

## Some more questions--p-Block Elements

(i) Nitrogen (N) does not form pentahalide while P forms  $\text{PCl}_5$ ,  $\text{PF}_5$ , and

$\text{PF}_6^-$

-. Why?

(ii) Sulphur (S) forms  $\text{SF}_6$  but oxygen does not form  $\text{OF}_6$ . Why?

(iii) Though nitrogen forms pentoxide but it does not form pentachloride.

Explain. Why?

(iv) Fluorine forms only one oxoacid while other halogens form a number

of oxoacids. Why?

**(NOTE** - The first member of p-block elements displays greater ability to form  $\text{p}^2$ -

$\text{p}^2$  bond (s) with itself, (e.g.,  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{N}=\text{N}$ ,  $\text{N}\equiv\text{N}$ ) and with the other

elements of second period (e.g.,  $\text{C}=\text{O}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{N}=\text{O}$ ) compared to the subsequent members of the group.

This is because p-orbitals of the heavier members are so large and diffuse

that they cannot have effective sideways overlapping. Heavier members

can form  $\text{p}^2\text{d}^2$  -  $\text{d}^2$  bonds with oxygen.

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(i) Nitrogen forms  $\text{N}_2$  but phosphorus forms  $\text{P}_4$  at room temperature.

Why?

(ii) Oxygen forms  $\text{O}_2$  but sulphur exists as  $\text{S}_8$ . Why?

(iii) Explain why  $(\text{CH}_3)_3\text{P}=\text{O}$  is known but  $(\text{CH}_3)_3\text{N}=\text{O}$  is not known.

+ are the pairs of isostructural species.

**Note Inert pair effect :** Due to poor shielding effect of intervening d and/ or f-electrons, the effective nuclear charge is increased. This increased nuclear charge holds the  $ns^2$  electrons of heavier elements to participate in bonding and the tendency of  $ns^2$  electrons to take part in bonding is more and more restricted down the group. Consequently, more stable lower oxidation state which is two units less than higher oxidation state becomes more and more stable than the higher oxidation state. For example, following questions can be explained with the help of inert pair effect.

(a) For N and P, + 5 oxidation state is more stable than + 3 oxidation state but for Bi, + 3 oxidation state is more stable than + 5. Explain why?

(b)  $NaBiO_3$  is a strong oxidising agent. Why?

(Hint : Bi(v) is least stable O.S.).

(c) In group 16 stability of + 6 oxidation state decreases and the stability

of + 4 oxidation increases down the group. Why?

(d)  $SO_2$  acts as reducing agent. Explain why?

(e) Why is  $BrO_4^-$  is a stronger oxidising agent than  $ClO_4^-$ ?

[Hint : It is because + 7 oxidation state is less stable in  $BrO_4^-$  due

to which Br - O bond becomes weaker.]

(f)  $BiCl_5$  is highly unstable.

(g) The stability of highest oxidation state of 4p element is less than those of 3p and 5p elements of the same group?

Increasing order of melting point and boiling point of hydrides is as given below :

$\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{NH}_3$  ; Melting point

$\text{PH}_3 < \text{AsH}_3 < \text{NH}_3 < \text{SbH}_3$  ; Boiling point

$\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te} < \text{H}_2\text{O}$  ; Melting point and Boiling point

$\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$  ; Boiling point

$\text{HCl} < \text{HBr} < \text{HF} < \text{HI}$  ; Melting point

**Thermal stability, reducing power and acid strength of hydrides** depend

upon bond dissociation enthalpy of E - H bond (E = group 15, group 16, and

group 17 element). Due to the increase in size down the group, bond dissociation

enthalpy of E - H bond decreases. Consequently, thermal stability, reducing

power and acid strength of hydrides increases down the group.

The following questions can be explained using the above concepts.

Explain why :

(i)  $\text{NH}_3$  has higher boiling point than  $\text{PH}_3$ .

(ii)  $\text{H}_2\text{O}$  is liquid and  $\text{H}_2\text{S}$  is gas or  $\text{H}_2\text{S}$  is more volatile than  $\text{H}_2\text{O}$ .

(iii) HE is weaker acid than HCl.

(iv) Among hydrogen halides, HI is the strongest reducing agent.

(v)  $\text{H}_2\text{Te}$  is more acidic than  $\text{H}_2\text{S}$ .

