The p-Block Elements

- General Electronic Configuration – $ns^2 np^{1-6}$
- The last e^- for an element if enters in the p-subshell then it is called a p-Block element.
- p-orbitals can accomodate 6 e^- thus 6 groups (13-18)

	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
2nd Period →	B	C	N	O	F	He
	Al	Si	P	S	Cl	Ne
	Ga	Ge	As	Se	Br	Ar
	In	Sn	Sb	Te	I	Kr
	Tl	Pb	Bi	Po	At	Xe
			Pnictogens	Chalcogens	Halogens	Rn
			Gases produced by them are suffocating & poisonous.	due to association with S & compounds formed by it	Salt forming compounds & majorly obtained from sea-water	Og. Noble Gases • Dont react even with themselves • do not participate in processes.

Reasons for Anomalous properties of 2nd Period Elements/ 1st Element of every Group.

1. Small Size (due to min. no. of shells).
2. Unavailability of d-orbitals so cannot expand octets (No 2d subshell) $2s + 2p = 1 + 3 = 4$ orbitals.
   Covalency can never exceed 4.
3. Most Electronegative (high Z_{eff})
4. High charge / size ratio, thus high polarising power
5. High I.E
6. Most negative $\Delta_{hyd}H$ (high charge/size ratio)
7. Should have most negative $\Delta_{eg}H$

Oxidation State / Numbers

- No. of e⁻ required / gained for noble gas configuration.

ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Group 15	Group 16	Group 17	Group 18
−3	−2 +2	−1, +3	0
$\boxed{+5}$	$\boxed{+6}$	$\boxed{+7}$, +1	−
+3	+4	+5	

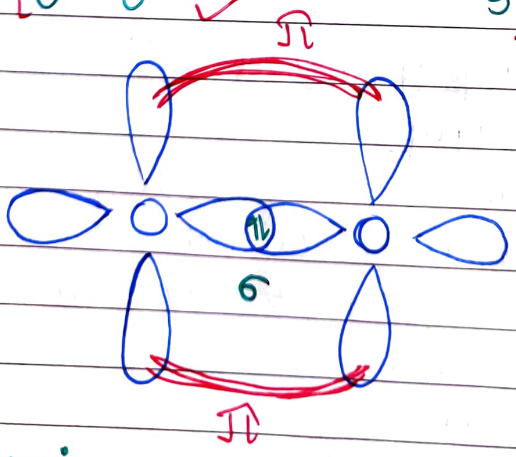
- Max O.S → no. of s e⁻ + no. of p e⁻
- 1st element → negative O.S, due to its max. electronegativity because of small size & high Z_{eff}.
- Heaviest Element → Due to inert pair effect stable O.S will be 2 less than max O.S / group O.S.

Bonding

- 1st elements of groups 14, 15, 16 show multiple bonding which other elements will not show.

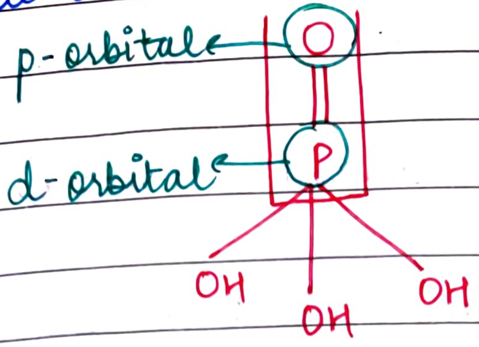
pπ-pπ bond
$N \equiv N$ ✓ $\cancel{P \equiv P}$

pπ-pπ bond
$O = O$ ✓ $\cancel{S = S}$



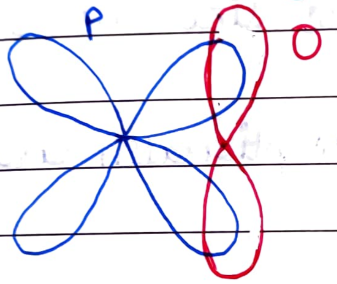
Reason:
2p - 2p π overlap is much stable & effective than 3p - 3p π-overlap due to small size of 2p subshell.

- O_2 & N_2 are gases because of $p\pi$-$p\pi$ bonding they exist as discrete diatomic molecules.



$d\pi$-$p\pi$ bond.

Heavier elements show $d\pi$-$p\pi$ bonds or $d\pi$-$d\pi$ bonds due to availability of a d-orbital.



N_2 is an inert molecule with bond energy of ~ 940 kJ/mol because of stable $p\pi$-$p\pi$ bonds formed & increase in overlapping area.

Catenation

- Self-linking property of an element.
- N & O do not show catenation due to small atomic sizes, there are inter-electronic repulsions so *weaker N-N & O-O bonds
- but P & S do show catenation due to high P-P & S-S bond energies.

  N—N ⇒ ~180 kJ/mol } lower value*
  P—P ⇒ ~200 kJ/mol

- Due to catenation in P & S because of stable/stronger P-P and S-S bonds respectively they exist as solids.

Covalency

- No. of covalent bonds formed.
- N, O, F can never show a covalency >4 due to absence of d-orbitals (2s, 2p but no 2d).
- Greater the O.N on the central atom, more will be its

polarising power and greater will be its the covalent character. (Fajan's Rule).

Ex: $\overset{+5}{P}Cl_5$ is more covalent than $\overset{+3}{P}Cl_3$.
$\overset{+6}{S}F_6$ is more covalent than $\overset{+4}{S}F_4$.
$IF_7 > IF_5 > IF_3$ (covalent character).

* **Note**: Highest O.S. for an element is established as its oxides or fluorides.

Atomic Size

- Down the group, generally, atomic size increases though the change in size is irregular.
- Elements of 3rd period have exceptionally large size like Al.

Density

- Down the group the density increases.

$$\rho = \frac{m}{V}$$

Increase in atomic mass is more than the increase in volume.

Ionisation Enthalpy

- Down the group it decreases because atomic size ↑ses & Z_{eff} ↓ses.

Electron Gain Enthalpy

- Generally $\Delta_{eg}H$ becomes less & less negative down the group because atomic size ↑ses & Z_{eff} ↓ses
- But $(\Delta_{eg}H)_O$ is less negative than $(\Delta_{eg}H)_S$ & $(\Delta_{eg}H)_F$ is less negative than $(\Delta_{eg}H)_{Cl}$

Due to small size & high charge density in O & F, the incoming e^- experience electronic repulsions.

Electronegativity

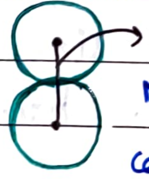
- Down the group it decreases due to ↑se in atomic size & ↓se in Z_{eff}.
- Halogens are most electronegative in their respective periods because across the period Z_{eff} increases and atomic size decreases.
- $F > O > \boxed{Cl > N}$ But Cl never make H-Bonds due to its large atomic size.

* **Note:** Noble gases have exceptionally large atomic sizes

OR

Noble gases are largest in their respective periods

Some common region of overlap.

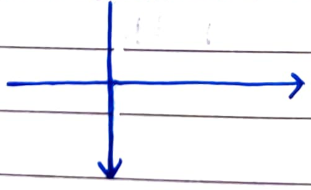


No region of overlap / complete atom is considered

(i) In noble gases Vander Waal's Radius is measured which is larges/greater than any other radius.

(ii) With pairing of e^-, shielding improves so due to completely filled orbitals, shielding effect is very high.

Metallic Character



Across the period (Decreases)
Electronegativity & IE ↑se

Down the group (Increases).
Electronegativity & IE ↓se.

N, P] - Non-metals
As, Sb] - Metalloids
Bi] - Metal

O, S] - Non-metals
Se, Te] - Metalloids
Po

Group 15 Elements

- Electronic Configuration → $ns^2 np^3$
- IE → ↓ ses
- Electronegativity → ↓ ses
- Oxidation States → $\boxed{-3}$, $+1$, $+3$, $\boxed{+5}$

Most stable for N
Due to its high electronegativity & non-metallic character.

↳ max O.S or group O.S

Order of stability for -3 O.S → $N^{3-} > P^{3-} > As^{3-} > Sb^{3-} >> \boxed{Bi^{3-}}$

high metallic character & electropositivity.

⇒ Bi is much more stable in +3 O.S than +5 O.S due to inert pair effect.

∴ Bi does not exist in −3 O.S & +5 O.S except in BiF_5 due to small size & high E.N. of F, it is able to unpair 6 e^- and make bonds with Bi.

- N & P do show +2 & +4 O.S in the form of their oxides & oxoacids.

Eg: $\underset{+2}{\underline{N}O}$, $\underset{+4}{\underline{N}O_2}$

* N & P show disproportionation reaction also as their particular O.S lies between 2 stable O.S.

Eg:

i) $3H\underset{+3}{\underline{N}}O_2 \longrightarrow H\underset{+5}{\underline{N}}O_3 + 2\underset{+2}{\underline{N}}O + H_2O$

ii) $3\underset{+4}{\underline{N}}O_2 \xrightarrow{+H_2O} 2H\underset{+5}{\underline{N}}O_3 + \underset{+2}{\underline{N}}O$

- Anomalous characteristics of N

i) N makes $p\pi - p\pi$ bond.
ii) Other elements makes $d\pi - p\pi$ and $d\pi - d\pi$ bonds.

iii) Nitrogen - gas (diatomic molecule - $p\pi - p\pi$ bonds).
Phosphorus - solid {catenation due to strong P-P bonds
So more coordinated.}

iv) ⓐ NCl_5 & NF_5 do not exist but PCl_5 & PF_5 do exist

ⓑ $R_3N=O$ does not exist but $R_3P=O$ does exist.

⇒ N does not have a d-orbital.

v) N can show hydrogen bonding in some of its compounds

Hydrides of Group 15 Elements

General formula for hydrides ⟶ EH_3

① Boiling Point

- F = ma

As atomic mass increases, magnitude of intermolecular forces of attraction increases, thus b.p increases.

∴ BiH_3 - max bp.

