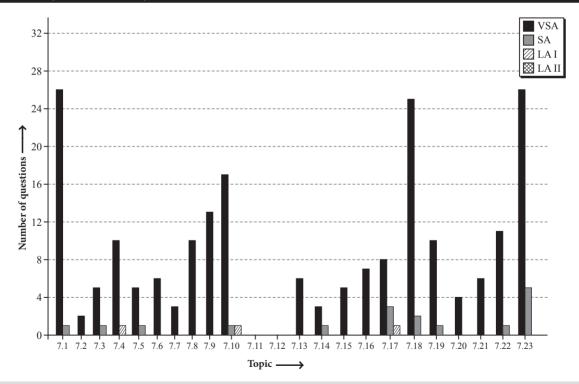
# The *p*-Block Elements (Group 15 to 18)

7.1 **Group 15 Elements** 7.8 **Phosphorus Halides** 7.16 Oxoacids of Sulphur 7.2 7.9 Oxoacids of Phosphorus 7.17 Sulphuric Acid Dinitrogen **Ammonia** 7.10 Group 16 Elements 7.18 Group 17 Elements 7.3 Oxides of Nitrogen 7.19 Chlorine 7.4 7.11 Dioxygen 7.5 Nitric Acid 7.12 Simple Oxides 7.20 Hydrogen Chloride Phosphorus - Allotropic **7.13** Ozone 7.21 Oxoacids of Halogens **Forms** 7.14 Sulphur - Allotropic Forms 7.22 Interhalogen Compounds **Phosphine** 7.7 7.15 Sulphur Dioxide 7.23 Group 18 Elements

# Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



- Maximum total weightage is of *Group 18 Elements*.
- Maximum VSA type questions were asked from Group 15 Elements, Group 17 elements and

Group 18 Elements.

 Maximum SA type questions were asked from Group 18 Elements.

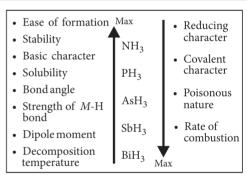
## **QUICK RECAP**

- Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shell are called *p*-block elements.
- **GROUP 15 ELEMENTS (NITROGEN FAMILY)**
- Group 15 elements are collectively called *pnictogens*.

General characteristics :

<b>Electronic configuration</b>	$ns^2 np^3$
Elements	<sub>7</sub> N, <sub>15</sub> P, <sub>33</sub> As, <sub>51</sub> Sb, <sub>83</sub> Bi, <sub>115</sub> Mc
Physical state and	N <sub>2</sub> (unreactive gas), P <sub>4</sub> (solid non-metal), As <sub>4</sub> and Sb <sub>4</sub> (Solid metalloids),
metallic character	Bi (metal)
Atomic radii	Increase down the group, smaller than that of group 14 elements due to
	increased nuclear charge.
Melting and	M.pt. increases from N to As and then decreases whereas b. pt. increases from
boiling points	N to Sb and decreases very slightly.
Ionisation enthalpy	Decreases regularly down the group due to increase in size.
Electronegativity	Decreases down the group.
Allotropy	Nitrogen ( $\alpha$ and $\beta$ -Nitrogen), phosphorus (white, red, scarlet, violet, $\alpha$ -black,
	$\beta$ -black), arsenic (grey, yellow, black), antimony (metallic, yellow, explosive)

- Chemical properties:
- ► Stability of +3 oxidation state increases and that of +5 decreases down the group due to *inert pair effect*.
- ▶ **Halides :** All the elements form trihalides of the type  $MX_3$  and except nitrogen, all form pentahalides of the type  $MX_5$ .
  - **Stability**:  $NF_3 > NCl_3 > NBr_3$
  - Lewis acid strength: PCl<sub>3</sub> > AsCl<sub>3</sub> > SbCl<sub>3</sub> and PF<sub>3</sub> > PBr<sub>3</sub> > PI<sub>3</sub>
  - Lewis base strength:  $NI_3 > NBr_3 > NCl_3 > NF_3$
  - Bond angle: PF<sub>3</sub> < PCl<sub>3</sub> < PBr<sub>3</sub> < PI<sub>3</sub>
     (increasing b.p. b.p. repulsions)
- ► **Hydrides**: All the elements form hydrides of the type *M*H<sub>3</sub> which are covalent and pyramidal in shape. Their general trends are:



▶ **Oxides**: All these elements form oxides of the type  $X_2O_3$ ,  $X_2O_4$  and  $X_2O_5$ .

$\begin{array}{c} N_2O_3\\N_2O_4\\N_2O_5 \end{array}$	$\begin{array}{c} P_2O_3 \\ P_2O_4 \\ P_2O_5 \end{array}$	$\begin{array}{c} As_2O_3 \\ As_2O_4 \\ As_2O_5 \end{array}$	Sb <sub>2</sub> O <sub>3</sub> Sb <sub>2</sub> O <sub>4</sub> Sb <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>3</sub> Bi <sub>2</sub> O <sub>4</sub> Bi <sub>2</sub> O <sub>5</sub>	Acidic nature increases
Acidic nature decreases					

# Preparation, properties and uses of some important compounds:

Compound	Preparation	Properties	Uses
N <sub>2</sub>	$NH_4Cl + NaNO_2 \longrightarrow N_2 \uparrow + 2H_2O$	$6\text{Li} + \text{N}_2 \xrightarrow{\text{Heat}} 2\text{Li}_3\text{N}$	Used in manufacture of nitric
	+ NaCl $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow +4H_2O$	$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$	acid, ammonia, calcium cyanamide and other nitrogen
$N \equiv N$	+ Cr <sub>2</sub> O <sub>3</sub>	$N_{2(g)} + 3H_{2(g)} = \frac{773 \text{ K}}{2NH_{3(g)}} $	compounds. Liquid dinitrogen is used
	$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2 \uparrow$	$N_{2(g)} + O_{2(g)} = \frac{\text{Heat}}{2NO_{(g)}}$	as a refrigerant to preserve
			biological materials, food items and in cryosurgery.

NH <sub>3</sub>	$NH_{2}CONH_{2} + 2H_{2}O \longrightarrow$ $(NH_{4})_{2}CO_{3} \Longrightarrow 2NH_{3} + H_{2}O + CO_{2}$ $2NH_{4}Cl + Ca(OH)_{2} \longrightarrow 2NH_{3}$ $+ 2H_{2}O + CaCl_{2}$ $(NH_{4})_{2}SO_{4} + 2NaOH \longrightarrow 2NH_{3}$ $+ 2H_{2}O + Na_{2}SO_{4}$ $+ 2H_{$	$ \begin{array}{c} Zn(OH)_{2(s)} + (NH_4)_2SO_{4(aq)} \\ (\text{white ppt.}) \end{array} $ $FeCl_{3(aq)} + NH_4OH_{(aq)} \longrightarrow \\ Fe_2O_3 \cdot xH_2O_{(s)} + NH_4Cl_{(aq)} \\ (\text{brown ppt.}) \\ Cu^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow \begin{bmatrix} Cu(NH_3)_4 \end{bmatrix}_{(aq)}^{2+} \\ (\text{blue}) \\ (\text{deep blue}) \end{array} $	Used in refrigerators, manufacturing of rayon, HNO <sub>3</sub> , NaHCO <sub>3</sub> , nitrogenous fertilizers.
H-O-N O	NaNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> $\longrightarrow$ NaHSO <sub>4</sub> + HNO <sub>3</sub> Ostwald's Process: $ \begin{array}{c} \text{Pt/Rh gauge} \\ \text{catalyst} \\ \text{500 K, 9 bar} \end{array} $ $ \begin{array}{c} \text{4NO + 6H2O} \\ \text{2NO + O2} \rightleftharpoons \text{2NO2} \\ \text{3NO2 + H2O} \longrightarrow \text{2HNO3 + NO} \end{array} $	$+ 2NO + 4H_2O$	fertilizers, explosives, perfumes and
PH <sub>3</sub>	$Ca_{3}P_{2} + 6H_{2}O \longrightarrow 3Ca(OH)_{2} + 2PH_{3}$ $Ca_{3}P_{2} + 6HCl \longrightarrow 3CaCl_{2} + 2PH_{3}$ $P_{4} + 3NaOH + 3H_{2}O \longrightarrow PH_{3}$ $+ 3NaH_{2}PO_{2}$ (sodium hypophosphite) $PH_{4}I + KOH \longrightarrow KI + H_{2}O + PH_{3}$	$3\text{CuSO}_4 + 2\text{PH}_3 \longrightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$ $3\text{HgCl}_2 + 2\text{PH}_3 \longrightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl}$ $2\text{PH}_3 + \text{HBr} \longrightarrow \text{PH}_4\text{Br}$	The spontaneous combustion of phosphine is technically used in Holme's signals. It is also used in smoke screens.
PCl₅  Cl Cl P   Cl Cl Cl Cl Cl Cl	$P_4 + 10Cl_2 \longrightarrow 4PCl_5$ (white or red)	$PCl_{5} \xrightarrow{\text{H}_{2}\text{O}} \text{H}_{3}\text{PO}_{4} + \text{HCl}$ $PCl_{5} \xrightarrow{\text{P}_{4}\text{S}_{10}} \text{PSCl}_{3}$ $PCl_{5} \xrightarrow{\text{SO}_{2}} \text{SOCl}_{2} + \text{POCl}_{3}$ $PCl_{5} \xrightarrow{\text{P}_{4}\text{O}_{10}} \text{POCl}_{3}$	Used as chlorinating and dehydrating agent.

PCl <sub>3</sub>	1 2 3		Used as reagent
	$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2$	3CH <sub>3</sub> COOH + PCl <sub>3</sub> →	in organic
	+ 2S <sub>2</sub> Cl <sub>2</sub>	, , , , , , , , , , , , , , , , , , , ,	
		$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl$	as a precursor
( )		+ H <sub>3</sub> PO <sub>3</sub>	of PCl <sub>5</sub> , POCl <sub>3</sub>
l Å			and PSCl <sub>3</sub> .
			It is used in
Cl Cl Cl			the synthesis of
			some organic
			compounds,
			e.g., C <sub>2</sub> H <sub>5</sub> Cl,
			CH <sub>3</sub> COCl.

# Preparation and properties of oxides of nitrogen:

Formula	O.S.	Preparation	Properties
N <sub>2</sub> O	+1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$	colourless gas, neutral
NO	+2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4$	colourless gas, neutral
		$+ 2H_2O + 2NO$	
$N_2O_3$	+3	$2NO + N_2O_4 \xrightarrow{250 \text{ K}} 2N_2O_3$	blue solid, acidic
NO <sub>2</sub>	+4	$2Pb(NO_3)_2 \xrightarrow{673 \text{ K}} 2PbO + 4NO_2 + O_2$	brown gas, acidic
$N_2O_4$	+4	$2NO_2 \stackrel{cool}{\longleftarrow} N_2O_4$	colourless solid/liquid, acidic
$N_2O_5$	+5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

# Allotropes of phosphorus :

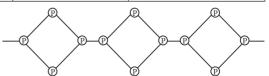
Property	White phosphorus	Red Phosphorus	Black phosphorus
Colour	White, but turns yellow on exposure	Dark red	Black
State	Waxy solid, can be cut with knife	Brittle powder	Crystalline with greasy touch
Smell	Garlic smell	Odourless	_
Density	1.84	2.1	2.69
Ignition temperature	307 K	543 K	673 K
Melting point	317 K	Sublimes in absence of air at 560 K	860 K

► White phosphorus consists of discrete tetrahedral P<sub>4</sub> molecule.



Structure of white phosphorus

► Red phosphorus is polymeric and consists of inter linked P<sub>4</sub> tetrahedra.



Structure of red phosphorus

Black phosphorus is thermodynamically most stable at room temperature and has two forms: α-black phosphorus and β-black phosphorus.

## Oxoacids of phosphorus:

$${
m H_3PO_4}$$
  
Orthophosphoric  
acid

$$H_4P_2O_7$$
  
Pyrophosphoric  
acid

H<sub>3</sub>PO<sub>3</sub> H<sub>3</sub>PO<sub>2</sub>
Orthophosphorous Hypophosphorous

(HPO<sub>3</sub>)<sub>3</sub> Cyclotrimetaphosphoric

 $(\mathrm{HPO_3})_n$ Polymetaphosphoric acid

#### **GROUP 16 ELEMENTS (OXYGEN FAMILY)**

Group 16 elements are collectively called *chalcogens*.