(vi)  $\text{NH}_3$  is mild oxidizing agent while  $\text{BiH}_3$  is the strongest reducing agent

among the group-15 hydrides.

(vii)  $\text{H}_2\text{S}$  is weaker reducing agent than  $\text{H}_2\text{Te}$ .

### **Basic nature of hydrides $\text{EH}_3$ of group 15 elements**

All the hydrides  $\text{EH}_3$  has one lone pair of electron. In ammonia the lone pair of

electron is present in,  $\text{sp}^3$  hybrid orbital of the N-atom. The  $\text{sp}^3$  hybrid orbital

is directional and further N is more electronegative than H, the bond pair of N - H is shifted towards N atom which further increases the electron density on N atom. In PH<sub>3</sub>, the lone pair of electron is present in large and more diffuse 3s orbital which is non-directional. As a result PH<sub>3</sub> is less basic than NH<sub>3</sub> and basic character decreases down the group. NH<sub>3</sub> donates electron pair more readily than PH<sub>3</sub>. (SiH<sub>3</sub>)<sub>3</sub>N has less Lewis basic nature than that of (CH<sub>3</sub>)<sub>3</sub>N because lone pair of electrons in p - orbital of N atom in (SiH<sub>3</sub>)<sub>3</sub>N is transferred to the vacant d - orbital of Si atom forming d<sup>2</sup> - p<sup>2</sup> bond.

### **COVALENT/IONIC CHARACTER OF HALIDES**

Pentahalides are more covalent than trihalides since the element (E) in higher oxidation state (+ 5) has more polarising power than element (E) in lower oxidation state (+ 3) in trihalides, Similarly SnCl<sub>4</sub>, PbCl<sub>4</sub>, SbCl<sub>5</sub> and UF<sub>6</sub> are more covalent than SnCl<sub>2</sub>, PbCl<sub>2</sub>, SbCl<sub>3</sub> and UF<sub>4</sub> respectively.

Following questions can be explained by using this concept. Explain why :

- (i) SnCl<sub>2</sub> has more b.p. than SnCl<sub>4</sub>.
- (ii) SbCl<sub>5</sub> is more covalent than SbCl<sub>3</sub>.
- (iii) PCl<sub>5</sub> has lower boiling point than that of PCl<sub>3</sub>.

### **Oxoacids of N, P and halogens :**

Strength of oxoacid depends upon the polarity of O-H bond which in turn, depends on the electron withdrawing power (or electronegativity) of the element

E. Strength of oxoacids increase if the number of oxygen atom bonded with E increases.

### VSA QUESTIONS (1 - MARK QUESTIONS)

1. In group 15 elements, there is considerable increase in covalent radius

from N to P but small increase from As to Bi. Why?

[Hint : Due to completely filled d- and / or f-orbitals in As, Sb and Bi.

2. The tendency to exhibit - 3 oxidation state, decreases down the group in

group 15 elements. Explain.

[Hint : Due to increase in size and decrease in electronegativity down the groups].

3. Maximum covalence of Nitrogen is '4' but the heavier elements of group

15 show covalence greater than '4'. Why?

4. Nitrogen exists as a diatomic molecule with a triple bond between the two

atoms, whereas the heavier elements of the group do not exist as E<sub>2</sub> at

room temperature. Assign a reason.

[Hint : p<sup>z</sup> - p<sup>z</sup> multiple bonds are formed by N due to its small size.]

5. The ionization enthalpies of group 15 elements are higher than those of

corresponding members of group 14 and 16 elements. Assign the reason.

6. The boiling point of PH<sub>3</sub> is lesser than NH<sub>3</sub>. Why?

7. NO<sub>2</sub> dimerises to form N<sub>2</sub>O<sub>4</sub>. Why?

[Hint : Due to presence of odd electron on N]

8. Draw the structure of N<sub>2</sub>O<sub>5</sub> molecule.

9. How does ammonia solution react with  $\text{Ag}^+$  (aq)? Write the balanced chemical equation.

10. Why does  $\text{NH}_3$  form intermolecular hydrogen bonds whereas  $\text{PH}_3$  does not?

[**Hint** : Due to strong electronegativity, small size of Nitrogen atom and presence of lone pair of electrons on N atom]

11. Write disproportionation reaction of  $\text{H}_3\text{PO}_3$ ?

12. How does  $\text{NH}_3$  act as a complexing agent?

[**Hint** : Metal hydroxides are dissolved in excess of  $\text{NH}_4\text{OH}$ . Ammonia acts as a Lewis base].

