

## CHEMISTRY OF MAIN GROUP ELEMENTS

### CLASSIFICATION OF PERIODIC TABLE

#### Classification -1

s-Block Elements	p-Block Elements	d-Block Elements	f-Block Elements
Group 1 & 2	Group 3 to 12	Group 13 to 18	
Alkali and Alkaline Earth Metals		Transition Elements	Inner transition Elements

#### Classification -2

Inert Gases	s&p block elements	d-block elements	f-block elements
$ns^2p^6$	$ns^1, ns^2 - np^{1-5}$	$(n-1)d^{1-9}ns^{1-2}$ exception Zn, Cd, Hg Group 12	$(n-2)f^{1-14} (n-1)d^{0-1} ns^2$ 4f - Lanthanide/Es 58 - 71 5f - Actinides 90 - 103
Inert Gases	Representative Elements	Transition Elements	Inner Transition Elements

#### DIAGONAL RELATIONSHIP

period 2- Li Be B C

These elements have similarity in Chemical behaviour

period 3- Na Mg Al Si

#### **Reason**

- In a period the atomic size and electropositive character decreases. Ionisation potential and electronegativity increases.
- Down a group atomic size and electropositive character increases. But Ionisation potential and electronegativity decreases.
- On moving in a diagonal these properties cancel each other. Therefore, similarly in behaviour.  
[eg. ionic size of  $Li^+ = 76\text{pm}$  & that of  $Mg^{2+} = 72\text{pm}$ ]

#### CHEMICAL PROPERTIES OF ALKALI METALS- GROUP -1

Oxidation state = +1 or - 1 = since it has only one 'S' electron

They are strong reducing agents being electropositive elements



They have very low ionisation potential (I.P)

#### REACTION OF ALKALI METALS WITH COMPOUNDS CONTAINING ACIDIC HYDROGEN



↑

(sodium hydroxide)

↑

(sodium acetylide)

All alkali metal hydroxides are stable except LiOH.

Alkali metals react with electronegative non metals to form **Electrovalent** or ionic Compounds.

e.g  $2M + X_2 \rightarrow 2MX$  (X= H or Cl );  $2Na + Cl_2 \rightarrow 2NaCl$

$4Li + O_2 \rightarrow 2Li_2O$  oxide ;

$4Na + O_2 \rightarrow 2Na_2O_2$  peroxide

$M + O_2 \rightarrow MO_2$  superoxide - K, Rb ,Cs

$K + O_2 \rightarrow KO_2$  superoxide  $Rb + O_2 \rightarrow RbO_2$

Oxide =  $O^{2-}$ , Peroxide =  $O_2^{2-}$ , Superoxide =  $O_2^-$

### ALKALI METALS AND AMMONIA

Alkali metals in Ammonia gives a blue solution due to the presence of solvated electrons.

$2M + 2NH_3 \rightarrow 2MNH_2 + H_2$  ;

$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$  ;

Formation of Metal Amide  $Li + (x+y) NH_3 \rightarrow [Li^+ NH_3^x] + [e^- (NH_3)_y]$

### ANOMALOUS BEHAVIOUR OF Li

Li is similar in its behaviour towards Mg - due to diagonal relationship

(1) Lithium reacts with  $N_2$  to form nitrides like Mg

$6Li + N_2 \rightarrow 2Li_3N$  /  $3Mg + N_2 \rightarrow Mg_3N_2$

(2)  $Li_2CO_3$ , LiOH ,  $LiNO_3$  decompose to give  $Li_2O$ . Other members of the group are stable.

$2LiOH$  on heating  $\Delta \rightarrow Li_2O + H_2O$

(3)  $Li_2CO_3$ , LiOH, LiF are much less soluble in water than the corresponding Na or K compounds due to its covalent character. That is, they are similar to Mg compounds.

(4) Polarising power :  $Li^{2+}$  ion has the highest polarising power. Therefore

Its tendency for covalent bond formation and solvation increases .

Li compounds are more soluble in organic solvents (Covalent Character)

(5) It is harder and lighter than other alkali metals.

(6) Flame colour

Li -Lilac, Na - golden yellow, K - violet

(7)  $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$  [ $LiNO_3$  decomposes on heating]

### GROUP -2: ALKALINE EARTH METALS

Be	Mg	Ca	Sr	Ba	Ra
4	12	20	38	56	88

e.g. Mg =  $1s^2, 2s^2, 2p^6, 3s^2$

General electronic configuration of the outer orbit =  $ns^2$

Like alkali metals they also predominantly form ionic compounds.

Be is slightly covalent in nature due to the small size of the atom therefore the polarising power is high.

Be resembles Al due to diagonal relationships

## CHEMICAL PROPERTIES

Oxidation state =  $M^{2+}$ ,  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$

Except Be- all other members are strong reducing agents that is obvious from their standard reduction potentials. The reducing character increases down the group. Due to their higher ionisation potential they are less reducing than group 1 elements.