# General characteristics:

Electronic	$ns^2np^4$	
configuration		
Elements	<sub>8</sub> O, <sub>16</sub> S, <sub>34</sub> Se, <sub>52</sub> Te, <sub>84</sub> Po, <sub>116</sub> Lv	
Physical state	O <sub>2</sub> (gas), S <sub>8</sub> (solid non-metal),	
and metallic	Se and Te (solid metalloid),	
characters	Po (radioactive)	
Atomic radii	Increase down the group	
Ionisation	Decreases down the group	
enthalpy		
Electronegativity	Decreases down the group	
Electron gain	Increases from oxygen to	
enthalpy	sulphur and then decreases.	
Melting and	Increase down the group	
boiling points	upto Te and then decreases.	
Allotropy	All elements show allotropy	

## Chemical properties:

- Stability of -2 oxidation state decreases down the group, stability of +4 oxidation state increases and that of +6 oxidation state decreases down the group due to *inert pair effect*.
- ► **Hydrides**: All the elements form stable hydrides of the type H<sub>2</sub>M. Their general trends are:
  - **Boiling point**:  $H_2O > H_2Te > H_2Se > H_2S$
  - Volatility:  $H_2S > H_2Se > H_2Te > H_2O$
  - **Bond angle**:  $H_2O > H_2S > H_2Se > H_2Te$
  - Acidic character : H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te
  - Reducing power:  $H_2Te > H_2Se > H_2S > H_2O$
- ▶ **Halides**: All elements form halides of the type  $EX_6$ ,  $EX_4$  and  $EX_2$ .

#### ▶ Oxides :

Simple oxides	MgO, Al <sub>2</sub> O <sub>3</sub>
Mixed oxides	Pb <sub>3</sub> O <sub>4</sub> , Fe <sub>3</sub> O <sub>4</sub>
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>
Basic oxides	Na <sub>2</sub> O, CaO, BaO
Amphoteric oxides	$Al_2O_3$
Neutral oxides	CO, NO, N <sub>2</sub> O

# Dioxygen $(O_2)$ :

## ▶ Preparation :

$$2KClO_{3} \xrightarrow{\Delta} 2KCl + 3O_{2}$$

$$2Ag_{2}O_{(s)} \xrightarrow{\Delta} 4Ag_{(s)} + O_{2(g)}$$

$$2Pb_{3}O_{4(s)} \xrightarrow{\Delta} 6PbO_{(s)} + O_{2(g)}$$

$$2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$$

$$2PbO_{2(s)} \longrightarrow 2PbO_{(s)} + O_{2(g)}$$

$$2H_{2}O_{2(aq)} \longrightarrow 2H_{2}O_{(l)} + O_{2(g)}$$

#### **▶** Properties:

- Dioxygen is colourless and odourless gas, soluble in water and paramagnetic in nature.
- Dioxygen directly reacts with most of the metals (except noble metals like Au, Pt), non-metals (except noble gases).

$$2\text{Ca} + \text{O}_2 \longrightarrow 2\text{CaO} \qquad \text{(Basic oxide)}$$

$$4\text{Al} + 3\text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3 \text{ (Amphoteric oxide)}$$

$$P_4 + 5\text{O}_2 \longrightarrow P_4\text{O}_{10} \qquad \text{(Acidic oxide)}$$

$$C + \text{O}_2 \longrightarrow \text{CO}_2 \qquad \text{(Acidic oxide)}$$

$$2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2 \text{ (Roasting)}$$

$$C\text{H}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \text{ (Combustion)}$$

$$2\text{SO}_2 + \text{O}_2 \longrightarrow \frac{\text{V}_2\text{O}_5}{2} + 2\text{SO}_3$$

(Catalytic oxidation)

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$
(Catalytic oxidation)

#### Uses:

- For artificial respiration in hospitals and by mountaineers, pilots and divers.
- In oxy-hydrogen and oxy-acetylene torches which are used for cutting and welding of metals.
- Liquid dioxygen is used as a rocket fuel.

# Ozone $(O_3)$ :

- **Preparation**:  $3O_2 \xrightarrow{\text{electric discharge}} 2O_3$
- **Properties:** It is a pale blue gas, dark blue liquid and violet black solid.

## Oxidising action:

$$O_3 \longrightarrow O_2 + O$$

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

$$2I_{(aq)}^- + H_2O_{(l)} + O_{3(g)} \longrightarrow 2OH_{(aq)}^- + I_{2(g)} + O_{2(g)}$$
 (used for estimation of  $O_3$  by reacting  $I_2$  with

hypo.)

#### Reducing action:

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$
  
 $BaO_2 + O_3 \longrightarrow BaO + 2O_2$ 

#### **Structure:**



Oxidation state of O is +1 and -1.

#### Uses:

- Used for bleaching ivory, flour, delicate fabrics, etc.
- As germicide and disinfectant for sterilising water.
- Manufacture of KMnO<sub>4</sub> and artificial silk.

# Allotropes of sulphur:

- **Rhombic sulphur** ( $\alpha$ -sulphur) : It has  $S_8$ molecules, yellow in colour, m.pt. 385.8 K, specific gravity 2.06 g cm<sup>-3</sup>, insoluble in water, soluble in CS<sub>2</sub>.
- Monoclinic sulphur (β-sulphur) : It has S<sub>8</sub> molecules, colourless, needle-shaped crystals, m.pt. 393 K, specific gravity 1.98 g cm<sup>-3</sup>, soluble in CS<sub>2</sub>.

# Sulphur dioxide (SO<sub>2</sub>):

#### **Preparation:**

- By heating sulphur in air:  $S + O_2 \xrightarrow{\Delta} SO_2$ 

**Lab method**: By heating Cu with conc. H<sub>2</sub>SO<sub>4</sub>.

 $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ It is also prepared by treating a sulphite with dilute H2SO4.

$$\mathrm{SO_3}^{2-}_{(aq)} + 2\mathrm{H}^+_{(aq)} \longrightarrow \mathrm{H_2O}_{(l)} + \mathrm{SO}_{2(g)}$$

#### **Properties:**

As reducing agent:

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$
  
 $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4$   
 $+ 2MnSO_4 + 2H_2SO_4$ 

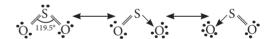
As oxidising agent :

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \downarrow$$

**Bleaching action:** Its bleaching action is due to reduction and is temporary.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2[H]$$
  
Coloured matter + [H]  $\longrightarrow$  Colourless

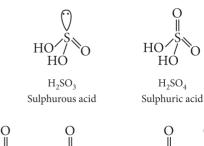
**Structure**:  $SO_2$  is a gas having  $sp^2$ hybridisation and V-shape.

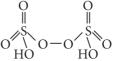


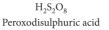
#### Uses:

- In the manufacture of sulphuric acid, sulphites and hydrogen sulphide.
- As a disinfectant, fumigant and preservative.
- For bleaching delicate articles.

# Oxoacids of sulphur:





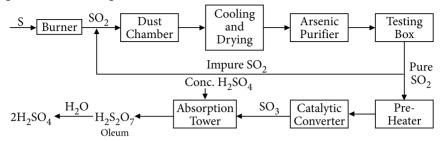




H2S2O2 Pyrosulphuric acid (Oleum)

# Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>):

#### Preparation (Contact process) :



Structure	Properties	Uses
Sulphuric acid Sulphate ion	$\begin{array}{c} & \underset{NaOH}{\overset{NaOH}{\longrightarrow}} & NaHSO_4 + H_2O \\ & \underset{NaOH}{\overset{NaOH}{\longrightarrow}} & Na_2SO_4 + 2H_2O \\ & \underset{C_{12}H_{22}O_{11}}{\overset{NaDH}{\longrightarrow}} & C + H_2O \\ & \underset{Na_2S}{\overset{S_8}{\longrightarrow}} & SO_2 + H_2O \\ & \underset{BaCl_2}{\overset{Na_2S}{\longrightarrow}} & Na_2SO_4 + H_2S \\ & \underset{K_4[Fe(CN)_6]}{\overset{NaDS}{\longrightarrow}} & BaSO_4 + 2HCl \\ & \underset{(NH_4)_2SO_4}{\overset{K_4[Fe(CN)_6]}{\longrightarrow}} & K_2SO_4 + FeSO_4 + \\ & (NH_4)_2SO_4 + CO \\ \end{array}$	It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.

#### **GROUP 17 ELEMENTS (HALOGEN FAMILY)**

Group 17 elements are collectively called halogens.

# General characteristics:

Electronic	$ns^2np^5$
configuration	
Elements	<sub>9</sub> F, <sub>17</sub> Cl, <sub>35</sub> Br, <sub>53</sub> I, <sub>85</sub> At, <sub>117</sub> Ts
Colour and physical state	F <sub>2</sub> (pale yellow gas), Cl <sub>2</sub> (greenish yellow gas), Br <sub>2</sub> (reddish brown liquid), I <sub>2</sub> (purple solid)
Atomic radii	Increase down the group
Ionisation enthalpy	Very high and decreases down the group
Electronegativity	Decreases down the group
Electron gain enthalpy	Cl > F > Br > I
Melting and boiling points	Increase down the group
Bond energy	$Cl_2 > Br_2 > F_2 > I_2$
Heat of hydration	$F^- > Cl^- > Br^- > l^-$

# Chemical properties:

► F shows only -1 oxidation state while other elements show -1, +1, +3, +5 and +7 oxidation states.

#### **▶** General trends :

- **Reactivity**:  $F_2 > Cl_2 > Br_2 > I_2$ 

- **Boiling points :** HF > HI > HBr > HCl

Melting points: HI > HF > HBr > HCl

- **Bond lengths**: HI > HBr > HCl > HF

Bond dissociation enthalpy:

HF > HCl > HBr > HI

- Acidic strength: HI > HBr > HCl > HF

- Thermal stability: HF > HCl > HBr > HI

incimal stability : 111 > 1101 > 11b1 > 111

- Reducing power: HI > HBr > HCl > HF

#### Oxides:

- Fluorine forms two oxides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub> called *oxygen fluorides*, other halogens form oxides in which oxidation states of these halogens range from +1 to +7.
- The higher oxides of halogens are more stable than the lower ones.

#### ► Metal halides :

- **Ionic character**: MF > MCl > MBr > MI
- For metals exhibiting more than one oxidation states, the halides in higher oxidation states will be more covalent than the one in lower oxidation states.

# Chlorine (Cl<sub>2</sub>):

#### **▶** Preparation:

$$\begin{array}{l} {\rm PbO_2 + 4HCl} \longrightarrow {\rm PbCl_2 + 2H_2O + Cl_2} \\ {\rm 2KMnO_4 + 16HCl} \longrightarrow {\rm 2KCl + 2MnCl_2} \\ {\rm + 8H_2O + 5Cl_2} \end{array}$$

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

#### **▶** Manufacture:

- Deacon's process: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of CuCl<sub>2</sub> at 723 K.
   4HCl + O<sub>2</sub> CuCl<sub>2</sub> > 2Cl<sub>2</sub> + 2H<sub>2</sub>O
- **Electrolytic process**: By the electrolysis of brine solution.
- Down's process: Obtained as by-product during manufacture of sodium by electrolysis of fused NaCl.
- ▶ **Properties :** It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as *chlorine water*.

#### - Bleaching action and oxidising property:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
  
 $HOCl \longrightarrow HCl + [O]$   
Coloured matter +  $[O] \longrightarrow Colourless$ 

The bleaching action of chlorine is permanent and is due to its oxidising nature.

- Action of hydrogen :

$$H_2 + Cl_2 \frac{U.V. light}{Charcoal catalyst} \rightarrow 2HCl$$

- Displacement reactions:

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$
  
 $2KI + Cl_2 \longrightarrow 2KCl + I_2$ 

- Action of NaOH:

$$2 NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O \\ (cold \ and \ dil.)$$

6NaOH + 3Cl<sub>2</sub>  $\longrightarrow$  5NaCl + NaClO<sub>3</sub> + 3H<sub>2</sub>O (hot and conc.)

- Addition reactions:

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$
  
 $CO + Cl_2 \longrightarrow COCl_2$ 

► Uses: It is used as a bleaching agent, disinfectant and in the manufacture of CHCl<sub>3</sub>, CCl<sub>4</sub>, DDT, bleaching powder, poisonous gas phosgene (COCl<sub>2</sub>), tear gas (CCl<sub>3</sub>NO<sub>2</sub>) and mustard gas (ClC<sub>2</sub>H<sub>4</sub>SC<sub>2</sub>H<sub>4</sub>Cl).

# Hydrochloric acid (HCl):

Preparation	Properties	Uses
$NaCl + H2SO4 \xrightarrow{420 \text{ K}} NaHSO4 + HCl$ $NaHSO4 + NaCl \xrightarrow{823 \text{ K}} Na2SO4 + HCl$	Colourless and pungent smelling gas, easily liquifiable, extremely soluble in water. $NH_3 + HCl \longrightarrow NH_4Cl$ $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ $Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$ 3 parts of conc. HCl and 1 part of conc. HNO <sub>3</sub> is used for dissolving noble metals <i>e.g.</i> , gold, platinum $Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$ $3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$	In manufacture of Cl <sub>2</sub> , NH <sub>4</sub> Cl and glucose, in medicine and as a laboratory reagent.  For extracting glue from bones and purifying bone black.