- NH_3 has exceptionally high bp. because of intermolecular H-bonds formed.
- $\boxed{PH_3} < AsH_3 < NH_3 < SbH_3 < BiH_3$

→ Most volatile

② Melting Point

- $PH_3 < AsH_3 < SbH_3 < NH_3$

(i) Most electronegative so highest magnitude of attractive forces.

(ii) Due to small size it fits well in the crystal lattice ⇒ high C.N.

③ Bond Length (E-H in pm)

As the size of central atom ↑ses, bond length ↑ses.

⇒ $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

④ Bond Dissociation Enthalpy ($\Delta_{diss}H$)

As the size of central atom ↑ses, Bond length ↑ses so $\Delta_{diss}H$ ↓ses.

$NH_3 > PH_3 > AsH_3 > SbH_3$.

⑤ Bond Angle

As the size of central atom ↑ses bp-bp repulsions btw E-H bonds ↓ses, thus bonds are pushed closer by lp.

$NH_3 > PH_3 > AsH_3 > SbH_3$.

⑥ Acidic Character

i) As the $\Delta_{diss}H$ ↓ses, acidic strength ↑ses.

ii) As the size of central atom ↑ses charge density ↓ses so a weaker base or ↑se in acidic behaviour.

⇒ K_a ↑ses or K_b ↓ses.

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ ← {pK_a ↑ses / pK_b ↓ses}

$pK_a = -\log(K_a)$

Acidic strength ↑ses ⇒ K_a ↑ses ⇒ pK_a ↓ses.

⑦ Enthalpy of Formation ($\Delta_f H$)

$\boxed{NH_3} < PH_3 < AsH_3 < SbH_3 < \boxed{BiH_3}$

Most stable in -3 state, so heat is evolved. (Small size & high EN of N).

Least stable in -3 state

* **Note:** BiH_3 is a very good reducing agent because it is unstable & oxidises to Bi releasing H_2 gas.

$$2\underset{-3}{BiH_3} \longrightarrow 2\underset{0}{Bi} + 3H_2(g).$$

$-3 \xrightarrow{\text{oxidation}} 0$

Oxides of Group 15 Elements

- General formula → E_2O_3 or E_2O_5
  E is in +3 O.S   E is in +5 O.S.

As the O.S of the central atom increases, ionic character decreases (Fajan's Rule) thus acidic strength of oxide increases.

⇒ E_2O_5 is more acidic than E_2O_3.

- Since O is more electronegative than group 15 elements thus oxides are formed.
- Oxides of N are also found in +2 & +4 O.S.
- Bi only forms Bi_2O_3 and not Bi_2O_5 due to inert pair effect +5 O.S for Bi is not stable.

Reactivity with Metals

- Since group 15 elements are more electronegative, so form

Nitrides → eg: Ca_3N_2, Li_3N, Mg_3N_2.
Phosphides → eg: Ca_3P_2
Arsenides → eg: Na_3As_2, K_3As_2
Antimonides → eg: Zn_3Sb_2
bismuthides → eg: Mg_3Bi_2

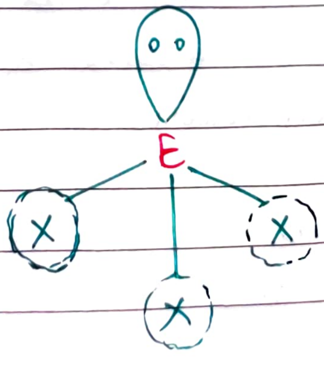
Not to be learned.

Reaction with Halogens

- General formula of halides → EX_3 & EX_5.

(E → group 15 elements
X → halogens - F, Cl, Br, I)

* EX_3



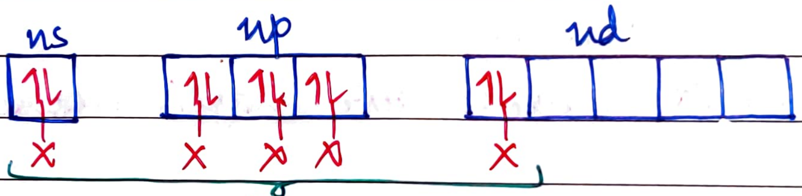
Hybridisation → sp^3
Geometry → tetrahedral
Shape → pyramidal.

- N will not for NX_5 as it does not have ~~emp~~ a d-orbital to expand its octet.
So, only NX_3 is formed.
- NF_3 is stable → F is small so can be accomadated around N.

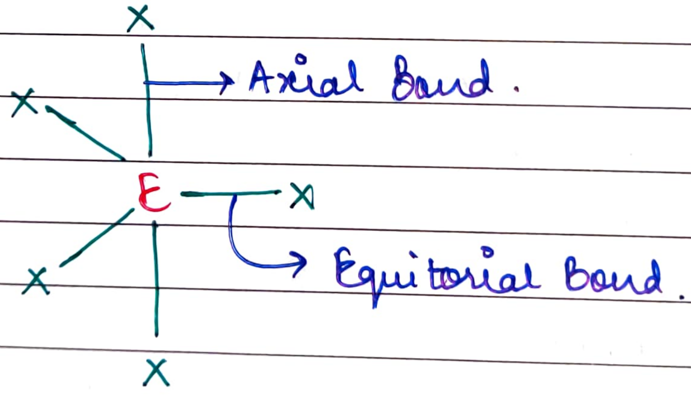
NCl_3 is explosive → Due to its unstability as Cl is larger in size and leads to increased interelectronic repulsions.

NBr_3 & NI_3 do not exist → Due to very large size of Br & I, they cannot be accomadated around N as they will cause strong interelectronic repulsions.

* EX_5



Hybridisation → sp^3d

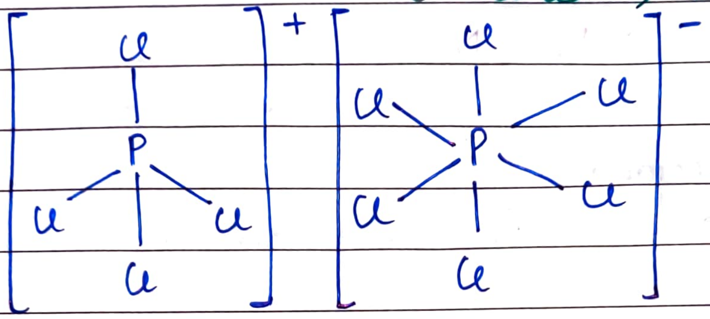


Geometry & shape → Trigonal bipyramidal.

- E–X bonds in EX_5 are non-equivalent as axial bonds are longer than equitorial bonds because of greater e^- pair repulsions experienced by them.

- PCl_5 & PF_5 exist due to small size of F & Cl, they can be accomadated around P atom but PBr_5 & PI_5 do not exist due to large size of Br & I, they cannot be accomodated around P as they will cause strong interelectronic repulsions.

- In gaseous state PCl_5 exists as it is but in solid state PCl_5 exists as $\underset{\substack{\Downarrow \\ 4e^- \text{ pair} \\ (\text{Tetrahedral})}}{[PCl_4]^+}\underset{\substack{\Downarrow \\ 6e^- \text{ pairs} \\ (\text{Octahedral}).}}{[PCl_6]^-}$



- PF_3, PCl_3, PBr_3 exist but PI_3 is unstable.
- EX_5 for Bi does not exist due to inert pair effect. (except BiF_5)
- Pentahalides are more covalent than trihalides for group 15 elements. (Fajan's Rule).

Dinitrogen (N_2)

Preparation

① Heat amm. chloride & sodium nitrite solution.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + \underline{\underline{N_2}}\uparrow + 2H_2O.$$

② By heating Ammonium dichromate.

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

③ Thermal decomposition of sodium or barium azide.

$$2NaN_3 \xrightarrow{\Delta} 2Na + \underline{\underline{3N_2}}$$
$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + \underline{\underline{3N_2}}. \quad \left\{(N\equiv N-N)^{\ominus} \longrightarrow N_3^{\ominus}\right\}$$

Physical Properties

- It is a gas.
- It is an inert molecule.

Chemical Reactions

① Formation of nitrides with metals.

$$6Li + N_2 \longrightarrow 2Li_3N$$

$$3Mg + N_2 \longrightarrow Mg_3N_2.$$

② Reaction with oxygen

$$N_2 + O_2 \rightleftharpoons 2NO(g).$$

③ Formation of Ammonia

$$N_2(g) + 3H_2(g) \underset{Fe_2O_3 \text{ or } Fe / \text{promoter}}{\rightleftharpoons} 2NH_3 + \Delta$$

$$\Delta_f H = -46.1 \text{ kJ/mol}.$$

Promoters → Mo OR K_2O / Al_2O_3.

* Conditions to maximise the yield of ammonia:
(Using Le chatelier's Principle).

1) Low Temperature - the rate of reacⁿ becomes very slow (sluggish reaction).

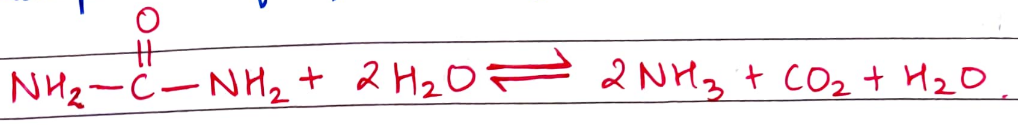
2) High Pressure - a furnace which can withstand the high pressure is very expensive.

In order to check upon the cost & rate of reaction the process is carried out at moderate temperature & pressure. ⟶ Yield of NH_3 is 60-70%.

Ammonia (NH_3)

Preparation

① Decomposition of aq. solⁿ of Urea.



$$NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + 2H_2O \rightleftharpoons 2NH_3 + CO_2 + H_2O.$$

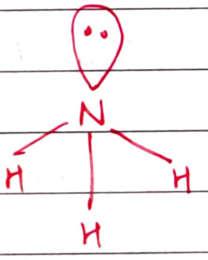
② Decomposition of Ammonium salts using NaOH or $Ca(OH)_2$.

$$NH_4^+ + NaOH \longrightarrow NH_3 + Na^+ + H_2O.$$

$$2NH_4^+ + Ca(OH)_2 \longrightarrow 2NH_3 + Ca^{2+} + 2H_2O.$$

③ Industrial manufacture by Haber's Process.