SOLUBILITY OF SALTS. Eg:  $M(OH)_2$ ,  $M SO_4$ ,  $MCO_3$  etc.\_

Hydroxides, Sulphates and Carbonates. Their solubility is influenced by (1)Lattice Energy and  
(2)Hydration energy

## LATTICE ENERGY $\Delta H_u$

It is the enthalpy change accompanying the formation of one mole of ionic solid from its constituent gaseous +ve and - ve ions.

eg.  $Na^+ + Cl^- \rightarrow NaCl(s)$   $\Delta H_u = -776KJ/mol$ .

## HYDRATION ENERGY:

It is defined as the enthalpy change accompanying the change of 1 mole of ions of an anhydrous salt into hydrated ions.

$Na^+ + Cl^- \rightarrow Na^+(aq) + Cl^-(aq)$ :  $\Delta H = -772KJ/mol$

Hydration and Lattice energy decreases with increase in ionic size. A compound will dissolve in a solvent only if free energy change ( $\Delta G$ ) accompanying the dissolution process is -ve

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

**Fajans Rule:** Smaller the size of the Cation Higher is the polarising power and larger the size of the Anion larger is the polarisability.

## ENTHALPY OF SOLUTION

( $\Delta H_{sol}$ ) is defined as the enthalpy change when one mole of a solute is dissolved in an excess of solvent, so that on further dilution there is no enthalpy change.

$NaCl(s) + Water(aq) \rightarrow Na^+(aq) + Cl^-(aq)$ ;  $\Delta H = +4 KJ/mol$ .

## Condition for solubility of ionic compounds in water:

Dissolution of a salt in water takes place when hydration energy is greater than the lattice energy of the ionic salt.

## OXIDES

e.g  $BeO$ ,  $MgO$ ,  $CaO$  Are obtained by burning these respective metals in oxygen

Examples of peroxides are  $SrO_2$ , and  $BaO_2$

Reactivity of the metals of the group towards oxygen increases down a group.

## HYDROXIDES

Solubility of hydroxides increases down a group. They are less basic than alkali metal hydroxides.

$Be(OH)_2$  is an amphoteric oxide and Basicity increases down a group.\*

## REACTIVITY TOWARDS WATER

Be does not react with water. Mg-reacts with hot water. Ca, Sr, Ba, reacts in the cold with water.\*

## SOLUBILITY OF SULPHATES AND CARBONATES

They decrease down a group.  $BeSO_4$  and  $MgSO_4$  are highly soluble in water due to the small size of the Cation.  $BaSO_4$  is insoluble in water.

**REASON:** The size of the cation is much smaller than anion  $CO_3^{2-}$ , and  $SO_4^{2-}$ . Lattice energy remains constant and solubility depends on hydration.

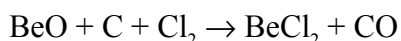
Hydration decreases down a group due to the increase in the size of the Cation.

The carbonates are not stable to heat;

eg.  $CaCO_3 \rightarrow CaO + O_2$ ;  $BeCO_3$  is highly unstable, therefore it is stored in an atmosphere of  $CO_2$ .

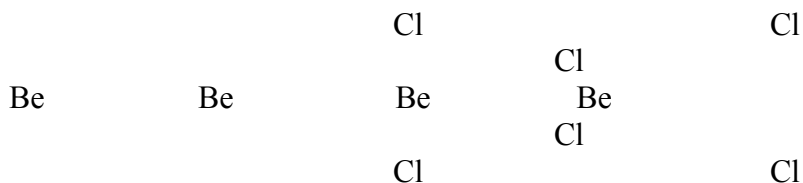
## ALKALINE EARTH HALIDES $\text{MX}_2$ .

They are formed by direct combination of metals with halogen.  $\text{BeCl}_2$  is prepared by heating its oxide with Carbon and Chlorine.

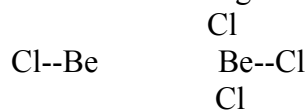


$\text{BeCl}_2$  has got a covalent character due to its small size and high polarisability of the cation and therefore it is soluble in organic solvents (Covalent solvents like dissolves in like). Melting point is lower than other halides.

It has a chain structure in the solid state.



In the vapour state it exists as a dimer and has a bridge structure.



This dissociates at 1200K to  $\text{BeCl}_2$  monomer (Cl-Be-Cl)

The halides from hydrated crystals eg.  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{BeCl}_2 \cdot 2\text{H}_2\text{O}$ . The fluorides are less soluble due to high lattice energy.

### SIMILARITY BETWEEN Be AND Al

Due to diagonal relationship

	Be	Al
(a) Charge on ion	+2	+3
(b) Ionic Radius $\text{Å}^0$	.31	.50
(c) Charge/Radius	$2/.31=6.4$	$3/.5=6.0$

Since Charge / radius ratio is a measure of deforming power. The deforming power of both  $\text{Be}^{2+}$  and  $\text{Al}^{3+}$  are same hence the similarity in behaviour.