13. Why HF is the weakest acid and HI is the strongest.

**Hint** :  $K_a$  : (HF) =  $7 \times 10^{-4}$  (HI) =  $7 \times 10^{11}$

Intermolecular H-bonds in H-F and high bond dissociation enthalpy of

H-F makes it weakest and weak bond in H-I makes it strongest.

14. Explain why halogens are strong oxidising agents.

[**Hint** : Ready acceptance of electron due to more negative electron gain enthalpy.]

15. Why is Bi(V) a stronger oxidant than Sb(V)?

[**Hint** : +3 oxidation state is more stable than +5 oxidation state in Bi].

16. Why  $\text{SF}_4$  is easily hydrolysed, whereas  $\text{SF}_6$  is resistant to hydrolysis?

[**Hint** : Water molecule can not attack 'S' atom due to steric hindrance and 'S' atom is also coordinately saturated in  $\text{SF}_6$  molecule.]

17. Bond dissociation enthalpy of  $\text{F}_2$  is less than that of  $\text{Cl}_2$ . Why?

18. Write the reaction of  $\text{PCl}_5$  with heavy water.

[Hint :  $\text{PCl}_5 + \text{D}_2\text{O} \rightleftharpoons \text{POCl}_3 + 2\text{DCl}$ ]

19. How many P – O – P bonds are there in cyclotrimetaphosphoric acid?

[Hint : 3 bonds]

20. In group 16, the stability of +6 oxidation state decreases and that of +4

oxidation state increases down the group. Why?

[Hint : due to inert pair effect]

21. Why we can not prepare HBr by heating KBr with sulphuric acid.

[Hint : As HBr readily reduces  $\text{H}_2\text{SO}_4$  forming  $\text{Br}_2$ ]

24. Fluorine exhibit only –1 oxidation state whereas other halogens exhibit

+ve oxidation states also. Explain.

25. Arrange the following oxoacids of chlorine in increasing order of acidic

strength.

$\text{HOCl}$ ,  $\text{HOClO}$ ,  $\text{HOClO}_2$ ,  $\text{HOClO}_3$

\*26. The majority of known noble gas compounds are those of Xenon. Why?

\*27. "Hypophosphorus acid is a good reducing agent." Justify with an example.

[Hint :  $4\text{AgNO}_3 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Ag} + \text{HNO}_3 + \text{H}_3\text{PO}_4$ .

\*28. Draw the structure of  $\text{H}_4\text{P}_2\text{O}_7$  and find out its basicity?

[Hint : Tetrabasic]

\*29. Arrange the following triatomic species in the order of increasing bond

angle.

$\text{NO}_2$ ,  $\text{NO}_2$

+,  $\text{NO}_2$

–

[Hint :

$\text{NO}_2$  has one non-bonding electron,  $\text{NO}_2$

– has two non-bonding electrons,

NO<sub>2</sub>

+ has no non-bonding electron on N atom. Bond angle of NO<sub>2</sub> is maximum that of NO<sub>2</sub> – minimum].

30. With what neutral molecule ClO<sup>-</sup> is isoelectronic?

31. Draw the structure of H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and find the number of S–S bond if any.

32. What is cause of bleaching action of chlorine water? Explain it with chemical equation?

[**Hint** : Formation of nascent oxygen]

\*33. Electron gain enthalpy of fluorine is more negative than that of chlorine.

[**Hint** . : Due to small size of F atom, there are strong interelectronic repulsions in the relatively smaller 2p orbitals of fluorine. So the incoming electron does experience less attraction than in Cl]

\*34. Which one of the following is not oxidised by O<sub>3</sub>. State the reason.

KI, FeSO<sub>4</sub>, K<sub>2</sub>MnO<sub>4</sub>, KMnO<sub>4</sub>

[**Hint** . : KMnO<sub>4</sub> since Mn is showing maximum oxidation state of +7.]

### **SA (I) TYPE QUESTIONS (2 - MARK QUESTIONS)**

2. Why is red phosphorus denser and less chemically reactive than white phosphorus?

3. Give chemical reaction in support of the statement that all the bonds in

PCl<sub>5</sub> molecule are not equivalent.

