# <u>UNIT 7</u> <u>P-BLOCK ELEMENTS</u>

### Points to remember

The general valence shell electronic configuration of p-block elements ns<sup>2</sup>np<sup>1-6</sup>

### **GROUP 15 ELEMENTS**

Group15 elements: N, P, As, Sb &Bi

General electronic configuration: ns<sup>2</sup>np<sup>3</sup>

## **Physical Properties**

Dinitrogen is a diatomic gas while all others are solids.

N & P are non-metals. As & Sb metalloids &Bi is a metals. This is due to decrease in ionization enthalpy and increase in atomic size.

Electro negativity decreases down the group.

### **Chemical properties**

Common oxidation states: -3, +3 & +5.

Due to inert effect ,the stability of +5 state decreases down the group & stability of +3 state increases in the case of nitrogen oxidation states from +1 to +4 tend to disproportionate in acid solution,

e.g.:-3HNO<sub>3</sub>  $\longrightarrow$  H<sub>2</sub>O+ 2NO

An anomalous behavior of Nitrogen:- due to its small size, high electro negativity, high ionization enthalpy and absence of d-orbital.

 $N_2$ has unique ability to form  $p\pi$ - $p\pi$  multiple bonds where as the heavier of this group do not form  $p\pi$ - $p\pi$  because there atomic orbital are so large and diffuse that they cannot have effective overlapping.

Nitrogen exists as diatomic molecule with triple bond between the two atoms where as other Elements form single bonds in elemental state.

N cannot form  $d\pi$ -p $\pi$  due to the non availability of d-orbital where as other elements can.

#### **Trends in Properties**

| Stability-                  | NH <sub>3</sub> >PH <sub>3</sub> >AsH <sub>3</sub> >SbH <sub>3</sub> >BiH <sub>3</sub>         |
|-----------------------------|--|
| Bond dissociation enthalpy- | NH <sub>3</sub> >PH <sub>3</sub> >AsH <sub>3</sub> >SbH <sub>3</sub> >BiH <sub>3</sub>         |
| Reducing character -        | NH <sub>3</sub> < PH <sub>3</sub> <ash<sub>3<sbh<sub>3<bih<sub>3</bih<sub></sbh<sub></ash<sub> |
| Basic character-            | NH <sub>3</sub> >PH <sub>3</sub> >AsH3>SbH3>BiH <sub>3</sub>                                   |
| Acidic character-           | $N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3 > B_{i_2}O_3$   |

### **DINITROGEN**

### **PREPARATION**

- 1. Commercial preparation-By the liquefaction & fractional distillation of air.
- 2. Laboratory preparation- By treating an aqueous solution NH<sub>4</sub>Cl with sodium nitrite.

$$NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$$

3. Thermal decomposition of ammonium dichromate Also give N<sub>2</sub>.

$$(NH_4)_2Cr_2O_7$$
 heat  $N_2 \neq 4H_2O + Cr_2O_3$ 

4. Thermal decomposition of Barium or Sodium azide gives very pure  $N_2$ .

### **PROPERTIES**

At high temperature nitrogen combines with metals to form ionic nitride  $(Mg_3N_2)$  & with nonmetals, covalent nitride.

### **AMMONIA PREPARATION**

Ammonia is prepared in the laboratory by heating ammonium salt with NaOH or lime.

 $2NH_4Cl+Ca(OH)_2$   $2NH_3+2H_2O+CaCl_2$ 

In large scale it is manufactured by Haber' process

 $N_2+3H_2 \longrightarrow 2NH_3;$  $\Delta H^0 = -46.1 \text{ kJ/mol}$ 

According to Le chatelier's principle the favorable conditions for the manufacture of NH<sub>3</sub> are :-Optimum temperature: 700K High pressure: 200atm, Catalyst : Iron Oxides, Promoter : K<sub>2</sub>O &  $Al_2O_3$ 

### **PROPERTIES**

Ammonia is a colorless gas with pungent odour. Highly soluble in water.

In solids & liquid states it exists as an associated molecule due to hydrogen bonding which accounts for high melting & boiling points of NH<sub>3</sub>

NH<sub>3</sub> molecule is trigonal pyramidal shape. Aqueous solution of ammonia is weakly basic due to the

formation of OH<sup>-</sup> ion.

 $\longrightarrow$  Zn (OH)<sub>2</sub> + (NH4)<sub>2</sub>SO<sub>4</sub> ZnSO<sub>4</sub>+2NH<sub>4</sub>OH

Ammonia can form coordinate bonds by donating its lone on nitrogen, ammonia forms complexes.  $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]_2SO_4$ 

| Name                   | Formula  | Oxidation state | Chemical nature |
|------------------------|--|-----------------|-----------------|
| Nitrous oxide          | N2O  | +1              | Neutral         |
| Nitric oxide           | NO   | +2              | Neutral         |
| Dinitrogen trioxide    | N <sub>2</sub> O <sub>3</sub>                    | +3              | Acidic          |
| Dinitrogen tetra oxide | N <sub>2</sub> O <sub>4</sub> or NO <sub>2</sub> | +4              | Acidic          |
| Dinitrogen penta oxide | N <sub>2</sub> O <sub>5</sub>                    | +5              | Acidic          |

