TOPIC : p-BLOCK ELEMENTS (HALOGEN & NOBEL GAS) EXERCISE # 1

SECTION (A)

1. s-block & p-block elements collectively comprise the representative elements. The valence shell electronic

configuration of halogen is ns² np⁵ and the last electron enters in p-subshell. Thus, halogens belongs to p-block elements.

- 6. According to their SRP.
- 7. HF has highest boiling point on account of intermolecular hydrogen bonding. But from HCl to HI the boiling point show a regular increase due to a corresponding increase in the magnitude of van der Waal's force of attraction as the size of the halogen increases.
- 8. As the size of anion increases the distance between the nucleus and valence shell electrons increases resulting into weak force of attraction between them. This leads to increase in the ease of the donation of electrons in the order $F^- < CI^- < Br^- < I^-$. Hence I^- acts as a strongest reducing agent.
- **14.** Bond length \propto 1/(bond dissociation energy) and bond dissociation energy \propto bond strength.

SECTION (B)

- $1 \ge (1) 2KMnO_4 (s) + 16 HCl (aq) \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$ $(2) 4HCl (g) + O_2 (g) \xrightarrow{CuCl_2}{723} 2Cl_2 + 2H_2O$ $(3) 4Cl⁻ (s) + Cr_2O_7^{2-} + 6H^+ \longrightarrow 2CrO_2Cl_2 + 3H_2O$ $(4) NaCl (s) + MnO_2(s) + H_2SO_4 (Conc.) \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$ $(4) Conc. (5) + Cl_2O_7^{2-} +$
- **2**⁽³⁾ is correct chemical composition of bleaching powder (NCERT).
- 3. (1) $SO_3^{2-} + H^+ \longrightarrow SO_2^{\uparrow} + H_2O^{\downarrow}$
 - (2) CO_3^{2-} + H⁺ $\longrightarrow CO_2^{\uparrow}$ + H₂O
 - (3) $NH_3 + HCI \longrightarrow NH_4CI^{\uparrow}$
 - (4) Conc. H_2SO_4 is used as it does not react with HCl.
- **4.** Chlorine gas reacts with CaO, NaOH and NH₃; so chlorine gas cannot be dried by passing over these compounds. H₂SO₄ have great affinity for water and therefore it is used for drying Cl₂.
- 5. $Ca(OH)_2$ (dry slaked lime) + $CI_2 \longrightarrow CaOCI_2 + H_2O$
- 7. $2CIO_2 + H_2O \longrightarrow HCIO_2 + HCIO_3$
- **11.** $SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$
- **12** $(2CIO_3 + H_2O \longrightarrow HCIO_3 + HCIO_4)$

SECTION (C)

1 In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First , he 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⁻¹) was almost identical with that xenon (1170 kJ mol⁻¹). He made efforts to prepare same type of compound with Xe⁺ PtF₆⁻ by mixing Pt F₆ and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

2. XeF_5 does not exist at all.

SECTION (D)

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

- 4. It is factual.
- 6. PF_5 is a fluoride ion acceptor so it yields cationic species with xenon fluorides. $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

EXERCISE # 2

- 2. Fluorine on account of low bond dissociation energy and high enthalpy of hydration of F⁻ acts as strong oxidising agent ; being the most electronegative, it exhibits only 1 oxidation state.
- **3.** HBr (or HI) cannot be prepared by heating bromide (iodide) with concentrated H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 to SO_2 and get themselves oxidised to bromine and iodine respectively.

 $KX + H_2SO_4 \longrightarrow KHSO_4 + HX$

 $H_2SO_4 + 2HX \longrightarrow SO_2 + X_2 + 2H_2O$ (X = Br or I)

Hence, HBr and HI are prepared by heating bromides and iodides respectively with concentrated $\rm H_3PO_4.$

$$3$$
KBr(KI) + H_3 PO $_4 \longrightarrow K_3$ PO $_4$ + 3 HBr (HI)

- **4.** CIO_4^- , conjugate base is most stable as charge is dispersed over four oxygen atom and so $HCIO_4$ is the strongest acid.
- **5.** CIO_2^- and CIF_2^+ both have 34 electrons and therefore are isoelectronic species.
- **6.** (1) 64 < 99 < 114 < 133 covalent radius/pm down the group size increases due to addition of new shells.