Properties



- Water soluble - due to intermolecular H- bonds formed with H_2O.
- Polar molecule so soluble in polar solvents.
- For some reactions liq. NH_3 can be used as a solvent.
- It is a Base.

Due to a lp of e^- on N which can be donated, it is a Lewis base.

$$\boxed{NH_3} + H_2O \rightleftharpoons NH_4^+ + \boxed{OH^-}$$

accepts a proton coming from water.

↪ hydroxide is released.

∴ Its a Bronsted Base.

Chemical Reactions

① Formation of hydroxide with Cations like (Al^{+3}, Fe^{3+}, Ce^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, etc.)

$$Fe^{3+} + 3NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3NH_4^+$$

$$\text{or } Fe_2O_3.xH_2O\downarrow$$

Reddish Brown Ppt.

$$Zn^{2+} + 2NH_4OH \longrightarrow \underset{\text{Dirty-white ppt}}{Zn(OH)_2\downarrow} + 2NH_4^+$$

② Formation of coordination compounds with some metal salts.

$$\underset{\text{(white ppt)}}{AgCl} + 2NH_3 \longrightarrow \underset{\text{(colourless).}}{[Ag(NH_3)_2]Cl}$$

$$CuSO_4 + 4NH_3 \longrightarrow \underset{\text{Deep blue colouration.}}{[Cu(NH_3)_4]SO_4}$$

- ∴ It plays a good role in detection of metals like Cu^{2+}, Ag^+, etc.

Nitric Acid (HNO_3)

Preparation

① In Laboratory

$$NO_3^- \text{ salt} + \text{Conc. } H_2SO_4 \rightarrow HNO_3$$

$$NO_3^- + H_2SO_4 \longrightarrow HNO_3 + HSO_4^-$$

② Industrial Method

The method of synthesis is called Ostwald's process.

$$NH_3 \xrightarrow{[O]} NO \xrightarrow{[O]} NO_2 \xrightarrow{H_2O} HNO_3$$

disproportionates

Key Step.

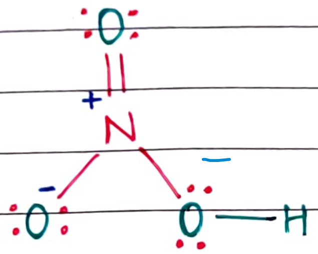
(i) $4NH_3 + 5O_2 \xrightarrow[500K]{\text{Rd-Pd Gauge}} 4NO(g) + 6H_2O(g)$

(ii) $2NO + O_2 \longrightarrow 2NO_2$.

(iii) $3\underset{+4}{NO_2} + H_2O \longrightarrow 2H\underset{+5}{NO_3} + \underset{+2}{NO}$

- By fractional distillation 68% HNO_3 is obtained.
- It can be further concentrated by using conc. H_2SO_4 (dehydrating agent) to 98%.

Structure



Hybridisation - sp^2
Geometry - trigonal planar.

- Each N-O bond in NO_3^- or HNO_3 is equivalent (has same bond length) due to resonance.
- Resonance is also involved in stabilisation of HNO_3.

Properties

① High acidic strength / strong acid.

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^- \quad (K_a = \text{large}).$$

Because O-H bond is highly polar due to resonance stabilisation of NO_3^- ion. (conjugate base).

② Decomposition of HNO_3.

$$2HNO_3 \xrightarrow{\Delta} 2NO_2 + H_2O + \frac{1}{2}O_2.$$

③ Oxidising Action

HNO_3 is a very good oxidising agent and its oxidising action depends upon

1. Concentration of HNO_3
    - Conc. HNO_3
    - Dil. HNO_3
    - V. Dil. HNO_3.
2. Temperature
3. Nature of substance / element undergoing oxidation

Metals
- Reactivity above H
- Reactivity below H

Non-metals
- No reacn with dil. HNO_3
- they only react with Conc. HNO

$$\text{Non-Metal} + HNO_3 \longrightarrow \text{Nitrate salt} + NO_2.$$

(HNO_3 reduces to NO_2).

* **Note:** HNO_3 does not react with noble metals like Au & Pt.

Chemical Reactions

1. An Oxidising Agent

ⓐ Metals that are more reactive than Hydrogen.
(eg.- Zn, Mg, Al, Fe, etc.)

$$M + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H$$
$$H + HNO_3 \longrightarrow \boxed{\text{Reduction Product}} + H_2O.$$

Dil. HNO_3	Conc. HNO_3	V. Dil. HNO_3
⇓	⇓	⇓
N_2O	NO_2	NH_4NO_3.

Eg:- $Zn + \text{Dil. } HNO_3 \longrightarrow$

$$(Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2[H]) \times 4$$
$$\underline{8H} + 2HNO_3 \longrightarrow N_2O + 5H_2O$$
$$\underline{4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O}$$

$Zn + \text{Conc. } HNO_3 \longrightarrow$

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + \underline{2H}$$
$$(H + HNO_3 \longrightarrow NO_2 + H_2O) \times 2$$
$$\underline{Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O}$$

ⓑ Metals with reactivity lesser than H

(eg - Cu, Ag, Bi, Hg).

$HNO_3 \longrightarrow$ Reduction product $+ H_2O + [O]$

$M + [O] + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2O$.

Reduction Products

Conc. HNO_3	Dil. HNO_3.
⇓	⇓
NO_2	NO

Eg:- Cu + Conc. HNO_3. $\longrightarrow$

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + [O]$$

$$Cu + [O] + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

$$\underline{Cu + 4NNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O}$$

Cu + Dil. $HNO_3 \longrightarrow$

$$2HNO_3 \longrightarrow 2NO + H_2O + 3[O]$$

$$(Cu + 2HNO_3 + [O] \longrightarrow Cu(NO_3)_2 + H_2O) \times 3$$

$$\underline{3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O}$$

ⓒ Reaction with Non-metals

- No reaction with dil. HNO_3.
- Non-metals react only with conc. HNO_3.

	Non-Metal	Oxidation Product
1.	C	CO_2
2.	P_4	H_3PO_4
3.	S_8	H_2SO_4
4.	I_2	HIO_3

* Conc. HNO_3 reduces to NO_2.

$6 \times 8 = 48 \times 1$

$$\underset{0}{S_8} + \underset{+5}{HNO_3} \longrightarrow 8\underset{+6}{H_2SO_4} + \underset{+4}{NO_2}.$$

$1 \times 1 = 1 \times 48$

$\Rightarrow S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O.$

Brown-Ring Test

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow 3Fe^{3+} + \boxed{NO} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underbrace{[Fe(H_2O)_5NO]^{2+} H_2O}_{\text{Brown ring}}$$

→ reason for brown colour.

A charge transfer complex is formed NO transfers e^- to Fe^{2+} & reduces it to +1 O.S & itself oxidises to NO^+ (Nitrosonium ion).

IUPAC name - Pentaaquanitrosonium iron (I) hydrate.

Group 16 Elements

Ionisation Enthalpy

- $\underbrace{(IE)_{Group16} < (IE)_{Group17}}$ higher Z_{eff}.
- $\underbrace{(IE)_{Group15}} > (IE)_{Group 16}$. half filled up subshell.

$\{ (IE)_{17} > (IE)_{15} > (IE)_{16}.$

Electron Gain Enthalpy

$\underbrace{(EGE)_{16}}$ is more -ve than $(EGE)_{grp15}$.
Higher Z_{eff}.

$\{(\Delta_{eg}H)_S$ is more -ve than $(\Delta_{eg}H)_O\}$

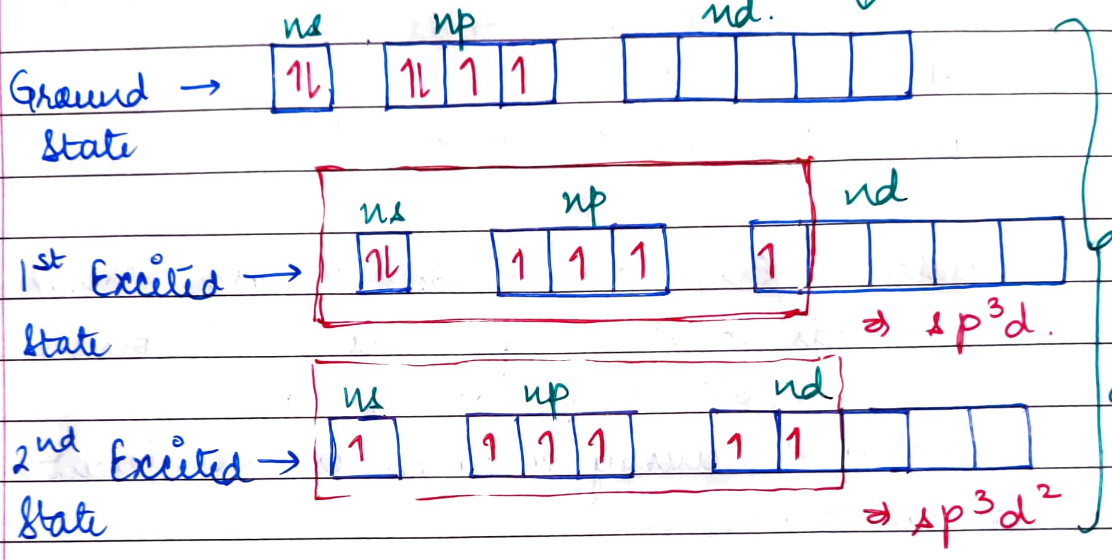
Electronegativity

Already discussed.

Oxidation States

-2, 0, +2, +4, +6 ($ns^2 np^4$).

species other than O.



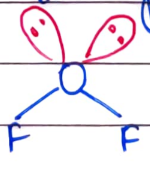
Only for Grp 16 elements with a d-orbital

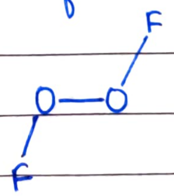
* **Note:**

O will never show +4 O.S or +6 O.S due to unavailability of d-orbitals.

