Bi, it can easily release H^+)

Thermal stability/ Bond dissociation energy
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
(Bi can easily release H^+ and hence have low thermal stability)

BP
$BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$
(As molecular mass ↑→ BP ↑)

MP
$NH_3 > SbH_3 > AsH_3 > PH_3$
(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

$N_2O < NO < N_2O_3 < NO_2 < N_2O_4 < N_2O_5$

- In a group thermal stability of oxides decreases down the group

$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$

Nature of Oxides

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

p-BLOCK ELEMENTS

OXYGEN FAMILY

PHYSICAL PROPERTIES

Electron affinity
- S > Se > Te > Po > O

CHEMICAL PROPERTIES

Hydrides

Bond Angle
$H_2O > H_2S > H_2Se > H_2Te$

Thermal Stability
$H_2O > H_2S > H_2Se > H_2Te$

Acidic Character
$H_2Te > H_2Se > H_2S > H_2O$

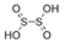
Reducing Power
$H_2Te > H_2Se > H_2S > H_2O$

B.P
$H_2O > H_2Te > H_2Se > H_2S$

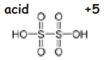
OXOACIDS OF SULPHUR

1) Thionous type

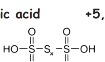
i) Dithionous acid +3
$H_2S_2O_4$
$(S_2O_4^{2-})$



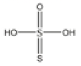
ii) Dithionic acid +5
$H_2S_2O_6$
$(S_2O_6^{2-})$



iii) Polythionic acid +5,0
$H_2S_4O_6$
$(S_4O_6^{2-})$



iv) Thiosulphuric acid +6, -2
$H_2S_2O_3$
$(S_2O_3^{2-})$

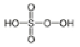


2) Sulphurous type

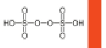
i) Sulphurous acid
H_2SO_3
ii) Sulphuric acid
H_2SO_4
iii) Pyrodisulphuric acid
$H_2S_2O_7$ (Oleum)

3) Peroxo type

i) Peroxomono sulphuric acid
H_2SO_5
(Caro's acid)



i) Peroxo disulphuric acid
$H_2S_2O_8$
(Marshall's acid)



H_2SO_4

Preparation

Contact process

$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$
$2SO_2 + O_2 \underset{Pt}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3$
$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$
$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4(98\%)$

Properties

Oxidising property

$3S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

SO_2

Properties

- Act as reducing agent(in aqueous medium)
$SO_2(aq) + HNO_3 + H_2O \rightarrow NO + H_2SO_4$
- Act as oxidizing agent in the presence of → Strong reducing agent
$\overset{+4}{S}O_2 + CO \rightarrow \overset{0}{S} + CO_2$
$\overset{+4}{S}O_2 + Fe \rightarrow Fe\overset{-2}{S} + FeO$

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

SO_3

Properties
$SO_3 \longrightarrow 6/2 = 3(3,0) \longrightarrow$ bent shape (120°)
100% oleum/sulphan ⟶ 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_2 molecule which has two unpaired electrons in π orbitals like O_2

HALOGENS & NOBLE GAS

PHYSICAL PROPERTIES

Electrom affinity/EGE
- Cl > F > Br > I

Oxidation State
- F shows only (-1) O.S. in its compounds
- All other shows -ve & +ve O.S

Bond dissociation energy
- $Cl_2 > Br_2 > F_2 > I_2$

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
- $F_2 > Cl_2 > Br_2 > I_2$ (OA)
- F_2 displaces Cl_2, Br_2 & I_2
- Cl_2 displaces Br_2 and I_2
- $Br_2 + 2KI \longrightarrow 2KBr + I_2$
- $I_2 + KBr \longrightarrow$ No reaction

2) With H_2O:
- $F + H_2O \longrightarrow HF + O_2$ (Release O_2 from H_2O, good oxidizing agent)
- $Cl_2/Br_2 + H_2O \longrightarrow HCl + HOCl$
  HBr + HOBr
- $I_2 + H_2O \longrightarrow$ No reaction

3) With H_2: **Hydrides**

Acidic Character
⟶ HI > HBr > HCl > HF

Reducing Power
⟶ HI > HBr > HCl > HF

Thermal Stability
⟶ HF > HCl > HBr > HI

BP ⟶ HF > HI > HBr > HCl

COMPOUNDS OF CHLORINE

1) Cl_2

Preparation : Commercial
Deacon's Process
$HCl + 1/2O_2 \xrightarrow[723\ K]{CuCl_2} H_2O + 1/2\ Cl_2$