(2) $515 > 391 > 347 > 305 - \Delta_{hvd}H(X^{-}) \text{ KJ mol}^{-1}$

Degree of hydration $\propto \frac{1}{size}$ of anion s

(3) 158.8 < 242.6 > 192.8 > 1.51 |-Bond dissociation enthalpy | (kJ mol⁻¹) F–F < Cl–Cl on account of large repulsion between non-bonded pairs of electron due to small F-F bond length. (4) 143 < 199 < 228 < 266 - X - X distance/pm as size of element increases the X-X distance

(4) 143 < 199 < 228 < 266 - X - X distance/pm as size of element increases the X-X distance increases.

- **8.** Halide ion is derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'_{3}), halate (when XX'_{5}) and perhalate (when XX'_{7}).
- 9.> (I) They do not form compounds readily as they are chemically inert on account of stable electron configuration.
 (II), (III) & (IV) are correct statement.
- **10.** Group No. 18 general valence shell electron configuration is ns²np⁶.
- **11.** It is argon which is used for creating inert atmosphere in Kroll and I.C.I process.
- **12.** $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$
- **13.** $2[HXeO_4]^- + 2OH^- \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2H_2O$

EXERCISE # 3 PART - I

1. Structure of XeF, as follows :



It involves sp³d² hybridisation in Xe atom. The molecule has square planar structure. Xe and four F atoms are coplanar. The lone pairs present on axial positions, minimise electron pair repulsion.

- 2. Due to strong H-F bond proton in not easily removed. So, HF is not a stronger acid than HCI. Order of halogen acids is HI > HBr > HCl > HF.
- 3. In BrF₃ molecule, Br is sp³d hybrid, but geometry is T-shaped due to distortion of geometry from trigonal-bipyramidal to T-shaped by the involvement of lone pair-lone pair repulsion. Here

:

ulsion = 2 bp-bp repulsion = 0

4. SiF_{4} and SF_{4} are not isostructural becuase SiF_{4} is tetrahedral due to sp^{3} -hybridisation of Si. $_{14}$ Si = 1s², 2s²2p⁶, 3s¹3p³ (in excited state)

Hence, four equivalent sp³ hybrid orbitals are obtained and they are oberlapped by four p-orbitals of four fluorine atoms on their axes. Thus it shows following structure :

While SF₄ is not tetrahedral but it is distorted tetrahedral because in it S is sp³d hybrid.

 $_{16}$ s = 1s², 2s²2p⁶, 3s²3p²_x3p¹_y3p¹_z (In groud state) $= 1s^2$, $2s^22p^6$, $3s^23p^2_x3p^1_y3p^1_z$, $3d^1_{xy}$ (sp³d - hybridisation) (In first excitation state)

- 5. The correct order of electron gain enthalpy (electron affinity) is 0 < S < FCI (electron affinity in eV) O < S < F CI < 1.48 2.07 3.45 3.61
- 7. In CIF₃ all bonds are not equal due to CIF₃ molecule has T-shape.



Trigonal-bipyramidal geometry BF_3 and AIF_3 show trigonal symmetry structure due to sp²-hybridisation.



Shows Trignoal pyramidal shape due to sp³ hybridiation.



- 8. Incorrect order of bond dissociation energy $F_2 > CI_2 > Br_2 > I_2$ due to following order of size I > Br > CI > F.
- **9.** OF_2 is oxygen difluoride.
- **11.** As oxidation number of central atom increases, acidic nature increases. HCIO < HCIO₂ < HCIO₃ < HCIO₄
- 12.