Oxygen

- Very stable -2 O.S as oxides due to its small size & high electronegativity.
- O_2^{2-} (peroxide) : OS = -1
  O_2^{-} (superoxide): OS = -0.5
- O shows positive O.S only with fluorines
  OR
  With fluorines oxygen forms fluorides and not oxides.
  This is due to higher EN of F than O.
  $\overset{+2}{O}F_2$
  $\overset{+1}{O_2}F_2$





- In +6 O.S covalent character is greater than that in +4 O.S.

- +6 O.S for group 16 elements are seen in form of their oxides and fluorides only (EO_3 or EF_6)

1) Small size of O & F.
2) High EN of O & F.
3) High charge / size ratio for O & F.
4) In case of O multiple bonds are formed with the element.
5) In case of F higher $\Delta_{diss}H$ or $\Delta_{bond}H$.

- SF_6 exists but SCl_6 does not due to large atomic size of Cl, it leads to steric repulsions / e-e repulsions.
- SF_6 exists but SH_6 does not due to:
  - less EN of H, energy released is insufficient for unpairing of e^-.
  - F makes back-bonds with S, that stabilizes the molecule.

Hydrides of Group 16 Elements

MP / BP

- H_2O shows exceptionally high bp due to intermolecular H-bonds.

mp :- $H_2S < H_2Se < H_2Te < H_2O$

bp :- $H_2S < H_2Se < H_2Te < H_2O$

Bond length

$H_2O < H_2S < H_2Se < H_2Te$.

$\Delta_{diss}H$

$H_2O > H_2S > H_2Se > H_2Te$.

Acidic nature

$H_2O < H_2S < H_2Se < H_2Te$.

⊙ Bond Angle

$H_2O > H_2S > H_2Se > H_2Te$.

Reactivity with Oxygen

- Formation of oxides ⟶ $\overset{+4}{EO_2}$ & $\overset{+6}{EO_3}$

EO_3 are more acidic than EO_2 as the ON of central atom ↑ses, ionic character ↓ses (Fajan's rule) so the acidic nature of oxides ↑ses.

- In +4 O.S or EO_2 are reducing but EO_3 are alway oxidising as EO_2 can oxidise to EO_3 so reducing whereas EO_3 cannot oxidise further indeed show reduction, thus oxidising in nature.

Reactivity with Halogens

$$\underbrace{\overset{+2}{E}X_2}_{\text{Oxygen shows it only as fluorides.}} \quad \underbrace{\overset{+4}{E}X_4 \quad \overset{+6}{E}X_6}_{\text{Not possible for O.}}$$

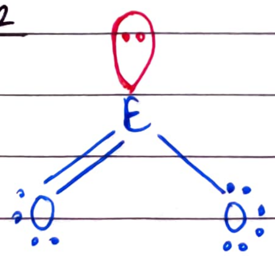
- SF_6 is kinetically inert. Why?

OR

SF_6 never gets hydrolysed. Why?

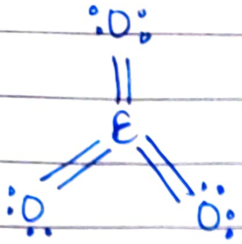
Because S is sterically surrounded by F from all 6 sides.

EO_2



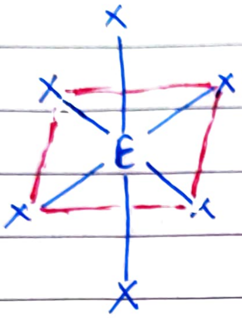
hybridisation - sp^2
Geometry - trigonal planar
Shape - bent

EO_3



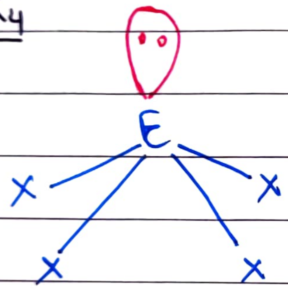
hybridisation - sp^2
Geometry & shape - trigonal planar.

EX_6



hybridisation - sp^3d^2
Geometry & shape - octahedral.

EX_4



Hybridisation - sp^3d
Geometry - trigonal bipyramidal
shape - see-saw.

- Group 16 elements also form monohalides but they are dimeric in nature.

Eg: Se_2Cl_2, S_2Cl_2, etc.

These monohalides undergo disproportionation.

3×1

$$\underset{+1}{Se_2Cl_2} \longrightarrow \underset{+4}{SeCl_4} + \underset{0}{Se}$$

3×1

$$\Rightarrow 2\,Se_2Cl_2 \longrightarrow SeCl_4 + 3\,Se$$

Oxygen

Preparation

i) Decomposition of Pottasium Chlorate, nitrate, permanganate.

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

ii) Auto-reduction of oxides of metals with low reactivity like Ag & Hg.

$2HgO \longrightarrow 2Hg(l) + O_2(g)$.

$2Ag_2O \longrightarrow 4Ag(s) + O_2(g)$.

iii) By decomposition of H_2O_2

$2H_2O_2 \longrightarrow 2H_2O + O_2$.

iv) By electrolysis of water / Aq. dilute sulphates.

$2H_2O \xrightarrow{\text{electricity}} 2H_2(g) + O_2$

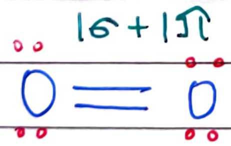
v) Industrial Method.

$\text{Air} \xrightarrow[\text{Pass through charcoal}]{} \text{Air} - (\text{oxide \& dust particles}) \xrightarrow[\text{removal of } CO_2 \text{ \& } H_2O]{} N_2 + O_2$

$N_2 + O_2 \xrightarrow[\text{fractional distillational}]{-N_2} O_2$.

Structure

- It is a gas due to pπ-pπ bonding between O atoms, a diatomic molecule is formed.



- High Bond Enthalpy due to pπ-pπ bonds formed between O atoms.
- It is paramagnetic in nature.

$(\sigma_{1s})^2, (\sigma_{1s}^*)^2, (\sigma_{2s})^2, (\sigma_{2s}^*)^2, (\sigma_{2p_z})^2, (\sigma_{2p_x}^{\,2}) = (\sigma_{2p_y}^{\,2})$

$\boxed{(\pi_{2p_x}^*)^1 = (\pi_{2p_y}^*)^1}$

Due to unpaired e^- in π^* molecular orbitals.

Properties

① It reacts with almost all metals & non-metals to form oxides.

② It doesn't react with noble metals like Au & Pt.

③ Formation of oxides is an exothermic process.

i) $C + O_2 \longrightarrow CO_2$

ii) $2Mg + O_2 \longrightarrow 2MgO$. (dazzling white flames).

iii) $CH_4 + 2O_2 \longrightarrow \underbrace{CO_2}_{\text{Combustion.}} + H_2O + \Delta$

iv) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$.

$\boxed{\text{v)}}$ $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3(g)$.

↳ Key step of contact process.

Oxides

Simple Oxides	Mixed Oxides.
Element forming oxide is present in only one O.S.	Element forming oxide is present in more than 1 O.S
Eg: ZnO, CO_2, Al_2O_3, etc.	Eg: Fe_3O_4, Pb_3O_4, etc.

- Basic oxides
- Acidic oxides
- Amphoteric oxides
- Neutral oxides.

Basic Oxides

(React with acids).

- These are usually the oxides formed by metals.
- When these oxides are added to water, they ~~are~~ form a base so called basic oxides.

Eg: $2Ca + O_2 \longrightarrow 2CaO$

$CaO + H_2O \longrightarrow \underset{\text{(base)}}{Ca(OH)_2}$.

Acidic Oxides

(React with bases)

- They are usually the oxides formed by non-metals.
- When these oxides are added to water, they form a base so called basic oxides.

Eg: $S + O_2 \longrightarrow SO_2 (g)$.

$SO_2 + H_2O \longrightarrow \underset{\text{(an acid)}}{H_2SO_3} (aq)$

Amphoteric Oxides

(React with both acids & bases)

Ex: $Al_2O_3 + 6HCl + 9H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$

$Al_2O_3 + 6NaOH + 3H_2O \longrightarrow 2Na_3[Al(OH)_6]$

Neutral Oxides

- They are neither acidic nor basic.

Eg: CO, N_2O, NO, H_2O, etc.

Ozone

- Upon thunder / lightening OR generation of a lot of energy oxygen forms ozone.

$$\underset{+\Delta}{3O_2} \longrightarrow 2O_3 \qquad \Delta H \simeq 140 \, kJ/mol.$$

Ozone is thermodynamically unstable.

$$\Delta G = \Delta H - T\Delta S$$

i) Formation of ozone is endothermic

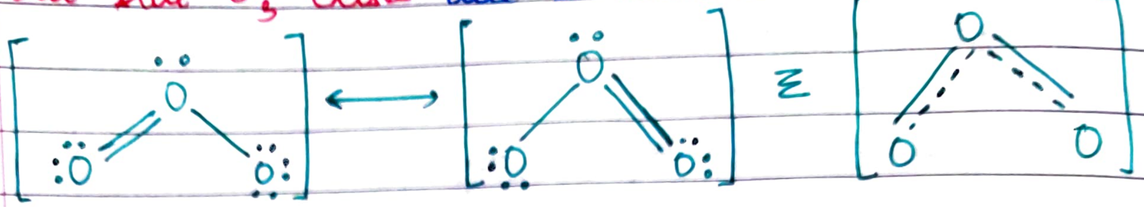
$\therefore \Delta H = +ve$ or $\Delta H > 0$.

ii) As no. of gaseous moles decreases from O_2 to O_3

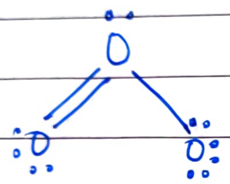
$\therefore \Delta S = -ve$ or $\Delta S < 0$.

So, at all temperatures, $\Delta G > 0$.
Hence, O_3 is thermodynamically unstable.

