p-Block Elements-II

Daily Tutorial Sheet	**Level - 0**

1. The bond 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. It reacts only at high temperature.

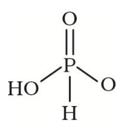
2. The $N-H$ bond in NH_3 is more polar than $P-H$ bond in PH_3. As a result NH_3 easily dissolves in polar solvent like water whereas PH_3 does not dissolves and shows bubbles.

3. Oxygen cannot expand its octet.

4. Since there are two $Xe-F$ covalent bonds in XeF_2. According to VSEPR they, the shape of XeF_2 is linear.

5. The acidic strength of compounds increases in the order $PH_3 < H_2S < HCl$ due to increase in EN.

6. Basicity of H_3PO_3 will be 2.

 H in the structure $2-H$ atom directly attach with oxygen.

7. In NO_2 molecule, hybrid orbital of nitrogen atom contains one unpaired electron which tends to get paired with other and form stable N_2O_4 molecule.

8. Hydrides of silicon are known as silanes. Examples: Monosilane (SiH_4) disilane (Si_2H_4) etc.

9. $2NH_3 + NaOCl \longrightarrow \underset{\text{Hydrazine}}{N_2H_4} + NaCl + H_2O.$

10. **(i)** sp^3d of P in PCl_5 **(ii)** sp^3d^2 of S in SF_6

11. **(i)** Flourine has higher standard reduction potential than chlorine, so it is more easily reduced and hence it is stronger oxidizing agent than chlorine.

(ii) In NO_2 unpaired electron is localized while in ClO_2 unpaired electron is delocalized.

12. Unlike GaX and InX halides, TlX does not undergo disproportionation reaction. Also TlX is more stable than TlX_3, whereas Ga and In halides are more stable in trivalent state.

13. Hot concentrated sulphuric acid oxidises sulphur to sulphur dioxide

$$S_8 + 16H_2SO_4 \longrightarrow 24SO_2 + 16H_2O$$

14. **(i)** $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(ii) $NaOH + SO_2(\text{excess}) \longrightarrow \underset{\text{Sodium hydrogen sulphite}}{NaHSO_3}$

15. **(i)** In the order of increasing base strength

$$\underset{\text{Least basic}}{SbH_3} < AsH_3 < PH_3 < \underset{\text{most basic}}{NH_3}$$

(ii) In the order of increasing acid strength

$$\underset{\text{weak acid}}{HF} < HCl < HBr < \underset{\text{strongest acid}}{HI}$$

16. **(i)** $2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$

(ii) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

17. $2NO_2 \xrightarrow{\text{dimerisation}} N_2O_4$

$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + \underset{\text{Brown}}{4NO_2} + O_2$

NO_2(Brown)

18. Pentahydrated stannic chloride, $SnCl_4 \cdot 5H_2O$ is known as 'butter of tin'.

19. Thermite is mixture of ferric oxide (Fe_2O_3) and aluminium in the ratio of 3 : 1 and is used in thermite welding.

20. Size of F is smaller than Cl therefore, SiF_6^{2-} has lesser steric repulsions. Moreover, the interaction of lone pair electrons of F with Si is stronger than that of the lone pairs of chlorine.

21. Sulphur exists as S_2 molecule in vapour state which has two unpaired electrons in the antibonding π^* orbital like O_2 molecule. Because of this reason Sulphur exhibits paramagnetism.

22. **(a)** Acid strength of oxoacid of the same halogen increases with increase in oxidation number of the halogen.

Thus the increasing order of the halogen.

$$\underset{+1}{HOCl} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4}$$

(b) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

This reaction is a disproportionation reaction as chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

(c) ClF_3 is used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3(l) \longrightarrow UF_6(g) + 3ClF(g)$$

23. **(a)** Fluorine and oxygen are the most electronegative elements and hence are very reactive. Therefore, they form compound with noble gases particularly xenon.

(b) Hydrolysis of XeF_6 with water gives $XeOF_4$ and XeO_3.

(i) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

(ii) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

24. **(i)** PCl_5 is ionic in the solid state because it exist as $[PCl_4]^+ [PCl_6]^-$ in which the cation is tetrahedral and anion is octahedral.

(ii) The size of central atom in H_2S is larger than H_2O. Hence H_2S is more acidic than H_2O.

(iii) Because fluorine is most electronegative element.

25. **(i)** Because of larger size of Sulphur atom than oxygen atom.

(ii) Because bond energy of F_2 is lower than Cl_2 and $N-F$ bond is smaller and stronger than $N-Cl$ bond.

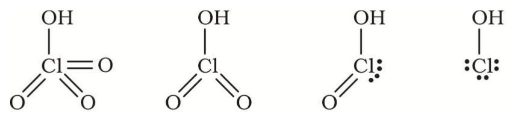
26. **(a)** **(i)** $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

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

(b) **(i)** Because down the group, +3 oxidation state becomes more and more stable due to higher energy involved to unpair the electrons or due to inert pair effect.