### NITRIC ACID

**PREPARATION**: Ostwald's process- it is based upon catalytic oxidation of ammonia by atmospheric oxidation. The main steps are

1)  $4NH_3+5O_2$  Pt as catalyst NO

2)  $2NO+O_2 \longrightarrow 2HNO_3+NO$ 

### **PROPERTIES:**

- I. Conc.HNO<sub>3</sub> is a strong oxidizing agent and attacks most metals gold &Pt.
- II. C r& Al do not dissolve HNO<sub>3</sub> because of the formation of a positive film of oxide on the surface.
- III. It oxidizes non metals like  $I_2$  to HIO<sub>3</sub>, C to CO<sub>2</sub>, S to  $H_2$ SO<sub>4</sub>
- IV. Brown ring test is used to detect  $NO_3^{-1}$ .

## **PHOSPHOROUS**

**ALLOTROPIC FORMS:**White/yellow, red and Black (α-black & β-black).

White phosphorous is more reactive red phosphorous because white P exists as discrete P<sub>4</sub>molecules.

In P several P4 molecules are linked to form polymeric chain.



# **PHOSPHINE**

Preparation: It is prepared in laboratory by heating white P with concentrated NaOH solution in an inert atmosphere of  $\rm CO_2$ 

 $[P_4+3NaOH+3H_2O \longrightarrow PH_3+3NaH_2PO_2]$ 

# PHOSPHOROUS HALIDES

Phosphorous forms two types of halides  $PX_3 \& PX_5 (X=F,I,Br)$ 

Trihalides have pyramidal shape and pentahalides have trigonal bipyramidal structure.

## **OXO ACIDS OF PHOSPHOROUS**

- 1. The acids in +3 oxidation state disproportionate to higher &lower oxidation.  $4H_3PO_3 \longrightarrow 3H_3PO_4+PH_3$
- 2. Acids which contains P-H bond have strong reducing properties. EX:-H<sub>3</sub>PO<sub>2</sub>
- 3. Are ionisable and cause the basicity.
- 4. Hydrogen atom which are attached with oxygen in P-OH form are ionisable

# **GROUP16 ELEMENTS (CHALCOGENS)**

Group 16 Elements: O, S, Se, Te, Po General electronic configuration: ns<sup>2</sup>np<sup>4</sup>

| Element | Occurrence   |
|---------|--|
| Sulphur | As sulphates such as gypsum CaSO4.2H2O, Epsom salt MgSO4.7H2O and    |
|         | sulphides such as galena PbS, zinc blende ZnS, copper pyrites CuFeS2 |
|         |  |

As metal selenides and telluride in sulphide ores.

Se & Te as a decay product of thorium and uranium minerals.

# ATOMIC & PHYSICAL PROPERTIES

- Ionization enthalpy decreases from oxygen to polonium.
- Oxygen atom has less negative electron gain enthalpy than S because of the compact nature of the oxygen atom. However from the S onwards the value again becomes less negative up to polonium.
- Electro negativity gradually decreases from oxygen to polonium, metallic character increases from oxygen to polonium.
- Oxygen & S are non-metals, selenium and tellurium are metalloids. Po is a radioactive metal.
- Oxygen is a diatomic gas while S, Se & Te are octaatomic S8, Se8 & Te8 molecules which has puckered' ring' structure.

# **CHEMICALPROPERTIES**

- Common oxidation state: --2,+2,+4 &+6.
- Due to inert effect, the stability of +6 decreases down the group and stability of +4 increases.

Oxygen exhibits +1 state in  $O_2F_2$ , +2 in  $OF_2$ .

Anomalous behavior of oxygen- due to its small size, high electro negativity and absence of d-orbital.

# TREND IN PROPERTIES

| Acidic character-              | H <sub>2</sub> O <h<sub>2S<h<sub>2Se<h<sub>2Te</h<sub></h<sub></h<sub> |
|--------------------------------|--|
| Thermal stability-             | H <sub>2</sub> O>H <sub>2</sub> S>H <sub>2</sub> Se>H <sub>2</sub> Te  |
| Reducing character-            | $H_2S < H_2Se < H_2Te$   |
| Boiling point-                 | H <sub>2</sub> S <h<sub>2Se<h<sub>2Te<h<sub>2O</h<sub></h<sub></h<sub> |
| Reducing property of dioxides- | SO <sub>2</sub> >SeO <sub>2</sub> >TeO <sub>2</sub>                    |
| Stability of halides-          | F>Cl>Br>I  |
|                                |  |

# <u>Halides</u>

Dihalides:  $sp^{3}hybridisation$  but angular structure. Tetra halides:  $sp^{3}hybridization$ -see-saw geometry Hexa halides:  $sp^{3}d^{2}$ , octahedral SF<sub>6</sub>

### DIOXYGEN

Prepared by heating oxygen containing salts like chlorates, nitrates

 $\longrightarrow$  2KCl+3O<sub>2</sub> KClO<sub>3</sub>  $2Fe^{3+}+SO_2+2H_2O \longrightarrow 2Fe^{2+}SO_4^{2-}+4H^+$ 

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

SO2 molecule is angular.