[**Hint** : PCl<sub>5</sub> + H<sub>2</sub>O → POCl<sub>3</sub> + 2HCl]

4. Account for the following :

(a) XeF<sub>2</sub> has linear structure and not a bent structure.

(b) Phosphorus show marked tendency for Catenation.

5. Draw the structures of  $\text{BrF}_3$ ,  $\text{XeOF}_4$ ,  $\text{XeO}_3$  using VSEPR theory.  
6. Write the conditions that favour the formation of ammonia gas along with the reactions involved in Haber's Process

7. Write the chemical equations of the following reactions

(a) Glucose is heated with conc.  $\text{H}_2\text{SO}_4$ .

(b) Sodium nitrate is heated with conc.  $\text{H}_2\text{SO}_4$ .

**Complete the following reactions :**

8. (i)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

$\xrightarrow{\text{heat}}$

(ii)  $\text{NH}_4\text{Cl (aq)} + \text{NaNO}_2 \text{ (aq)}$

9. (i)  $\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$

(ii)  $\text{FeCl}_3 \text{ (aq)} + \text{NH}_4\text{OH}$

10. (i)  $\text{Ca}_3\text{P}_2 + \text{H}_2\text{O (l)}$

(ii)  $\text{I}_2 + \text{HNO}_3 \text{ (conc.)}$

11. (i)  $\text{Ba(N}_3)_2$

$\xrightarrow{\text{heat}}$

(ii)  $4\text{H}_3\text{PO}_3$

$\xrightarrow{\text{heat}}$

12. (i)  $\text{PH}_4\text{I} + \text{KOH}$

(ii)  $\text{HgCl}_2 + \text{PH}_3$

13. (i)  $\text{PCl}_3 + 3\text{H}_2\text{O}$

(ii)  $\text{S} + \text{H}_2\text{SO}_4 \text{ (conc.)}$

14. (i)  $\text{Al}_2\text{O}_3\text{(s)} + \text{NaOH (aq)} + \text{H}_2\text{O(l)}$

(ii)  $\text{HCl} + \text{O}_2 \xrightarrow{2\text{CuCl}}$

15. (i)  $\text{Ca(OH)}_2 + \text{Cl}_2$

(ii)  $\text{XeF}_4 + \text{H}_2\text{O}$

16. (i)  $\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O}$

(ii)  $\text{NaHCO}_3 + \text{HCl}$

17. (i)  $\text{XeF}_6 + \text{H}_2\text{O}$  Complete

hydrolysis

(ii)  $\text{XeF}_6 + \text{H}_2\text{O}$  Partial

hydrolysis  $\text{Fe}^{2+}$

18. (i)  $\text{NO}_3^-$

$\text{Fe}^{2+} + \text{H}^+$

(ii)  $\text{Zn} + \text{HNO}_3$  (dil)

19. (i)  $\text{Zn} + \text{HNO}_3$  (conc)

(ii)  $\text{P}_4 + \text{HNO}_3$  (conc)

20. (i)  $\text{NH}_3 + \text{O}_2$

$\text{Pt/Rh}$

(ii)  $\text{P}_4 + \text{NaOH} + \text{H}_2\text{O}$

21. (i)  $\text{P}_4 + \text{SOCl}_2$

(ii)  $\text{P}_4 + \text{SO}_2\text{Cl}_2$

22. (i)  $\text{PbS} + \text{O}_3$

(ii)  $\text{KI} + \text{H}_2\text{O} + \text{O}_3$

23. (i)  $\text{MnO}_4^-$

$\text{SO}_2 + \text{H}_2\text{O}$

(ii)  $\text{Zn} + \text{HNO}_3$

(dil)

24. (i)  $\text{NH}_3$  (Excess) +  $\text{Cl}_2$

(ii)  $\text{NH}_3 + \text{Cl}_2$  (Excess)

25. (i)  $\text{Cl}_2 + \text{NaOH}$  (cold and dil)

(ii)  $\text{Cl}_2 + \text{NaOH}$  (hot & conc)

26. (i)  $\text{Fe} + \text{HCl}$

(ii)  $\text{Cl}_2 + \text{F}_2$  (Excess)

27. (i)  $\text{U} + \text{ClF}_3$

(ii)  $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{Cl}_2$

28. (i) What is the covalency of N in  $\text{N}_2\text{O}_5$ ?

(ii) Explain why phosphorus forms pentachloride whereas nitrogen and

bismuth do not?