(ii) Because halogens readily accept an electron.

27. Fluorine cannot expand its octet so form only one oxy acid HOF. The other halogen form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.



$HClO_4$ $HClO_3$ $HClO_2$ $HClO$

28. **(i)** $2NH_3 + \underset{\text{sodiumhypo chlorite}}{NaOCl} \longrightarrow \underset{\text{hydrazine}}{N_2H_4} + NaCl + H_2$

(ii) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$

29. On warming, NaOCl solution undergoes disproportionation reaction i.e., the oxidation state of chlorine increases as well as decreases, thus NaOCl solution becomes unstable on warming.

$$\underset{\text{Sodium hypochlorite}}{3NaOCl} \xrightarrow{\text{Heat}} \underset{\text{Sodium chlorate}}{NaClO_3} + \underset{\text{Sodium chloride}}{2NaCl}$$

30. $\underset{\text{Lowest thermal stability}}{HIO_4} < HBrO_4 < \underset{\text{Highest thermal stability}}{HClO_4}$

31. **(i)** Carbon does not contain d-subshell whereas silicon does contain. Therefore, silicon can accommodate lone pair of electrons donated by oxygen atom of water for co-ordinate bond formation. Therefore, unlike to $SiCl_4$, CCl_4 does not hydrolyse.

(ii) Nitrogen does not possess d-subshell. Therefore, it can accommodate one pair of electrons donated by chlorine atoms, for co-ordinate bond formation. (i.e., Nitrogen cannot expand its octet). In phosphorus the state of affair is just opposite, as it does contain d-subshell.

(iii) SF_6 is much more stable than SH_6. As fluorine is more electronegative than hydrogen.

(iv) Because of stronger backbond in BF_3.

32. **(i)** This is because of the lowest ionization energy of xenon and due to the presence of vacant d-orbitals for the promotion of electron.

(ii) Chlorine atom has vacant d-orbitals so ClF_3 is formed. F atom has no d-orbitals.

(iii) H_2O is a colourless liquid while other hydrides of group 16 elements are colourless poisonous gases with unpleasant smell. The low volatile character of water is due to the association of water molecule through hydrogen bonding. This in turn, is due to low atomic size and high electronegativity of oxygen.

(iv) Nitrogen shows little tendency towards catenation. It is due to the weak $N-N$ single bond. The tendency of phosphorus to show catenation is due to its unexpectedly high bond energy.

33. **(a)** Laboratory preparation of phosphine PH_3 : It is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

(b) When phosphine reacts with copper sulphate and mercuric chloride solution, the corresponding phosphides are obtained.

(i) $$\underset{\text{Copper sulphate}}{3CuSO_4} + 2PH_3 \longrightarrow \underset{\text{Copper phosphides}}{Cu_3P_2} + 3H_2SO_4$$

(ii) $$\underset{\text{Mercuric chloride}}{3HgCl_2} + 2PH_3 \longrightarrow \underset{\text{Mercuric phosphide}}{Hg_3P_2} + 6HCl$$

(c) PH_3 reacts with acids like HI to form PH_4I, which shows that it is basic in nature

$$PH_3 + HI \longrightarrow PH_4I$$

34. **(i)** As a result of sp^3d hybridization, there are two axial bonds and three equatorial bonds in PCl_5 molecule. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore, the axial bonds are slightly elongated and hence slightly weaker than the equatorial bonds.

(ii) Xenon has the lowest ionization energy among the noble gases except radon which is however, radioactive.

(iii) Due to inert pair effect, the lower oxidation state gets more stabilized with the increase in atomic number in the same group of p-block, elements. Hence PbO_2 is a stronger oxidizing agent than SnO_2.

35. Halogens react with each other to form interhalogen compounds. They are obtained by direct combination between the halogens or by action of a halogen on a lower halogen.
General composition:

(i) XX' (ClF, BrF, BrCl) **(ii)** XX'_3 (ClF_3, BrF_3, IF_3)

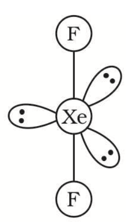
(iii) XX'_5 (ClF_5, BrF_5) **(iv)** XX'_7 (IF_7)

36. **(i)** H_3PO_2 is having 2 hydrogens attached to phosphorus while H_3PO_4 having no hydrogen attached to phosphorous. So H_3PO_2 is a stronger reducing agent than H_3PO_4.

(ii) Because of stronger $S-S$ bonds as compared to $O-O$ bonds, sulpher has greater tendency for catenation than oxygen.

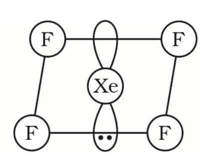
(iii) Since the stability of hydrides decreases from HF to HI, reducing property increases in the same order. HF is not reducing agent at all.