# **OXIDES**

A binary compound of oxygen with another element is called oxide. Oxides can be classified on the basis of nature

- Acidic Oxides:- Non metallic oxides. Aqueous solutions are acids. Neutralize bases to form salts. Ex: SO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> etc.
- Basic Oxides: metallic oxides. Aqueous solutions are alkalis. Neutralize acids to form salts. Ex: • Na<sub>2</sub>O, K<sub>2</sub>O, etc.
- Amphoteric oxides:- Some metallic oxides exhibit a dual behavior. Neutralize both acids & • bases to form salts.

Ex: Al<sub>2</sub>O<sub>3</sub>, SbO<sub>2</sub>, SnO etc

## **OZONE PREPARATION**

Prepared by subjecting cold, dry oxygen to silent electric discharge.

 $3O_2 = 2O_3$ at low temp only

## **PROPERTIES**

Due to the ease with which it liberates atoms of nascent oxygen, it acts as a powerful oxidizing agent. For eg: -it oxidizes lead sulphide to lead sulphate and iodide ions to iodine.

 $PbS+4O_3$  $\longrightarrow$  PbSO<sub>4</sub>+4O<sub>2</sub>

## **SULPHURDIOXIDE**

## PREPARATION

Burning of S in air  $S+O_2 \longrightarrow SO_2$ Roasting of sulphide minerals (Iron pyrites)  $4\text{FeS}_2+110_2 \longrightarrow 2\text{Fe}_2\text{O}_3+8\text{SO}_2$ (Zinc blende)  $2ZnS+3O_2 \longrightarrow 2ZnO+2SO_2$ 

### PROPERTIES

- Highly soluble in water to form solution of sulphurous acid  $SO_2+H_2O \longrightarrow H_2SO_3$
- SO<sub>2</sub> reacts with Cl<sub>2</sub> to form sulphuryl chloride  $SO_2+Cl_2 \longrightarrow SO_2Cl_2$
- It reacts with oxygen to form  $SO_3$  in presence of  $V_2O_5$  catalyst  $2SO_2+O_2 \longrightarrow 2SO_3$
- Moist SO<sub>2</sub> behaves as a reducing agent. It converts Fe(III) ions to Fe(II) ions & decolorizes acidified potassium permanganate(VII) solution (It is the test for the gas).

## **SULPHURIC ACID:**

# **PREPARATION**

It is manufactured by contact process which involves 3 steps

- 1. Burning of S or Sulphide ores in air to generate  $SO_2$ .
- 2. Conversion of SO<sub>2</sub>to SO<sub>3</sub> in presence of  $V_2O_5$  catalyst
- 3. Absorption of  $SO_3$  in  $H_2SO_4$  to give oleum.

# **PROPERTIES**

1. In aqueous solution it ionizes in 2 steps

 $H_2SO_4+H_2O$  $HSO_4^++H_2O$  $HSO_4^-+H_2O$  $H_3O^++SO_4^{-2}$ 

2. It is a strong dehydrating agent Eg :-charring action of sugar

 $C_{12}H_{22}O_{11} \xrightarrow{H SO}{2} 12C+11H_{2}O$ 

3. It is a moderately strong oxidizing agent.  $Cu+2H_2SO_4$  (conc.)  $\longrightarrow$   $CuSO_4+SO_2+2H_2O$  $C+2H_2SO_4$ (conc.)  $\longrightarrow$   $CO_2+2SO_2+2H_2O$ 

## GROUP17 ELEMENTS(HALOGENS)

Group17elements: F, Cl, Br, I, At General electronic configuration: ns<sup>2</sup>np<sup>5</sup>

| Element     | Occurrence  |
|-------------|---|
| Fluorine(F) | As in soluble fluorides (fluorspar CaF2, Cryolite and fluoroapattie)  |
| Cl, Br ,I   | Sea water contains chlorides, bromides and iodides of Sodium,<br>potassium magnesium and calcium, but is mainly sodium chloride<br>solution (2.5% by mass).<br>Certain form so f marine life(various sea weeds) |

# ATOMIC & PHYSICAL PROPERTIES

- i. Atomic & ionic radii increase from fluorine to iodine.
- ii. Ionization enthalpy gradually decreases from fluorine to iodine due to increase in atomic size.
- iii. Electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine & repulsion between newly added electron & electrons already present in its small 2 p orbital.
- iv. Electro negativity decreases from fluorine to iodine. Fluorine is the most electro negative element in the periodic table.
- v. The color of halogens is due to absorption of radiations invisible region which results in the excitation of outer electrons to higher energy level.
- vi. Bond dissociation enthalpy of fluorine is smaller than that of chlorine is due to electronelectron repulsion among the lone pair in fluorine molecules where they are much closer to each other than in case of chlorine. The trend: Cl-Cl>Br-Br>F-F>I-I.

