

**p-block elements:** Elements belonging to group 13 to 18 of the periodic table are called p-block elements. In p-block elements last incoming electron enters

p-orbitals.,

Group	→ 13	14	15	16	17	18	
						He	
	5	6	7	8	9	10	
	В	С	Ν	0	F	Ne	
	13	14	15	16	17	18	
	Al	Si	Р	S	Cl	Ar	
	31	32	33	34	35	36	
	Ga	Ge	As	Se	Br	Kr	
	49	50	51	52	53	54	
	In	Sn	Sb	Те	Ι	Xe	
	81	82	83	84	85	86	
	ΤI	Рb	Bi	Ро	At	Rn	

**Position :** Extreme Right of periodic table **General electronic configuration:** ns<sup>2</sup>np<sup>1-6</sup>

#### **Representative elements :**

Element belonging to the s and p-block in the P. T. are called p-block elements or main group element.

**Inert pair effect :** The tendency of ns<sup>2</sup> electrons to take part in bond formation decreases with increase in atomic size. It is called inert pair effect.

#### Anomalous behaviour :

The first element of each group shows more anomalous behaviour due to the following reasons.

- 1. Very small size
- 2. High I.E.
- 3. High electronegativity
- 4. Absence of d-orbitals

#### Exceptions:

Atomic Mass : Ar > K	
Effective nuclear charge :	Decreases from
group 17 to 18	
Electron affinity : F < Cl,	inert gases is zero
(+ve)	

**Ionisation energy :** N > O, In < TI, Sn < Pb. **Oxidising power :** Inert gases have zero oxidising power.

## GROUP –15

т

(N, P, As, Sb, Bi)

Allotropy : Shown by all elements except N common oxidation state : -3, +3, +5**Down the group:** Tendency to show – 3 decreases (due to increase in size and metallic character) Tendency to show + 5 decreases, + 3 increases (due to inert pair effect) N exhibits +1, +2, +4 (oxides of N) P exhibits +1, &+4 (in oxoacids) **Disproportionation Reaction.**  $3HNO_{2} \rightarrow HNO_{3} + 3NO + H_{2}O$  $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ **Maximum Covalency:** (due to absence of d-orbitals) N is 4. other elements - More than 4. N forms  $p\pi - p\pi$  bonds whereas other elements forms  $d\pi$ - $p\pi$  and  $d\pi$ - $d\pi$  eq.  $R_{2}P = O$ **Chemical properties Reaction with Hydrogen – Form hydrides** 

NH₃	ì	
$PH_3$		Stability decreases
AsH <sub>3</sub>		Basicity decreases
SbH <sub>3</sub>	Ŷ	Reducing character increases
BiH₃	В	



Reaction with Oxygen : Forms oxides E,O, and  $E_{2}O_{r}$  Oxides with higher oxidation states are more acidic than lower oxidation state.

E,0,  $N_2O_3$ ,  $P_2O_3$  – Acidic oxides As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub> – Amphoteric oxides

Structure of N<sub>2</sub>O<sub>5</sub>

Bi<sub>2</sub>O<sub>3</sub> – Basic oxides

Reaction with halogen : Form halides  $EX_3$  and  $EX_5$ N does not form pentahalides. Covalent nature of  $EX_{5} > EX_{3}$ All trihalides are stable except those of N (Only NF<sub>3</sub> is stable)

Reaction with metal : Form binary compounds showing - 3 oxidation state. Ca<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>P<sub>2</sub>, Na<sub>3</sub>As<sub>2</sub>, Zn<sub>3</sub>Sb<sub>2</sub>, Mg<sub>3</sub>Bi<sub>2</sub>

## DINITROGEN : $N_2$ ( $N \equiv N$ )

#### Preparation

1. Commercial Method : Liquifaction and fractional distillation of air.

Lab - Method : 2.

 $\rm NH_4Cl_{(aq)}$  +  $\rm NaNO_{2(aq)}$   $\rightarrow$   $\rm N_{2(g)}$  +  $\rm 2H_2O_{(/)}$  +  $\rm NaCl_{(aq)}$  NO and HNO\_3 are formed as impurity which are removed by passing the gas through aqueous H<sub>2</sub>SO<sub>4</sub> containing K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

Thermal decomposition of Ammonium 3. dichromate.

 $(NH_4)_2 Cr_2O_7 \xrightarrow{\Lambda} N_2 + 4H_2O + Cr_2O_3$ 

4. Thermal decomposition of azides of Ba & Na.  $Ba(N_3)_2 \rightarrow Ba + 3N_2$ 

 $2NaN_{3} \rightarrow 2Na + 3N_{2}$ 

#### **Properties of N**<sub>2</sub>

Colourless, odourless, tasteless. non-toxic 1. gas.

- Low solubility in H<sub>2</sub>O 2.
- It is inert due to high bond energy 3. 4.
  - At high T form nitrides

 $6Li + N_2 \longrightarrow 2Li_3N$ 

 $3Mg + N_2 \longrightarrow Mg_3N_2$ 

 $N_2 + 3H_3 \ge 2NH_3$  (Habers process) 5.

N<sub>2</sub> + O<sub>2</sub> 2000 K 2NO 6.

#### Uses of dinitrogen

Making NH<sub>3</sub> and calcium cyanamide 1.

2. Liquid nitrogen is used as refrigerant

**OXIDES OF NITROGEN** 

Oxides	Nature	Oxidation state	Preparation	Structure
N <sub>2</sub> O	Neutral	+1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$	N≡N – Ö:
NO	Neutral	+2	$2NaNO_{2} + 2FeSO_{4} + 3H_{2}SO_{4} \rightarrow Fe_{2}(SO_{4})_{3} + 2NaHSO_{4} + 2H_{2}O + 2NO_{4}O_{4} + 2H_{2}O + 2NO_{4}O_{4} + 2H_{2}O_{4} + 2H_$	N = O
NO <sub>2</sub>	Acidic	+4	$2Pb(NO_3)_2 \xrightarrow{673 \text{ K}} 4NO_2 + 2PbO$	N N
N <sub>2</sub> O <sub>3</sub>	Acidic	+3	$2NO + N_2O_4 \xrightarrow{250 \text{ K}} 2N_2O_3$	0 N - N 0
N <sub>2</sub> O <sub>4</sub>	Acidic	+4	$2NO_2 \xrightarrow{cool} N_2O_4$	0 N-N 0
N <sub>2</sub> O <sub>5</sub>	Acidic	+5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	



It oxidises non metals and their compounds. 6.  $I_2 + 10 \text{ HNO}_3 \longrightarrow 2 \text{HIO}_3 + 10 \text{ NO}_2 + 4 \text{ H}_2 \text{O}$ Iodic acid  $\begin{array}{cccc} C + & 4HNO_3 & \longrightarrow & CO_2 + & 4NO_2 + & 2H_2O\\ S_8 + & 48HNO_3 & \longrightarrow & 8H_2SO_4 + & 48NO_2 + & 16H_2O\\ P_4 + & 20HNO_3 & \longrightarrow & 4H_3PO_4 + & 20NO_2 + & 4H_2O \end{array}$ (conc.)

#### Brown ring test: For nitrates

The test is carried out by adding dil FeSO, solution to an aqueous solution containing nitrate ion and then carefully adding conc.  $H_2SO_4$  along the sides of the test tube. A brown ring at the interface b/ w the solution and  $H_2SO_4$  layers indicate the presence of nitrate ion. . ΝΩ <sup>-</sup> + 3Fe<sup>+2</sup> + 4H<sup>+</sup> → ΝΩ + 3Fe<sup>+3</sup> + 2H Ω

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$$
  
brown ring

#### Uses of nitric acid

- Making fertlizers (NH<sub>4</sub>NO<sub>3</sub>), explosives -1. nitroglycerin, TNT.
- As oxidiser in Rocket fuel. 2.

#### PHOSPHOROUS

Allotropic forms - White, Red and Black.