1. Al & Be are not attacked by acids- due to oxide film.

2.  $\text{Be}^{2+}$  dissolves in alkalis to form  $[\text{Be}(\text{OH})_4]^{2-}$

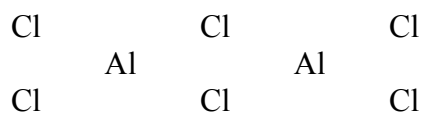


3. Oxides  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$  are hard high melting insoluble solids. The oxides as well as hydroxides are amphoteric and dissolve in NaOH.

4. Be forms complex  $\text{BeF}_4^-$ ; Al forms  $\text{AlF}_6^{3-}$  in solution.

5.  $\text{BeCl}_2$  is covalent and has bridged structure.

$\text{AlCl}_3$  is covalent forming a bridged dimer  $\text{Al}_2\text{Cl}_6$



They have a tendency to form complexes .e.g Mg, the metal present in chlorophyll.

## FLAME COLOURATION

Halides of alkali metal impart characteristic colour to flame.

Ca- Brick Red ; Sr - Crimson , Ba - Green

## GROUP - 13 ELEMENTS: BORON FAMILY

B	Al	Ga	In	Tl
5	13	31	49	81

$Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

*Oxidation States* = +3, +1 = [ ]  $ns^2 np^6$  (B  $\rightarrow$  B<sup>+3</sup>)

Metallic character steadily increases from boron to thallium. Boron exhibits diagonal relationship.

### CHEMICAL PROPERTIES

First three I.P of boron is high. It shows covalent character [Fajan's rule] - Boron forms electron deficient compounds.  $1s^2 2s^2 2p^1$ . They are good Lewis acids. [smaller the size of the cation, greater is the tendency towards covalence- Fajan's rule ]

### OXIDATION STATES OF Al

#### IN AQUEOUS SOLUTION:

The compounds of Al from Al<sup>3+</sup> ions in aqueous solution because the hydration energy available from its aqueous solution is greater than the third Ionisation Potential.

#### IN SOLID STATE

Al does not exist as Al<sup>3+</sup> ions in its compounds due to the high I.P

In gaseous state Al compounds are covalent due to small size and high charge.

### STABILITY OF OXIDATION STATE

Gallium, Indium, Thallium shows Oxidation state of +1 and +3.

The stability of +I oxidation state increases down a group. The oxidation state of +1 is due to **Inert pair effect**. This is the tendency of the  $ns^2$  electron pair not to take part in reaction since it gives a stable electronic configuration. **In Tl- +I is more stable than +3.**

### HYDRIDES

Boron forms boranes. [general formula -  $B_n H_{n+4}$  ]

Compounds with general formula  $B_n H_{n+4}$  are called Hydroboranes.

eg. Borane  $BH_3$ , Diborane =  $B_2H_6$

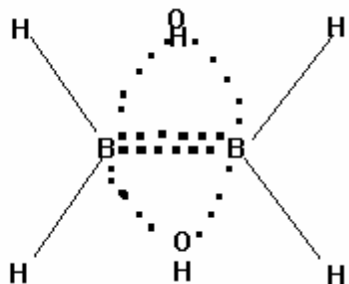
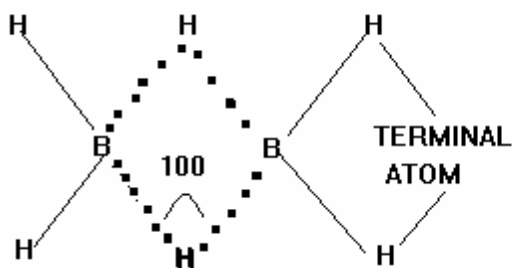
Preparation  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

Large scale Preparation -  $6LiH(s) + 2BF_3(g) \rightarrow B_2H_6(g) + 6LiF(s)$

These compounds are electron deficient species.

#### BONDING IN DIBORANES

#### THE HYDROGEN BRIDGE



The other elements of the group do not form stable hydrides.

ATOMIC RADIUS: They do not show a regular trend.

The order of Atomic radii in pico meter (pm)

B(85) < Al(143) > Ga(135) < In(167) < Tl(170)

Al > B - Because greater no of shells than B.

Al > Ga - Presence of d - orbitals- The effective nuclear charge increases- The screening effect is not effective since the d - orbital is larger. Therefore the atomic radius of Ga is < Al.

Ga > In > Tl - Regular increase - Normal screening effect.

IONISATION POTENTIAL

The order of First ionisation energies in kJ/gm atom down the group is as given below:

B(800) > Al(577) < Ga(578) > In(558) < Tl(590)

Reason:

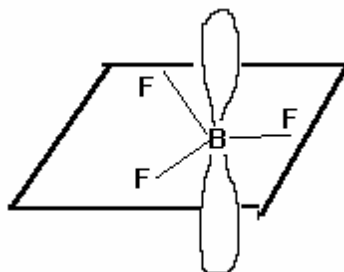
The I.E of B > Al as expected due to large size and greater screening effect than effective nuclear charge of Al than boron. In going from Al to Ga there are ten first transition series elements. In these elements the d subshell is being filled. These intervening d electrons do not screen the nuclear charge effectively. The effective nuclear charge becomes greater in Ga than Al. Hence IE of Al is less than Ga. The further trend can be similarly explained on the basis of effective nuclear charge and screening effect.