# **CHEMICAL PROPERTIES**

**OXIDATION STATES**:-1.However, chlorine, bromine & iodine exhibit +1, +3, +5, +7 oxidation states also.

Fluorine forms two oxides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. These are essentially oxygen fluorides because of the higher electro negativity of fluorine than oxygen.

Anomalous behavior of fluorine-due to its small size, highest electro negativity, low F-F bond dissociation enthalpy and absence of d-orbitals.

# TRENDS IN PROPERTIES

Oxidizing property –  $F_2$ > $Cl_2$ > $Br_2$ > $I_2$ 

Acidic strength-HF<HCl<HBr<HI

Stability & bond dissociation enthalpy-HF>HCl>HBr>HI Stability of oxides of halogens-I>Cl>Br Ionic character of halides–MF>MCl>MBr>MI

# <u>CHLORINE</u>

# PREPARATION

- 1.  $MnO_2+4HCl \longrightarrow MnCl_2+Cl_2+H2O$
- 2. 4NaCl+MnO<sub>2</sub>+4H<sub>2</sub>SO<sub>4</sub>  $\longrightarrow$  MnCl<sub>2</sub>+4NaHSO<sub>4</sub>+2H<sub>2</sub>O+Cl<sub>2</sub>
- 3.  $2KMnO4+16HCl \longrightarrow 2KCl+2MnCl_2+8H_2O+5Cl_2$
- 4. DEACON'S PROCESS  $4HCl+O_2 \xrightarrow{CuCl_2} 2Cl_2+2H_2O$
- 5. By electrolysis of brine solution.  $Cl_2$  is obtained at a node.

# **PROPERTIES**

a) With cold and dilute alkalies Cl<sub>2</sub> produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies gives chloride and chlorate.
 2NaOH+Cl<sub>2</sub>(cold) \_\_\_\_\_ NaCl + NaOCl + H2O

6NaOH(hot) +3Cl<sub>2</sub> -5NaCl+NaClO<sub>3</sub>+3H<sub>2</sub>O

- b) With dry slaked lime it gives bleaching powder.  $2Ca(OH)_2+2Cl_2 \longrightarrow Ca(OCl)_2+CaCl_2+2H_2O$
- c) It is a powerful bleaching agent; bleaching action is due to oxidation Cl<sub>2</sub>+H<sub>2</sub>O → 2HCl+[O] Colored substance +[O] colorless substance
- d) Action of concentrated  $H_2SO_4$  on NaCl give HCl gas. NaCl + $H_2SO_4$  420K NaHSO<sub>4</sub>+HCl

3:1 ratio of conc. HCl & HNO<sub>3</sub> is known as aquaregia & it is used for dissolving noble metals like Au and Pt.

# **OXO ACIDS OF HALOGENS**



### Inter halogen

Inter halogen compounds are prepared by direct combination of halogens. Ex: CIF, CIF<sub>3</sub>, BrF<sub>5</sub>, IF<sub>7</sub> They are more reactive than halogens because X-X' is weaker than X-X bonds in halogens (except F-F).

| TYPE | STRUCTURE               |
|------|-------------------------|
| XX'3 | Bent T-shaped           |
| XX'5 | Square pyramidal        |
| XX'7 | Pentagonal bi pyramidal |

## **GROUP 18 ELEMENTS**

Group18 elements: He, Ne, Ar, Kr, Xe & Rn

General electronic configuration: ns<sup>2</sup>np<sup>6</sup>

Atomic radii- large as compared to other elements in the periods in ce it corresponds to Van der Waal radii.

Inert-due to complete octet of outer most shell, very high ionization enthalpy & electron gain enthalpies a real most zero.

The first noble compound prepared by Neil Bartlett was XePtF<sub>6</sub> & Xenon.  $O_2^+PtF_6^-$  leads to the discovery of XePtF<sub>6</sub> since first ionization enthalpy of molecular oxygen (1175kJmol<sup>-1</sup>) was almost identical with that of xenon (1170kJmol<sup>-1</sup>).

### **PROPERTIES**

 $Xe + F_{2} \xrightarrow{673 \text{ K, 1bar}} XeF_{2}$   $Xe + 2F_{2} \xrightarrow{873 \text{ K}} XeF_{4}$   $Xe + 3F_{2} \xrightarrow{573 \text{ K}} XeF_{6}$   $XeF_{4} + O_{2}F_{2} \longrightarrow XeF_{6} + O_{2}$   $XeF_{6} + MF \longrightarrow M^{+}[XeF_{7}]^{-}$   $XeF_{2} + PF_{5} \longrightarrow [XeF]^{+}[PF_{6}]^{-}$   $6 XeF_{4} + 12H_{2}O \longrightarrow 4Xe + 2XeO_{3} + 24HF + 3O_{2}$   $XeF_{6} + 3H_{2}O \longrightarrow XeO_{3} + 6HF$   $XeF_{6} + 2H_{2}O \longrightarrow XeO_{2}F_{2} + 4HF \text{ (partial hydrolysis)}$ 