#### White Phosphorous:

- translucent, Poisonous white waxy solid. 1.
- 2. Insoluble in H<sub>2</sub>O
- Soluble in CS<sub>2</sub> 3.
- 4. Glows in dark (Chemilumenescence)
- More reactive, less stable (due to angular 5. strain in P<sub>4</sub> molecule where angles are only 60°
- 6. Catches fire in air.
- $P_4 + 5 O_2 \rightarrow P_4 O_{10}$ Dissolves in boiling NaOH to form phosphine 7.  $P_4$  + 3NaOH + 3H<sub>2</sub>O  $\rightarrow$  PH<sub>3</sub> + 3NaH<sub>2</sub>PO<sub>2</sub> (sodium hypophosphite)
- 8. Consiste of discrete tetrahedral  $P_{4}$  molecule.



#### **Red Phosphorous**

- 1. Iron grey lustre
- 2. Non poisonous
- 3. insoluble in H<sub>2</sub>O
- insoluble in CS 4.
- 5. Does not glow
- Less reactive 6.
- It is polymeric , consisting of chains of 7.  $P_4$  tetrahedral.



8. Red P is prepared by heating white P at 573 K in inert atmosphere.

Black Phosphorous : least reactive allotrope of P \*Two forms

#### (I) α-black Phosphorous

- formed when Red P is heated in sealed tube 1. at 803 K
- 2. It sublimes in air
- 3. have monoclinic or Rhombohedral crystals
- 4. Does not conduct electricity.

#### (II) β-black Phosphorous(Orthorhombic)

Prepared by heating white P at 473 K 1.



- 2. Does not oxidise upto 673 K
- 3. Good conductor of electricity like graphite

## PHOSPHINE (PH<sub>3</sub>)

#### Preparation

- $\begin{array}{c} \mathsf{Ca}_{3}\mathsf{P}_{2} + \mathsf{6H}_{2}\mathsf{O} \longrightarrow \mathsf{3Ca}(\mathsf{OH}_{2}) + \mathsf{2PH}_{3} \\ \mathsf{Ca}_{3}\mathsf{P}_{2} + \mathsf{6HCI} \longrightarrow \mathsf{3CaCI}_{2} + \mathsf{2PH}_{3} \end{array}$ 1.
- 2.
- 3. Lab Method  $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (white)
- $\begin{array}{c} \mathsf{PH}_{4}\mathsf{I} + \mathsf{KOH} \xrightarrow{} \mathsf{KI} + \mathsf{H}_{2}\mathsf{O} + \mathsf{PH}_{3} \\ \mathsf{4H}_{3}\mathsf{PO}_{3} \xrightarrow{} \mathsf{473}\,\mathsf{K} \xrightarrow{} \mathsf{3}\,\mathsf{H}_{3}\mathsf{PO}_{4} + \mathsf{PH}_{3}\,\uparrow \end{array}$ 4.
- 5.

#### Properties of PH,

- Colourless gas with rotten fish smell. 1.
- Highly poisonous 2.
- 3. Explodes in contact with traces of oxidising agents like HNO<sub>3</sub>, Cl<sub>2</sub>, Br<sub>2</sub> vapours.
- Slightly soluble in water. 4.
- 5. Weakly basic  $PH_3 + HBr \rightarrow PH_4Br$
- Solution of PH<sub>3</sub> in water decomposes in 6. presence of light giving red P and H<sub>2</sub> gas.
- 7.  $3 \text{ CuSO}_4 + 2\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$  $3 \text{ HgCl}_2 + 2\text{PH}_3 \rightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl}$



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(H<sub>3</sub>PO<sub>2</sub>) is a good reducering agent as it contais two P - H bonds. It reduces AgNO<sub>3</sub> to Ag,  $4 \text{ AgNO}_3 + 2 \text{H}_2\text{O} + \text{H}_3\text{PO}_2 \rightarrow 4 \text{Ag} + 4 \text{HNO}_3 \text{H}_3\text{PO}_4$ P-H bonds are non-ionisable to give H<sup>+</sup>. Only those H atoms which are attached with oxygen in P-OH are ionisable and cause basicity. GROUP –16 1. (CHALCOGENS) (O, S, Se, Te, Po) 2. Occurence: Oxvgen – Most abundant of all the elements 3. on earth 4. Sulphur – Gypsum CaSO<sub>4</sub>. 2H<sub>2</sub>O 5. Epsom salt MgSO<sub>4</sub>. 7H<sub>2</sub>O Baryte BaSO Zinc blende ZnS. Copper pyrite CuFeS, as H<sub>2</sub>S in volcanoes in eggs, onion, mustard, proteins, wool C etc. Se and Te - As metal selenides or tellurides in sulphide ores. C **Polonium** – Decay product of throium and uranium minerals. **Oxidation state:** oxygen exhibit ; -2 (In OF, +2 and in O,F, +1) other elements; +2, +4, +6Stability of +6 decreases down the group and +4 1. increases. (due to inert pair effect) 2. **Reaction with Hydrogen :** form hydrides  $H_{2}E(E = S, E)$ 3. Se, Te, Po) H<sub>2</sub>O , H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te 4. Acidic character increases H– E bond energy decreases Reducing property increases Thermal stability decreases Reaction with oxygen : form oxides EO<sub>2</sub> and EO<sub>3</sub>. (E = S, Se, Te, Po) both oxides are acidic in nature. from SO, to TeO, Reducing property decreases SO, is reducing while TeO, is an oxdising agent Reaction with halogens form halides  $EX_6$ ,  $EX_4$ ,  $EX_2$ Order of stability of halides  $F^- > Cl^- > Br^- > I^$ amongst haxahalides, hexafluorides are the only

stable halides.  $SF_4$  – gas SeF<sub>4</sub> – liquid  $TeF_4$  – solid

sp<sup>3</sup>d Hybridisation sea-saw geometry Monohalides are dimeric in nature S<sub>2</sub>F<sub>2</sub> , S<sub>2</sub>Cl<sub>2</sub> ,  $S_2Br_2$  ,  $Se_2Cl_2 Se_2Br_2$ . These dimeric halides undergo disproportionation  $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$ 

#### DIOXYGEN : 0<sub>2</sub>

#### Preparation

- $2\text{KCIO}_3 \xrightarrow{\text{heat}} 2\text{KCI} + 3\text{O}_2$
- $2Ag_2O \longrightarrow 4Ag + O_2$ ;  $2Pb_3O_4 \rightarrow 6PbO + O_2$ 2HgO  $\_\_$  2Hg + O<sub>2</sub>; 2PbO<sub>2</sub>  $\rightarrow$  2PbO + O<sub>2</sub>
- $2H_2O_2 \rightarrow 2H_2O + O_2$
- Electrolysis of water (large scale)
- Liquifection and fractional distllartion (industrial Method)

#### Properties of Dioxygen

Reacts with nearly all metals and non metals. except noble gases and Au, Pt,

$$\begin{array}{c} \text{Ca} + \text{O}_2 \rightarrow 2\text{CaO} \\ \text{A} + 3\text{O} \rightarrow 2\text{A} \\ \end{array}$$

 $P_4 + 5O_2 \rightarrow P_4O_{10}$ 

$$+ O_2 \rightarrow CO_2$$

$$2 \text{ 2 nS} + 30_2 \rightarrow 22 \text{ nO} + 2 \text{ SO}_2$$

$$\Box\Pi_4 + 2U_2 \rightarrow UU_2 + 2\Pi_2 U$$

 $SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$ 

 $4 \text{ HCI} + \text{O}_2 \xrightarrow{\text{CuCl}_2} 2\text{Cl}_2 + 2\text{H}_2\text{O}$ 

#### Uses of Dioxygen:

Respiration and combustion process.

- Used in oxyacetylene welding
- Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering
- Hydrazines in liquid oxygen, provides tremendous thrust in rockets.

#### Simple oxides eg. MgO, Al<sub>2</sub>O<sub>2</sub>

Classified as Acidic oxides - SO<sub>2</sub>, Cl<sub>2</sub>O<sub>7</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, Mn<sub>2</sub>O<sub>7</sub>, CrO<sub>3</sub>,  $V_2O_5$  etc.

Basic oxides - Na<sub>2</sub>O, CaO, BaO etc Amfhoteric oxides – Al<sub>2</sub>O<sub>3</sub> . etc. Neutral oxides - CO, NO, N<sub>2</sub>O etc Mixed oxides –  $Pb_3O_4$ .  $Fe_3O_4$  etc.