METALLIC NATURE.

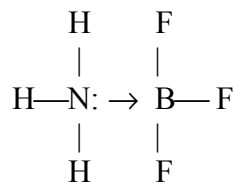
Electropositive character increases from boron to aluminium and then decreases from Aluminium to thallium.

HALIDES: BCl<sub>3</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>

B in BCl<sub>3</sub> & BF<sub>3</sub> is sp<sup>2</sup> hybridised with a vacant p orbital. Therefore they act as Lewis acids, they form NH<sub>3</sub> → BF<sub>3</sub>. Therefore they form Coordinate compounds.

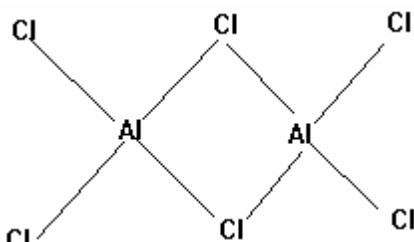


All the other elements form trihalides and are known, except Tl(III). Tl has a stable +I oxidation state



AlCl<sub>3</sub>: It is a Lewis acid because it is an electron deficient species.

Al halides (except AlF<sub>3</sub>) are covalent in aqueous solution, but they can form Al<sup>3+</sup> ions in aqueous solutions.



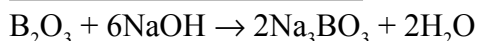
$\text{AlCl}_3$  exists as a dimer in  $\text{Al}_2\text{Cl}_6$ .

Boron halides do not form dimers because of the small size of boron.

OXIDES AND HYDROXIDES-general formula -  $\text{M}_2\text{O}_3$  &  $\text{M}(\text{OH})_3$

Acid character decreases down a group and basic character increases down a group, because of the decrease in I.P and electronegativity.

REACTIONS OF OXIDES



$\text{B}_2\text{O}_3$  = Boric oxide is an acidic oxide which is also a good dehydrating agent



Boric oxide reacts with water to form  $\text{H}_3\text{BO}_3$  or  $(\text{B}(\text{OH})_3)$  ortho boric acid which is soluble in water. where as  $\text{Al}(\text{OH})_3$  is a gelatinous precipitate.  $\text{B}(\text{OH})_3$  acts as a Lewis acid by forming  $[\text{B}(\text{OH})_4]^- + \text{H}^+$  and dissolves in water easily.

SIMILARITIES BETWEEN BORON AND SILICON (diagonal relationship)

- 1) Both elemental B and Si are semi conductors. Al is metallic .
- 2)  $\text{B}_2\text{O}_3$  and  $\text{SiO}_2$  are acidic- borates and silicates( $\text{BO}_4$  and  $\text{SiO}_4$ ) have a tetrahedral structure. However  $\text{BO}_3$  can form planar structure.
- 3) Boron halides like Si-halides are readily hydrolysed by water. Al halides are only partially hydrolysed.
- 4) Boron form compounds with metals called borides and silicon forms silicides.
- 5) Boron and Silicon form numerous volatile hydrides and spontaneously catch fire on exposure to air and are easily hydrolysed.

#### GROUP - 14 : CARBON FAMILY.

C	Si	Ge	Sn	Pb
6	14	32	50	82
Non-metals		Metalloid	Metals	

Oxidation states (+II) & (+IV)

( ) Uncommon Oxidation States.

C	Si	Ge	Sn	Pb
+4 (+2)	+4 (+2)	+2, +4	+2, +4	+2, (+4)
$\text{CH}_4$	$\text{SiH}_4$	$\text{GeF}_4, \text{GeF}_2$	$\text{SnCl}_2, \text{SnCl}_4$	$\text{PbCl}_2$ stable. * $\text{PbF}_4, \text{PbCl}_4,$ $\text{Pb}(\text{C}_2\text{H}_5)_4$

\*The tetravalent compounds of lead are less stable.

INERT PAIR EFFECT

The inert pair effect is prominent in the heavier element. Therefore +2 state is quite stable.

## CATENATION

It is the ability of like atoms to form covalent bonds with one another. Also referred to as the self linking property of an element.

### CONDITIONS FOR CATENATION

- 1) The valence must be 2 or greater than 2.
- 2) The element must form strong covalent bonds between its own atoms as compared to the bond with another atom especially oxygen.

In carbon we can see



The tendency of catenation decrease in the order  $C > Si > Ge > Sn \approx Pb$ .

### ALLOTROPY

Carbon exhibits allotropy examples of the Allotropes are Graphite, Diamond, Fullerene, Carbon Black, Coal

The properties of Graphite viz. Conduction of electricity, Usage as a lubricant etc. Can be explained on the basis of its structure The C atom under goes  $SP^2$  hybridisation  $\therefore$  in graphite there is  $p\pi - p\pi$  bonding.