But still O_3 exists due to resonance stabilisation.



- In O_3, each O-O bond is equivalent (has same bond order & bond length) due to resonance.



Hybridisation - sp^2
Geometry - trigonal planar
Shape - bent OR Inverted V.

Ozone (O_3)

Tropospheric Ozone	Stratospheric Ozone
Bad Ozone	Good Ozone.
As it is a pollutant & causes nausea, respiratory ailments, etc.	As it protects the Earth from UV radiations.

$$2O_3 \xrightarrow[\text{UV Radiations}]{h\nu} 3O_2$$

- The exhaust of jet planes leads to ozone depletion as it releases oxides of N like NO which react with O_3 and increases the rate of its conversion to O_2.

$$O_3 + NO \longrightarrow NO_2 + O_2$$

Properties

- $O_3 \longrightarrow O_2 + \boxed{[O]} \rightarrow$ can oxidise other substances, thus O_3 is a powerful/good oxidising agent.

$$PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$$

oxidation.

$$\boxed{2I^- + O_3 + H_2O \longrightarrow I_2 + O_2 + 2OH^-}$$

oxidation

↳ used for estimation of ozone.

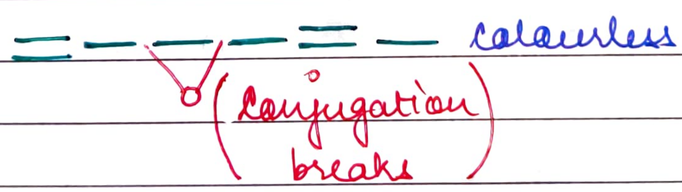
Quantitative Estimation of Ozone

(i) Ozone gas is passed through aq. solⁿ of excess KI in presence of borate buffer. (pH = 9.2) iodine gas gets released.

(ii) Thus I_2 liberated in titrated against standard sodium thiosulphate solⁿ. (hypo solⁿ).

Coloured substance + [O] ⟶ colourless } oxidative bleaching.

∴ O_3 also shows bleaching action.



Ques. S_2 molecule is paramagnetic in nature. Why?

$(KK^*), (LL^*), (\sigma 3s)^2, (\sigma 3s^*)^2, (\sigma 3p_z)^2, (\pi 3p_x)^2 = (\pi 3p_y)^2$
$(\pi 3p_x^*)^1 = (\pi 3p_y^*)^1$

Due to unpaired e^- present in π^* molecular orbitals of S_2, it is paramagnetic in nature.

Sulphur Dioxide (SO_2)

Preparation

① Burning Sulphur in air

$S + O_2 \longrightarrow \textcircled{SO_2}$ ⟶ smells like burning sulphur (crackers).

② Reacⁿ of Sulphite salts with dil. H_2SO_4

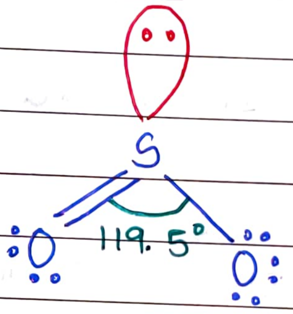
$SO_3^{2-} + 2H^+ \longrightarrow SO_2\uparrow + H_2O$.

③ Industrial Preparation by roasting sulphide ores

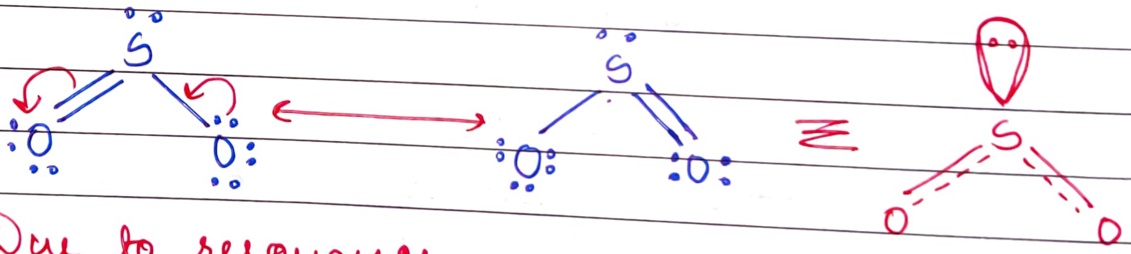
$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
(Zinc blende)

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$.
(Iron pyrite)

Structure



hybridisation - sp^2
geometry - trigonal planar
shape - bent or Inverted V.



Due to resonance
i) SO_2 is a stable molecule.
ii) the bond length of S—O bonds is equal
OR
the S—O bonds are equivalent.

Properties

① It is acidic in nature
i) $SO_2 + H_2O \rightleftharpoons H_2SO_3$
Sulphurous acid.

Reaction with Base
* ii) $SO_2 + NaOH \longrightarrow Na_2SO_3 + H_2O$.
Due to excess passage of SO_2.

$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$

* iii) $SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$ } Lime water becomes cloudy.

Due to excess passage of SO_2.

$CaSO_3 + H_2O + SO_2 \longrightarrow Ca(HSO_3)_2$

Cloudiness dissapears.

② Detection of SO_2 / Reducing Action of SO_2.

i) $\underset{+4}{SO_2} + \underset{+7}{MnO_4^-} \longrightarrow \underset{+2}{Mn^{2+}} + \underset{+6}{SO_4^{2-}}$

5×2

Permanganate (purple) Manganese ions (colourless).

2×5

$\Rightarrow 2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

ii) $\underset{+3}{Fe^{3+}} + \underset{+4}{SO_2} \longrightarrow \underset{+2}{Fe^{2+}} + \underset{+6}{SO_4^{2-}}$

1×2

2×1

[decolourisation of yellow colour of Fe^{3+}].

$\Rightarrow 2Fe^{3+} SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

iii) $\overset{+6}{Cr_2O_7^{2-}} + \overset{+4}{SO_2} \longrightarrow 2Cr^{3+} + \overset{+6}{SO_4^{2-}}$

(orange) (green).

3×2 = 6×1

Dichromate ions. Chromium ions.

2×1 = 2×3

$\Rightarrow Cr_2O_3^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$.

③ $SO_2 + Cl_2 \xrightarrow{Charcoal} SO_2Cl_2$

Sulphuryl chloride.

④ $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

⑤ **Bleaching Action**

Reductive Action.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + \underbrace{2[H]}_{\text{leads to reduction}}$$

$$\text{Coloured Substance} \overset{2[H]}{\rightleftharpoons} \text{Colourless.}$$

$$H_2O \qquad O_2 .$$

⇒ The process is reversible so the bleaching action is temporary.

Oxoacids of Sulphur

- The following 2 conditions should be fulfilled for a substance to be termed an oxoacid:

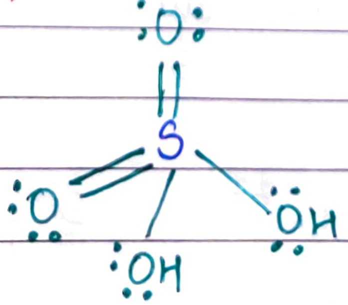
i) Presence of atleast one $S=O$

ii) Presence of atleast one $S-OH$.

Types

- Sulphurous Acid Family.
- Sulphuric Acid Family
- Thioacids
- Peroxyacids

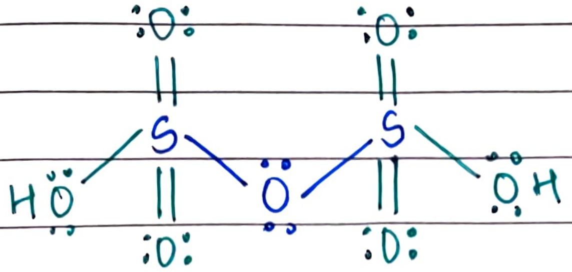
⊙ **Sulphuric Acid Family**



① Sulphuric Acid - H_2SO_4.

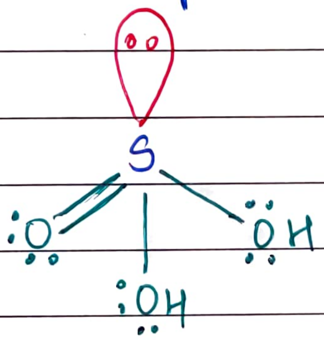
② $H_2S_2O_7$ - Pyrodisulphuric Acid or Oleum.

↳ anhydride linkage.



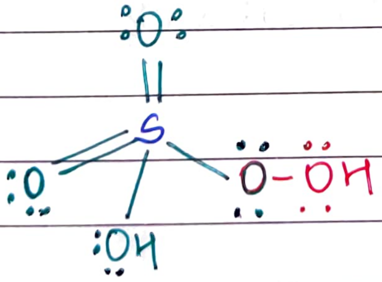
⊙ Sulphurous Acid Family

◦ H_2SO_3 - Sulphurous Acid

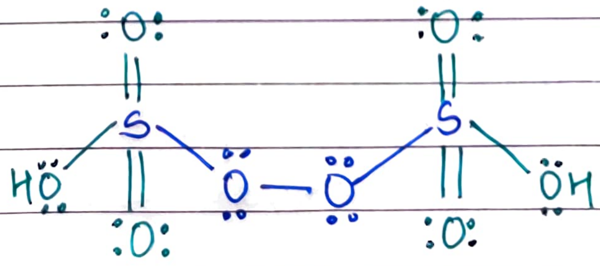


⊙ Peroxy acids

① H_2SO_5 - peroxysulphuric Acid or Caro's Acid

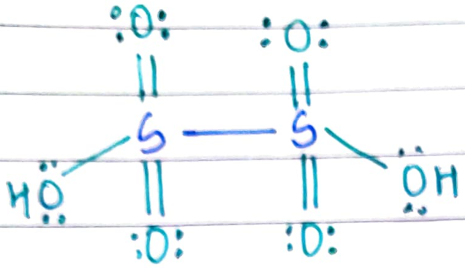


② $H_2S_2O_8$ - Peroxydisulphuric acid or Marshall's Acid.