#### OZONE : O3

Allotropic form of oxygen formed from atmospheric oxygen in the presence of sunlight.

#### **Preparation of Ozone**

When slow stream of oxygen is passed through a silent electrical discharge conversion of oxygen to  $30_2 \rightarrow 20_3$ Ozone occur : ;  $\Delta H(298K) = +142 \text{ kJmol}^{-1}$ 

#### **Properties of Ozone**

- 1. Pure ozone is pale blue gas, dark blue liquid and violet black solid .
- 2. Small concentration is harmless. Its concentration above 100 parts per million causes headache and nausea.
- 3. Act as powerful oxidising agent (due to liberation of atoms of nascent oxygen  $O_3 \rightarrow O_2 + O$ )
  - $\begin{array}{l} PbS_{(s)} \stackrel{+}{+} 4O_{3(g)} \rightarrow PbSO_{4(s)} + 4O_{2(g)} \\ 2I_{(ag)} \stackrel{-}{+} H_2O_{(l)} + O_{3(g)} \rightarrow 2 OH_{(aq)} \stackrel{+}{+} I_{2(s)} + O_{2(g)} \end{array}$
- When ozone reacts with excess of KI solution 4. buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate . This is a quantitative method for estimation of  $O_{2}$ 5. Depletion of ozone layer Due to

#### (1) Freons

(2) Nitric oxide emitted from exhaust of superjet planes.

 $NO + O_3 \rightarrow NO_2 + O_2$ 

**Resonance structure of ozone** 



#### Uses of Ozone:

- As germicide disinfectant and for sterilising 1. water
- 2. For bleaching oils, ivory, flour, starch etc.
- 3. as oxidising agent in making of KMnO<sub>4</sub>.
- 4. Ozone layer protects from ultraviolet radiations.

#### SULPHUR

#### Rhombic sulphur ( $\alpha$ -sulphur)

- 1. yellow colour solid
- 2. m.p. 385.8 K
- 3. Specific gravity 2.06
- 4. Rhombic S crystals are formed on evaporating the solution of roll S in CS<sub>2</sub>.
- 5. Insoluble in water but dissolves to some extent in benzene, alcohol, ether.
- 6. Readily soluble in CS,
- Stable below 369 K 7.

#### **Monoclinic Sulphur** (β–sulphur)

Prepared by melting rhombic S in a dish and 1. cooling till crust is formed. Two holes are made in the crust and the remaining liquid proured out on removing the curst, colourless needle shaped crystals of β-sulphur are formed

- 2. m. p. 393 K, Specific gravity 1.98
- 3.
- Soluble in CS $_{\rm 2}$  Stable above 369 K and transforms into  $\alpha-$ 4. sulphur below it.

\* At 369 K both forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic S have S<sub>8</sub> molecules S<sub>8</sub> ring in both form is puckered (crown shape)



#### Other modifications of S

- S<sub>6</sub> chair form 1.
- S<sub>2</sub> (at 1000K) is Paramagnetic like O<sub>2</sub> In vapour 2. state.

S

### SULPHUR DIOXIDE

#### **Preparation**

- $S + 0_2 \rightarrow SO_2$ 1.
- Treating sulphite with dil H<sub>2</sub>SO<sub>4</sub> (Lab. Method) 2.  $SO_3^{-2}(aq) + 2H^+(g) \rightarrow H_2O(l) + SO_2(g)$
- 3. As by -product of roasting of sulphide ores (industrial method)

$$4\text{FeS}_2(s) + 11 \text{ O}_2(g) \rightarrow \text{Fe}_2\text{ O}_3(s) + 8\text{SO}_2(g)$$

The gas is stored in steel cylinders

#### **Properties:**

- 1. Colourless gas with pungent smell.
- 2. highly soluble in water.
- 3. liquifies at room T under a pressure of 2 atmospheres
- 4. b.p. 263K.
- 5.  $SO_2 + H_2O \rightarrow H_2SO_3$
- 6.  $2NaOH + SO_2 \rightarrow 2Na_2SO_3 + H_2O$  $Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$
- $SO_2 + CI_2 \xrightarrow{charcoal}$ 7. SO<sub>2</sub>Cl<sub>2</sub> sulphuryl chloride
- 8.  $SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$
- 9. Moist SO<sub>2</sub> behaves as reducing agent  $2Fe^{+3} + SO_2 + 2H_2O \rightarrow 2Fe^{+2} + SO_4^{-2} + 4H^+$  $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{-2} + 4H^+ + 2Mn^{2+}$ (decolourises acidified KMnO<sub>4</sub> it is used as test for SO, gas)

#### SO, molecule - Shape Angular **Resonance structures**



#### Uses of SO,

- 1. Refining petroleum and sugar.
- 2. In bleaching wool and silk
- 3. As anti -chlor, disinfectant and preservative
- 4. In making  $H_2SO_4$ , NaHSO<sub>3</sub>, Ca(HSO<sub>3</sub>)<sub>2</sub>
- 5. Liquid SO<sub>2</sub> to dissolve organic and inorganic chemical

#### Oxoacids of Sulphur.





Sulphurous aicd Sulphuric acid Peroxodisulphuric acid H<sub>2</sub>SO<sub>3</sub> H<sub>2</sub>SO<sub>4</sub> H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>



Pyrosulphuric acid (oleum) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>

#### SULPHURIC ACID





**Step3.**  $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ 

**Step4.**  $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 



## Flow diagram for the manufacture of sulphuric acid

#### **Properties of sulphuric acid**

- 1. Colourless dense oily liquid
- 2. Specific gravity 1.84 at 298 K

3. Freezes at 28 K and boils at 611 K

4. It dissolves in water with the evolution of a large quantity of heat. Hence concentrated acid must be added slowly into water with constant stirring while preparing  $H_2SO_4$  solution.

- 5. Low volatility
- 6. ability to act as oxidising agent

 $H_2SO_4(aq) + H_2O(I) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$ ; Ka<sub>1</sub> = very large (Ka<sub>1</sub> > 10)

$$HSO_{4}^{-}(aq) + H_{2}O(I) \longrightarrow H_{3}O^{+}(aq) + SO_{4}^{2-}(aq)$$
  
: Ka<sub>2</sub> = 1.2 × 10<sup>-2</sup>

8. 
$$2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4 (X = F, CL, NO) (M = Metal.)$$

9. Act as strong dehydrating agent. Many wet gases are dried by passing through it

10. It removes water from organic componds

 $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12 C + 11 H_2O$ 

11. It Oxidises metals and non metals and reduces itself to  $SO_2$ 

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$35 + 2H_2SU_4 \longrightarrow 3SU_4 + 2H_2U$$

 $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O_2$ 

#### Uses of sulphuric acid :

- 1. Manufacture fertilizers (eq. ammonium
- sulphate, superphosphate)
- 2. Petroleum refining
- Making paints pigments
- 4. Detergent industry
- 5. Cleansing metals
- 6. In storage, batteries
- 7. Making nitrocellulose products
- 8. As laboratory reagent.

#### GROUP –17

#### [Known as halogens (salt producer)] [Elements- F, Cl Br, I, At (radiactive)] Occurence

F – Insoluble fluorides – Fluoraptite  $3Ca_3(PO_4)_2$ . CaF<sub>2</sub>, fluorspar (CaF<sub>2</sub>) Cryolite (Na<sub>3</sub>AIF<sub>6</sub>), in river water plant, bones and teeth of animals Cl – NaCl & Karnalite (KCl MgCl<sub>2</sub> . 6H<sub>2</sub>O) in drived up seas.

. Br – sea water.

I - sea weeds (0.5%).

#### **Physical Properties**

 $\begin{array}{ll} \mathsf{F_2} \text{ , } \mathsf{Cl}_2 \rightarrow \text{gases} \\ \mathsf{Br}_2 & \rightarrow \text{ liquid} \\ \mathsf{I_2} & \rightarrow \text{ solid} \end{array}$ 

#### **Chemical properties**

#### **Oxidation states**

All elements exhibit – 1

Cl, Br, I exhibit +1, +3, +5, +7 also (when in combination of highly electronegative atom F & O) +4, +6 occurs in oxides and acids of Cl, Br.