# Oxyacids of halogens:

Variation of the general properties of oxyacids of halogens							
Halogen	Hypohalous acids (O.S. of halogen = +1)	Halous acids (O.S. of halogen = +3)	Halic acids (O.S. of halogen = +5)	Perhalic acid (O.S. of halogen = +7)	decreases — decreases — decreases — decreases —		
F	HOF	_	_	_	Electronegativity Thermal stability Oxidising power - Acidic strength		
Cl	HClO	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>	negat Il stal ng po		
Br	HBrO	_	$HBrO_3$	$\mathrm{HBrO}_4$	Electrone Thermal Oxidisin		
I	HIO	_	$HIO_3$	$HIO_4$	- Ele - Th - Ox - Ox		
——Oxidation number of the central atom increases (+1, +3, +5, +7) —→  ——Thermal stability increases —→  ——Covalent character of <i>X</i> —O bond increases —→  ——Oxidising power decreases —→							

—— Acidity increases —→
- Electronegativity of the central atom remains the same -

Interhalogens compounds: Halogens combine amongst themselves to form a number of interhalogens of the type XX', XX'<sub>3</sub>, XX'<sub>5</sub> and XX'<sub>7</sub>, where X is a larger size halogen (more electropositive) and X' is smaller size halogen.

# **▶** Preparation :

$$\begin{array}{c} \text{Cl}_2 + \text{F}_2 \xrightarrow{437 \text{ K}} \text{2ClF}; \ I_2 + 3\text{Cl}_2 \longrightarrow 2\text{ICl}_3 \\ \text{(equal volume)} \qquad \qquad \text{(excess)} \\ \text{Cl}_2 + 3\text{F}_2 \xrightarrow{573 \text{ K}} \text{2ClF}_3; \ \text{Br}_2 + 3\text{F}_2 \longrightarrow 2\text{BrF}_3 \\ \text{(excess)} \\ \text{I}_2 + \text{Cl}_2 \longrightarrow 2\text{ICl}; \qquad \text{Br}_2 + 5\text{F}_2 \longrightarrow 2\text{BrF}_5 \\ \text{(equimolar)} \qquad \qquad \text{(excess)} \end{array}$$

#### **▶** Structures:

Туре	Hybridi- sation	Shape	Structure
XX'	sp³	Linear	X $X'$
XX' <sub>3</sub>	sp³d	T-shaped	

XX' <sub>5</sub>	sp³d²	Square pyramidal	X' $X'$ $X'$ $X'$ $X'$
XX' <sub>7</sub>	sp³d³	Pentagonal bipyramidal	X' $X'$ $X'$ $X'$ $X'$ $X'$ $X'$

#### **GROUP 18 ELEMENTS (NOBLE GASES)**

- These are monoatomic gases and are also known as *rare gases* or *aerogens*.
- General characteristics:

Electronic configuration	ns²np <sup>6</sup>
Elements	<sup>2</sup> He, <sub>10</sub> Ne, <sub>18</sub> Ar, <sub>36</sub> Kr, <sub>54</sub> Xe, <sub>86</sub> Rn, <sub>118</sub> Og
Physical state	Gases
Atomic radii	Increase down the group.
Electron gain enthalpy	Positive
Melting and boiling points	Very low due to weak dispersion forces

- Chemical properties: Noble gases are least reactive due to high ionization enthalpy and more positive electron gain enthalpy.
- ► Xenon-fluorine compounds :

$$\begin{array}{c} \text{Xe} \\ \text{(excess)} \\ \text{Xe} \\ + & \text{F}_2 \\ \text{(1:5 ratio)} \\ \text{Xe} \\ + & 2\text{F}_2 \\ \text{(1:5 ratio)} \\ \text{Xe} \\ + & 3\text{F}_2 \\ \text{(1:20 ratio)} \\ \end{array} \xrightarrow{673 \text{ K}, 7 \text{ bar} \atop \text{A0-70 bar}} \text{XeF}_4$$

**▶** Xenon-oxygen compounds :

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF$$

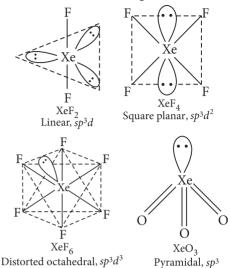
$$+ 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

# Structures of some compounds of xenon:



#### Uses:

# **Previous Years' CBSE Board Questions**

# 7.1 Group 15 Elements

#### VSA (1 mark)

1. Why is the single N—N bond weaker than the single P—P bond?

(1/5, Delhi 2019, Foreign 2014)

2. Give reason:

Nitrogen does not form pentahalide. (1/3, *Delhi 2017*, 1/3, *Delhi AI 2016*, 1/3 *AI 2011C*)

Arrange the following in the increasing order of property mentioned:
 NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> (Base strength)

<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> (Base strength) (1/5, Delhi 2016)

4. Account for the following:
BiH<sub>3</sub> is the strongest reducing agent amongst all the hydrides of group 15.

(1/5, Foreign 2015)

- 5. Why does  $R_3P = O$  exist but  $R_3N = O$  does not? (R = alkyl group) (1/5, Delhi 2015C)
- **6.** Why is  $NH_3$  more basic than  $PH_3$ ? (1/5, AI 2015C, 2014C)
- 7. Give reasons for the following:  $(CH_3)_3P = O$  exists but  $(CH_3)_3N = O$  does not. (1/3, AI 2014)
- 8. Account for the following:
  Bi is a strong oxidizing agent in the +5 state.

  (1/5, Foreign 2014)
- Account for the following:
   PCl<sub>5</sub> is known but NCl<sub>5</sub> is not known.

(1/5, Foreign 2014)

**10.** Arrange the following in the increasing order of their basic character:

NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> (Foreign 2014)

**11.** Arrange the following group of substances in the order of the property indicated against each group:

NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, SbH<sub>3</sub> – increasing order of boiling points. (1/5, Delhi 2014C)

**12.** Assign reasons for the following: NF<sub>3</sub> is an exothermic compound whereas NCl<sub>3</sub> is not. (1/5, AI 2014C, 2013C, 2012, 2011, 1/3, Delhi 2011)

13. Why is nitrogen gas very unreactive?

(AI 2014C)

**14.** Give reasons for the following: PH<sub>3</sub> has lower boiling point than NH<sub>3</sub>.

(1/5, Delhi 2013)

**15.** Explain the following: BiCl<sub>3</sub> is more stable than BiCl<sub>5</sub>.

(1/2, Delhi 2013C)

**16.** Account for the following : Nitrogen is found in gaseous state.

(1/5, Delhi 2013C)

**17.** Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Why?

(1/2, AI 2013C, Delhi 2012C)

**18.** Account for the following: NF<sub>3</sub> is an exothermic compound but NCl<sub>3</sub> is an endothermic compound.

(1/3, AI 2013C, 2012, 2011, 1/5, Delhi 2011)

**19.** Bismuth is a strong oxidising agent in the pentavalent state. Explain.

(1/3, AI 2013C, 1/5, Delhi 2012C)

**20.** Explain the following observations: The molecules NH<sub>3</sub> and NF<sub>3</sub> have dipole moments which are of opposite direction. (1/5, Delhi 2012)

- **21.** Explain the following observation: Phosphorus has greater tendency for catenation than nitrogen. (1/5, AI 2012)
- **22.** Why is BiH<sub>3</sub> the strongest reducing agent amongst all the hydrides of group 15 elements? (1/5, AI 2012C)
- 23. Account for the following:

  Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

  (1/5, Delhi 2011)
- **24.** Draw the structure of the following molecule:  $NF_3$  (1/3, Foreign 2011)
- 25. Explain the following:
  +3 oxidation state becomes more and more stable from As to Bi in the group.
  (1/5, Delhi 2011C)

**26.** Account for the following : BiCl<sub>3</sub> is less covalent than PCl<sub>3</sub>.

(1/5, Delhi 2011C)

#### SA (2 marks)

- **27.** Among the hydrides of group-15 elements, which have the
  - (a) lowest boiling point
  - (b) maximum basic character
  - (c) highest bond angle
  - (d) maximum reducing character? (2018)

# **7.2** Dinitrogen

#### VSA (1 mark)

- **28.** What happens when  $(NH_4)_2Cr_2O_7$  is heated? (1/2, Delhi 2017)
- **29.** Give reasons for the following :  $N_2$  is less reactive at room temperature.

(1/3, AI 2015)

#### 7.3 Ammonia

# VSA (1 mark)

- **30.** On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved which forms a blue coloured complex with Cu<sup>2+</sup> ion. Identify the gas. (*Delhi 2016*)
- 31. Account for the following:
  Bond angle in NH<sub>4</sub> is higher than NH<sub>3</sub>.

(1/5, Foreign 2015)

- 32. What happens when ammonium chloride is treated with  $Ca(OH)_2$ ? (1/5, AI 2015C)
- 33. Why does NH<sub>3</sub> act as a Lewis base?

(AI 2014)

**34.** Mention the optimum conditions for the industrial manufacture of ammonia by Haber's process. (1/3, Foreign 2011)

#### SA (2 marks)

35. How is ammonia prepared on the large scale? Name the process and mention the optimum conditions for the production of ammonia by this process. (2/5, AI 2014C)

# **7.4** Oxides of Nitrogen

#### VSA (1 mark)

**36.** Give reasons for the following :  $N_2O_5$  is more acidic than  $N_2O_3$ . (1/3, AI 2017)

- 37.  $Pb(NO_3)_2$  on heating gives a brown gas which undergoes dimerisation on cooling? Identify the gas. (AI 2016)
- **38.** Draw the structure of the following compound:  $N_2O_5$  (1/3, Delhi 2014, AI 2012)
- **39.** Why does NO<sub>2</sub> dimerise? (AI 2014, 2012C)
- **40.** Using VSEPR theory predict the probable structure of the following:  $N_2O_3$

(1/5, Delhi 2014C)

- **41.** What is the covalency of nitrogen in  $N_2O_5$ ? (Delhi 2013)
- **42.** Explain the following : NO<sub>2</sub> readily forms a dimer. (1/2, Delhi 2013C)
- 43. Explain the following: The bond angles (O-N-O) are not of the same value in  $NO_2^+$  and  $NO_2^+$ .

(1/5, Delhi 2012)

- **44.** Give reason: Nitric oxide becomes brown when released in air. (1/5, Delhi, AI 2012C)
- **45.** State reasons for the following:

  The N—O bond in NO<sub>2</sub> is shorter than the N—O bond in NO<sub>3</sub>. (1/2, AI, Delhi 2011)

#### LA I (3 marks)

- **46.** When concentrated sulphuric acid 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 to this test tube. On cooling, the gas (*A*) changed into a colourless solid (*B*).
  - (i) Identify (A) and (B).
  - (ii) Write the structures of (A) and (B).
  - (iii) Why does gas (A) change to solid on cooling? (3/5, 2018)

# 7.5 Nitric Acid

#### VSA (1 mark)

- 47. Write the formula of the compound of phosphorus which is obtained when conc.HNO<sub>3</sub> oxidises P<sub>4</sub>. (AI 2017)
- **48.** Write the formula of the compound of sulphur which is obtained when conc.  $HNO_3$  oxidises  $S_8$ . (AI 2017)
- **49.** Write the formula of the compound of iodine which is obtained when conc. HNO<sub>3</sub> oxidises I<sub>2</sub>. (AI 2017)

- **50.** Complete the following chemical equation; Cu + HNO<sub>3(dilute)</sub>  $\longrightarrow$  (1/5, Delhi 2015C, AI 2012)
- ${\bf 51.} \ \ Complete \ the \ following \ chemical \ equation:$

 $I_2 + HNO_3 \longrightarrow (1/5, Delhi 2011)$ (Conc.)

#### SA (2 marks)

**52.** When dilute ferrous sulphate solution is added to an aqueous solution containing nitrate ion followed by careful addition of concentrated sulphuric acid along the sides of test tube, a brown ring is formed at the interface between the solution and sulphuric acid layers. Which anion is confirmed by the appearance of brown ring? What is the composition of the brown ring? (AI 2019)

# 7.6 Phosphorus – Allotropic Forms

#### VSA (1 mark)

- 53. Give reason for the following:
  Red phosphorus is less reactive than white phosphorus. (1/3, AI 2017, 1/3 Foreign 2011)
- **54.** Which allotrope of phosphorus is more reactive and why? (1/5, Delhi 2015)
- **55.** Write the structural difference between white phosphorus and red phosphorus.

(1/3, Delhi 2014)

**56.** Complete the following equation :

 $P_4 + H_2O \longrightarrow (1/2, AI\ 2014)$ 

57. Draw the structure of the following : Red  $P_4$  (1/5, Foreign 2014)

**58.** White phosphorus is more reactive than red phosphorus. Explain (1/5, *Delhi 2012C*)

# 7.7 Phosphine

# VSA (1 mark)

**59.** Complete the following chemical reaction equation:

 $P_4 + NaOH + H_2O \longrightarrow$ 

(1/5, Delhi 2015C, 2014C)

- **60.** Complete the following chemical equation:  $Ca_3P_2 + H_2O \longrightarrow (1/3, Delhi \ 2014)$
- **61.** Complete the following equation:  $HgCl_2 + PH_3 \longrightarrow (1/3, AI\ 2011)$

# 7.8 Phosphorus Halides

## VSA (1 mark)

- **62.** Account for the following: Solid PCl<sub>5</sub> is ionic in nature. (1/5, AI 2019, Delhi 2016)
- 63. What happens when PCl<sub>5</sub> is heated? Write the equation involved.