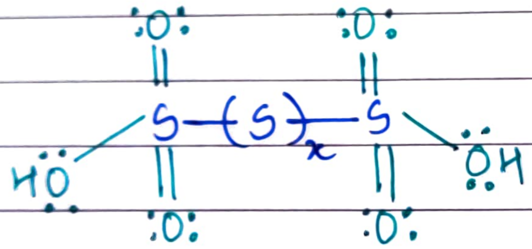


⊙ Thioacids

① $H_2S_2O_6$ - **Thionic Acid.**



② $H_2(S_2)_x O_6$ - **Polythionic Acid** ($x = 0, 1, 2, 3 \ldots$)



Sulphuric Acid (H_2SO_4)

Properties

a) **Low volatility:**

Does not boil off easily and the salts of sulphuric acid also have low volatilities.

b) **Dehydrating Agent:**

$$C_{12}H_{22}O_4 \xrightarrow{\text{Conc. } H_2SO_4} 12C + 11H_2O$$

(Cane sugar) (Carbon black.)

} Charring of Sugar.

$$CuSO_4 . 5H_2O \xrightarrow{\text{Conc. } H_2SO_4} CuSO_4 + 5H_2O$$

(hydrated). (anhydrous).

c) Strong Acidic Nature:

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$ Ka_1 = Very large.

$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$ $Ka_2 \simeq 10^{-2}$

Due to large Ka_1, a complete ionisation making it a strong acid.

- $Ka_1 >> Ka_2$. Why?

- SO_4^{2-} is a stronger base than HSO_4^- thereby affecting the acidic strength of the Bronsted acid to which it is paired.

$SO_4^{2-} \rightarrow$ conjugate base of HSO_4^- making it a weaker acid so low Ka_2.

$HSO_4^- \rightarrow$ conjugate base of H_2SO_4 making it a stronger acid to large Ka_1.

- After the loss of first H^+ / formation of HSO_4^- it is difficult for a -vely charged species to lose a proton, as being a strong/good base it would try to accept H^+.

d) Salt Formation:

Acidic Sulphates	Normal Sulphates
• Ex: $NaHSO_4$, $Ca(HSO_4)_2$, etc.	• Ex: $CuSO_4$, Na_2SO_4, etc.
• Salts with HSO_4^- / bisulphate or hydrogen sulphate.	• Salts with SO_4^{2-} / sulphates.

e) An Oxidising Agent:

- It is able to oxidise low reactivity metals like Cu & some non-metals like C, P, S, etc.

- $Cu + 2H_2SO_4 (conc.) \longrightarrow CuSO_4 + SO_2 + 2H_2O$.
- $C + 2H_2SO_4 (conc.) \longrightarrow CO_2 + 2SO_2 + 2H_2O$.
- $S + 2H_2SO_4 (conc) \longrightarrow 3SO_2 + 2H_2O$.

f) Uses:

① Manufacture of Fertilizers - eg Ammonium Sulphate.
② Storage Batteries - eg. Electrolyte in Pb storage batteries.
③ Metallurgical processes - eg. galvanisation, electroplating, etc.
④ Industrial application - Used in manufacture of paints, dyes, pigments & some other acids.

∴ Due to (a) to (f), it is called the 'King of Acids'.

Group 17 Elements

Occurrence

- Sea-water is the richest source for group 17 elements.
- Sea-water contains chlorides, bromides & iodides in the form of their soluble sodium, potassium, calcium, and Magnesium salts.
- Insoluble fluorides are obtained from the river plants, weeds and teeth & bones of animals.
- Some marine animals contain iodides in them like seaweeds, diatoms, etc.

General Electronic Configuration → $ns^2 np^5$

Physical Properties

- Halogens are obtained as a diatomic molecule X_2.
- Halogens are coloured

F_2 - yellow

Cl_2 - greenish yellow

Br_2 - Reddish-brown

I_2 - violet.

These molecules absorb light in the visible region and reflect complementary colour.

⊙ M.P & B.P

$I_2 > Br_2 > Cl_2 > F_2$

↳ Max. atomic mass

↳ min. atomic mass.

Greater the atomic mass, higher will be the magnitude of intermolecular forces of attraction.

⊙ Bond Length

$I_2 > Br_2 > Cl_2 > F_2$

↳ max. atomic size

↳ Min. atomic size.

As the atomic size increases, bond length increases.

⊙ Bond Dissociation Enthalpy

- As bond length increases, $\Delta_{diss}H$ decreases.

  ∴ I_2 should have least $\Delta_{diss}H$ due to max. bond length.

- F_2 has an exceptionally ~~high~~ low $\Delta_{diss}H$ (F−F) due to small size of F there are electron-electron repulsions which make the molecule unstable.

∴ Order will be: $I_2 < F_2 < Br_2 < Cl_2$

↳ exceptional behaviour

Reduction Potential OR Oxidising Nature ($E^\circ_{X_2/X^-}$)

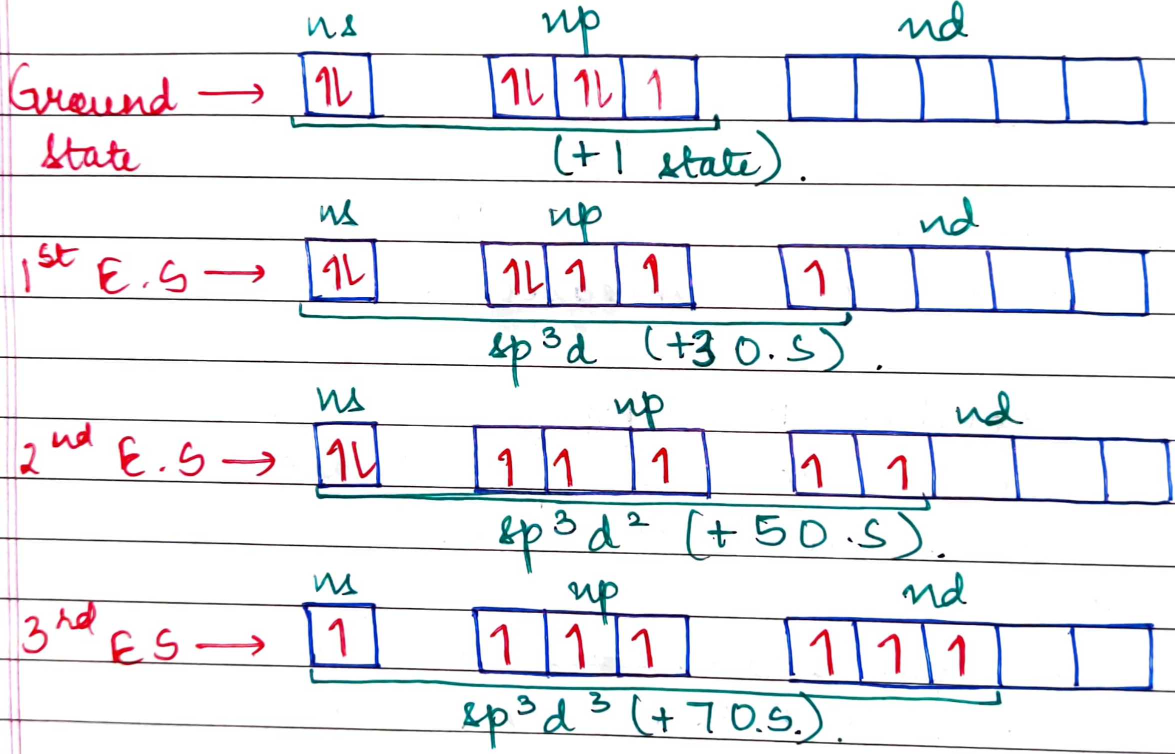
$$\begin{tikzcd}
\frac{1}{2}X_2(g) \arrow[r, "E^\circ_{red}"] \arrow[d, "\frac{1}{2}\Delta_{diss}H"] & X^{\ominus}(aq) \\
X(g) \arrow[r, "\Delta_{eg}H"'] & X^{\ominus}(g) \arrow[u, "\Delta_{hyd}H"']
\end{tikzcd}$$

$$E^\circ_{red} = \underbrace{\frac{1}{2}\Delta_{diss}^\circ H}_{+} + \underbrace{\Delta_{eg}H}_{-} + \underbrace{\Delta_{hyd}H}_{-}$$

Despite of more negative $\Delta_{eg}H$ of chlorine, fluorine is a better oxidising agent / is more oxidising because:

i) low $\Delta_{diss}H$ of F — F

ii) high $\Delta_{hyd}H$ for $F^{\ominus}_{(g)}$.



- But F only shows -1 & 0 O.S & never shows +1, +3, +5 and +7.

① Most Electronegative element

② Does not have an available d-orbital.

- $F_2 + H_2O \longrightarrow 2HF + \frac{1}{2}O_2$. $[F^{\ominus}\cdots\cdots H—F]$

$X_2 + H_2O \longrightarrow HX + HOX$

(X = Cl and Br).

* **Note**: Reac^{n} with fluorine / formation of fluorides is always an exothermic reaction.

Reaction with Hydrogen

i) Bond length: HF < HCl < HBr < HI

ii) $\Delta_{diss}H$: HF > HCl > HBr > HI

iii) Acidic strength: HF < HCl < HBr < HI

iv) $pK_a = -\log K_a$: HF > HCl > HBr > HI

v) HF is a liquid whereas HCl is a gas.

vi) mp / bp: HF > HI > HBr > HCl.

Reaction with Oxygen

All halogens except F react with oxygen to form oxoanions / oxides.

XO_2^-
XO_3^-
XO_4^-
XO^-

XO
XO_2
XO_3

Because of (i) high electronegativity of O.
(ii) small size of O.

- Oxides of Cl* $\longrightarrow$ Cl_2O, ClO, Cl_2O_6, Cl_2O_7

- Oxides of Br $\longrightarrow$ Br_2O, BrO, BrO_2, BrO_3. No stabilising factor.

- Oxides of I $\longrightarrow$ I_2O_4, I_2O_5, I_2O_7

These oxides are highly stable due to polarisability between I & O bond.