\* Halogens are highly reactive. Their reactivity decreases down the group.

\*  $F_2$  is the strongest oxidising halogen as it oxidises other halide in solution or solid phase

 $F_2 + 2X^- \rightarrow 2F^- + X_2(X_2 = CI, BrI)$ 

 $CI_2 + 2X^- \rightarrow 2CI^- + X_2(X_2 = Br \text{ or } I)$ 

 $Br_{2}^{-} + 2I^{-} \rightarrow 2Br^{-} + I_{2}$ 

\* Öxidising ability of halogens decreases down the group.

\* Fluorine oxidises water to oxygen whereas  $Cl_2$  and Br, react with water to form haydrohalic and hypohalous acids. I<sup>-</sup> can be oxidised by oxygen in acidic medium.

$$2F_{2}(g) + 2H_{2}O(I) \rightarrow 4H^{+}(aq) + 4F^{-}(aq) + O_{2}(g)$$
  

$$X_{2}(g) + H_{2}O(I) \rightarrow HX(aq) + HOX(aq)$$
  
[where X = Cl, Br, ]

$$4I^{-}(aq) + 4H^{+}(aq) + O_2 \rightarrow 2I_2(s) + 2H_2O$$

Reactivty towards hydrogen : Form hydrogen halide.

Affinity for hydrogen decreases from F to I Acidic strength HF < HCI < HBr < HIStability HF > HCI > HBr > HI (due to dicrease in bond (H – X) dissociation enthalpy down the group) Reducing character HF < HCI < HBr < HI

#### **Reactivity towards oxygen :** – form oxides but most of them are unstable. F forms $OF_2$ and $O_2F_2$ (OF, is thermally stable at 298 K)

\* These oxides are essentially oxygen flourides because of the higher electronegativity of flourine than oxygen.  $(O_2F_2 \text{ oxidises Pu to PuF_6} \text{ and the}$ reaction is used in removing Pu as  $PuF_6$  from spent nuclear fuel).

Decreasing order of stability of oxides formed by helogene

#### I > CI > Br

Higher oxides of halogens are more stable than lower ones.

**Chlorine oxides Cl\_2O, ClO\_2, Cl\_2O\_6, Cl\_2O\_7** are highly reactive oxidesing agents & tend to explode.  $ClO_2$  is used as bleaching agent and in water treatment.

Bromine oxides :  $Br_2O$ ,  $BrO_2$ ,  $BrO_3$  (are least state and exist at low T).

Are powerful oxidising agents.

Iodine oxides :  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$  (decompose on heating)

 $\rm I_2O_5$  – Very good oxidesing agent and is used in estimation of CO.



**Reactivity towards metals :** Form Metal halides  $Mg(s) + Br_2(I) \rightarrow MgBr_2(s)$ Ionic character MF > MCl > MBr > MI ( M =

Monovalent metal) If metal exhibts more than one oxidetion state,

the halides in higher oxidation state are more covalent.

eq.  $SnCl_4 > SnCl_2$   $PbCl_4 > PbCl_2$   $SbCl_5 > SbCl_3$  $UF_6 > UF_4$ 

#### CHLORINE : CI<sub>2</sub>

Discovered by Sheele (1774) by action of HCl on  $MnO_2$  (Chlorous = greenish yellow)

#### Preparation of Cl,

1. 
$$MnO_2 + 4HCI \rightarrow MnCl_2 + Cl_2 + 2H_2O$$
  
(conc.)  
2.  $MnO_2 + NaCl + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4$   
 $+ Cl_2 + 2H_2O$   
3.  $2KMnO_2 + 16HCI \rightarrow 2KCI + 2MnCl_2 + 5Cl_2$   
 $+ 8H_2O$ 

#### Manufacture

1. **Deacons Process :** Oxidation of HCl gas by atomospheric oxides

$$HCI + O_2 \xrightarrow{CuCl_2}{723 \text{ K}} 2Cl_2 + 2H_2O$$

2. Electrolysis of brine : (NaCl solution )  $2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$ (Anode)

#### Properties of Cl<sub>2</sub>

- 1. Greenish yellow gas with pungent and suffocating
- 2. 2–5 times heavier than air.
- 3. liquified easily
- 4. soluble in water.
- 5. With number of metals and non metals forms chlorides

$$\begin{array}{l} \mathsf{2AI} + \mathsf{3CI}_2 \rightarrow \mathsf{2AICI}_3 \text{ ; } \mathsf{P}_4 + \mathsf{6CI}_2 \rightarrow \mathsf{4PCI}_3 \\ \mathsf{2Na} + \mathsf{CI}_2 \rightarrow \mathsf{2NaCI} \text{ ; } \mathsf{S}_8 + \mathsf{4CI}_2 \rightarrow \mathsf{4S}_2\mathsf{CI}_2 \\ \mathsf{2Fe} + \mathsf{3CI}_2 \rightarrow \mathsf{2FeCI}_3 \end{array}$$

6. Reacts with H containing compound to form HCl

 $\begin{array}{l} \mathsf{H_2} + \mathsf{Cl}_2 \rightarrow 2\mathsf{HCl} \\ \mathsf{H_2S} + \mathsf{Cl}_2 \rightarrow 2\mathsf{HCl} + \mathsf{S} \\ \mathsf{C_{10}H_{16}} + 8\mathsf{Cl}_2 \rightarrow 16 \; \mathsf{HCl} + 10 \; \mathsf{C} \end{array}$ 

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- 9.  $8 \text{ NH}_3 + 3\text{Cl}_2 \rightarrow 6\text{NH}_4\text{Cl} + 3\text{HCl}$ (excess) (Nitrogen trichloride)
- 10. NaOH + Cl<sub>2</sub>  $\rightarrow$  NaCl + NaOCl + H<sub>2</sub>O (cold dilute) (sodium hypochlorite) 6NaOH + 3Cl<sub>2</sub>  $\rightarrow$  5NaCl + NaOCl<sub>3</sub> + 3H<sub>2</sub>O

(disproportionation reaction ) (hot conc.) (sodium chlorite)

11.  $2Ca(OH)_2 + 2CI_2 \rightarrow Ca(OCI)_2 + CaCI_2 + H_2O$ (Dry slaked lime) (bleaching powder) The composition of bleaching powder is

Ca(OCI), . CaCl, Ca(OH), . 2H,O

12. With hydrocarbons

 $CH_4 + Cl_2 \xrightarrow{\cup v} CH_3Cl + HCl$ 

 $C_2H_4 + Cl_2 \xrightarrow{\text{Room T}} C_2H_4Cl_2$ 

1,2 Dichloro ethane

13. Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. (Hyprochlorous acid). HOCl formed gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

 $\begin{array}{l} 2\mathsf{FeSO}_4 + \mathsf{H}_2\mathsf{SO}_4 + \mathsf{Cl}_2 \rightarrow \mathsf{Fe}_2(\mathsf{SO}_4)_3 + 2\mathsf{HCl} \\ \mathsf{Na}_2\mathsf{SO}_3 + \mathsf{Cl}_2 + \mathsf{H}_2\mathsf{O} \rightarrow \mathsf{Na}_2\mathsf{SO}_4 + 2\mathsf{HCl} \\ \mathsf{SO}_2 + 2\mathsf{H}_2\mathsf{O} + \mathsf{Cl}_2 \rightarrow \mathsf{H}_2\mathsf{SO}_4 + 2\mathsf{HCl} \\ \mathsf{I}_2 + 6\mathsf{H}_2\mathsf{O} + 5\mathsf{Cl}_2 \rightarrow 2\mathsf{HIO}_3 + 10 \ \mathsf{HCl} \end{array}$ 

14. It is a powerful bleaching agent; bleaching action is due to oxidation

 $Cl_2 + H_2O \rightarrow 2HCI + O$ 

Coloured substance +  $O \rightarrow$  Colourless substance. Bleaching action is permanent. Bleaches vegetables and organic matter in the presence of moisture.