## VERY SHORT ANSWER TYPE QUESTION (1 marks)

- 1. Nitrogen does not form pentahalide although it exhibit +5 oxidation state. Due to absence d-orbitals N can not extend its valency beyond four
- 2. NH<sub>3</sub>acts as Lewis base. Because N has a lone pair electron so NH3 acts as a Lewis base
- 3. **NH<sub>3</sub> is stronger base than PH<sub>3</sub>** Due to smaller size of nitrogen there is high electron density on nitrogen so electron pair is easily available.
- 4. All the five P-Cl bonds are not equal in PCl5. The two axial bonds suffer more repulsion from equatorial bonds and hence are elongated.
- 5. H3PO3 is dibasic (diprotic) but H3PO4 is tribasic. In H<sub>3</sub>PO<sub>3</sub>only two H atoms are linked to O which are ionisable the third H is attached to P and not ionisable because P is less electronegative. In H3PO4 all the three H atoms are with O and ionisable
- 6. PCl<sub>5</sub> is ionic in solid state

It is due to the following conversion:  $2PCl5 \square [PCl4]^{+}[PCl6]^{-1}$ 

- **7.** Nitrogen shows little catenation but phosphorous distinctly shows catenation property Due to smaller size of N there is repulsion between the lone pairs and N-N single bond is weaker than P-P
- 8. +5 oxidation state of Bi is less stable than +3 Because inert pair effect is very prominent in Bi , so +5 oxidation state is not stable
- 15 Bi in +5 oxidation state is strong oxidizing agent Because inert pair effect is very prominent in Bi so Bi<sup>5+</sup> can be easily converted into Bi<sup>3+</sup>
- 10.  $N_2$  is less reactive at room temperature

Due to having triple bond and hence high bond dissociation energy(946 kJ/mol

- 11. N exists as N2 and gas form but P exists as P4 and solid Due to smaller size N can form  $p\pi$ -d $\pi$  multiple bonding and exists as discrete N<sub>2</sub> molecule but P can not form  $p\pi$ -p $\pi$  multiple bonding.
- 12.  $H_2S$  is acidic while  $H_2O$  is neutral. H-S bond is weaker due to larger size of S so proton release easier in  $H_2S$
- Compound of F & O is fluoride of oxygen not oxide of fluorine . F is more electronegative than O.
- 14. SCl<sub>6</sub> is not known but SF<sub>6</sub> is knownF is strongest oxidizing agent so it can oxidizes S to its maximum oxidation state +6. Cl can not. Again Cl has larger size so steric repulsion is there in SCl6
- **15.**  $H_2O$  is liquid but  $H_2S$  is gas O is electronegative so there is intermolecular H-bonding in water so it is liquid.
- 16. O<sub>2</sub> is gas but sulphur is solid Due to smaller size O can form pπ-pπ multiple bond and exists as discrete diatomic molecule.
  17. Group 16 elements are called chalcogens
- 17. Group to elements are called chalcogens Chalcogen means ore forming elements. They form several ores 18. Halogens have maximum negative electron gain enthalpy( $\Delta_{eg}$ H)

Because they have smallest size in their respective periods

19. F has less electron gain enthalpy than that of Cl but fluorine is stronger oxidizing agent than chlorine.

F has very small size so there is inter-electronic repulsion. F is stronger oxidizing agent due to its low bond dissociation energy and high hydration energy

- **20.** F exhibits only -1 oxidation state, other halogen shows +1, +3, +5, +7 oxidation states F is most electronegative element and due to absence of d-orbitals it can not expand its octet so it does not exhibit positive oxidation state.
- 21. Bond dissociation energy of  $F_2$  is less than  $Cl_2$

Due to very small size of F there is interelectronic repulsion in  $F_2$  so it has low bond dissociation energy

22. HF has lower acid strength than HI

Due to larger size of I the H-I bond is weaker than H-F bond so HI is stronger

- **23. He, Ne do not form compound with F.** Due to high IE
- 24. Noble gases have very low b.pt

Because there is only weak dispersion force between their atoms.

- **25.** Ne used as warning signal Because Ne – light has high fog penetration power
- 26. Noble gases form compounds only with fluorine and oxygen Because F & O are the most electronegative elements
- **27. Out of noble gases only Xe forms compounds** Because Xe has comparatively low IE and vacant orbitals for promotion of electrons
- **28. Noble gases are mostly inert** Because they have completely filled valence orbitals i.e octet configuration
- **29. He is used as diving apparatus .** Because it is less soluble in blood with compare to nitrogen
- **30. It is difficult to study the chemistry of Rn.** Because Rn is radioactive and hence very unstable
- **31. Noble gases have comparatively large atomic size.** They are mono atomic so their van der Walls radii measured which is longer than covalent/ionic or metallic radii.