(1/2, Delhi 2017, 1/2, Delhi 2013)

**64.** Account for the following : PCl<sub>3</sub> is more covalent than PCl<sub>3</sub>.

(1/2, Delhi 2014)

- 65. Complete the following equation:  $Ag + PCl_5 \longrightarrow (1/2, AI\ 2014)$
- **66.** Draw the structure of the following : Solid  $PCl_5$  (1/2, Delhi 2014C, AI 2014C)
- **67.** Complete the following chemical equation:  $P_4 + SO_2Cl_2 \longrightarrow (1/2, AI\ 2014C, 1/5, (Delhi\ 2012, 1/3, Foreign\ 2011)$
- **68.** Why does PCl<sub>3</sub> fume in moisture? (*Delhi 2013C*, 2012C)
- **69.** Which one of PCl<sub>4</sub><sup>+</sup> and PCl<sub>4</sub><sup>-</sup> is not likely to exist and why? (*Delhi 2012*)
- 70. Explain the following observation: All the bonds in PCl<sub>5</sub> molecule are not equivalent. (Delhi 2012)
- 71. Account for the following: PCl<sub>5</sub> acts as an oxidising agent.

(1/5, AI 2012C)

# **7.9** Oxoacids of Phosphorus

# VSA (1 mark)

**72.** Give reasons :

 $H_3PO_3$  undergoes disproportionation reaction but  $H_3PO_4$  does not. (1/5, 2018)

**73.** What happens when  $H_3PO_3$  is heated? Write the equation.

(1/2 Delhi 2017, Delhi 2013)

- 74. Draw the structure of the following :  $H_3PO_2$  (1/2, Delhi 2017, Delhi 2013C, 2012, AI 2013C)
- 75. Draw the structure of the following :  $H_4P_2O_7$  (1/2, Delhi 2017, 1/5, Foreign 2015)
- **76.** Arrange the following in the increasing order of property mentioned :

- H<sub>3</sub>PO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>2</sub> (Reducing character) (1/5, Delhi 2016)
- 77. What is the basicity of  $H_3PO_4$ ? (Delhi 2015)
- **78.**  $H_3PO_2$  is a stronger reducing agent than  $H_3PO_3$ .(1/3, Delhi, 1/3, AI, 1/5, Foreign 2014)
- **79.** What is the basicity of  $H_3PO_3$ ?

(1/3, AI 2014)

- **80.** Draw the structure of the following molecule:  $(HPO_3)_3$  (*Delhi 2013*)
- 81. Draw the structure of the following molecule:  $H_3PO_3$  (1/2, Delhi 2013)
- **82.** Account for the following :  $H_3PO_2$  has reducing nature. (1/5, Delhi 2013C)
- 83. What is the basicity of  $H_3PO_2$  acid and why? (1/5, 2012, AI 2011)
- **84.** Write a reaction to show the reducing behaviour of H<sub>3</sub>PO<sub>2</sub>. (*Delhi 2012C*)

# 7.10 Group 16 Elements

#### VSA (1 mark)

**85.** Give reason:

Sulphur is a polyatomic solid whereas oxygen is a diatomic gas.

(1/5, 2020, 1/5, 2018, Delhi 2015C, AI 2012)

**86.** Account for the following:

Tendency to show -2 oxidation state decreases from oxygen to tellurium.

(1/5, 2020)

- 87. Give reason:
  - $SO_2$  is reducing while  $TeO_2$  is an oxidising agent. (1/5, 2020, 1/3, AI 2016)
- **88.** Arrange the following in the order of property indicated :
  - H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te increasing acidic character (1/2, Delhi 2019, 1/3, Delhi 2014)
- **89.** Arrange the following in increasing order of property indicated, giving reason.
  - Hydrides of group 16 reducing character (1/5, AI 2019)
- **90.** Account for the following: SF<sub>6</sub> is inert towards hydrolysis. (1/5, 2018C, AI 2014C, Delhi 2013C, 1/2 Delhi, AI 2011)
- 91. Give reason:

Thermal stability decreases from  $H_2O$  to  $H_2Te$ . (1/3, Delhi 2017)

**92.** Account for the following:

There is large difference between the melting and boiling points of oxygen and sulphur.

(1/5, Delhi 2015)

**93.** Give reason for the following:

H<sub>2</sub>Te is the strongest reducing agent amongst all the hydrides of group 16 elements.

(1/3, AI 2015)

- **94.** Elements of group 16 generally show lower value of first ionization enthalpy compared to the corresponding elements of group 15. Why? (1/5, AI 2015C, 1/3, AI 2011C)
- **95.** Give reason for the following:

  Oxygen has less electron gain enthalpy with negative sign than sulphur. (1/3, AI 2014)
- **96.** Arrange the following group of substances in the order of the property indicated against the group:

O, S, Se, Te – increasing order of electron gain enthalpy with negative sign.

(1/5, Delhi 2014C)

 $\textbf{97.} \ \ \text{Assign reason for the following}:$ 

H<sub>2</sub>S is more acidic than H<sub>2</sub>O

(1/5, AI 2014C, 2011)

**98.** Assign reason for the following: Sulphur has a greater tendency for catenation than oxygen.

(1/5, AI 2014C, Delhi 2013, AI 2012)

**99.** Account for the following:

H<sub>2</sub>S is less acidic than H<sub>2</sub>Te.

(1/5, Delhi 2013C)

**100.** Account for the following:

Boiling point of water is much higher than that of hydrogen sulphide. (1/3, AI 2013C)

**101.** Account for the following:

Thermal stability of water is much higher than that of  $H_2S$ . (1/5, Delhi 2012C)

#### SA (2 marks)

- **102.** Account for the following:
  - (i) H<sub>2</sub>S has lower boiling point than H<sub>2</sub>O.
  - (ii) Reducing character decreases from SO<sub>2</sub> to TeO<sub>2</sub>. (2/3, Foreign 2015)

#### LA | (3 marks)

**103.** Among the hydrides of group 16, write the hydride

- (i) Which is a strong reducing agent?
- (ii) Which has maximum bond angle?
- (iii) Which is most thermally stable? Give suitable reason in each. (3/5,

Give suitable reason in each. (3/5, 2020)

# **7.13** Ozone

## VSA (1 mark)

104. Give reason for the following:

Ozone is thermodynamically less stable than oxygen.

(1/5, Delhi 2019)

 $\textbf{105.} \ \mathsf{Complete} \ \mathsf{the} \ \mathsf{following} \ \mathsf{reaction}:$ 

$$PbS_{(s)} + O_3 \longrightarrow$$

(1/5, AI 2019)

 $\textbf{106.} \ \textbf{Account for the following:}$ 

Ozone is thermodynamically unstable.

(1/5, Delhi 2016)

**107.** How the supersonic jet aeroplanes are responsible for the depletion of ozone layers? (1/5, *Delhi 2015*)

**108.** Account for the following:

The two O—O bond lengths in the ozone molecule are equal. (1/3, Delhi 2014)

**109.** Account for the following:

O<sub>3</sub> acts as a powerful oxidising agent.

(1/5, AI 2011C)

# 7.14 Sulphur – Allotropic Forms

#### VSA (1 mark)

**110.** Account for the following:

Sulphur in vapour form exhibits paramagnetic behaviour.

(1/5, Delhi 2019, 1/3, AI 2014,

1/5, Foreign 2014, 2011, 1/5, Delhi 2012, 2011C)

**111.** Give reason for the following:

Above 1000 K sulphur shows paramagnetism. (1/5, AI 2019)

**112.** Which allotrope of sulphur is thermally stable at room temperature? (Foreign 2015)

#### SA (2 marks)

**113.** Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated about 370 K?

(*Foreign 2014*)

# 7.15 Sulphur Dioxide

## VSA (1 mark)

- 114. Account for the following: Moist  $SO_2$  gas acts as a reducing agent. (1/5, 2020)
- 115. Write a chemical reaction to test sulphur dioxide gas. Write chemical equation involved. (1/5, Delhi 2019)
- **116.** Complete the following chemical equation :  $Fe^{3+} + SO_2 + H_2O \longrightarrow$

(1/5, 2018C, Foreign 2011, Delhi 2011C)

117. What happens when:

SO<sub>2</sub> gas is passed through an aqueous solution Fe<sup>3+</sup> salt?

(1/2, AI 2016, 1/3, AI 2011)

118. What happens when sulphur dioxide reacts with chlorine in the presence of charcoal? (1/3, Delhi 2015)

# 7.16 Oxoacids of Sulphur

#### VSA (1 mark)

**119.** Account for the following : Sulphurous acid is a reducing agent.

(1/3, 2020)

- **120.** Draw the structure of an oxoacid of sulphur containing S—O—S linkage. (1/5, 2020)
- 121. Draw the structure of the following :  $H_2S_2O_8$

(1/5, AI 2019, 1/2, AI 2017, 1/5, Foreign 2014, 2011, 1/3, Delhi 2013, 2012)

**122.** Draw the structure of the following :  $H_2S_2O_7$  (1/2, *Delhi 2017*, 1/3, *AI 2013*, 1/5, *Delhi 2012*)

**123.** Draw the structure of the following :  $H_2SO_3$  (1/2, AI 2017, 2015)

**124.** Draw the structure of the following :  $H_2SO_4$  (1/5, Delhi 2015C, 2014)

**125.** Predict the shape and the asked angle (90° or more or less) in the following case:  $SO_3^{2-}$  and the angle O - S - O

(1/5, Delhi 2012)

# **7.17** Sulphuric Acid

## VSA (1 mark)

**126.** Complete the following equation :

$$S + H2SO4 \longrightarrow (Conc.)$$
 (1/5, 2020)

127. Write the conditions to maximize the yield of H<sub>2</sub>SO<sub>4</sub> by Contact process.

(1/5, Delhi 2016)

**128.** Complete the following equation:

 $Cu + conc. H_2SO_4 \longrightarrow$ (1/3, AI 2014)

**129.** Complete the following equation:

$$CaF_2 + H_2SO_4 \longrightarrow (1/2, AI\ 2014)$$

**130.** Complete the following equation :

 $C + conc. H<sub>2</sub>SO<sub>4</sub> \longrightarrow$ 

(1/2, AI 2014, Delhi, Foreign 2011)

**131.** Why is  $K_{a_1} \ll K_{a_1}$  for  $H_2SO_4$  in water?

(1/2, Foreign 2014)

**132.** Account for the following:

Concentrated sulphuric acid has charring action on carbohydrates. (1/3, AI 2013C)

**133.** Complete the following equation:

$$SO_3 + H_2SO_4 \longrightarrow$$

(1/5, AI 2011)

#### SA (2 marks)

- 134. Write one reaction as an example of each, to show that conc. H<sub>2</sub>SO<sub>4</sub> acts as
  - (i) an oxidising agent, and
  - (ii) a dehydrating agent.

(2/3, 2020)

- 135. What happens when
  - (i) conc. H<sub>2</sub>SO<sub>4</sub> is added to Cu?
  - (ii) SO<sub>3</sub> is passed through water?

Write the equations. (Delhi 2017)

136. With the help of chemical equation explain the principle of Contact process in brief for the manufacture of sulphuric acid.

(2/3, AI 2013C)

#### LA I (3 marks)

137. Describe the Contact process for the manufacture of sulphuric acid with special reference to the reaction conditions, catalysts used and yield in the process. (No diagram is (3/5, Delhi 2015C, 2012C) required.)

# **7.18** Group 17 Elements

# VSA (1 mark)

138. Assertion (A) : F - F bond in  $F_2$  molecule is weak.

**Reason (R):** F atom is small in size.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement. (2020)
- **139.** Assertion (A):  $F_2$  has lower bond dissociation enthalpy than Cl<sub>2</sub>.

Reason (R): Fluorine is more electronegative than chlorine.

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement. (2020)
- **140.** Complete the following chemical reaction:

$$I_{(aq)}^- + H_{(aq)}^+ + O_{2(g)} \longrightarrow (1/3, 2020)$$

**141.** Account for the following : Acidic character increases from HF to HI.

(1/5, 2020, Delhi 2015)

**142.** Account for the following:

Hydration enthalpy of F- ion is more than (1/5, 2020, 1/3, Delhi 2017)

143. Arrange the following in order of property indicated:

> HF, HCl, HBr, HI – decreasing bond enthalpy (1/2, Delhi 2019, AI 2011C)

**144.** Explain the following observation:

Despite lower value of its electron gain enthalpy with negative sign, fluorine (F2) is a stronger oxidising agent than Cl<sub>2</sub>.

(1/5, Delhi 2019, AI 2019, 2012)

**145.** Arrange the following in increasing order of property indicated, giving reason. Hydrides of group 17 - acidic strength

(1/5, AI 2019)

146. Arrange the following in the decreasing order of their reducing character:

- **147.** Complete the following chemical equation :  $F_2 + 2Cl^- \rightarrow (1/2, Delhi\ 2017)$
- 148. Give reason for the following:

  Electron gain enthalpies of halogens are largely negative. (1/3, AI 2017)
- **149.** F<sub>2</sub> has lower bond dissociation enthalpy than Cl<sub>2</sub>. Why? (1/5, Delhi 2015, 2013)
- 150. Why are halogens coloured?