37. **(i)**



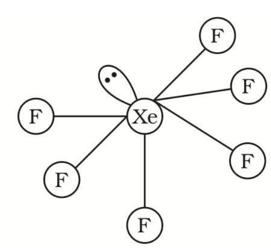
XeF_2
Geometry : Linear

(ii)



XeF_4
Geometry : Square planar

(iii)



XeF_6
Geometry : Distorted octahedral

38. Sulphur exists in a number of allotropic forms. Some of the important forms are discussed as under:

(i) Rhombic or Octahedral or α-sulphur : It is the common forms of Sulphur which is stable below 95.6°C.Its colour is pale yellow. It is soluble in carbon disulphide but insoluble in water. Its melting point is 114°C (when heated rapidly) and specific gravity is 2.06 g cm^{-3}.

(ii) Monoclinic, prismatic or β-sulphur : This forms is stable above 95.6°C and is prepared by melting rhombic Sulphur in a dish and cooling it until a crust is formed. Two holes are pierced in the crust and the liquid lying below the crust is poured out. On removing the crust, monoclinic sulphur is obtained in the form of needle like crystals of amber yellow colour. Its melting point is 120° and specific gravity is 1.94 g cm^{-3}. It is also soluble in carbon disulphide.

(iii) Plastic or γ-sulphur : It is obtained when boiling Sulphur (upto 350°) is poured into cold water. It is a soft rubber like mass which hardens on standing and gradually changes to rhombic sulphur. Its colour is amberbrown and its specific gravity is 2.19 g cm^{-3}. It does not have any sharp melting point. It is also soluble in carbondisulphide. It is considered to be a supercooled liquid i.e., it has no time to settle in crystalline form due to rapid cooling below its melting point.

(iv) Colloidal or δ-sulphur : It is prepared by passing hydrogen sulphide gas into a solution of an oxidising agent like HNO_3, $KMnO_4$ etc.

$$H_2S + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + \underset{\text{Colloidal sulphur}}{S\downarrow}$$

(v) Liquid Sulphur : Thin pale-yellow liquid Sulphur is obtained on heating rhombic Sulphur gradually between $113° - 115°C$. At about 180°C, this liquid becomes dark brown and highly viscous. On further heating, its viscosity decreases rapidly and the liquid starts flowing is 444.5°C. The above changes are exactly reversed on cooling this liquid.

39. **Preparation:** Chloric acid is known only in solution. It is prepared by the following methods.

(i) By the action of sulphuric acid on barium chlorate.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow 2HClO_3 + \underset{\text{(white ppt)}}{BaSO_4\downarrow}$$

After filtering off the precipitate of $BaSO_4$, the filterate is treated with baryta water to precipitate the unused H_2SO_4. When the filterate free from H_2SO_4 is evaporated in a vacuum dessicator over conc. H_2SO_4, a dilute solution of chloric acid is obtained. Excessive evaporation should be avoided because the chloric acid may decompose to chlorine and perchloric acid.

$$3HClO_3 \xrightarrow{\text{Heat}} HClO_4 + Cl_2 + 2O_2 + H_2O$$

(ii) By the reaction of potassium chlorate and hydrofluosilicic acid

$$2KClO_3 + H_2SiF_6 \longrightarrow K_2SiF_6\downarrow + 2HClO_3$$

Properties :

(i) Its solution is colourless having pungent smell.

(ii) Heating effect: On heating it decomposes and give perchloric acid

$$3HClO_3 \xrightarrow{\text{Heat}} HClO_4 + Cl_2 + 2O_2 + H_2O$$

(iii) Reaction with I_2 : When a mixture of iodine and 25% $HClO_3$ is evaporated iodic acid is formed.

(iv) $HClO_3$ is a strong oxidizing agent and powerful bleaching agent. Some of the reactions in which it acts as an oxidizing agent are given below.

(a) $HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O$

(b) $2HClO_3 + 5H_2S \longrightarrow Cl_2 + 5S + 6H_2O$
hydrogen sulphide

(v) Organic substances like cotton, wool, paper etc. catch fire when they come in contact with chloric acid.

Uses :

(i) Its salt $KClO_3$ is used in the manufacture of matches, fire work and gun powder etc.

(ii) As a bleaching agent and oxidizing agent.

40. In 1962, Neil Bartlett noticed that platinum hexafluoride is a powerful oxidizing agent. He observed that an ionic compound is formed when PtF_6 reacts with O_2 i.e., PtF_6 is capable to oxidise O_2 into O_2^+.

$$O_2 + PtF_6 \longrightarrow O_2^+[PtF_6]^-$$

He also noticed that the oxygen and xenon have some markable similarities, like nearly same ionization energies $(O = 1{,}170 \text{ kJ mol}^{-1} \text{ and } Xe = 1{,}180 \text{ kJ mol}^{-1})$ and both have same molecular diameters. He thought that because of above similarities O_2 could be replaced by Xe. He did the same and obtained an orange yellow solid $Xe[PtF_6]$, after the reaction of PtF_6 and Xe (in excess).

$$Xe(g) + PtF_6(g) \longrightarrow Xe^+[PtF_6]^-(s)$$