#### **32.** Complete and balance the following reaction:

- (i)  $NH_4Cl + NaOH \rightarrow 2NH_3 + 2H_2O + 2Na_2SO_4$
- (ii)  $2FeCl_3 + 3 NH_4OH \rightarrow Fe_2O_3 .xH_2O(s) + 3NH_4Cl$
- (iii)  $Cu+2(aq) +4NH_3 \rightarrow [Cu (NH3)_4]^{+2} (aq)$
- (iv)  $3Cu + dil. HNO_3 \rightarrow Cu (NO_3)_2 + 2NO + 4 H_2O$
- (v)  $Zn + dil. HNO_3 \rightarrow 4Zn (NO_3)_2 + NH_4(NO_3) + 3 H_2O$
- (vi) Zn + conc. HNO<sub>3</sub>  $\rightarrow$  Zn (NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> + 2 H<sub>2</sub>O
- (vii)  $XeF_6+3H_2O \rightarrow XeO_3+6HF$
- (viii)  $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$
- (ix)  $Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + Ca (OH)_2$
- (x)  $P_4 + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3$

## SHORT ANSWER TYPE QUESTION (2 marks)

## **1**. Bond angle in PH<sub>4</sub><sup>+</sup> is higher than that in PH<sub>3</sub>.Why?

**Sol:** Both  $PH_4^+$  and  $PH_3$  involve sp<sup>3</sup> hybridization of P atom. In  $PH_4^+$  all the four orbitals are bonded whereas in PH<sub>3</sub> there is a lone pair of electrons on P. In  $PH_4^+$  the HPH bond angle is tetrahedral angle of 109.5<sup>°</sup>. But in PH<sub>3</sub> the lone pair-bond pair repulsion is more than bond pair-bond pair repulsion so that bond angle becomes less than normal tetrahedral angle of 109.5<sup>°</sup>. The bond angle in PH<sub>3</sub> has been found to be 93.6<sup>°</sup>.

## 2. $H_2O$ is a liquid and $H_2S$ is a gas. Explain why.

**Sol:** In  $H_2O$  hydrogen is bonded to highly electronegative element oxygen. Therefore there is strong intermolecular H-bonding in water. As, a result molecules exist as associated water is a liquid at room temperature. Whereas in case of  $H_2S$  there is negligible hydrogen bonding because of low electro negativity of Sulphur. Hence,  $H_2S$  is a gas at room temperature.

## 3. Why is BiH<sub>3</sub> the strongest reducing agent among all the hydrides of group 15?

**Sol:** Among the hydride of group 15  $BiH_3$  is least stable because Bi has largest size in the group and has least tendency to form covalent bonds with small hydrogen atom. Therefore it can readily lost H atom and hence has strongest tendency to act as reducing agent.

### 4. Fluorine shows anomalous behavior among Halogens. Give instances.

**Sol:** (i) Since fluorine is the most electronegative element, it shows only a negative oxidation state of -1. It does not show any positive oxidation state. On the other hand, other Halogens show positive oxidation states also such as, +1, +3, +5, +6 and +7.

(ii) Maximum covalency of Fluorine is 1 because it cannot expand its valence shell. On the other hand, other elements can exercise covalencies up to 7 because of availability of vacant d-orbitals.

## 6. Why H<sub>2</sub>S is less acidic than H<sub>2</sub>Te?

**Sol:** In  $H_2Te$  the size of central Te is more than that of S in  $H_2S$  and therefore the distance between the central atom and the hydrogen atom in Te-H is more than that of S-H. As a result of large bond length, the bond disassociation enthalpy of Te-H is less than that of S-H and bond cleavage of  $H_2Te$  is easy. Hence,  $H_2Te$  is more acidic than  $H_2S$ .

## 7. What do you mean by Clathrates?

**Sol:** A compound formed by physical trapping of molecules of one substance in holes in the crystal lattice of another. Clathrates are produced by crystallizing a mixture of two substances. Quinol, for example, has holes in its lattice and can hold noble gases, oxygen methane, etc. Ice can form clathrate compounds with argon, krypton and xenon. In such compounds no chemical bond is formed between the host compound and the trapped molecule.

8. Fluorine does not undergo disproportionation reaction but other Halogens do. Why?

**Sol:** Disproportionation means simultaneous oxidation-reduction. Fluorine being most electronegative element undergoes only reduction but not oxidation As a result it only shows -1 oxidation state while other halogens show both negative (-1) and positive (+1,+3,+5,+7) oxidation states. Thus, Fluorine does not show disproportionation reaction while other halogens do.

### 9. Why interhalogens are more reactive than halogens?

**Sol:** This is because the bond in interhalogens (X-X') is weaker than (X-X). This is on account of lees effective overlapping between orbital of dissimilar atoms than those of similar atoms. Hence, the X-X' bond can be broken easily and therefore Interhalogens are more reactive than halogens.

### 10. Helium and Neon doesn't form compounds with fluorine as Xenon does. Why?

**Sol:** Helium and Neon does not contain d-orbital in their valence shell and hence their electrons cannot be promoted to higher energy levels like that in Xenon to form bonds. Therefore Helium and Neon does not form bond with fluorine whereas Xenon does.

## 11. Give reasons for inertness shown by the Noble gases.

**Sol:** (i) The noble gases have completely filled  $ns^2np^6$  electronic configuration in their valence shell. (ii) The noble gases have high ionization energy.

(iii) The electron affinities of noble gases are almost zero.