#### **Uses of chlorine:**

- (a) As bleaching agent.
- (b) estrection of gold & Pt
- Making dyes, drugs, organic compound.
   (CCl<sub>4</sub>, CHCl<sub>3</sub> DDT)
- (d) Sterilising drinking water.
- (e) Making poisonous gases like Phosgene COCl<sub>2</sub>, tear gas (CCl<sub>3</sub>NO<sub>2</sub>) mustard gas (CICH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl).

#### HYDROGEN CHLORIDE : HCI

Glauber prepared it by heating common salt with conc.  $H_2SO_4$ .

NaCl +  $H_2SO_4$  420 K NaHSO<sub>4</sub> + HCl

NaHSO<sub>4</sub> + NaCl  $\xrightarrow{823 \text{ K}}$  Na<sub>2</sub>SO<sub>4</sub> + HCl

\*HCl gas can be dried by passing it through conc.  $\rm H_2SO_4$ 

#### **Properties of HCl**

- 1. Colourless, pungent smelling gas.
- 2. Freezing point 159 K, b.p. 189 K,
- 3. Extremely soluble in water. HCl(g) + H<sub>2</sub>O (*I*)  $\rightarrow$  H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup> (aq) ; Ka = 10<sup>7</sup>

- 4. Its aqueous solution is called hydrochloric acid
- 5. Reacts with  $NH_3$  to give white fumes of  $NH_4CI$  $NH_3 + HCI \rightarrow NH_4CI$

6. Aqua -regia : When 3 parts of conc HCl and one part of conc.  $HNO_3$  are mixed.

- It is used for dissolving noble metals (Au, Pt) Au + 4H<sup>+</sup> + NO<sub>3</sub><sup>-</sup> + 4Cl<sup>-</sup>  $\rightarrow$  AuCl<sup>-</sup><sub>4</sub> + NO + 2H<sub>2</sub>O 3Pt + 16H<sup>+</sup> + 4NO<sub>3</sub><sup>-</sup> + 18Cl<sup>-</sup>  $\rightarrow$  3PtCl<sub>6</sub><sup>2-</sup> + 4NO + 8H<sub>2</sub>O
- 7.  $NaCO_{3} + 2HCI \rightarrow 2NaCI + H_{2}O + CO_{2}$   $NaHCO_{3} + HCI \rightarrow NaCI + H_{2}O + CO_{2}$  $Na_{2}SO_{3} + 2HCI \rightarrow 2NaCI + H_{2}O + SO_{2}$

#### Uses of HCI :

- 1. Manufacture of Cl<sub>2</sub>, NH<sub>4</sub>Cl, glucose,
- 2. For extracting glue from bones & purifying bone black
- 3. As laboratory reagent

CI

4. In medicines.

#### Oxoacids of Chlorine

0

(H)



Hypochlorous acid (HOCI) Chlorous acid(HClO<sub>2</sub>)





Chloric acid (HClO<sub>3</sub>)

Perchloric acid(HClO<sub>4</sub>)

Acidic strength of oxoacids HClO <  $HClO_2 < HClO_3 < HClO_4$ Acidic strength HClO > HBrO > HIO

**Interhalogen compounds:** When two different halogens react with each other .

Types – XX', XX'<sub>3</sub>, XX'<sub>5</sub>, XX'<sub>7</sub> (where X is halogen of larger size, X' of smaller size .

X is more electropositive than X')

As ratio b/w radii of X and X' increases, the number of atoms per molecule also increases eg.  $IF_7$  has maximum number of atoms as the ratio of radii b/w I and F is maximum.

Interhalogen compounds are more reactive than halogens (except  $F_2$ ) because X - X' bond is weaker than X - X, except F - F.

#### Preparation of Interhalogen compounds:

 $\begin{array}{ll} \text{Cl}_2 + \text{F}_2 & \xrightarrow{473\text{K}} & 2\text{ClF} \ ; & \text{I}_2 + \text{Cl}_2 \rightarrow 2\text{ICl} \\ (\text{equal volume}) & (\text{equimolar}) \\ \text{Cl}_2 + 3\text{F}_2 & \xrightarrow{573\text{K}} & 2\text{ClF}_3 \ ; \ \text{I}_2 + 3\text{Cl}_2 \rightarrow 2\text{ICl}_3 \end{array}$ 

	EOOR ELEMENTS		
I	(excess) (excess) $Br_2 + 3F_2 \longrightarrow 2BrF_3$ (diluted with water )		$Br_{2} + 5F_{2} \longrightarrow 2BrF_{5}$ (excess) * ICl <sub>3</sub> dimerises as Cl – bridged dimer (I <sub>2</sub> Cl <sub>6</sub> )
	Туре	Hybridisation	Interhalogen computities undergo hydrolysis
	XX'(CIE BrE ICI)		Giving halide ion derived from smaller halogen and
	$XX'_3(ClF_3, BrF_3, IF_3)$	sp <sup>3</sup> d	T-Shape
	XX' <sub>5</sub> (IF <sub>5</sub> , BrF <sub>5</sub> , ClF <sub>5</sub> )	sp <sup>3</sup> d <sup>2</sup>	Square Pyramidal
	XX'7(IF2)	sp <sup>3</sup> d <sup>3</sup>	Pentagonal bipyramidal
r H H f Use (() () () () () () () () () () () () ()	AX $_7(IF_7)$ hypohalite (when XX'), halite ( halate (when XX' <sub>5</sub> ) perhalate (XX' <sub>7</sub> ) a rom larger halogen. <b>s of Interhalogen compounds :</b> 1) As non aqueus solvent 2) Useful flourinating agents 3) CIF <sub>3</sub> , BrF <sub>3</sub> are used for the prod in the enrichment of U <sup>235</sup> . U <sub>(s)</sub> + 3CIF <sub>3(f)</sub> → UF <sub>6(g)</sub> + 3CIF <sub>(g)</sub> <b>GROUP –18</b> <b>, Ne, Ar, Kr, Xe, Rn</b> ) <b>Noble gases:</b> They react with only f ike F <sub>2</sub> and O <sub>2</sub> to form compounds stable electronic configuration. <b>Decurence :</b> 1 % by volume (a constituent) in atomsphere (Except R He & Ne in minearls of Radioactive bitch blende, monazite, clevite etc. He – Commercial source is natural ga Rn) – decay product of Radium. $^{226}_{38}$ Ra $\rightarrow^{222}_{38}$ Rn $+^4_2$ He (By Dorn) <b>sical Properties</b> 1. Monoatomic 2. Colourless , Odourless, tasteless 3. Sparingly soluble in water. 4. Very low m. p. and b.p. (wea orcess) eg. <b>He</b> has lowest m.p. (4.2 conown substance. It has unusual diffusing through rubber, glass or plas <b>Chemical properties :</b> least reactive s due to (i) completely filled valer	ew elements due to their rgon major adon) origen eq. s Radon s Radon	Pentagonal bipyramidal Compounds of Krypton are fewer . Only KrF <sub>2</sub> studied in detail. Compound of Rn are identified (eg. RnF <sub>2</sub> ) by radiotracer technique. No compounds of Ar, Ne or He are known Xe and F Compounds Xe(g) + F <sub>2</sub> (g) $\xrightarrow{673 \text{ K}}$ XeF <sub>2</sub> (s) (excess) Xe(g) + 2F <sub>2</sub> (g) $\xrightarrow{873 \text{ K}}$ XeF <sub>4</sub> (s) (1 : 5 ratio) Xe(g) + 3F <sub>2</sub> (g) $\xrightarrow{573 \text{ K}}$ XeF <sub>6</sub> (s) (1 : 2 ratio) Properties of compound of noble gases (XeF <sub>2</sub> , XeF <sub>4</sub> , XeF <sub>6</sub> ) (1) colourless crystalline solids (2) sublimes readily at 298 K (3) Are powerful fluorinating agents (4) Readily hydrolysed eq. 2XeF <sub>2</sub> + 2H <sub>2</sub> O $\rightarrow$ 2Xe(g) + 4HF(aq) + O <sub>2</sub> (g) Xenon Flourides react with flouride acceptors to form flouroanions XeF <sub>2</sub> + PF <sub>5</sub> $\rightarrow$ [XeF] <sup>+</sup> [PF <sub>6</sub> ] <sup>-</sup> XeF <sub>4</sub> + SbF <sub>5</sub> $\rightarrow$ [XeF] <sup>+</sup> [PF <sub>6</sub> ] <sup>-</sup> XeF <sub>4</sub> + SbF <sub>5</sub> $\rightarrow$ [XeF] <sup>+</sup> [M = Na, K, Rb ) Compound of Xe and O 6XeF <sub>4</sub> + 12H <sub>2</sub> O $\rightarrow$ 2Xe + 4HF(aq) + O <sub>2</sub> (g) XeF <sub>6</sub> + 3H <sub>2</sub> O $\rightarrow$ XeO <sub>3</sub> + 6HF 2XeF <sub>6</sub> + 2H <sub>2</sub> O $\rightarrow$ 2Xe + 4HF(aq) + O <sub>2</sub> (g)
high I. E. (iii) More + ve electron gain enthalpy. <b>Neil Bartlett</b> prepared first compound of Xe $PtF_6 + Xe \rightarrow Xe^+[PtF_6]$ (I. E. of Xe = 1170 kJ/ mol, I. E. of oxygen = 1175 kJ/mol) (red)			Partial hydrolysis of XeF <sub>6</sub> gives Oxyfluorides, XeOF <sub>4</sub> and XeO <sub>2</sub> F <sub>2</sub> , XeF <sub>6</sub> + H <sub>2</sub> O $\rightarrow$ XeOF <sub>4</sub> + 2HF (Colourless volatile liquid) XeF <sub>6</sub> + 2H <sub>2</sub> O $\rightarrow$ XeO <sub>2</sub> F <sub>4</sub> + 4HF