In diamond the carbon atom undergoes  $SP^3$  hybridisation and the 4 valences of the C atom are satisfied by 4 other C atoms which are tetrahedrally linked to each other and forms a 3 dimensional network covalent bond.

HYDRIDES: Except Pb all other elements form hydrides of the formula  $MH_4$ . Their stability decreases down the group. Carbon forms Hydrocarbons, Silicon forms Silanes, and Germanium forms Germanes.

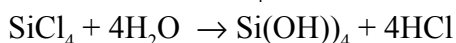
Preparation of ultra pure Silicon:

$SiH_4$  Pyrolysis  $\rightarrow Si + 2H_2$ . The silicon thus obtained is further purifies by zone refining.

HALIDES:

$MX_4$  - Tetrahedral and covalent.

The chlorides except  $CCl_4$  are hydrolysed by water



$PbBr_4$  and  $PbCl_4$  are unstable but  $PbI_4$  is not known

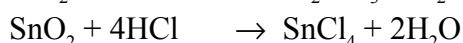
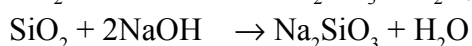
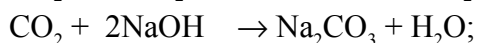
Oxides

They form monoxides  $MO$  and dioxides  $MO_2$ .  $CO$  is a gas at room temperature and forms a number of coordination compounds or organometallic compounds

e.g.  $Ni(CO)_4$ ;  $Fe(CO)_5$  and  $Cr(CO)_6$  in these compounds it is bonded to transition metals.  $CO$  is neutral while other oxides are basic. Silicon does not form monoxide.

Dioxide  $MO_2$

$CO_2$  and  $SiO_2$  are acidic while  $GeO_2$  and  $SnO_2$  and  $PbO_2$  are amphoteric.  $PbO_2$  is a powerful oxidant.

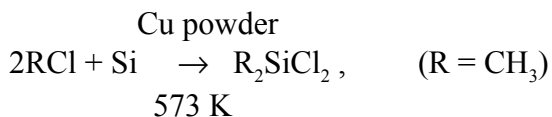


Why is  $SiO_2$  is a solid where as  $CO_2$  is a gas ?

## SILICATES AND SILICONES

Silicones are organosilicon compounds containing Si-O-Si linkages called silicones. These have high thermal stability for Si-O-Si chains and are also called high temp. polymers. Since it contains a ketone group, it is called silicone. General formula  $(R_2SiO)_x$  where  $R = CH_3; C_2H_5; C_6H_5$

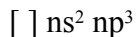
## METHODS OF PREPARATION



## GROUP 15 ELEMENTS - NITROGEN FAMILY

N	P	As	Sb	Bi
7	15	33	51	83

General electronic configuration



N and P forms covalent compounds - They can also form phosphide( $\text{Na}_3\text{P}$ ) and nitride( $\text{Li}_3\text{N}$ ) by accepting 3 electrons

The covalent character decreases in the order  $\text{P} > \text{As} > \text{Sb} > \text{Bi}$ .

Nitrogen exists as  $\text{N}(\text{triple bond})\text{N}$ . P, As and Sb form tetrahedral molecules in the elemental state.

Why is trimethyl amine pyramidal while tri amine is planar.

$(\text{CH}_3)_3\text{N}$ :

HYDRIDES PREPARATION:-



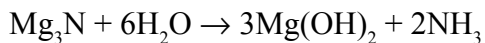
$\text{NH}_3$ -Ammonia,  $\text{PH}_3$ -Phosphine,  $\text{AsH}_3$ -Arsine,  $\text{SbH}_3$ -Stibine,  $\text{BiH}_3$ -Bismuthine



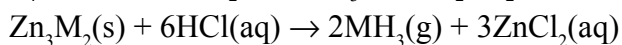
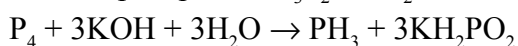
$\text{N}_2\text{H}_4$ -Hydrazine;  $\text{P}_2\text{H}_4$ -Diphosphine.

$\text{As}_2\text{H}_4$ -Diarsine;  $\text{Sb}_2\text{H}_4$ -Distibine.

METHODS OF PREPARATION:-



calcium phosphide  $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$ -Phosphine



where  $\text{M} = \text{As}, \text{Sb}, \text{Bi}$

HYDRAZINE PREPARATION



It is a strong reducing agent and its derivatives are used as rocket fuel [ $\text{NaOCl}$ = sodium oxychloride].