# Q12. Explain why ClF<sub>3</sub> exists whereas FCl<sub>3</sub> does not.

**Ans**. Electronic configuration of Cl is  $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$ . An electron from 3p can jump to 3d orbitals. So it can show an oxidation state of 3 and combine with the more electronegative fluorine. Electronic configuration of F is  $1s^2 2s^2 2p^2_x 2p_y^2 2p_z^1$ . No d-orbital is available for excitation of electron. Moreover it is most electronegative element. So it shows an oxidation state of -1 only.

### SHORT ANSWER QUESTIONS (3MARKS)

1. Arrange the following:

(i) F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>. Increasing bond disassociation enthalpy.

(ii) HF, HBr, HCl, HI. Increasing acid strength.

(iii) NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub>. Increasing base strength.

**Sol:** (i)  $I_2 < F_2 < Br_2 < Cl_2$ .

(ii) HF < HCl < HBr < HI.

(iii)  $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$ .

### 2. Draw the structure of followings and name the geometry

- 1. XeO<sub>3</sub>, PCl<sub>5</sub>
- 2. NH<sub>3</sub>, ClF<sub>3</sub>
- 3. H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>3</sub>PO<sub>4</sub>







### Q.3. Draw the structure of followings and name the geometry

- 1.  $H_3PO_3$ ,  $H_2SO_4$
- 2.  $XeOF_4$ ,  $N_2O_5$
- 3. XeF<sub>2</sub>, XeF<sub>4</sub>



H<sub>3</sub>PO<sub>3</sub> Orthophosphorous acid







0





### 4.Explain why (i) He is used in diving apparatus? (ii)Noble gases have very low boiling points.Why? (iii)Why is ICl moe reactive than I<sub>2</sub>?

Ans- (i)It is not soluble in blood even under high pressure. (ii)Being monoatomic they have weak dispersion forces.

(iii)I-Cl bond is weaker than l-l bond

5. Account for the following.

# (i) $SF_6$ is less reactive than.

(ii) of the noble gases only xenon chemical compounds.

# (iii) NO2 is coloured and readily dimerises

Ans- (i)In SF<sub>6</sub> there is less repulsion between F atoms than In SF<sub>4</sub>.

(ii)Xe has low ionisation enthalpy & high polarising power due to larger atomic size.
(iii) NO2 contains odd number of valence electrons. It behaves as a typical odd molecules On dimerization; it is converted to stable N<sub>2</sub>0<sub>4</sub> molecule with even number of electrons.

## 6. Complete the following equations.

(i)XeF4+H2O $\rightarrow$ (ii)Ca<sub>3</sub>P<sub>2</sub>+H<sub>2</sub>O $\rightarrow$ 

(iii)AgCl<sub>(s)</sub> +NH3 (aq) $\rightarrow$ 

Ans- (i)  $6XeF4+12H_2O \rightarrow 4Xe+2XeO_3+24HF+3O_2$ 

(ii)Ca<sub>2</sub>P<sub>2</sub>+6H<sub>2</sub>O $\rightarrow$ 3Ca (OH) <sub>2</sub>+2PH<sub>3</sub>

(iii)AgCl<sub>(s)</sub> +2NH<sub>3 (aq)</sub> $\rightarrow$ [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>(aq)</sub>

## 7. (i)How is XeOF4 prepared ?Draw its structure.

(ii)When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride ,Why?

Ans- (i)Partial hydrolysis of XeOF<sub>4</sub>

 $XeF_6+H_2O \rightarrow XeOF_4+2HF$ 

Structure-square pyramidal.

(ii) Its reaction with iron produces h2

 $Fe+2HCl \rightarrow FeCl_2+H_2$ 

Liberation of hydrogen prevents the formation of ferric chloride.

# LONG ANSWER TYPE QUESTION (5marks)

1. Account for the following.

(i)Noble gas form compounds with  $F_2$ &O<sub>2</sub> only.

(ii)Sulphur shows paramagnetic behavior.

(iii)HF is much less volatile than HCl.

(iv)White phosphorous is kept under water.

## (v)Ammonia is a stronger base than phosphine.

**Ans-** (i) $F_2$ &O<sub>2</sub> are best oxidizing agents.

(ii)In vapour state sulphur partly exists as  $S_2$  molecule which has two unpaired electrons in the antibonding pi \*orbitals like  $O_2$  and, hence, exhibit paramagnetism.

- (iii)HF is associated with intermolecular H bonding.
- (iv) Ignition temperature of white phosphorous is very low (303 K). Therefore on explosure to air, it spontaneously catches fire forming  $P_4O_{10}$ . Therefore to protect it from air, it is kept under water.
- (v)Due to the smaller size of N, lone pair of electrons is readily available.