(1/5, Delhi 2015C, AI 2012)

- **151.** Answer the following :

  Why are halogens strong oxidising agents?

  (1/5, AI 2015C)
- **152.** Arrange the following in the order of property indicated:

  HF, HCl, HBr, HI increasing bond dissociation enthalpy

  (1/2, Delhi 2014)
- **153.** Arrange the following groups of substances in the order of the property indicated : F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> increasing order of bond dissociation enthalpy.

(1/5, Delhi 2014C, 2011C)

- **154.** Why is  $F_2$  a stronger oxidising agent than  $Cl_2$ ? (AI 2014C, 1/3, AI 2011C)
- 155. Assign reason for the following:

  HCl is a stronger acid than HF though
  fluorine is more electronegative than
  chlorine. (1/5, AI 2014C, AI 2013C)
- Fluorine does not exhibit positive oxidation state. (1/5, Delhi 2013, 2011C, 1/5, AI 2012)
- **157.** Fluorine exhibits only –1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation state also. Why is it so? (*Delhi 2013C*)
- **158.** Account for the following :

  HF is not stored in glass bottles but is kept in wax-coated bottles. (1/3, AI 2013C)
- **159.** Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water. (1/5, AI 2012)
- 160. Explain giving reason for the following situation:

  In aqueous medium HCl is stronger acid than HF. (1/2, Foreign 2011)

**161.** Suggest a possible reason for the following observation:

Fluorine forms the largest number of interhalogen compounds amongst the halogens. (Delhi 2011C)

**162.** Account for the following: Electron gain enthalpy with negative sign for fluorine is less than that for chlorine.

(1/3, AI 2011C)

#### SA (2 marks)

- **163.** Write the reaction of  $F_2$  with water. Why does  $I_2$  not react with water? (2/5, 2020)
- 164. Compare the oxidizing action of F<sub>2</sub> and Cl<sub>2</sub> by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy. (2/5, Delhi 2016)

#### 7.19 Chlorine

#### VSA (1 mark)

- **165.** Complete the following reaction equation : NaOH (cold and dilute) +  $Cl_2 \longrightarrow$  (1/5, 2020, 1/5, Delhi 2018C, 1/3, Delhi 2011C)
- **166.** Complete the following reaction :  $NH_3 + 3Cl_{2(excess)} \longrightarrow (1/2, Delhi 2017)$
- **167.** Complete the following reaction:  $Cl_2 + H_2O \longrightarrow (1/2, Delhi\ 2017)$
- **168.** Write balanced equation for the following reaction:

Chlorine reacts with dry slaked lime.

(1/3, Delhi 2015C)

- **169.** Name two poisonous gases which can be prepared from chlorine gas. (AI 2013)
- 170. Account for the following:

  Bleaching of flowers by Cl<sub>2</sub> is permanent while that of SO<sub>2</sub> is temporary?

(1/3, AI 2013C)

- 171. Complete the following chemical equation : NaOH +  $Cl_2 \longrightarrow$  (hot and conc.) (1/5, Delhi 2012)
- 172. Account for the following:

  Chlorine water loses its yellow colour on standing.

  (1/5, AI 2012C)
- 173. Complete this reaction :  $6\text{NaOH} + 3\text{Cl}_2 \longrightarrow (1/3, AI\ 2011C)$

**174.** Complete the following reaction equation :

 $I_2 + H_2O + Cl_2 \longrightarrow$ (AI 2011C)

#### SA (2 marks)

175. How can you prepare Cl<sub>2</sub> from HCl and HCl from Cl<sub>2</sub>? Write reactions only. (AI 2019)

# **7.20** Hydrogen Chloride

## VSA (1 mark)

**176.** Complete the following chemical reaction:  $MnO_2 + 4HCl \longrightarrow$ (1/3, 2020)

177. Write balanced chemical equations for the following process:

MnO<sub>2</sub> is heated with conc. HCl.

(1/2 Delhi 2019)

178. What happens when HCl is added to MnO<sub>2</sub>? (1/2, Delhi 2017)

**179.** Account for the following: Iron dissolves in HCl to form FeCl2 and not (1/5, Foreign 2015, 2014)

# **7.21** Oxoacids of Halogens

#### VSA (1 mark)

**180.** Account for the following: Fluorine forms only one oxoacid.

(1/3, 2020, 1/5, Delhi 2016)

181. Give reason:

HClO<sub>4</sub> is a stronger acid than HOCl.

(1/5, 2020, 1/5, Foreign 2015)

**182.** Draw the structure of the following: (1/5, AI 2019, 2018, 1/2 AI 2017) HClO<sub>3</sub>

**183.** Draw the structure of the following: HClO<sub>4</sub> (1/2, AI 2014, 2011, 1/5 Foreign 2014)

**184.** Account for the following:

Fluorine does not form oxoacids.

(1/5, AI 2012C)

**185.** How would you account for the following: The oxidising power of oxoacids of chlorine follows the order:

HClO<sub>4</sub> < HClO<sub>3</sub> < HClO<sub>2</sub> < HClO

(1/2, Foreign 2011)

# **7.22** Interhalogen Compounds

#### VSA (1 mark)

**186.** Draw the shape of the following molecule: (1/2, 2020, 1/5, Delhi 2015C, 2014, BrF<sub>3</sub> 2014C, 2013, 2011, AI 2014, 2011) 187. Give reason:

When Cl<sub>2</sub> reacts with excess of F<sub>2</sub>, ClF<sub>3</sub> is formed and not FCl<sub>3</sub>. (1/5, 2018)

**188.** Draw the structure of the following: BrF<sub>5</sub> (1/2, 2018C, AI 2017, 1/5, Delhi 2016)

**189.** Draw the structure of the following: (1/2, AI 2017, Delhi 2015, AI 2012)

**190.** Give reason: ICl is more reactive than  $I_2$ . (1/3, AI 2016, 2012, AI 2012C, 2011C)

**191.** Complete the following chemical equation :

 $F_2(Excess) + Cl_2 \xrightarrow{300^{\circ}C}$ (1/5, AI 2014C)

192. F<sub>2</sub> is more reactive than ClF<sub>3</sub> but ClF<sub>3</sub> is more reactive than Cl<sub>2</sub>. Give reason.

(1/5, Delhi 2013C)

193. Predict the shape and the asked angle (90° or more or less) in the following cases.

 $ClF_3$  and the angle F - Cl - F

(1/5, Delhi 2012)

194. Account for the following: BrCl<sub>3</sub> is more stable than BrCl<sub>5</sub>.

(1/5, AI 2012C)

195. Why does fluorine not play the role of a central atom in interhalogen compounds?

(AI 2011)

**196.** Complete the following chemical equation :  $Br_2 + F_2 \longrightarrow$ (Foreign 2011) (excess)

#### SA (2 marks)

**197.** How are interhalogen compounds formed? What general compositions can be assigned to them? (AI 2013)

# **7.23** Group 18 Elements

# VSA (1 mark)

198. Draw the shape of the following molecule: XeOF<sub>4</sub>

> (1/2, 2020, 1/2, Delhi 2017, 1/5, AI 2017C, 2015,2015C, 2013, 2012, Foreign 2014)

199. Complete the following chemical reaction:  $XeF_6 + KF \longrightarrow$ (1/3, 2020)

200. Give reason:

Helium does not form compounds like (1/5, 2020)

201. Boiling point of noble gases increase from He to Rn (1/3, 2020) **202.** Complete the following equation :

 $XeF_2 + H_2O \rightarrow (1/5, 2020, 1/2, Delhi 2017,$ AI 2014, 1/5, Delhi 2011, 2011C)

**203.** Draw the structure of  $XeF_2$ . (1/5, 2020, 1/2, 2018C, 1/5, Foreign 2015, Delhi 2014, 2012, 2013, 2011, AI 2014)

**204.** Draw the structure of the following:

(1/5, Delhi 2019, 2018, 2016, 2014, XeF₄ 1/2, Delhi 2017, AI 2016, 2014)

205. Write balanced chemical equations for the following processes:

XeF<sub>2</sub> undergoes hydrolysis.

(1/2, Delhi 2019, 1/5, 2018C)

**206.** Complete the following reaction:

 $XeF_6 + NaF \longrightarrow$ (1/5, AI 2019)

**207.** Complete the following reaction:

 $XeF_4 + SbF_5 \longrightarrow$ (1/5, 2018)

**208.** Complete the following equation :  $XeF_4 + O_2F_2 \longrightarrow (1/5, 2018 C, 1/2, Delhi$ 

2014C, 2012, 1/2, AI 2014, 2012)

**209.** Complete the following reaction:

 $XeF_6 + 2H_2O \longrightarrow$ (1/2, Delhi 2017)

**210.** Draw the structure of the following:

XeF<sub>6</sub> (1/2, Delhi 2017, AI 2013, 1/5, Delhi 2012)

**211.** Complete the following reaction:

 $XeF_6 + 3H_2O \longrightarrow$ (1/2, Delhi 2017)

**212.** What happens when  $XeF_4$  reacts with  $SbF_5$ ? (AI 2016)

**213.** Give reason for the following:

Helium is used in diving apparatus as a diluent for oxygen. (1/3, AI 2015, 2013C)

**214.** Draw the structure of the following: XeO<sub>3</sub>

(1/5, AI 2015C, 2014)

**215.** Account for the following:

Unlike xenon, no distinct chemical compound of helium is known. (1/5, Foreign 2014)

**216.** Write the formula and describe the structure of noble gas species which is isostructural with BrO<sub>3</sub>. (1/5, Delhi 2014C)

217. Complete the following chemical reaction equation:  $XeF_4 + H_2O$  —

> (1/2, AI 2014C, 2012, 2011, 2011C, 1/5, Delhi 2012)

218. What inspired N.Bartlett for carrying out reaction between Xe and PtF6?

(Delhi 2013)

219. Complete the following chemical reaction equation:

 $XeF_6 + H_2O \longrightarrow$ (1/5, Delhi 2012, 1/3, Foreign 2011)

220. Predict the shape and asked angle (90° or more or less) in the following case.

XeF<sub>2</sub> and the angle F - Xe - F

(1/5, Delhi 2012)

**221.** Explain the following observations:

Helium forms no real chemical compound.

(1/5, AI 2012)

222. Noble gases have low boiling points. Why?

(Delhi 2012C, AI 2011)

223. Complete the following reaction equation:

$$XeF_2 + PF_5 \longrightarrow$$

(1/5, Delhi 2011C, 1/2, AI 2011C)

#### SA (2 marks)

**224.** Write the products of the following reaction:  $6XeF_4 + 12H_2O \rightarrow$ 

Is this reaction a disproportionation reaction? Give reasons in support of your

225. (i) Which noble gas is used in filling balloons for meteorological observations?

(ii) Complete the equation:

$$XeF_2 + PF_5 \longrightarrow (2/5, Delhi 2015)$$

226. Write the balanced chemical equations for obtaining XeO<sub>3</sub> and XeOF<sub>4</sub> from XeF<sub>6</sub>.

(1/5, Delhi 2013C)

**227.** Explain the following:

- (i) Xenon does not form such fluorides as XeF<sub>3</sub> and XeF<sub>5</sub>.
- (ii) Out of noble gases, only xenon is known to form real chemical compounds.

(Delhi 2012C)

228. How is XeO<sub>3</sub> obtained? Write the related chemical equations. Draw the structure of XeO<sub>3</sub>. (AI 2012C)

### **Detailed Solutions**

- 1. The single N—N bond is weaker than the single P—P bond because of high interelectronic repulsion of the non-bonding electrons, occurring due to the small bond length.
- **2.** Nitrogen cannot expand its octet due to absence of *d*-orbitals.
- 3. Increasing (Lewis) base strength order is :  $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

The reason for this order is that as we move from NH<sub>3</sub> to BiH<sub>3</sub>, the size of the central atom increases. Hence, lone pair is not easily available for donation. The electron density on the central atom decreases on moving from NH<sub>3</sub> to BiH<sub>3</sub> and so the basic strength also decreases.

- 4. Among hydrides of group-15 elements, the bond length increases from N-H to Bi-H with increasing size of element. Bi-H bond is longest and weakest, it can break more easily and evolve  $H_2$  gas which acts as the reducing agent.
- 5.  $R_3N = O$  molecule has five covalent bonds with N atom. The octet in N cannot be extended as it does not have *d*-orbitals for the formation of  $p\pi$ - $d\pi$  bond.

In the case of  $R_3P = O$ , P can extend its octet since it has empty d-orbitals in its valence shell and form  $p\pi$ - $d\pi$  bond.

- 6. Lewis basic nature of  $NH_3$  and  $PH_3$  molecules is due to the presence of lone pairs on N and P atoms, respectively. P atom is much larger than N atom and also has empty d-orbitals. Electron density due to lone pair on P gets diffused because of the presence of d-orbitals and so the lone pair is not easily available for donation. Hence,  $PH_3$  is less basic than  $NH_3$ .
- 7. Refer to answer 5.
- **8.** On moving down the group, the stability of +5 oxidation state decreases while +3 oxidation state increases due to inert pair effect.