* Oxides of Cl are stable due to multiple bonding between Cl & O.

∴ The order of thermal stability of oxides is :

oxides of I > oxides of Cl > oxides of Br.

The oxides of Br are highly unstable due to middle row anomally.

Reaction with Metals (formation of salts)

$$Mg + Br_2 \longrightarrow MgBr_2$$

- Ionic character of metal salts of halogens decreases as : M-F > M-Cl > M-Br > M-I.

Acc. to Fajan's Rule as size of anion increases covalent character ↑es.

Formation of Interhalogen Compounds

XX', XX'_3, XX'_5, XX'_7

$(\chi_{x'} > \chi_x)$ & $(\text{size})_{x'} < (\text{size})_x$

⇒ Difference in electronegativities & size.

Chlorine

Preparation

Laboratory Preparation

i) Reac^n of MnO_2 with HCl.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

ii) From chloride salts.

$$(Cl^- + H_2SO_4\,(\text{conc}) \longrightarrow HSO_4^- + HCl) \times 4$$

$$4HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$\Rightarrow 4Cl^- + 4H_2SO_4 + MnO_2 \longrightarrow 4HSO_4^- + MnCl_2 + Cl_2 + 2H_2O$$

Industrial Preparation

i) Electrolysis of Brine Solution

Aq. NaCl.

Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2(g)$.

ii) Deacon's Process

$$2HCl + \frac{1}{2}O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O.$$

Properties

① Reacⁿ with metals, non-metals & metalloids to form chlorides

- $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
- $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$
- $P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(s)$.
- $P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(s)$
- $S_8(l) + 4Cl_2(g) \longrightarrow 4S_2Cl_2$.

② Reacⁿ with NH_3

$$NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

$$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

③ Reacⁿ with Alkalis / Bases.

Mild Conditions $\{ Cl_2 + \underset{\text{(cold \& dil)}}{2NaOH} \longrightarrow NaCl + NaOCl + H_2O.$

1×5

$$\text{Vigorous Conditions}\left\{\; 3\underset{0}{Cl_2} + 6NaOH \xrightarrow[\text{(hot \& conc.)}]{\Delta} 5Na\underset{-1}{Cl} + Na\underset{+5}{Cl}O_3 + 3H_2O \right.$$

5×1

Synthesis of Bleaching powder:

$$2Cl_2 + 2Ca(OH)_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

* **Composition of Bleaching powder** -

$$Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O.$$

④ Oxidising & Bleaching Action of chlorine

$$Cl_2 + H_2O \longrightarrow HCl + HOCl.$$

$$HOCl \longrightarrow HCl + \underbrace{[O]}_{}$$

→ oxidises other species present in the solution.

$$\underset{\text{Substance}}{\text{Coloured}} + [O] \xrightarrow{\text{Oxidising Action}} \text{Colourless} \left.\right\} \text{Oxidative Bleaching.}$$

Since the above process is irreversible, so a permanent bleaching action.

Ques. Bleaching action of SO_2 is temporary whereas that of chlorine is permanent. Why?

$$\left.\begin{array}{l} \text{Ferrous} \longrightarrow \text{Ferric} \\ SO_3^{2-} \longrightarrow SO_4^{2-} \\ SO_2 \longrightarrow H_2SO_4 \end{array}\right\} \text{Under the action of } Cl_2.$$

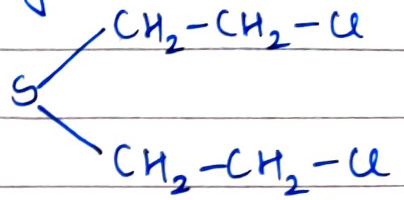
- $Fe^{2+} + Cl_2 \longrightarrow Fe^{+3} + 2HCl$

  $+ 2H^+$

- $SO_3^{2-} + Cl_2 + H_2O \longrightarrow SO_4^{2-} + 2HCl$

Uses

① Used as a bleaching agent for woodpulp, textiles, etc.
② Used in the extraction of Au & Pt.
③ Used for refrigeration as it forms CFCs.
④ It is used in synthesis of poisonous gases like
  i) Phosgene → $COCl_2$
  ii) Mustard gas
  iii) Tear gas → CCl_3NO_2.



(Mustard gas).

HCl

Preparation

⇒ From chloride salts.

$$Cl^- + H_2SO_4\,(conc) \longrightarrow HSO_4^- + HCl$$
$$Cl^- + HSO_4^- \longrightarrow SO_4^{2-} + HCl.$$

Properties

① A strong acid

proton donated.

$$\underset{(acid)}{HCl} + H_2O \rightleftharpoons \underset{\left(\substack{conjugate\\ base}\right)}{Cl^-} + H_3O^+ \;;\; K_a \approx 10^7.$$

② Reacⁿ with CO_3^{2-}, HCO_3^-, SO_3^{2-}, S^{2-}.

$$CO_3^{2-} + 2HCl \longrightarrow 2Cl^- + H_2O + CO_2\uparrow$$
$$HCO_3^- + HCl \longrightarrow Cl^- + H_2O + CO_2\uparrow$$
$$SO_3^{2-} + 2HCl \longrightarrow 2Cl^- + H_2O + SO_2\uparrow$$
$$S^{2-} + 2HCl \longrightarrow 2Cl^- + H_2S\uparrow$$

③ Reacⁿ with NH_3

$$NH_3 + HCl \longrightarrow NH_4Cl$$

④ Formation & reac^{n} of Aqua Regia

3 parts of conc. HCl
+
1 part of conc. HNO_3.

- A very strong oxidising agent that reacts with noble metals like Au & Ag.

$$3HCl + HNO_3 \longrightarrow \underbrace{NOCl}_{\text{Nitrosyl chloride}} + 2Cl + 2H_2O$$

$Au \rightarrow Au^{3+}$
$Pt \rightarrow Pt^{4+}$

$$Au + 4H^+ + 4Cl^- + NO_3^- \longrightarrow [AuCl_4]^- + NO + 2H_2O$$
$$3Pt + Cl^- + 4NO_3^- + 16H^+ \longrightarrow 3[PtCl_6]^{2-} + 4NO + 8H_2O$$

⑤ Reac^{n} with Iron

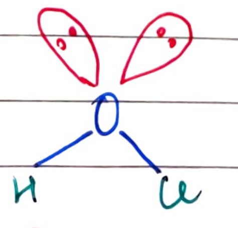
$$Fe + 2HCl \longrightarrow FeCl_2 + \boxed{H_2}$$ $\rightarrow$ reduces Fe^{3+} to Fe^{2+}.

Oxoacids of Halogens

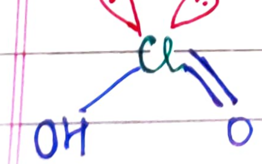
$\boxed{HOX}$ $\longrightarrow$ F will only form HOF
i) small size
ii) high electronegativity
iii) absence of d-orbital.

HOXO
$HOXO_2$
$HOXO_3$

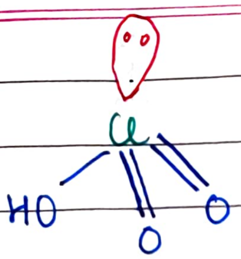
Structure:



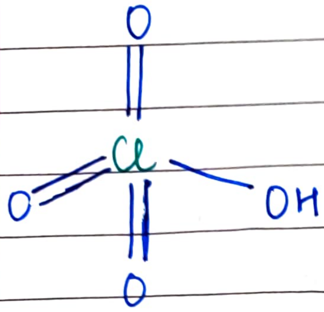
hypochlorous acid
sp^3, angular/bent



Chlorous acid. sp^3, angular/bent



Chloric acid. , sp^3, pyramidal.



Perchloric acid. sp^3, tetrahedral.

Acidic strength : $HClO_4 > HClO_3 > HClO_2 > HOCl$.

Due to more resonating str O–H bond polarity is more.

Acid	No. of conjugating structures with conjugate base formed
$HOCl$	Nil
$HClO_2$	2
$HClO_3$	3
$HClO_4$	4.

Greater the no. of resonating structures more will be the stability of conjugate base formed and thus higher will be the O-H bond polarity.

Reducing Nature :

$HO\overset{+1}{\underline{Cl}} > H\overset{+3}{\underline{Cl}}O_2 > H\overset{+5}{\underline{Cl}}O_3 > \boxed{H\overset{+7}{\underline{Cl}}O_4} \rightarrow$ Cl will not oxidise further.

Acidic strength :

$HOCl > HOBr > HOI$

Electronegativity order :– $Cl > Br > I$

Greater the electronegativity of halogen, more will be its tendency to pull e$^-$ from O which will increase the O—H bond polarity.

Interhalogen Compounds

Preparation

$Cl_2 + F_2 \xrightarrow{\Delta} 2ClF$
(equal volume)

$Cl_2 + 3F_2 \xrightarrow{\Delta} 2ClF_3$
(excess)

Due to small size of Cl it cannot accomadate more than 3 F-atoms around it.

$Br_2 + F_2 \longrightarrow 2BrF$

$Br_2 + 3F_2 \longrightarrow 2BrF_3$

$Br_2 + 5F_2 \longrightarrow 2BrF_5$
excess

Due to comparatively larger size of Br than Cl, it can accomadate 5F atoms around it.

$I_2 + Cl_2 \longrightarrow 2ICl$
(equimolar)

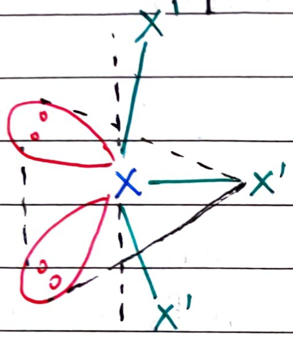
$I_2 + 7F_2 \longrightarrow 2IF_7$
(excess)

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$
(excess)

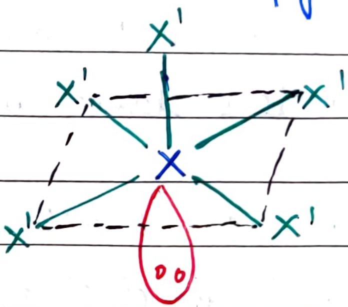
Due to larger size of Cl than F it will lead to steric hindrance thus I cannot accomadate more than 3 Cl atoms around it.