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## **SOLVED PROBLEMS**

5.

6.

Sol.

1. H<sub>3</sub>PO<sub>3</sub> is diprotic (or dibasic). Why?

Sol.

Its structure is  $HO \sim IOH^{P} H$ 

Ο

Since it contains only two ionizable H-atoms which are present as OH groups, it behaves as a dibasic acid.

### 2. $NH_3$ has a higher proton affinity than $PH_3$ . Explain.

#### or NH<sub>3</sub> is more basic than PH<sub>3</sub>.

Sol. Due the presence of a lone pair of electrons on N and P, both NH<sub>3</sub> and PH<sub>3</sub> act as Lewis bases and accept a proton to form an additional N – H and P – N bonds respectively

$$H_{3}N:+H^{+}\longrightarrow NH_{4}$$

 $H_3P: + H^+ \longrightarrow PH_{4^+}$ 

However, due to smaller size of N over P, N – H bond thus formed is much stronger than the P – H bond. Therefore,  $NH_3$  has higher proton affinity than  $PH_3$ . In order words,  $NH_3$  is more basic than  $PH_3$ .

- 3. NO (Nitric oxide) is paramagnetic in the gasesous state but diamagnetic in the liquid and solid states. Why ?
- **Sol.** NO has an odd number of electrons (7 + 8 = 15 electrons) and hence is paramagnetic in the gaseous state. But in liquid and solid states, it exists as a dimer and hence is diamagnetic in these states.
- 4. Give the chemical reaction to support that +5 oxidation state of Bi is less stable than +3 state.
- **Sol.** Due to inert pair effect, Bi can show +3 and +5 oxidation states. Since the inert pair effect is maximum in case of Bi, therefore, its +5

oxidation state is less stable than +3 oxidation state. This is evident from the observation that  $BiCl_3$  even on prolonged heating with  $Cl_2$  does not form  $BiCl_5$ 

$$BiCl_3 + Cl_2 \longrightarrow BiCl_5$$

- In the structure of NHO<sub>3</sub> molecule, N O bond (121 pm) is shorter than N — OH bond (140 pm).
- **Sol.** HNO<sub>3</sub> is a resonance hybride of the following two canonical structures :



Due to resonance N - O bond has some double bond character. In contrast, N - OH has only pure single bond character. Since single bonds are longer than double bonds, therefore, N - OH bond is longer

(140 pm) than N — O bond (121 pm) in NHO<sub>3</sub>.

#### Why H<sub>2</sub>S is acidic while H<sub>2</sub>o is neutral?

- The S H bond is weaker than O H bond because the size of S - atom is bigger than that of O-atom Hence.  $H_2s$  can dissociate to give H<sup>+</sup> ions in aqueous solution.
- 7. Why the compounds of fluorine with oxygen are called fluorides of oxygen and not the oxides of fluorine ?

**Sol.** This is because fluorine is more electronegative than oxygen.

8. Give reasons for the following observations :

(i) Why SF<sub>4</sub> undergoes hydrolysis but not SF<sub>6</sub>?

(ii) Sulphur exhibits greater tendency for calenation than selenium.

(iii) Sulphur has a higher tendency for

#### catenation than oxygen.

**Sol.** (i) In  $SF_6$ , S sterically proctected by six F atoms and hence does not allow  $H_2O$  molecules to attack the S atom. Furthermore. F does not have d -orbitals to accept the electrons denotes by  $H_2O$  molecules. As a result of these two reason.  $SF_6$  does not undergo hydrolysis. In contrats, in  $SF_4$ . S is not sterically protected since it is surrounded by only four F atoms. As a result, attack of  $H_2O$  molecules on S atoms can take place easily and hence hydrolysis occurs.

(ii) As we move from S to Se, the atomic size increase and hence the strength of E - E bond decreases. As a result, S - S bond is much stronger than Se -Se bond and consequently, S show greater tendency for catenation than selenium.

(iii) Due to small size, the lone pairs of electrons on the O atoms repel the bond pair of the O – O bond to a greater extend that the lone pairs of electrons on the S atom in S – S bond. As a result, S – S bond is much stronger (213 kJ mol<sup>-1</sup>) than O – O bond (138 kJ mol<sup>-1</sup>) and hence S has a such stronger tendency for catenation than O.

## 9. Bond dissociation energy of $F_2$ is less than that of $Cl_2$ . Explain.

- Sol. Due to smaller size, the lone pairs of electrons on the F-atoms repel the bond pair of the F – F bond. In contrast, because of comparatively larger size of Cl atoms, the lone pairs on the Cl atoms doe not repel the bond pair of Cl – Cl bond. As a result, F – F bond energy is lower than that of Cl – Cl bond energy.
- 10. F-atom is more electronegative than Iatom, yet HF has lower acid strength than HI. Explain.
- Sol. F atom being smaller in size than I atom, the bond dissociation energy of H – F is very high as compared to that of H – I bond. Consequently, H – I bond breaks more easily than H – F bond and thus HI is a stronger acid than HF.

### 11. Iodine is more soluble in KI than in water. Why ?

- **Sol.** Iodine combines with KI to form the soluble complex,  $KI_3$  (KI +  $I_2 \rightarrow KI_3$ ).
- 12. Arrange HClO<sub>4</sub>, HClO<sub>3</sub>, HClO<sub>2</sub>, HClO in order of (i) acidic strength (ii) oxidizing power. Give reasons.

**Sol.** (i) Acidic strength :  $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$ 

Reason : As the stability of the oxoanion (conjugate base) left after the removal of a proton increases, the acid strength increases in the same order. Since the stability of the anions decreases in the order :

 $CIO_4^- > CIO_3^- > CIO_2^- > HCIO^-$ , therefore, acid strength decreases in the same order :

 $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$ 

Oxidising power :  $HCIO_4 < HCIO_3 < HCIO_2 < HCIO$ Reason : As the stability of the oxoanion increases, its tendency to decompose to give  $O_2$  decrease and hence its oxidising power decreases. Since the stability of the oxoanion decreases in the order :

 $CIO_4^- > CIO_3^- > CIO_2^- > CIO^-$ , therefore, the oxidising power of their oxoacids increases in the reverse order, i.e.,  $HCIO_4 < HCIO_3 < HCIO_2 < HCIO$ .

## 13. Why HF acid is stored in wax coated glass bottles

**Sol**. This is because HF does not attack wax but reacts with glass. It dissolves  $SiO_2$  present in glass forming hydrofluorosilicic acid

 $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2 H_2O$ 

14. Assign appropriate reasons for each of the following statements.

Perchloric acid is a stronger acid than sulphuric acid.