Thus, +5 oxidation state of Bi is less stable and Bi(V) is a stronger oxidising agent.

- **9.** Nitrogen cannot expand its valency beyond 4 due to absence of *d*-orbitals whereas phosphorus show pentavalency due to presence of *d*-orbitals.
- **10.** *Refer to answer 3.*

11.  $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$ 

The abnormally high boiling point of NH3 is due to the intramolecular H-bonding. Further as we move from  $PH_3$  to  $BiH_3$  the molecular mass increasing. As a result, the van der waals forces of attraction increase and the boiling points increase regularly from  $PH_3$  to  $BiH_3$ .

- **12.** In case of nitrogen, only NF<sub>3</sub> is known to be stable. N-F bond strength is greater than F-F bond strength, therefore, formation of NF<sub>3</sub> is spontaneous. In case of NCl<sub>3</sub>, N—Cl bond strength is lesser than Cl—Cl bond strength. Thus, energy has to be supplied during the formation of NCl<sub>3</sub>.
- 13. The bond dissociation enthalpy of triple bond in  $N \equiv N$  is very high due to  $p\pi p\pi$  overlap. Hence,  $N_2$  is less reactive at room temperature.
- 14. Unlike  $NH_3$ ,  $PH_3$  molecules are not associated through hydrogen bonding in liquid state. Therefore, the boiling point of  $PH_3$  is lower than  $NH_3$ .
- **15.** BiCl<sub>3</sub> is more stable than BiCl<sub>5</sub>. On moving down the group, the stability of +5 oxidation state decreases while +3 oxidation state increases due to inert pair effect.
- 16. Nitrogen exists as a diatomic molecule with a triple bond between two atoms. These  $N_2$  molecules are held together by weak van der Waals force of attraction which can be easily broken by the collision of the molecules at room temperature. Therefore,  $N_2$  is a gas at room temperature.
- 17. Refer to answer 2.
- **18.** Refer to answer 12.
- **19.** Refer to answer 8.

20.



In NH<sub>3</sub> the bond moment and lone pair moment work in same direction. Hence, net dipole moment is higher.



In NF<sub>3</sub> the bond moment and lone pair moment work in opposite direction. Hence, net dipole moment is lower.

- 21. The property of catenation depends upon the strength of the element element bond. Since, P P (213 kJ mol<sup>-1</sup>) bond strength is much more than N N (159 kJ mol<sup>-1</sup>) bond strength so, phosphorus shows marked catenation properties than nitrogen.
- 22. Refer to answer 4.
- 23. Due to inert pair effect the stability of +5 oxidation state decreases down the group in group 15. Hence, tendency to form pentahalide decreases down the group 15 of the periodic table.
- **24.** Total no. of electrons around the central N atom = 5

No. of bond pairs = 3

No. of lone pairs = 1

Hybridisation =  $sp^3$ 

Therefore, according to VSEPR theory; NF<sub>3</sub> should be pyramidal.



- **25.** On moving down the group, the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to inert pair effect.
- **26.** BiCl<sub>3</sub> is less covalent than PCl<sub>3</sub> because the size of Bi<sup>3+</sup> is much larger than P<sup>3+</sup> (According to Fajan's rule)
- 27. (a) PH<sub>3</sub> (Phosphine)
- (b) NH<sub>3</sub> (ammonia)
- (c) NH<sub>3</sub> (ammonia)
- (d) BiH<sub>3</sub> (Bismuth hydride)
- **28.** When orange red crystals of ammonium dichromate are heated, these crystals decompose violently evolving nitrogen and green coloured chromic oxide is formed.

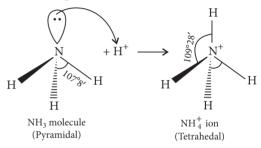
$$\begin{array}{c} (NH_4)_2Cr_2O_7 \xrightarrow{\quad \Delta \quad} Cr_2O_3 + N_2 + 4H_2O \\ (Orange\ red) \qquad \qquad (Green) \end{array}$$

**29.** In  $N_2$  molecule N atoms are held by triple bonds. It has very high bond dissociation energy (941.4 kJ mol<sup>-1</sup>). Therefore  $N_2$  is inert at room temperature.

30. 
$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta}$$
  
 $2NH_3 + Na_2SO_4 + 2H_2O$   
(colourless and pungent odoured gas)

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$
(Blue colour)

**31.** N in NH<sub>3</sub> is  $sp^3$ -hybridized. It has three bond pairs and one lone pair around N. Due to stronger lone pair-bond pair repulsions than bond pair-bond pair replusions, the tetrahedral angle decreases from 109°28′ to 107°8′. As a result, NH<sub>3</sub> is pyramidal. However, when it reacts with a proton, it forms NH<sub>4</sub> ion which has four bond pairs and no lone pair. Due to the absence of lone pair-bond pair repulsion and presence of four identical bond pair-bond pair interaction, NH<sub>4</sub> assumes tetrahedral geometry with a bond angle of 109°28′. This explains why the bond angle in NH<sub>4</sub> is higher than in NH<sub>3</sub>.



- 32.  $2NH_4Cl+Ca(OH)_2 \longrightarrow 2NH_3+2H_2O+CaCl_2$
- **33.** NH<sub>3</sub> has a lone pair of electrons on the N-atom which it can donate to an electron acceptor. Hence, NH<sub>3</sub> acts as a Lewis base.
- **34.** Optimum conditions for the production of ammonia are:

Temperature = about 700 K

Pressure = about 200 atm  $(200 \times 10^5 \text{ Pa})$ 

Catalyst = iron oxide with small amounts of  $K_2O$  and  $Al_2O_3$  (as promoters).

**35.** Ammonia is manufactured industrially by Haber's process.

 $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ ;  $\Delta_r H^\circ = -46.1$  kJ mol<sup>-1</sup> This is a reversible exothermic reaction. High pressure about 200 atm, low temperature about 700 K and use of catalyst such as iron oxide with small amounts of  $Al_2O_3$  and  $K_2O$  would favour the formation of ammonia according to Le-Chatelier's principle.

**36.** Oxidation state of N in  $N_2O_5 = +5$ Oxidation state of N in  $N_2O_3 = +3$ 

As the oxidation number of central element increases, acidic strength increases. Hence,  $N_2O_5$  is more acidic than  $N_2O_3$ .

37. 
$$2Pb(NO_3)_2 \xrightarrow{673 \text{ K}} 4NO_2 + 2PbO + O_2$$
Brown

NO2 dimerises as:

$$2NO_2 \frac{\underline{Cool}_{\searrow}}{\underline{\ \ }} \, N_2O_4$$

**38.** The structure of  $N_2O_5$  is

$$\sum_{O} N - O - N$$

**39.** Because NO<sub>2</sub> contains odd number of valence electrons and on dimerisation, it is converted to stable N<sub>2</sub>O<sub>4</sub> molecule with even number of electrons.

$$\begin{array}{ccc}
N & & & & & & & & & & & \\
N & & & & & & & & & & \\
\hline
N & & & & & & & & & \\
N & & & & & & & & \\
\end{array}$$
Planar structure

41. In  $N_2O_5$  covalency of nitrogen is four.  $O \searrow N \longrightarrow O$   $N \searrow O$ 

- 42. Refer to answer 39.
- **43.** In  $NO_2^-$ , 'N' atom has  $sp^2$ -hybridisation whereas in  $NO_2^+$ , 'N' atom has sp-hybridisation.

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Hence, bond angles are not of the same value.

- 44. Nitric oxide forms brown fumes of nitrogen dioxide (NO<sub>2</sub>) instantaneously in the presence of air.  $2NO + O_2 \longrightarrow 2NO_2$
- **45.** In NO<sub>2</sub>, the average N—O bond order is 1.5 due to two resonating structures whereas in NO<sub>3</sub>, the average N—O bond order is 1.33 due to three resonating structures. Higher the bond order, shorter is the bond length.

**46.** (i) Light brown fumes of nitrogen dioxide are evolved on heating the nitrate with concentrated  $H_2SO_4$ .

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
  
 $4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$   
Brown  
fumes (A)

These fumes intensify when copper turnings are added.

$$\begin{array}{c} \text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O} \\ 2\text{NO}_2 & & \\ \hline & \text{Brown gas} & & \\ & & \text{(A)} & & \text{Colourless solid} \\ & & & \text{(B)} \end{array}$$

- (iii) Refer to answer 39.
- **47.** H<sub>3</sub>PO<sub>4</sub> (phosphoric acid) is obtained when conc. HNO<sub>3</sub> oxidises P<sub>4</sub>.

$$P_4 + 20HNO_{3(conc.)} \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

**48.** When conc.  $HNO_3$  oxidises  $S_8$ , it forms sulphuric acid.

$$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O_3$$

**49.** Iodic acid ( $HIO_3$ ) is formed when conc.  $HNO_3$  oxidises  $I_2$ .

$$I_2 + 10 \text{HNO}_3 \longrightarrow 2 \text{HIO}_3 + 10 \text{NO}_2 + 4 \text{H}_2 \text{O}$$

$$Iodic acid$$

50. 
$$3 \text{ Cu} + 8 \text{HNO}_{3 \text{ (dilute)}} \longrightarrow 3 \text{Cu}(\text{NO}_3)_2 + 2 \text{NO} + 4 \text{H}_2 \text{O}$$

- **51.**  $I_2 + 10 \text{HNO}_{3(conc.)} \rightarrow 2 \text{HIO}_3 + 10 \text{NO}_2 + 4 \text{H}_2 \text{O}$
- **52.** The brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$
  
 $[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$   
Brown

**53.** White phosphorus is made up of discrete  $P_4$  tetrahedra which are subjected to very high angular strain as the angles are 60°. Red phosphorus is a polymer of  $P_4$  tetrahedra, which has much less angular strain. This high angular strain makes white phosphorus unstable and highly reactive.

- **54.** White phosphorus is most reactive of all the allotropes because it is unstable due to the angular strain on  $P_4$  molecule with bond angle of  $60^\circ$ .
- **55.** White phosphorus consists of discrete tetrahedral P<sub>4</sub> molecule.

Red phosphorus is polymeric, consisting of chains of  $P_4$  tetrahedra linked together.

**56.**  $P_4 + H_2O \longrightarrow No reaction$ 

**58.** Refer to answer 53.

**59.** 
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$

**60.** 
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

**61.** 
$$3\text{HgCl}_2 + 2\text{PH}_3 \longrightarrow \text{Hg}_3\text{P}_2 + 6\text{HCl}$$

**62.** Phosphorus pentachloride is a salt containing the tetrahedral cation  $[PCl_4]^+$  and the octahedral anion  $[PCl_6]^-$  therefore, it is ionic in solid state.

$$\begin{bmatrix} Cl \\ P \\ Cl \end{bmatrix}^{\dagger} \begin{bmatrix} Cl & Cl \\ Cl & P \end{bmatrix}^{-1}$$

**63.** PCl<sub>5</sub> on heating, sublimes but it decomposes into phosphorus trichloride and chlorine on stronger heating.

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

**64.** In +5 oxidation state charge/radius ratio is higher than that in +3 oxidation state. Hence, +5 oxidation state has more polarising power than that of +3 oxidation state and pentahalides (in O.S. +5) are more covalent than trihalides.

**65.** 
$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$

66. Cl
$$\begin{vmatrix} a & & Cl \\ & & Cl \end{vmatrix}$$

$$Cl \qquad \qquad CCl \qquad CCl$$

In PCl<sub>5</sub>, there are three equatorial and two axial bonds present. Since, three equatorial bonds are repelled by two bond pairs and two axial bonds are repelled by three bond pairs so, axial bonds are weaker and longer than the equatorial bonds.

**67.** 
$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

**68.** PCl<sub>3</sub> hydrolyses in the presence of moisture giving fumes of HCl.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

**69.** PCl<sub>3</sub> because PCl<sub>3</sub> cannot form bond with Cl<sup>-</sup> ions.

70. Refer to answer 66.

- 71. The oxidation state of phosphorus in  $PCl_5$  is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons. It can decrease its oxidation number from +5 to +3 or some lower value. So,  $PCl_5$  acts as an oxidising agent.
- **72.** The oxoacid of phosphorus containing +3 oxidation state, undergoes disproportionation to yield compounds in higher and lower oxidation states. Hence, H<sub>3</sub>PO<sub>3</sub> undergoes disproportionation reaction but H<sub>3</sub>PO<sub>4</sub> does not, as in it phosphorus is already in highest oxidation state (+5).

$$4H_{3}^{+3}PO_{3} \xrightarrow{\Delta} PH_{3} + 3H_{3}^{+5}PO_{4}$$

**73.** When phosphorus acid (H<sub>3</sub>PO<sub>3</sub>) is heated, it forms orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{200 \text{ °C}} 3H_3PO_4 + PH_3$$

**75.**  $H_4P_2O_7$  (Pyrophosphoric acid):

- 76. Reducing character of oxyacids of phosphorus depends on the number of P–H bonds. More the number of P–H bonds in oxyacid, more is the reducing character.  $H_3PO_2$  has two P–H bonds,  $H_3PO_3$  has one P–H bond and  $H_3PO_4$  has no P–H bond. Thus, order of reducing character is  $H_3PO_2 > H_3PO_3 > H_3PO_4$ .
- 77. Basicity of oxoacids of P is equal to the number of P—OH bonds in the molecule.