Interhalogen Compound	Examples	Geometry	Shape	Hybridisation
XX'	ClF			
	BrF			
	IF(unstable)	—	—	
	BrCl			
	ICl			
	IBr.			

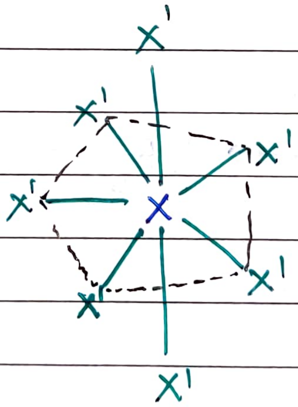
Interhalogen Compound	Examples.	hybridisation.	Geometry	shape.
XX'_3	ClF_3 BrF_3 IF_3 $BrCl_3$ ICl_3	sp^3d	Trigonal bipyramidal	T-shaped.
XX'_5	BrF_5 IF_5	sp^3d^2	Octahedral	square pyramidal
XX'_7	IF_7	sp^3d^3.	Pentagonal Bipyramidal	pentagonal bipyramidal



XX'_3



XX'_5



XX'_7

Properties

1. They are covalent compounds.
2. They are volatile solids or liquids except ClF which is a gas.
3. They are diamagnetic in nature.
4. They are soluble in polar solvents (like dissolves like)
5. Reac^n with water

$$XX' + H_2O \xrightarrow[H-OH]{} HX' + HOX$$

More electronegative halogen will form hydride and less electronegative halogen will form ~~hydroxide~~ oxoacid.

6. Their mp & bp are more than expected.
7. They do not conduct electricity.
8. **Volatality**

Interhalogen compounds are more reactive than pure diatomic halogen molecule.

OR

XX' is more reactive than X_2.

$X-X \longrightarrow$ non polar molecule

$X-X' \longrightarrow$ due to electronegativity difference between X & X', high bond polarity.

$\therefore XX'$ is less stable due to low $\Delta_{diss}H$.

But F_2 is more reactive / less stable than XX'.
Due to electron-electron repulsions in F_2 molecule it has an exceptionally low $\Delta_{diss}H$.

9. **Good fluorinating Agents**

eg. $U(s) + 3ClF_3 \longrightarrow UF_6 + 3ClF$

or

$3BrF_3$

Group 18 Elements

- Noble gases have very low boiling points due to weak London forces or dispersion forces present between the atoms of noble gases.
- Noble gas liquify at very low temperature. It is due to their low critical temp. which is due to low value of vander Waal's coefficient 'a'.

Chemical Properties

- Xe forms compounds with F & O, due to:

i) its comparatively large atomic size
ii) low I.E.

Compounds formed by Xe are only with F and O because of:

i) their small size.

ii) high electronegativity.

iii) high charge/size ratio.

iv) ability of O to form multiple bonds.

v) high $\Delta_{diss}H$ with F.

* Other than this KrF_2 also exists.

- In 1962

Neil Bartlett was carrying out a reacⁿ between O_2 & PtF_6 which then gave a compound with red colouration.

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^-$$

red colouration.

- Due to comparable ionisation enthalpies of Xe & O_2 (Xe = 1165 kJ/mol & O_2 = 1170 kJ/mol) he thought of performing the reacⁿ of PtF_6 with Xe and was successful in obtaining a red colouration compound.

$$Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$$

red.

This showed that compounds can be made by noble gases like Xe & Kr.

~~Compounds of Xe~~ Xe

Preparation

i) $Xe + F_2 \longrightarrow XeF_2$
(Xe in excess).

ii) $Xe + 2F_2 \longrightarrow XeF_4$
(1 : 5 ratio).

iii) $Xe + 3F_2 \longrightarrow XeF_6$
(1 : 20 ratio).

} Xenon fluorine compounds.

iv) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$. - Xenon Fluorine Compounds

Xenon Oxygen Compounds

v) Hydralysis of XeF_4

$6XeF_4 + 12H_2O \longrightarrow \boxed{2XeO_3} + 4Xe + 24HF + 3O_2$.

vi) Hydralysis of XeF_6

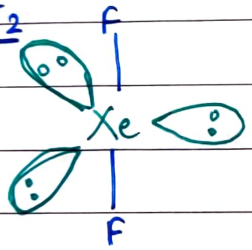
$XeF_6 + H_2O \longrightarrow \boxed{XeOF_4} + 2HF$

$XeF_6 + 2H_2O \longrightarrow \boxed{XeO_2F_2} + 4HF$

$XeF_6 + 3H_2O \longrightarrow \boxed{XeO_3} + 6HF$.

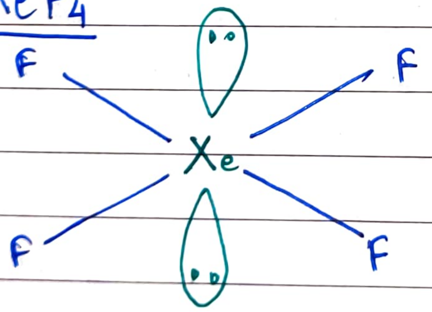
Structures

i) XeF_2



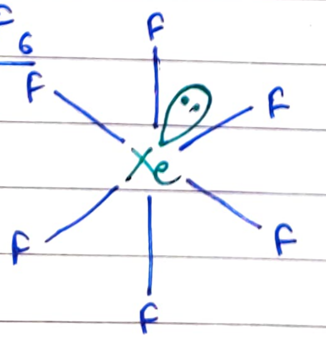
Hybridisation - sp^3d.
Geometry - trigonal bipyramidal.
Shape - linear.

ii) XeF_4



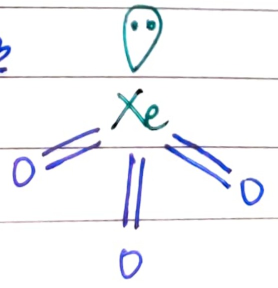
hybridisation - sp^3d^2
Geometry - Octahedral.
Shape - Square planar.

iii) XeF_6



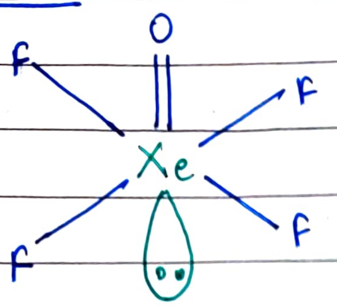
Hybridisation - sp^3d^3
Geometry - pentagonal bipyramidal
Shape - distorted octahedral.

iv) XeO_3



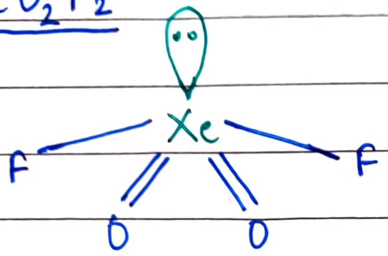
Hybridisation - sp^3
Geometry - tetrahedral
Shape - pyramidal.

v) $XeOF_4$



Hybridisation - sp^3d^2
Geometry - Octahedral.
Shape - Square pyramidal.

vi) XeO_2F_2



Hybridisation - sp^3d
Geometry - trigonal bipyramidal
Shape - see - saw.

Chemical Reactions

① Hydrolysis of Xe – F compounds.

i) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$.
ii) $6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 24HF + 3O_2$.
iii) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$
$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$.

② Acceptor or Donar of F-atoms

$XeF_6 + MF \longrightarrow M^+[XeF_7]^-$
(M - alkali metals except Li).

$XeF_4 + SbF_5$ or $PF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$

Uses

① Helium gas

- filling of meterological balloons / weather balloons.
- diluent in gas cylinders.
- essential part in instruments like MRI, NMR, etc.
- coolants in nuclear reactors.

② **Neon Gas**

- used in botanical gardens and green houses.
- used in discharge tubes and fluorescent tubes / bulbs.

③ **Argon**

- used in metallurgical purposes like arc welding of metals & alloys.
- filling electric bulbs.
- In laboratory devices with air sensitivity.

NCERT Exercises

7.34 $ClO^- = (17+9)\ e^-$

It should be ClF.

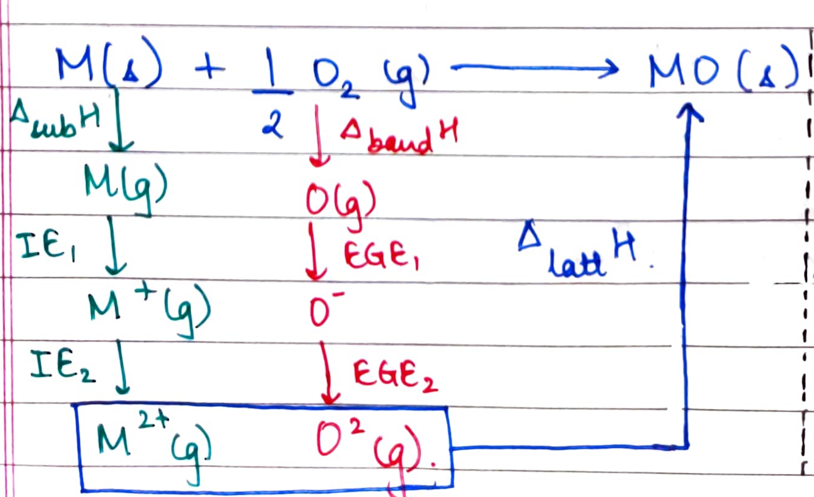
Yes, it is a Lewis base.

7.38 i) 2 lp + 4 bp, XeF_4

ii) 3 lp + 2 bp, XeF_2.

iii) 3 bp + 1 lp, XeO_3

7.19



As charge on ion increases $\Delta_{latt}H$ increases and this energy released more than compensates the energy required to convert $O^-(g) \longrightarrow O^{2-}(g)$.