**Sol.** (v) The oxdation state of Cl in perchloric acid is +7 while that of S in sulphuric acid is +6



Due to higher oxidation sate and higher electronegativity of Cl,  $ClO_3$  part of  $HClO_4$  pulls the electrons of the O — H bond more strongly and hence can break the O — H bond more easily to liberate a proton than  $SO_2$  part in  $H_2SO_4$ . Thus, perchloric acid is a stronger acid than sulphuric acid.

### **15.** CF<sub>3</sub> exists but FCl<sub>3</sub> does not.

**Sol.** Reasons are : (i) Cl has vacant d - orbitals and hence can show an oxidation state of +3 but F has d - orbitals, therefore, it cannot show positive oxidation state. Further, since F can show only – 1 oxidation state, therefore, it can form only CIF and not FCl<sub>3</sub>.

(ii) Because of bigger size, Cl an accommodate three small F atoms around it while F being smaller cannot accommodate three bigger sized Cl atoms around it.

## 16. What prompted Bartlett to the discovery of noble gas compounds ?

**Sol.** Since  $PtF_6$  oxidises  $O_2$  to  $O_2^+$ , Bartlett thought that  $PtF_6$  should also oxidise Xe to Xe<sup>+</sup> because the ionization enthalpies of  $O_2$  (1175 kJ mol<sup>-1</sup>) and Xe

(1170 kJ mol<sup>-1</sup>) are quite close.

- 17. The majority of noble gas compound are those of xenon. Explain.
- **Sol.** Except radon which is radioactive, Xe has the lowest ionization enthalpy among noble gases and hence can be easily oxidised by strong oxidising agents like  $O_2$  and  $F_2$ . That is why majority of noble gas compounds are those of xenon.

### XeF<sub>2</sub> has straight linear structure and not a bent structure.

Sol. In the formation of XeF<sub>2</sub> molecule, Xe undergoes sp<sup>3</sup>d - hybridization. Two of the five sp<sup>3</sup>d - orbitals overlap



- **19.** PH<sub>3</sub> has lower boiling than NH<sub>3</sub>. Why ?
- **Sol.** The electronegativity of N (3.0) is much higher than that of P (2.1). Therefore,  $NH_3$  undergoes extensive intermolecular H - bonding and hence it exists as an associated molecule. To break these H-bonds, a large amount of energy is needed. On the other hand,  $PH_3$  does not undergo H - bonding and thus exists as discrete molecules. Therefore, the boiling point of  $PH_3$ is much lower than that of  $NH_3$ .

### Q.20 Why does NO<sub>2</sub> dimerise?

**Sol.**  $NO_2$  is an odd electron (7 + 2 × 8 = 23) molecule. In the valence shell, N has seven electron and hence is less stable. To become more stable by aquiring inert gas configuration having 8 electrons in the valence shell, it undergoes dimerization to form  $N_2 O_4$ .



### 21 When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why ?

Fe reacts with HCl to form  $\text{FeCl}_2$  and  $\text{H}_2$ , Fe + 2 HCl  $\rightarrow$  FeCl<sub>2</sub> + H<sub>2</sub>

 $\rm H_{2}$  thus liberated prevents the oxidation of  $\rm FeCl_{2}$  to  $\rm FeCl_{3}$ 

#### 22 Why is $K_{a_2}$ less than $K_{a_1}$ for $H_2SO_4$ in water

**Sol.**  $H_2SO_4$  is a dibasic acid, it ionizes in two stages and hence has two dissociation constants. (i)  $H_2SO_4(aq) + H_2O(1) \rightarrow H_3O^+(aq) + HSO_4^-$ 

(aq) :  $K_{a_1} > 10$ 

(ii) 
$$\text{HSO}_4^-$$
 (aq) +  $\text{H}_2\text{O}(1) \rightarrow \text{H}_3\text{O}^+$  (aq) +  $\text{SO}_4^{2-}$ 

(aq); 
$$K_{a_2} = 1.2 \times 10^{-3}$$

 $K_{a_2}$  is less than  $K_{a_1}$  because the negatively charged HSO<sub>4</sub><sup>-</sup> ion has much less tendency to donate a proton to H<sub>2</sub>O as compared to netural H<sub>2</sub>SO<sub>4</sub>.

Sol.

## 23 Given the reason for the bleaching action of Cl<sub>2</sub>.

**Sol.** In presence of moisture or in aqueous solution.  $Cl_2$  liberates nascent oxygen.  $Cl_2 + H_2O \rightarrow 2HCI + [O]$ Nascent oxygen

#### 24 Why is ICl more reactive than I<sub>2</sub>?

**Sol.** ICl is more reactive than  $I_2$  because I - Cl bond is weaker than I - I bond. Consequently, ICl breaks easily to form halogen atoms which readily bring about the reactions.

## 25 Can $PCl_{s}$ act as an oxidising as well as reducing agent ? Justify.

**Sol.** The oxidation state of P in  $PCl_5$  is + 5. Since P has five electrons in ts valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore,  $PCl_5$ cannot act as a reducing agent. However, it can decrease its oxidation number from + 5 to + 3 or some lower value, therefore,  $PCl_5$  acts as an oxidising agent. For example, it oxidises Ag to AgCl, Sn to SnCl<sub>4</sub> and H<sub>2</sub> to HCl.

 $2\overset{0}{A}g + \overset{+5}{P}Cl_3 \longrightarrow 2\overset{+1}{A}gCl + \overset{+3}{P}Cl_3$ ;

 $\overset{0}{\text{Sn}} + 2\overset{+5}{\text{PCI}}_{5} \longrightarrow \overset{+4}{\text{Sn}} \overset{-}{\text{CI}}_{4} + 2\overset{+3}{\text{PCI}}_{3}$ 

## $P\overset{+5}{\text{Cl}_5} + \overset{0}{\text{H}_2} \xrightarrow{+3} P\overset{+1}{\text{Cl}_3} + 2\overset{+1}{\text{HCl}}$

26 Why is dioxygen gas but sulphur is a solid small Sol. Due to size and high electronegativity, oxygen forms  $p\pi - p\pi$  multiple bonds. As a result, oxygen exists as diatomic  $(O_2)$  moleucles. These molecules are held together by weak van der Walls force of attraction whcih can be easily overcome by collisions of the molecules at room temperature. Therefore,  $O_2$  is a gas at room temperature. Sulphur because of its higher tendency for catenation and lower tendency for  $p\pi - p\pi$ multiple bonds, forms octa-atomic  $(S_8)$ molecules having eight-membeed puckered ring structure (Figure shown) Because of bigger size, the force of attraction holding the  ${\rm S}_{_{\rm 8}}$  molecules together are much stronger which cannot be overcome by collisions of molecules at room temperature. Consequently, sulphur is a solid at room temperature.

#### 27 Why are halogens stong oxidising agents ?

Sol.

28

Sol.

29

Sol.

Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy halogens have a strong tendency to accept electrons and thus get reduced.

## $X_2 + 2e^- \longrightarrow 2X^-$

As a result, halogens act as strong oxidising agents.

## Explain why fluorine forms only one oxoacid, HOF.

Due to high electronegativity and small size, F cannot act as central atom in hgher oxoacids such as HOFO, HOFO<sub>2</sub> and HOFO<sub>3</sub> in which the oxidation state of F would be +3, +5 and +7. It just forms one oxoacid, i.e., HOF in which the oxidation state of F is +1.

#### Why are halogens coloured ?

Because their molecules absorb light in the visible region as a result of which their electrons get excited to higher energy levels while the remaining light is transmitted. The colour of the halogens is actually the colour of this transmitted light. The amount of energy needed for excitation decreases progressively from F to I as the size of the atom increases. Consequently, the energy of the transmitted light goes on increasing from F to I. In other words, the colour of the halogens deepens from F, to I,. For example, F, absorbs violet light (higher excitation energy) and hence appears pale yellow while iodine absorbs yellow and green light (lowe excitation energy) and hence appears deep violet. Similarly, we can account for greenish yellow colour of Cl<sub>2</sub> and orange red colour of bromine.