HALIDES:  $\text{MX}_3$ ;  $\text{MX}_3$                        $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{F}$

$\text{MX}_3$  SERIES:

$\text{NF}_3$	$\text{NCl}_3$	$\text{NBr}_3$	
$\text{PF}_3$	$\text{PCl}_3$	$\text{PBr}_3$	$\text{PI}_3$
$\text{AsF}_3$	$\text{AsCl}_3$	$\text{AsBr}_3$	$\text{AsI}_3$
$\text{SbF}_3$	$\text{SbCl}_3$	$\text{SbBr}_3$	$\text{SbI}_3$
$\text{BiF}_3$	$\text{BiCl}_3$	$\text{BiBr}_3$	$\text{BiI}_3$

**MX5 SERIES:**

PF <sub>5</sub>	PCl <sub>5</sub>	PBr <sub>5</sub>	PI <sub>5</sub>
AsF <sub>5</sub>	AsCl <sub>5</sub>		
SbF <sub>5</sub>	SbCl <sub>5</sub>		
BiF <sub>5</sub>			

Nitrogen does not form NCl<sub>5</sub>, NF<sub>5</sub> etc. since it does not contain 'd' orbitals.

Penta halides of group 15 elements are fewer in number as compared to trihalides- PCl<sub>5</sub> is used as an intermediate for many phosphorous compounds. It has a trigonal bipyramidal structure- sp<sup>3</sup>d hybridisation. In solid state PCl<sub>5</sub> exists as ionic [PCl<sub>4</sub>]<sup>+</sup>, [PCl<sub>6</sub>]<sup>-</sup>- [PCl<sub>4</sub>]<sup>+</sup> is tetrahedral, [PCl<sub>6</sub>]<sup>-</sup> is octahedral.

PCl<sub>3</sub> acts as a Lewis acid and base.



OXIDES:

	N	P	As	Sb	Bi
+1					
+2					
+3	N <sub>2</sub> O <sub>3</sub>	P <sub>4</sub> O <sub>6</sub>	As <sub>4</sub> O <sub>6</sub>	Sb <sub>4</sub> O <sub>6</sub>	Bi <sub>2</sub> O <sub>3</sub>
+4	N <sub>2</sub> O <sub>4</sub>	P <sub>4</sub> O <sub>8</sub>			
+5	N <sub>2</sub> O <sub>5</sub>	P <sub>4</sub> O <sub>10</sub>	As <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>5</sub>	
+6 (NO <sub>3</sub> ) <sub>2</sub>	N <sub>2</sub> O <sub>6</sub>	VERY STABLE			

Structures of acids to be given here.

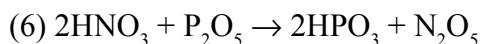
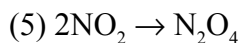
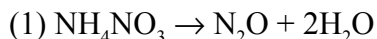
Phosphorous forms Phosphorous trioxide P<sub>4</sub>O<sub>6</sub> and Phosphorous pentoxide P<sub>4</sub>O<sub>10</sub>

Phosphorus does not enter into pπ - pπ bonds as in nitrogen dioxide



Structure of above Compounds.

#### METHODS OF PREPARATION OF OXIDES OF NITROGEN



OXO ACIDS OF:-

NITROGEN	OXID.STATE	REMARK
Hydronitrous acid-H <sub>2</sub> NO <sub>2</sub>	+1	Weak
Nitroxyl acid - H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	+2	Explosive
Nitrous acid - HNO <sub>2</sub>	+3	Weak, unstable
Nitric acid - HNO <sub>3</sub>	+5	Strong, stable
Peroxynteric acid HNO <sub>4</sub>	+7	Unstable, explosive

PHOSPHOROUS	OXID.STATE	REMARK
HypoPhosphorous acid-H <sub>3</sub> PO <sub>2</sub>	+1	Monobasic S.R.A.
Phosphorous acid - H <sub>3</sub> PO <sub>3</sub>	+3	Dibasic .R.A
Orthophosphoric acid-H <sub>3</sub> PO <sub>4</sub>	+5	Tribasic not R,A
Metaphosphoric acid - HPO <sub>3</sub>	+5	Monobasic
Hypophosphoric acid -H <sub>4</sub> P <sub>2</sub> O <sub>6</sub>	+4	Tetrabasic
Pyrophosphoric acid-H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	+4	Tetrabasic

### GROUP-16 : OXYGEN FAMILY

O	S	Se	Te	PO
8	16	34	52	84

Electronic configuration of S is 1s<sup>2</sup>,2s<sup>2</sup>,2p<sup>6</sup>,3s<sup>2</sup>,3p<sup>4</sup>;

General electronic configuration [ ] ns<sup>2</sup> np<sup>4</sup>

The first four elements are called Chalcogens meaning ore forming. Oxygen is the most electronegative element of the group (3.5) and smallest in size. Therefore it shows difference in properties from other elements of the group. It resembles N & F. It can form pπ - pπ bonds and hydrogen bonds.

OXIDATION STATES:-

-ve oxidation state when electrons are gained

+ve oxidation state when electrons are lost.

O	S	Se	Te	Po
+II, (-I)	-II +IV,+VI	(-II,+II) +IV, +VI	+II,+IV +VI	(+II,+IV)

( ) less common

Oxygen can show + ve oxidation state only with fluorine since F has electronegativity of 4 > 3.5 of oxygen.