XX'	(e.g. CIF)	(i)	Linear
XX ₃ '	(e.g. CIF ₃)	(ii)	T-shape
XX ₅ '	(e.g. IF ₅)	(iii)	Square-pyramidal
XX ₇ '	(e.g. IF ₇)	(iv)	Pentagonal bipyramidal
	XX' XX ₃ ' XX ₅ ' XX ₇ '	XX' (e.g. CIF) XX_3' (e.g. CIF_3) XX_5' (e.g. IF_5) XX_7' (e.g. IF_7)	XX' (e.g. CIF) (i) XX_3' (e.g. CIF_3) (ii) XX_5' (e.g. IF_5) (iii) XX_7' (e.g. IF_7) (iv)

13. However HOF is the only known oxyacid of fluorine but it is unstable at room temperature forming HF and O₂. So we can say that all halogens except fluorine form monobasic oxyacids.

PART - II

- 1.XeOF4, square planar (sp3d2 hybridisation)Trigonal pyramidal
(sp3 hybridisation)Distorted octahedral
(sp3d3 hybridisation)
- 3. As the size of the anion increases from F^- to I^- , the covalent character increase and hence the solubility in non-polar solvent increases. Lil > LiBr > LiCl > LiF.
- **8.** F₂ is more reactive because of higher E^o value.

PART - III

- 1. In phosphorous the vacant 3 d-orbitals are available. So it can increase its covalence beyond three.
- **2.** $4\text{HCI} + \text{O}_2 \rightarrow 2\text{CI}_2 + 2\text{H}_2\text{O}$ white fumes cloud
- **3.** The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- **4.** Helium is twice as heavy as hydrogen. But it is a non-inflammable gas has 92% lifting power to that of hydrogen.

CHEMISTRY FOR NEET

- 5. The bond dissociation energy of F–F bond is very low. The weak F–F bond makes fluorine the strongest oxidising halogen.
- 6. As the size of the halogen atom increases from F to I, H X bond length in HX molecules also increases from H F to H I (H F < H CI < H Br < H I). The increase in H X bond length decreases the strength of H X bond from H F to H I. The decrease in the strength of H X bond is evident from the fact that H X bond dissociation energies decrease from H F to H I. Due to successive decrease in the strength of H X bond from H F to H I, thermal stability of HX molecules also decreases from HF to HI (HF > HCI > HBr > HI).

7. Higher is the oxidation state of the central atom, greater is the acidity.

Hence, HCIO₄ is a stronger acid than HCIO₃. HNO₃ is a stronger acid than HNO₂.

Now greater is the electronegativity and higher is the oxidation state of the central atom, greater is the acidity. Hence H_2SO_3 is a stronger acid than H_3PO_3 .

Due to higher dissociation energy of H–F bond and molecular association due to hydrogne bonding in Hf, HF is a weaker acid than HCI.

8. +2 +5 -1

3HCIO (aq) \rightarrow HCIO₃ (aq) + 2HCI (aq).

It is disproportionation reaction of hypochlorus acid where the oxidation number of CI changes from +1 (in CIO⁻) to +5 (in CIO₃⁻) and -1 (in CI⁻).

9. $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

 $O_3 + SO_2 \rightarrow O_2 + SO_3$

Si + 2NaOH + $O_2 \rightarrow NaSiO_3 + H_2O$

Cl₂ reacts with excess of ammonia to produce ammonium chloride and nitrogen.

$$2NH_3 + 3CI_2 \rightarrow N_2 + 6HCI$$

$$6NH_3 + 6HCI \rightarrow 6NH_4CI$$

$$8NH_3 + 3CI_2 \rightarrow N_2 + 6NH_4CI$$

10 This reaction is not feasible because XeF₆ formed will get hydrolysed according to the following reaction,

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

11. In general, interhalogen compounds are more reactive than halogens except fluorine (as per NCERT)

12.
$$Cl_2$$
 + 2NaOH \longrightarrow Cl⁻ + ClO⁻ + Na⁺ + H₂O

Cold & dil.

Disproportionation reaction.

13. NaOH + Cl₂ \longrightarrow NaCl + NaClO₃ Hot & conc.