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## What is laughing gas ? s. N<sub>2</sub>O

## 33. Give an example of a disproportionation reacton of F, ?

**ol.**  $F_2$  when passed over ice at 233 K, undergoes a disproportionation reaction, i.e.,  $F_2$  is both oxidised and reduced. In HOF, the oxidatino state of F is + 1 while in HF is -1.

 $\overset{0}{\mathsf{F}}_{2}(g) + \mathsf{H}_{2}\mathsf{O}(s) \xrightarrow{233\mathsf{K}} + \overset{1}{\mathsf{O}}\mathsf{F}(l) + \overset{-1}{\mathsf{H}}\mathsf{F}(l)$ 

- **34.** Iodine forms  $I_3^-$  but  $F_2$  does not form  $F_3^-$  ions. Why
  - $I_2$ , because of the presence of vacant d orbitals, accepts electrons from I<sup>-</sup> ions to form  $I_3^-$  ions but  $F_2^-$  because of the absence of d orbitals does not accept electrons from F<sup>-</sup> ions to form  $F_3^-$  ions.

### **Can FCl<sub>3</sub> exist ? Comment.**

No. because F cannot exhibit valency more than one due to the absence of d - orbitals. Further, three big sized Cl atoms cannot be accommodated around a small F atom.

### Which is more stable PCl<sub>5</sub> or PCl<sub>3</sub>?

 $PCI_3$  is more stable than  $PCI_5$  because on heating  $PCI_5$  decomposes to form  $PCI_3$  and  $CI_2$ 

$$\mathsf{PCI}_5 \xrightarrow{\Delta} \mathsf{PCI}_3 + \mathsf{CI}_2$$

# 37. Which of the following hydride has largest bond angle ?

#### H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se or H<sub>2</sub>Te

As the electronegativity of the central atom decreases, the repulsions between element-hydrogen bond pairs decreases and hence the angle decreases accordingly. Thus  $H_2O$  has the largest bond angle (104-5°).

### 8. IF<sub>7</sub> exists but BrF<sub>7</sub> does not, why ?

**ol.** The atomic size of I is much bigger than Br. Therefore, 7 small sized F atoms can be arranged around big sized I atom but not around small sized Br atom.

E	(ERCISE-I UN	ISOL	
Q.1	The negative value of electron gain enthalpy is less for fluorine than for chlorine.	Q.15	Write the order of thermal stability of the hydrides of group 16 elements.
Q.2	$F_2$ is stronger oxidising agent than $Cl_2$ .	Q.16	Why is $H_2O$ is liquid and $H_2S$ is gas ?
Q.3	Arrange HClO, HBrO and HIO in order of decreasing acidic strength giving reason.	Q.17	How is $O_3$ estimated quantitatively ?
Q.4	Why interhalogens are more reactive than halogens?	Q.18 Q.19	Give the resonating structures of NO <sub>2</sub> and N <sub>2</sub> O <sub>5</sub> . Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group )?
Q.5	Why do noble gases form compounds with fluorine and oxygen only ?	Q.20	Give the dsiproportionation reaction of $H_3PO_3$ .
Q.6	Write the reaction of thermal decomposition of sodium azide.	Q.21	How are $XeF_2$ , $XeF_4$ and $XeF_6$ obtained ?
Q.7	In what way can it be proved that $\mathrm{PH}_{\mathrm{3}}$ is basic in nature ?	Q.22 Q.23	How are $XeO_3$ and $XeOF_4$ prepared ? Arrange the following in order of priority indicated for each set :
Q.8	Why does PCl <sub>3</sub> fume in moisture ?		(i) $F_2$ , $Cl_2$ , $Br_2$ , $I_2$ - increasing bond dissociation enthalpy.
Q.9	Which form of sulphur shows paramagnetic behaviour? or Sulphur in the vapour state exhibits paramagnetism		(ii) HF, HCl, HBr, 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.
Q.10	How does ammonia react with a solution of $Cu^{2+}$ 2	Q.24	Why do noble gases have comparatively large atomic sizes ?
Q.11	What happens when white phosphorus is	Q.25	Why is red phophorus more reactive than white phosphorus ?
	inert atmosphere of $CO_2$ ?	Q.26	How is ammonia prepared industrially?
Q.12	What happens when $PCl_5$ is heated ?	Q.27	Write balanced eq <sup>n</sup> for the following (i) NaCl is heated with sulphuric acid in the
Q.13	What is the basicity of $H_3PO_4$ ?		(ii) Chlorine gas is passed into a solution of
Q.14	What happens when $H_3PO_3$ is heated ?		sodium iodide in water.

EXERCISE-II BO				DARD PROBLEMS		
Q.1	Why is red phosph phosphorous ?	orous less reactive than white		equations. (i) $I_2 + HNO_3 \rightarrow$ (conc.)		
Q.2	Complete the for equations (i) $XeF_2 + H_2O \rightarrow$ (ii) $PH_3 + HgCl_2 \rightarrow$	ollowing chemical reaction	Q.11	(ii) $\text{HgCl}_2 + \text{PH}_3 \rightarrow$ How would you account for the following : (i) $\text{H}_2\text{S}$ is more acidic than $\text{H}_2\text{O}$ (ii) The N=O bond is NOT is charter than		
Q.3	(a) Draw the structure (i) $H_2S_2O_8$ (ii) $HCIO_4$ (b) How would ye (i) $NH_3$ is stronger (ii) Sulphur has graph than oxygen (iii) $F_2$ is a stronger	ictures of the following bu account for the following base than $PH_3$ reater tendency for catenation er oxidising agent than $Cl_2$ .	Q.12	(ii) Both $O_2$ and $F_2$ stabilise high oxidation states but the ability of oxygen to stablise the higher oxidation state exceeds that of fluorine. (a) Mention the optimum conditions for the industrial manufacture of ammonia by Haber's process		
Q.4	(a) Draw the structure (i) $H_2S_2O_7$ (b) Explain the for (i) In the structure (121 pm) is short pm). (ii) All the P – equivalent	icture of the following (ii) $HCIO_3$ llowing observations re of $HNO_3$ , the N – O bond er than the N – OH bond (140 Cl bonds in $PCI_5$ are not	Q.13	<ul> <li>(b) Explain the following giving appropriate reasons.</li> <li>(i) Sulphur vapour exhibits paramgnetic behaviour</li> <li>(ii) Red phosphorus is less reactive than white phosphorus</li> </ul> Draw the structures of the following molecules		
Q.5	(iii) ICl is more re Nitrogen is relat phosphorous ? W	eactive than I <sub>2</sub> lively inert as compared to hy	Q.14	(i) $H_2S_2O_8$ (iii) $H_3PO_3$ Complete the following chemical equations :		
Q. 6	Draw the structure compounds. (i) $H_4P_2O_5$ (ii) XeF	aral formula of the following		(i) $C + H_2SO_4 (conc.) \longrightarrow$ (ii) $P_4 + NaOH + H_2O \longrightarrow$ (iii) $Cl_2 + F_2 \longrightarrow$ (excess)		
Q.7	Complete the for equations (i) NaOH + Cl <sub>2</sub> $\rightarrow$ (ii) XeF <sub>6</sub> + H <sub>2</sub> O $\rightarrow$ (excess)	ollowing chemical reaction	Q.15 Q.16	What is the basicity of H <sub>3</sub> PO <sub>3</sub> and why ? How are interhalogen compounds formed ? What general compositions can be assigned to them?		
Q.8	How would you a (i) NCl <sub>3</sub> is an endo is an exothermic (ii) $XeF_2$ is a linea (iii) The electron	ccount for the following othermic compound while NF <sub>3</sub> one. In molecule without a bend.	Q.17 Q.18	Draw the structures of the following molecules (i) $N_2O_5$ (ii) $XeF_2$ Give reasons for the following : (i) Though nitrogen exhibits +5 oxidation state		
Q.9 Q.10	(III) The electron sign is less than t is a stronger oxid Fluorine does not state . Why? Complete the fo	exhibit any positve oxidation chemical reaction		<ul> <li>it does not form pentahalide.</li> <li>(ii) Electron gain enthalpy with negative sign of fluorine is less than that of chlorine.</li> <li>(iii) The two oxyen-oxygen bond lengths is ozone molecule are identical.</li> </ul>		