In O<sub>2</sub>F<sub>2</sub> O = +1,

In OF<sub>2</sub> O = +2

In all other compounds the oxidation state is -2. Other elements show valency of + 4 and +6, since it contains vacant 'd' orbitals

### METALLIC CHARACTER:-

(1) O \_\_\_\_\_ S                      Se \_\_\_\_\_ Te                      Po  
non metallic                      semiconductor                      metallic

(2) Stability of hydrides  $H_2O > H_2S > H_2Se > H_2Te > H_2PO$

(3) Tendency for catenation decreases down a group.  
e.g of catenation Polysulphides =  $Sn_2$ , Sulphanes H-Sn-H,  
Polysulphuric acid  $HO_3S-Sn-SO_3H$ .

In allotropes Sn rings and chains are present.

(4) The tendency to form multiple bonds to C,N,O decreases as we descend down the group. Stability of these compounds  $S = C = S > Se = C = Se > Te = C = Te$  unknown.

### ALLOTROPY:

Oxygen has two forms  $O_2$  and  $O_3$  or Ozone

Allotropes of Sulphur:

$S_8$  sulphur exist as Rhombic, Monoclinic, Plastic and Colloidal Sulphur.

$Se_8$  Selenium = Rhombic, Monoclinic, & Grey the most stable.

### HYDRIDES:

All elements form hydrides e.g  $H_2X$  [ $X = O, S, Se, Te \& Po$ ]

The most stable is water the other hydrides have unstable odour and is poisonous. The hydrides are acidic and the order is  $H_2O < H_2S < H_2Se < H_2Te$

### HALIDES:-

e.g  $S_2X_2$                       ( $X = F, Cl, Br, I$ )                       $SX_4$                       ( $X = F, Cl$ )  
 $SX_6$  ( $X = F$ )

Se and Te form halides in the +1, +2 and +4 oxidation states.

$SF_4$  is prepared by flourinating  $SCl_2$  with NaF.

structure-  $sp^3d$ - is distorted, trigonal bipyramidal. One of the equatorial positions is occupied by a lone pair.

$SF_6$  is prepared by the combustion of S in a stream of Fluorine. The compound is stable and is used as an insulator in switch gears and high voltage generators.

Structure of the molecule is Octahedral since Sulphur undergoes  $SP^3d^2$  hybridisation.

### OXIDES:

ELEMENT	MONOXIDE	DIOXIDE	TRIOXIDE	HEPTOXIDE
S	SO	SO <sub>2</sub>	SO <sub>3</sub>	S <sub>2</sub> O <sub>7</sub>
Se	-	SeO <sub>2</sub>	SeO <sub>3</sub>	
Te	TeO	TeO <sub>2</sub>	TeO <sub>3</sub>	
Po	PoO	PoO <sub>2</sub>		

## STRUCTURE OF OXIDES

To be drawn.

### Oxo Acids of Group 16

SULPHUR	SELENIUM	TELLURIUM
Sulphurous Acid $H_2SO_3$	Selenous acid $H_2SeO_3$	Tellurous acid $H_2TeO_3$
Sulphuric Acid $H_2SO_4$	Selenic acid $H_2SeO_4$	Telluric acid $H_2TeO_4$
Permono Sulphuric acid $H_2SO_5$		
ThioSulphuric acid $H_2S_2O_3$		
Dithionic Acid $H_2S_2O_6$		
Di Sulphuric acid $H_2S_2O_7$		
Per di Sulphuric acid or Marshalls acid $H_2S_2O_8$		

KING OF CHEMICALS  $H_2SO_4$

Structures of Acids of Sulphur.

To be drawn.

## GROUP -17: HALOGENS

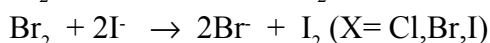
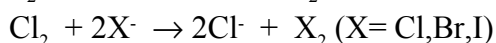
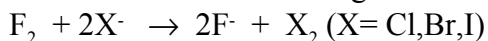
F	Cl	Br	I	Pt
9	17	35	53	85
-1	-1,+1,+3, +4,+5,+6,+7	+1,+2,+3 +4,+5,+6	-1,+1,+3 +5,+7	

Electronic configuration of Chlorine Z is 17  $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

General Electronic configuration.  $[ ] ns^2 np^5$

Halogens are very reactive electronegative elements:

Lower members oxidise higher members in a group.



The reduction potential values decrease down a group.

HALIDES: All elements form halides except He, Ne and Ar

IONIC CHARACTER:  $M-F > M-Cl > M-Br > M-I$

LOW I.P: Ionic compounds with high m.p and b.p e.g NaCl, NaF, NaBr, NaI

Elements with higher oxidation no are covalent.

e.g  $SnCl_4$ ,  $PbCl_4$ ,  $SbCl_4$ ,  $UF_6$  more covalent than  $SbCl_2$ ,  $SbCl_3$ ,  $PbCl_2$

Explanation of oxidation state of +1,+3,+5,+7 of Cl, Br, I

(\*DO BOXES\*)

+4 and +6 are seen in oxides

HALO ACIDS e.g The strength of the haloacids increase in the order

HF < HCl < HBr < HI.