2. Arrange the following in the increasing order of the property mentioned.
(i)HOCl, HClO<sub>2</sub>, HClO<sub>3</sub>, HClO<sub>4</sub> (Acidic strength)
(ii)As<sub>2</sub>O<sub>3</sub>, ClO<sub>2</sub>, GeO<sub>3</sub>, Ga2O3 (Acidity)
(iii)NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub> (HEH bond angle)
(iv)HF, HCl, HBr, HI (Acidic strength)
(v)MF, MCl, MBr, MI (ionic character)

Ans- (i)Acidic strength: HOCl<HClO<sub>2</sub><HClO<sub>3</sub><HClO<sub>4</sub> (ii)Acidity: Ga<sub>2</sub>O<sub>3</sub><GeO<sub>2</sub><AsO<sub>3</sub><ClO<sub>2</sub> (iii)Bond angle: SbH<sub>3</sub><AsH<sub>3</sub><PH<sub>3</sub><NH<sub>3</sub> (iv)Acidic strength: HF<HCl<HBr<HI (v)Ionic character: MI<MBr<MCl<MF

3. When Conc.  $H_2SO_4$  was added to an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were added in to test tube. On cooling gas (A) changed in to a colourless gas (B). (a)Identify the gases 'A' and 'B' (b)Write the equations for the reactions involved Ans- The gas 'A' is NO<sub>2</sub> whereas 'B' is N<sub>2</sub>O<sub>4</sub>. XNO<sub>3</sub> +  $H_2SO_4 \rightarrow XHSO_4 + HNO_3$ Salt (conc.) Cu + 4HNO<sub>3</sub> (Conc.)  $\rightarrow$ Cu (NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub> + 2H<sub>2</sub>O Blue Brown (A) 2NO<sub>2</sub> (on cooling)  $\rightarrow$ N<sub>2</sub>O<sub>4</sub> Colourless(B)

#### 4.Account for the following.

(i)Noble gas form compounds with  $F_2$ &O<sub>2</sub>only.

(ii)Sulphur shows paramagnetic behavior.

(iii)HF is much less volatile than HCl.

#### (iv)White phosphorous is kept under water.(v)Ammonia is a stronger base than phosphine.

Ans: (i)  $F_2$  O<sub>2</sub> are best oxidizing agents.

(ii)In vapour state sulphur partly exists as S<sub>2</sub>molecule which has two unpaired electrons in

the anti bonding  $pi^*\pi$  orbitals like O<sub>2</sub> and, hence, exhibit paramagnetism.

(iii)HF is associated with intermolecular H bonding.

(iv)Ignition temperature of white phosphorous is very low(303 K). Therefore on exposure to air, it spontaneously catches fire forming  $P_4O_{10}$ . Therefore to protect it from air, it is kept under water.

(v)Due to the smaller size of N, lone pair of electrons is readily available.

#### VALUE BASED QUESTIONS

1. Ammonium nitrate is used as a high nitrogen fertilizer in agriculture. It is also used in instant cold packs. It is mixed with fuel oil and used as explosive. Due to its various uses its production cannot be banned.

- (a) What are cold packs?
- (b) What steps Indian government has taken to avoid the misuse of ammonium nitrate by terrorists?
- (c) What values are needed by an individual while handling such chemicals?

Ans: (a) They contain ammonium nitrate and water . Endothermic reaction gives cooling effect and relieves pain

(b) Only authorized dealers can sell ammonium nitrate

(c)Proper knowledge about the properties of the chemicals, misuse should be avoided, Chemical should be used only for the welfare of mankind

2. In recent years, the excessive uses of some aerosol propellants and refrigerants have depleted the ozone layer.

(a)Name two chemicals which deplete the ozone layer in the stratosphere.

(b)What is the importance of ozone in the stratosphere?

(c)Suggest some measures for minimizing global warming.

Ans.(a) NO, CFC'S

(b)Prevents entry of harmful ultraviolet radiations in earth's atmosphere.

(c)Minimising the usage of CFC'S, fossil fuels etc.

3. Student accidently spills concentrated  $H_2SO_4$  on his hand. Before the teacher gets to know, his friend washed his hands with water and also with soap but the burning sensation on hand was still going on. The friend then rubs solid sodium bicarbonate on his hand and then washed with water; finally the burning sensation is relieved.

(i) Mention the values shown by student's friend.

(ii) Can you recommend any other substance available in the laboratory which can be used instead of sodium bicarbonate?

Ans.(i)Concern and care for others and application of scientific knowledge

(ii) Slaked lime

4.India's top court ruled that authorities must regulate the sale of acid used in a spate of attacks on women. An acid called "Tezaab", which is designed to clean rusted tools but is often used in the attacks, can currently be bought across the counter. But the judges said the buyer of such acids should in future have to provide a photo identity card to any retailer when they make a purchase. The retailers must register the name and address of the buyer.

- (a) Why are acid burns harmful?
- (b) What are the values associated with the above discussion?
- (c) What are responsibilities of the citizens in this regard?
- Ans(a) Stringent measures to prevent misuse of acid

(b)They are highly corrosive.

(c) Help in preventing such incidences and helping victims , bringing to the notice of authorities such incidences

5. In a paper industry hydrogen peroxide is used bleaching agent. Satish asked his friend about using chlorine as bleaching agent. His friend told that using hydrogen peroxide was better.

- (a) What is the disadvantage of using chlorine as bleaching agent?
- (b) Why is use of hydrogen peroxide better?
- Ans: (a) HCl is the bye product in case Cl is used as a bleaching agent
  - (b) Water is the bye product.