It is tribasic due to the presence of three replaceable hydrogen atoms.

**78.** The acids which contain more P—H bond, have strong reducing properties. Hypophosphorus acid  $(H_3PO_2)$  contains two P—H bonds, whereas orthophosphorus acid  $(H_3PO_3)$  has one P—H bond. Hence,  $H_3PO_2$  is stronger reducing agent than  $H_3PO_3$ .

(H<sub>3</sub>PO<sub>3</sub>) Orthophosphorus acid

It is dibasic due to the presence of two replaceable hydrogen atoms.

- **81.** Refer to answer 78.
- 82. Refer to answer 78.

It is monobasic acid due to the presence of one replaceable hydrogen.

**84.** 
$$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$$

85.  $O_2$  molecules are held together by weak van der Waals' forces because of the small size and high electronegativity of oxygen. Sulphur shows catenation and the molecule is made up of eight atoms ( $S_8$ ) with strong intermolecular attractive forces. Hence, sulphur exists as solid at room temperature.

**86.** Tendency to show –2 oxidation state decreases from oxygen to tellurium because electronegativity decreases on moving down the group.

87. The +6 oxidation state of S is more stable than +4 therefore,  $SO_2$  acts as a reducing agent. Further, since the stability of +6 oxidation state decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases.

Thus, TeO<sub>2</sub> acts as an oxidising agent.

**88.** 
$$H_2O < H_2S < H_2Se < H_2Te$$

As the atomic size increases down the group, the bond length increases and hence, the bond strength decreases. Consequently, the cleavage of M — H bond (M = O, S, Se, Te, etc.) becomes easier. As a result, the tendency to release hydrogen as proton increases i.e., acidic strength increases down the group.

- **89.** Reducing character:  $H_2S < H_2Se < H_2Te$  Hydrides of all elements of group 16 except that of oxygen, *i.e.*, water are reducing agents. The reducing character, however, increases from  $H_2S$  to  $H_2Te$  because of increasing size of atoms from S to Te which results in weaker M-H bond.
- **90.** In SF<sub>6</sub>, S atom is sterically protected by six F atoms and does not allow any reagent to attack on the S atom. Due to these reasons, SF<sub>6</sub> is kinetically an inert substance.
- **91.** As the size of central atom increases, M-H bond becomes weaker and longer and hence, thermal stability decreases while going from  $H_2O$  to  $H_2Te$ .
- **92.** Oxygen molecules are held together by weak Van der Waals' forces because of the small size and high electronegativity of oxygen. Sulphur shows catenation and the molecule is made up of 8 atoms with strong intermolecular forces. Hence, there is large difference in the melting and boiling points of oxygen and sulphur.
- 93. Bond dissociation enthalpy and hence thermal stability of hydrides decreases from  $H_2O$  to  $H_2Te$ . Therefore,  $H_2Te$  releases hydrogen readily. Hence,  $H_2Te$  is the strongest reducing agent amongst all the hydrides of group 16.

- **94.** The first ionization enthalpy of group 16 elements is lower than those of group 15 elements despite their smaller atomic radii and higher nuclear charge. This is due to the relatively symmetrical and more stable configuration of the elements of group 15 as compared to those of the elements of group 16.
- **95.** The electron gain enthalpy of oxygen is less negative than sulphur. This is due to its small size. As a result of which the electron-electron repulsion in the relatively small 2*p*-subshell are comparatively

larger and hence the incoming electrons are not accepted with same ease as in case of other (sulphur) elements of this group.

**96.** Electron gain enthalpy of oxygen is less negative than sulphur due to compact size of oxygen atom (inter-electronic repulsion is more in O). From sulphur onwards enthalpy again becomes less negative upto Po.

O < Po < Te < Se < S   
 
$$\Delta_{eg}H({\rm kJ\ mol^{-1}})$$
 -141 -174 -190 -195 -200   
 (-ve sign shows release of energy)

- 97. Refer to answer 88.
- **98.** The property of catenation depends upon E E bond strength of the element. As S S bond is much stronger (213 kJ mol<sup>-1</sup>) than O O bond (138 kJ mol<sup>-1</sup>), sulphur has greater tendency for catenation than oxygen.
- 99. Refer to answer 88.

100. 
$$H_2O$$
  $H_2S$   
Boiling point 373 K > 213 K

The abnormally high boiling point of H<sub>2</sub>O is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

- 101. Refer to answer 91.
- **102.** (i) Refer to answer 100.
  - (ii) Refer to answer 87.
- **103.** (i) Bond dissociation enthalpy and hence thermal stability of hydrides decreases from  $H_2O$  to  $H_2Te$ . Therefore,  $H_2Te$  releases hydrogen readily. Hence,  $H_2Te$  is the strongest reducing agent amongst all the hydrides of group 16.
- (ii) All the group 16 hydride have angular shape involving  $sp^3$  hybridisation due to stronger lone pair-lone pair repulsions than bond pair-bond

pair repulsions, the bond angle in water decreases from the tetrahedral value. As we move down the group from O to Te, the size of central atom increases and its electronegativity decreases. As a result the position of the two bond pairs shifts away from the central atom as we move from  $H_2O$  to  $H_2Te$ . Consequently the repulsions between the bond pairs decreases from  $H_2O$  to  $H_2Te$  and therefore bond angle decreases. Thus  $H_2O$  has the highest bond angle among group 16 hydrides.

(iii) As the size of the element increases down the group, the E—H bond dissociation energy decreases and hence E—H bond breaks more easily. Thus H<sub>2</sub>O has the highest thermal stability among group 16 hydrides.

**104.** Ozone is thermodynamically unstable and decomposes into oxygen.

$$2O_3 \xrightarrow{\Delta} 3O_2$$
;  $\Delta H = -ve$ 

The above conversion is exothermic *i.e.*,  $\Delta H$  is negative. Also, entropy increases *i.e.*,  $\Delta S = +$  ve. Thus,  $\Delta G$  for the decomposition of ozone is negative. Hence, it is thermodynamically unstable.

**105.** 
$$PbS_{(s)} + 4O_{3(g)} \longrightarrow PbSO_{4(s)} + 4O_{2(s)}$$

**106.** *Refer to answer 104.* 

**107.** Nitrogen oxide emitted from the exhausts of supersonic jet aeroplanes readily combines with ozone to form nitrogen dioxide and diatomic oxygen. Since supersonic jets fly in the stratosphere near the ozone layer, they are responsible for the depletion of ozone layer.

**108.** The two O - O bond lengths in the ozone molecule are equal as it is a resonance hybrid of the following two forms:

$$0 \longrightarrow 0$$

**109.** Ozone is a powerful oxidising agent because ozone has higher energy content than dioxygen hence, decomposes to give dioxygen and atomic oxygen.

The atomic oxygen thus liberated brings about the oxidation while molecular oxygen is set free.

110. At elevated temperature, sulphur vapour exists as  $S_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$ -orbitals like  $O_2$  hence, exhibits paramagnetism.

111. Refer to answer 110.

112. Rhombic sulphur

113. Sulphur exists in numerous allotropes of which yellow, rhombic ( $\alpha$ -sulphur) and monoclinic ( $\beta$ -sulphur) are most important. The stable form is rhombic, which transforms to monoclinic sulphur, when heated around 370 K.

114. In presence of moisture, SO<sub>2</sub>, acts as a reducing agent due to the evolution of nascent hydrogen.

**115.** Sulphur dioxide turns acidified potassium dichromate solution from orange to green.

$$\label{eq:K2Cr2O7} \begin{split} K_2Cr_2O_7 + H_2SO_4 + 3SO_2 &\longrightarrow K_2SO_4 + Cr_2(SO_4)_3 \\ \text{(orange)} & \text{(green)} \\ &+ H_2O \end{split}$$

116.  $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$ 

117. Refer to answer 116.

118.  $SO_2 + Cl_2 \rightarrow SO_2Cl_2$ 

**119.** Due to the presence of a lone pair of electrons on the sulphur atom, sulphurous acid can be easily oxidised to sulphuric acid therefore, it acts as a reducing agent.

$$H_2O + Br_2 + H_2SO_3 \longrightarrow 2HBr + H_2SO_4$$

**120.** H<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (Pyrosulphuric acid)

**122.** *Refer to answer 120.* 

**124.**  $H_2SO_4$  (Sulphuric acid) : O  $\parallel$  S HO

sp<sup>3</sup> Hybridisation

Shape : Pyramidal; O-S-O angle >  $90^{\circ}$ 

**126.** 
$$S_8 + 16H_2SO_4 \rightarrow 24SO_2 + 16H_2O$$
(Conc.)

127. In Contact process, the rate determining step

is  $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$ ,  $\Delta H^\circ = -196.6 \text{ kJ mol}^{-1}$ This reaction is reversible and exothermic *i.e.*,  $\Delta H$  is negative. Thus, according to Le-Chatelier's principle, the conditions to maximise the yield are as follows:

(a) At low temperature: As heat is evolved in the reaction so, at lower temperature the reaction proceeds more in forward direction.

(b) At high pressure: As three moles of gaseous reactants give two moles of gaseous products thus, at higher pressure reaction moves in forward direction.

128. 
$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$
(conc.)

129. 
$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

130. C + 
$$2H_2SO_4$$
 (conc.)  $\longrightarrow$   $CO_{2(g)} + 2H_2O_{(l)} + 2SO_{2(g)}$ 

131. 
$$\text{H}_2\text{SO}_{4(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}_{(aq)}^+ + \text{HSO}_{4(aq)}^-$$
  
 $K_{a_1} > 10$ , very large

$$\begin{split} \text{HSO}^-_{4(aq)} + \text{H}_2\text{O}_{(l)} &\to \text{H}_3\text{O}^+_{(aq)} + \text{SO}^{2-}_{4(aq)} \\ & K_{a_2} = 1.2 \times 10^{-2} \end{split}$$

 $K_{a_2}$  is smaller than  $K_{a_1}$  because dissociation of HSO<sub>4</sub><sup>-</sup> is less probable due to presence of negative charge on the ion.

**132.** Concentrated H<sub>2</sub>SO<sub>4</sub> removes water from organic compounds hence, it has charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} > 12C + 11H_2O$$
  
Sugar Sugar charcoal

133. 
$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

**134.** (i) 
$$\overset{0}{\text{C}} + 2\text{H}_2\overset{+6}{\text{SO}}_4 \longrightarrow 2\overset{+4}{\text{SO}}_2 + \overset{+4}{\text{CO}}_2 + 2\text{H}_2\text{O}$$

(ii) HCOOH 
$$\xrightarrow{\text{Conc. H}_2\text{SO}_4}$$
 H<sub>2</sub>O + CO

**135.** (i) When conc.  $H_2SO_4$  reacts with Cu, CuO is formed which gets further converted into  $CuSO_4$ .

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

(ii) When SO<sub>3</sub> is passed through water, it dissolves SO<sub>3</sub> to give H<sub>2</sub>SO<sub>4</sub>.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

136. Contact process: It involves three stages:

(i) Burning of sulphur or sulphide ore in air to generate SO<sub>2</sub>.

$$S + O_2 \rightarrow SO_2$$

$$4\text{FeS}_2 + 11\text{O}_2 \rightarrow 8\text{SO}_2 + 2\text{Fe}_2\text{O}_3$$

(ii) Conversion of SO<sub>2</sub> to SO<sub>3</sub> by reaction with oxygen in the presence of V<sub>2</sub>O<sub>5</sub> catalyst.

$$2SO_{2(g)} + O_{2(g)} = V_2O_5 = 2SO_{3(g)};$$

$$\Delta_r H^{\circ} = -196 \text{ kJ mol}^{-1}$$

(iii) The  $SO_3$  gas from the catalytic converter is absorbed in conc.  $H_2SO_4$  to form oleum ( $H_2S_2O_7$ ). Dilution of oleum with water gives  $H_2SO_4$  of desired concentration.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$
 (Oleum)  
 $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$ 

**137.** Refer to answers 127 and 136.

**138.** (b) : Due to small size, the lone pairs of electrons on F-atoms repel the bond pair between F-atoms. Therefore, F—F bond in  $F_2$  molecule is weak.

**139. (b)** : Increasing bond dissociation enthalpy order is

$$I_2 < F_2 < Br_2 < Cl_2$$

Bond dissociation enthalpy of  $F_2$  is less than that of  $Br_2$  and  $Cl_2$  due to the lone pair - lone pair repulsion.

**140.** 
$$4I_{(aq)}^{-} + 4H_{(aq)}^{+} + O_{2(g)} \longrightarrow 2H_{2}O + 2I_{2}$$

**141.** The acidic strength of the hydrohalic acids is in the order :

This order is a result of bond dissociation enthalpies of H - X bond which decreases from H - F to H - I as the size of halogen atom increases.