Properties
- Greenish yellow coloured gas
- $Cl_2 + H_2O \rightarrow \underbrace{HOCl + HCl}_{\text{colourless}}$
  greenish yellow
- With NH_3
  1) NH_3 (excess) $+ Cl_2 \rightarrow NH_4Cl + N_2$
  2) $NH_3 + Cl_2$ (excess) $\rightarrow NCl_3 + HCl$
- With Alkali
  a) $NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$ (Cold & dilute)
  $NaOH + Cl_2 \rightarrow NaClO_3 + NaCl + H_2O$ (Cold & Conc.)
  b) $Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$ (calcium hypochlorite)
  $Ca(OCl)_2 + CaCl_2 \rightarrow$ Bleaching powder

uses
- Powerful bleaching agent due to oxidizing property
- Bleaching powder $\rightarrow Ca(OCl)_2 + CaCl_2$
- Preparation of poisonous gas
  1) Tear gas $\rightarrow CCl_3NO_2$
  2) Phosgene $\rightarrow COCl_2$
  3) Mustard gas $\rightarrow Cl\text{-}(CH_2)_2\text{-}S\text{-}(CH_2)_2\text{-}Cl$

2) HCl

$NH_3 + HCl \rightarrow NH_4Cl$
Aqua regia ($HCl:HNO_3 = 3:1$) dissolve Au and Pt by release of nitric oxide
$Au \xrightarrow{\text{Aqua regia}} [AuCl_4]^- + NO$
$Pt \xrightarrow{\text{Aqua regia}} [PtCl_6]^{2-} + NO$
HCl is a strong acid which decomposes salt of weak acid

OXOACIDS OF HALOGEN

F ⟶ HOF
Cl ⟶ HOCl, $HClO_2$, $HClO_3$, $HClO_4$
Br ⟶ HOBr, $HBrO_2$, $HBrO_3$, $HBrO_4$
I ⟶ HOI, HIO_2, HIO_3, HIO_4

1) Acidic character
→ $HClO < HClO_2 < HClO_3 < HClO_4$
2) Oxidising character
→ $HClO < HClO_2 < HClO_3 < HClO_4$
3) Stability:
→ $HClO < HClO_2 < HClO_3 < HClO_4$

INTERHALOGEN COMPOUNDS

Compounds formed b/w 2 different halogens

Types: $XX^1 \longrightarrow$ ICl, BrF
$XX_3^1 \longrightarrow ClF_3$, BrF
$XX_5^1 \longrightarrow BrF_5$
$XX_7^1 \longrightarrow IF_7$, ClF_7

Properties and uses
- ClF_3 & $BrF_3 \longrightarrow$ Uranium enrichment for flurinating (U^{235})
- IF ⟶ Spectroscopically detected
- ICl ⟶ Exist in 2 polymeric form α & β
- Inter halogens are very reactive than halogens (except F_2)

Structure

$XX' \longrightarrow X\text{-}X \longrightarrow$ linear
$XX_3' \longrightarrow \frac{7+3}{2} = 5(3,2)$ T-Shaped
$XX_5' \longrightarrow \frac{7+5}{2} = 6(5,1)$ Square Pyramidal
$XX_7' \longrightarrow \frac{7+7}{2} = 7(7,0)$ Pentagonal bipyramidal

NOBLE GASES

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

Physical properties
- Atomic radii → ↑ down the group
- IE → ↓ down the group
- He is having maximum ionisation energy of all known substances
- Ne is having high positive value of electron gain enthalpy
- B.P → ↑ down the group
- He is having lowest B.P among all known substance (4.2K)

COMPOUNDS OF Xe

Xenon Fluoro compounds

Preparation:
- $Xe(g) + F_2(g) \xrightarrow{673\ K, 1\ bar} XeF_2(S)$ (Xenon in excess)
- $Xe(g) + 2F_2(g) \xrightarrow{673\ K, 1\ bar} XeF_4(S)$ [1:5 ratio]
- $Xe(g) + 3F_2(g) \xrightarrow{573\ K, 60\text{-}70\ bar} XeF_6(S)$ [1:20 ratio]
- $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

Structure
$XeF_2 \longrightarrow \frac{8+2}{2} = 5(2,3) \longrightarrow$ linear
$XeF_4 \longrightarrow \frac{8+4}{2} = 6(4,2) \longrightarrow$ square planar
$XeF_6 \longrightarrow \frac{8+6}{2} = 7(6,1) \longrightarrow$ Distorted Octahedral

Properties On reacting with H_2O, they get hydrolysed when XeF_2 hydrolyses, it gives Xe, HF & O_2
- $XeF_2 + H_2O \longrightarrow Xe + HF + O_2$

XENON-OXYGEN COMPOUND

Structure $XeO_3 \longrightarrow 8/2 = 4(3,1)$ Pyramidal
$XeOF_4 = \frac{8+4}{2} = 6(5,1)$ Sq. Pyramidal
$XeO_2F_2 = \frac{8+2}{2} = 5(4,1)$ Sea saw

Preparation
$XeF_6 + H_2O \longrightarrow XeOF_4 + HF$
$XeF_6 + 2H_2O$ (excess) $\longrightarrow XeO_2F_2 + HF$