I.P: Ionic compounds with high m.p and b.p

## OXIDES & OXO ACIDS

### OXIDATION STATE

Oxidation State	F	Cl	Br	I
+1	-	Cl <sub>2</sub> O	Br <sub>2</sub> O	-
+2	-	-	-	-
+3	-	Cl <sub>2</sub> O <sub>3</sub>	-	-
+4	-	ClO <sub>2</sub>	BrO <sub>2</sub>	I <sub>2</sub> O <sub>4</sub>
+5	-	-	-	I <sub>2</sub> O <sub>5</sub>
+6	-	Cl <sub>2</sub> O <sub>6</sub>	-	-
+7	-	Cl <sub>2</sub> O <sub>7</sub>	-	-

All oxides are powerful oxidising agents which explode on a shock or heat. ClO<sub>2</sub> and Cl<sub>2</sub>O used as bleaching agents.

$\bar{F}_2O_2$  and F<sub>2</sub>O are called oxygen fluorides, fluorine being more electronegative.

oxo acids of fluorine e.g. HOF hypofluorous acid.

$X_2 + H_2O \rightarrow HOX(\text{hypohalous acid}) + HX$

$Cl_2 + H_2O \rightarrow HOCl(\text{hypochlorous acid}) + HCl$

### STRUCTURE

#### FORMATION OF HALATES $XO_3^-$



hypohalate      halate

#### REACTION OF HALATES



halates                      halogen

Potassium Chlorate

e.g KClO<sub>3</sub> used in fire works and safety matches.

Perhalates MXO<sub>4</sub> e.g KClO<sub>4</sub> Potassium perchlorate

Per halates are strong oxidising agents.

#### INTER HALOGEN COMPOUNDS:-

The binary diamagnetic compounds made by direct combination of halogen elements among themselves under suitable conditions of temperature and pressure are called inter halogen compounds.

General formula is AX<sub>n</sub> A is an halogen atom less electronegative than X.

$$n = 1,3,5,7$$

The compounds are considered as halides of less electronegative halogen atom.

e.g ClF chlorine monofluoride

Cl(3) F(4) therefore F<sup>-</sup> ion is formed.

Most of the compounds are Fluorides except BrCl, ICl, IBr, ICl<sub>3</sub> the other interhalogen compounds are

ClF, ClF<sub>3</sub>, ClF<sub>5</sub>, BrF, BrF<sub>3</sub>, BrF<sub>5</sub>, IF, IF<sub>3</sub>, IF<sub>5</sub>

polyhalogen anion and action are(?)

General formula = xy<sub>2n</sub> n = 1,2,3,4 xy<sup>+2n</sup>

Molecular structures are explained using VSEPR.

XF<sub>3</sub>, XF<sub>5</sub>, IF<sub>5</sub>

#### GROUP - 18: NOBLE GASES

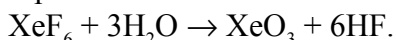
He	Ne	Ar	Kr	Xe	Rn
2	10	18	36	54	86

Generally they are very inert due to a stable electronic configuration viz. ns<sup>2</sup> np<sup>6</sup>

Only clathrate compounds were known of Ar, Kr, Xe. Niel Bartlett observed that the I.P of O<sub>2</sub> and Xe were close to that of each other i.e 1175 KJ/mol and 1170 KJ/mol and he could prepare Xe<sup>+</sup>[PtF<sub>6</sub>].

COMPOUNDS OF XENON: XeF<sub>2</sub>, XeF<sub>4</sub>, XeF<sub>6</sub>, XeO<sub>3</sub>, XeOF<sub>4</sub>

Preparation of Xenon fluorides:



STRUCTURE OF COMPOUNDS:

XeF<sub>2</sub> (Linear) XeF<sub>4</sub> (Square planar) XeO<sub>3</sub> (Trigonal pyramidal)

XeF<sub>6</sub>

XeOF<sub>4</sub>

Distorted

Square pyramidal

pentagonal bipyramidal

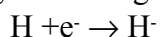
#### HYDROGEN

The first element has got some unique properties.

(1) Like alkali metals it loses an electron to form H<sup>+</sup> proton with 1S<sup>0</sup> as its electronic configuration.



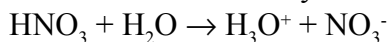
(2) Like halogens it can gain an electron to form H<sup>-</sup>(hydride ion) with He gas configuration 1s<sup>2</sup>.



It differs from alkali metal since it has high I.P of 1310 KJ/mole which is greater than that of Xe. Therefore compounds are covalent in character.

e.g. in C-H, HCl, H<sub>2</sub>S, NH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>.

H<sup>+</sup> ions are formed only when the solvent can solvate the proton.



Such compounds (e.g H<sub>2</sub>SO<sub>4</sub>, HCl) are known as protonic solvents.

H<sup>-</sup> ion is formed with elements with low I.P e.g NaH, or alkali earth metals