**142.** As the size of halogen increases down the group from F to I, the hydration enthalpy of corresponding halide ion decreases. Hence, F<sup>-</sup> ion has higher hydration enthalpy (524 kJ mol<sup>-1</sup>) than Cl<sup>-</sup> ion (378 kJ mol<sup>-1</sup>).

143. HF > HCl > HBr > HI

As the size of halogen atom increases from F to I, bond dissociation enthalpies of H—X bond decreases from H—F to H—I.

**144.** Fluorine is the strongest oxidising agent because of its low bond dissociation and high heat of hydration as compared to those of chlorine. It oxidise other halide ions in solution or even in solid phase.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 (X = Cl, Br \text{ or } I)$$
  
 $Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 (X = Br \text{ or } I)$   
 $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$ 

**145.** *Refer to answer 141.* 

**146.** The decreasing order of reducing character of the given hydrogen halides is

HI > HBr > HCl > HF

**147.** 
$$F_2 + 2Cl^- \rightarrow 2F^- + Cl_2$$

**148.** Halogens have the smallest size in their respective periods and therefore have high effective nuclear charge. As a result, they readily accept one electron to acquire noble gas configuration. Hence, electron gain enthalpies of halogens are largely negative.

**149.**  $F_2$  has lower bond dissociation enthalpy than  $Cl_2$  because F atom is very small and hence the electron-electron repulsions between the lone pairs of electrons are very large.

**150.** Halogens absorb radiations in visible region which results in excitation of outer electrons to higher level resulting in different colours.

**151.** General electronic configuration of halogens is  $ns^2np^5$ . They easily accept one electron to complete their octet. This makes them good oxidising agent.

**153.** Increasing bond dissociation enthalpy order is

$$I_2 < F_2 < Br_2 < Cl_2$$

Bond dissociation enthalpy of  $F_2$  is less than that of  $Br_2$  and  $Cl_2$  due to the lone pair - lone pair repulsion.

154. Refer to answer 144.

**155.** HF is the weakest acid because of its high bond dissociation energy due to small size of fluorine atom.

**156.** Since, fluorine is the most electronegative element, it shows only a negative oxidation state of -1, and does not show any positive oxidation state (except +1 in HOF).

**157.** Fluorine is most electronegative element and it cannot exhibit any positive oxidation state (except +1 in HOF). Other halogens have d-orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

**158.** HF acid attacks glass with the formation of fluoro silicate ions. Thus, it is stored in wax-coated glass bottles to prevent the reaction.

**159.** Higher boiling point of  $H_2O$  is due to the extensive H-bonding in  $H_2O$  than HF.

**160.** In aqueous medium HCl is stronger acid than HF because bond dissociation enthalpy of H—Cl is lower than that of HF.

**161.** Fluorine is the most electronegative element among halogens and it cannot exhibit any positive oxidation state. Therefore, it form largest number of interhalogen compounds.

**162.** The electron gain enthalpy of fluorine is less negative than that of chlorine due to the small size of fluorine atom.

**163.** 
$$2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$$
  
 $3F_2 + 3H_2O \longrightarrow 6H^+ + 6F^- + O_3$ 

The electrode potential of  $F_2/F^-$  couple is the maximum while that of  $I_2/I^-$  is minimum, *i.e.*,  $F_2$  is reduced most easily but  $I_2$  is reduced least easily.  $F_2$  reduces  $H_2O$  to  $O_2$  and  $O_3$  but  $I_2$  does not react with water.

164. Oxidising power of a substance depends on the factors like bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy. Due to small size of fluorine, its electron gain enthalpy is less than that of chlorine. However, its low bond dissociation enthalpy and high hydration enthalpy compensate the low electron gain enthalpy. Fluorine because of its small size has higher hydration enthalpy than chlorine. Also, due to repulsion between electrons it has lower bond dissociation energy. Thus, fluorine has better oxidising action than chlorine.

165. 2NaOH 
$$_{(dil.)}$$
 +  $\text{Cl}_{2(aq)}$   $\rightarrow$   $\text{NaCl}_{(aq)}$  +  $\text{NaClO}_{(aq)}$  +  $\text{H}_2\text{O}_{(l)}$ 

**166.** NH<sub>3</sub> + 3Cl<sub>2(excess)</sub> 
$$\longrightarrow$$
 NCl<sub>3</sub> + 3HCl  
Nitrogen  
trichloride  
(explosive)

**167.** 
$$Cl_2 + H_2O \longrightarrow HCl + HOCl \longrightarrow Hydrochloric Hypochlorous acid acid$$

168. 
$$2Cl_2 + 2Ca(OH)_{2(dil.)} \xrightarrow{Cold} CaCl_2 + Ca(OCl)_2 + 2H_2O$$

169. (i) Phosgene

(ii) Calcium hypochlorite

**170.** The bleaching action of  $Cl_2$  is due to oxidation of coloured substances to colourless substances by nascent oxygen. Since, the bleaching action of  $Cl_2$  is due to oxidation and that of  $SO_2$  is due to reduction, therefore, bleaching effect of  $Cl_2$  is permanent while that of  $SO_2$  is temporary.

171. 6NaOH + 
$$3Cl_2 \rightarrow 5NaCl + NaClO_3 + H_2O$$
 (hot and conc.)

**172.** Chlorine water on standing loses its yellow colour due to the formation of HCl and HClO.

173. Refer of answer 171.

174. 
$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$
Iodic acid

175. 
$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$
  
 $Cl_2 + H_2S \longrightarrow 2HCl + S$ 

176. 
$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

177. Refer to answer 176.

**178.** *Refer to answer 176.* 

179. Its reaction with iron produces  $H_2$ . Fe + 2HCl  $\rightarrow$  FeCl<sub>2</sub> +  $H_2$ 

Liberation of hydrogen prevents the formation of ferric chloride.

**180.** Fluorine forms only one oxoacid HOF. Because for the formation of other oxoacids d-orbitals are required for the multiple  $p\pi - d\pi$  bonding between extra oxygen atoms and fluorine.

High electronegativity and small size of fluorine also favours the formation of only one oxoacid.

**181.** As the number of oxygen bonded to the central atom increases, the oxidation number of the central atom increases causing a weakening of

the O—H bond strength and an increase in the acidity. Hence, HClO<sub>4</sub> is stronger acid than HClO.

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

184. Refer to answer 180.

**185.** As the stability of the oxoanion increases, its tendency to decompose to give  $O_2$  decreases and hence its oxidising power decreases. Since, the stability of the oxoanion decreases in the order:  $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$  therefore oxidising power of their oxoacids increases in the reverse order:

**187.** Because of smaller size of F and bigger size of Cl, chlorine can accomodate three fluorine atoms around it but fluorine does not. Also Cl has vacant d-orbitals and hence can show +3 oxidation state, but F has no d-orbitals.

$$Cl_2 + 3F_2 \xrightarrow{250 \text{ °C}} 2ClF_3$$
Excess

**190.** Interhalogen compounds are more reactive than halogens (except flourine) because X - X' bond (I—Cl bond) in interhalogens is weaker than X - X bond (I—I bond) in halogens except F—F bond. In other words, I—Cl bond is weaker than I—I bond. Thus, ICl is more reactive than I<sub>2</sub>.

**191.** 
$$3F_2$$
 (excess) +  $Cl_2 \xrightarrow{300^{\circ}C}$  **2**  $2ClF_3$ 

192. Interhalogen compounds are more reactive than halogen because the X'-X bond in interhalogens is weaker than X-X bond in halogens. But in case of flourine, the F-F bond is weaker. This is because of the small size of fluorine atoms, the F-F bond distance is very small due to which there is appreciable inter-electronic repulsion. This repulsion weakens the bond between two fluorine atoms. Hence,  $F_2$  is more reactive than  $ClF_3$  but  $ClF_3$  is more reactive than chlorine.

**193.** Refer to answer 189.

ClF<sub>3</sub> is T-shaped molecule.

Angle F — Cl — F : Less than 90°

**194.** Oxidation state of Br in BrCl<sub>5</sub> is +5, whereas in case of BrCl<sub>3</sub> is +3. As Br is more stable in +3 oxidation state than +5, due to inert pair effect. Therefore, it is unstable and readily reduces from +5 to +3 oxidation state.

**195.** Fluorine does not have *d*-orbitals and it cannot show higher oxidation state. Therefore, it does not play the role of a central atom in interhalogen compounds.

196. 
$$Br_2 + 5F_2$$
 (excess)  $\longrightarrow 2BrF_5$ 

**197.** Interhalogen compounds are formulated as XX',  $XX'_3$ ,  $XX'_5$  and  $XX'_7$  where, X is halogen of larger size and X' of smaller size.

The interhalogen compounds can be prepared by direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, for example,

$$Cl_{2} + F_{2} \xrightarrow{437 \text{ K}} 2\text{ClF}$$
(Equal volume)
$$Cl_{2} + 3F_{2} \xrightarrow{573 \text{ K}} 2\text{ClF}_{3}$$
(Excess)
$$I_{2} + Cl_{2} \rightarrow 2\text{ICl}$$

(equimolar)

$$I_2 + 3Cl_2 \rightarrow 2ICl_3$$
  
Excess

$$Br_2 + 3F_2 \rightarrow 2BrF_3$$
 (diluted with water)

$$Br_2 + 5F_2 \rightarrow 2BrF_5$$
(excess)

**198.** 
$$XeOF_4: F \xrightarrow{V} Xe \xrightarrow{V} F$$

**199.** 
$$XeF_6 + KF \longrightarrow K^+ [XeF_7]^-$$

**200.** Extremely small size and fully filled outer orbital makes helium very stable and resistant to chemical reactions and hence, it does not form compounds unlike bigger atoms of other elements of noble gas family.

**201.** As the size of noble gases increases, van der Waals' forces of attraction increase accordingly and hence, the boiling point increases from He to Rn.

**202.** 
$$2XeF_{2(s)} + 2H_2O_{(l)} \rightarrow 2Xe_{(g)} + 4HF_{(aq)} + O_{2(g)}$$

**203.** 
$$XeF_2$$
:  $Xe$ 

204. 
$$F \xrightarrow{Xe} F$$

**205.** *Refer to answer 202.* 

**206.** 
$$XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$$

**207.** 
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

**208.** 
$$XeF_4 + O_2F_2 \xrightarrow{143 \text{ K}} XeF_6 + O_2$$

**209.** 
$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

**210.** XeF<sub>6</sub>: (Xenon hexafluoride)



**211.**  $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$ 

212. Refer to answer 207.

**213.** Helium is used in diving apparatus as diluent for oxygen because of its low solubility (as compared to N2) in blood, a mixture of oxygen and helium is used in diving apparatus used by deep sea divers.

**214.** XeO<sub>3</sub>:

Hybridisation = 
$$sp^3$$
  
Geometry = Tetrahedral  
Shape = Pyramidal



215. Refer to answer 200.

**216.** The central atom Br has seven electrons. Four of these electrons form two double bonds or coordinate bonds with two oxygen atoms while the fifth electron forms a single bond with  $O^-$  ion. The remaining two electrons form one lone pair. Hence, in all there are three bond pairs and one lone pair around Br atom in  $BrO_3^-$ . Therefore, according to VSEPR theory,  $BrO_3^-$  should be pyramidal.

Here,  $BrO_3^-$  has  $26(7 + 3 \times 6 + 1 = 26)$  valence electrons. A noble gas species having 26 valence electrons is  $XeO_3(8 + 3 \times 6 = 26)$ . Thus, like  $BrO_3^-$ ,  $XeO_3$  is also pyramidal.

**217.**  $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2 + 4\text{Xe}$ 

**218.** Neil Bartlett first prepared a red compound which is formulated as  $O_2^+PtF_6^-$ . He then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ/mol) is almost identical with Xe (1170 kJ/mol). He made efforts to prepare same type of compound with Xe and was successful in preparing another red compound Xe<sup>+</sup>PtF $_6^-$ .

**219.** 
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

**220.** *Refer to answer 203.* 

**221.** Helium has completely filled  $ns^2$  electronic configurations in its valence shell. Due to its small size and high IE, helium is chemically unreactive. Thus, it forms no real chemical compound.

**222.** Noble gases being monoatomic gases are held together by weak London dispersion forces, therefore they have low boiling points.

**223.** 
$$XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$$

224. Refer to answer 217.

It is a disproportionation reaction in which  $XeF_4$  (+4) undergoes disproportionation giving xenon (0) and xenon trioxide (+6).

- **225.** (i) Helium is used for filling balloons for meteorological observations because it is non-inflammable.
- (ii) Refer to answer 223.

226. 
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$
  
 $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$   
 $5s^2 \qquad 5p^6$ 

All the orbital of Xe have paired electrons. The promotion of one, two or three electrons from 5*p*-filled orbitals to the 5*d*-vacant orbitals will

give rise to two, four and six-half filled orbitals. Therefore, xenon can combine with even number of fluorine atoms, not odd. Thus, it cannot form  $XeF_3$  and  $XeF_5$ 

- (ii) Except radon which is radioactive, Xe has least ionisation energy among noble gases and hence it readily forms chemical compounds particularly with oxygen and fluorine.
- **228.**  $XeO_3$  can be obtained by hydrolysis of  $XeF_4$  and  $XeF_6$ .

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

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