29. (i) The acidic character of hydrides of group 15 increases from  $\text{H}_2\text{O}$  to

$\text{H}_2\text{Te}$ . Why?

(ii) Dioxygen is a gas while sulphur (S<sub>8</sub>) is a solid. Why?

30. (i) Interhalogen compounds are more reactive than halogens except

F<sub>2</sub>. Why?

(ii) Give one important use of ClF<sub>3</sub>.

31. (i) Write the composition of bleaching powder.

(ii) What happens when NaCl is heated with conc. H<sub>2</sub>SO<sub>4</sub> in the presence

of MnO<sub>2</sub>. Write the chemical equation.

32. Arrange the following in the decreasing order of their basicity.

Assign the

reason :

PH<sub>3</sub>, NH<sub>3</sub>, SbH<sub>3</sub>, AsH<sub>3</sub>, BiH<sub>3</sub>.

\*33. A colourless and a pungent smelling gas which easily liquifies to a colourless

liquid and freezes to a white crystalline solid, gives dense white fumes with

ammonia. Identify the gas and write the chemical equation for its laboratory

preparation. [**Hint** : HCl]

\*34. Complete following disproportionation reactions.

(a)  $P_4 + NaOH + H_2O \rightarrow \text{?} \text{?} \text{?}$

(b)  $HNO_2$

$H^+ \rightarrow \text{?} \text{?} \text{?} \text{?}$

35. Arrange the following trichlorides in decreasing order of bond angle NCl<sub>3</sub>

PCl<sub>3</sub>, AsCl<sub>3</sub>, SbCl<sub>3</sub>

36. Suggest reason why only known binary compounds of noble gases are

fluorides and oxides of Krypton, Xenon.

[**Hint** : F and O are most electronegative elements. Kr and Xe both have

low ionisation enthalpies.]

37. Which fluorinating agent are oftenly used instead of F<sub>2</sub>? Write two chemical

equations showing their use as fluorinating agents.

[Hint :  $\text{BrF}_5 + 3\text{H}_2\text{O} \rightleftharpoons \text{HBrO}_3 + 5\text{HF}$

$2\text{IF}_7 + \text{SiO}_2 \rightleftharpoons 2\text{IOF}_5 + \text{SiF}_4$ ]

38. (a) Hydrolysis of XeF<sub>6</sub> is not regarded as a redox reaction. Why?

(b) Write a chemical equation to represent the oxidising nature of XeF<sub>4</sub>.

[Hint : (b)  $\text{XeF}_4 + 2\text{H}_2 \rightleftharpoons \text{Xe} + 4\text{HF}$ ]

39. Write Chemical equation :

(a) XeF<sub>2</sub> is hydrolysed

(b) PtF<sub>6</sub> and Xenon are mixed together.

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### **SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)**

1. (i) How is HNO<sub>3</sub> prepared commercially?

(ii) Write chemical equations of the reactions involved.

(iii) What concentration by mass of HNO<sub>3</sub> is obtained?

2. (i) How does O<sub>3</sub> react with lead sulphide? Write chemical equation.

(ii) What happens when SO<sub>2</sub> is passed in acidified KMnO<sub>4</sub> solution?

(iii) SO<sub>2</sub> behaves with lime water similar to CO<sub>2</sub>.

3. Assign reason for the following :

(i) Sulphur in vapour state exhibits paramagnetism.

(ii) F<sub>2</sub> is strongest oxidising agent among halogens.

(iii) In spite of having same electronegativity, oxygen forms hydrogen

bond while chlorine does not.

4. Give appropriate reason for each of the following :

(i) Metal fluorides are more ionic than metal chlorides.

(ii) Perchloric acid is stronger than sulphuric acid.

(iii) Addition of chlorine to KI solution gives it a brown colour but excess

of Cl<sub>2</sub> makes it colourless.

**[Hint :**

(i) According to Fajan's Rule, bigger ions more are polarised than the

smaller ion by a particular cation.

(ii)  $\text{ClO}_4^-$

– is more resonance stabilised than  $\text{SO}_4^{2-}$

2– since dispersal of

negative charge is more effective in  $\text{ClO}_4^-$

– as compared with  $\text{SO}_4^{2-}$

2–

(iii)  $2\text{KI} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{I}_2$

Excess  $5\text{Cl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{HIO}_3 + 10\text{HCl}$  (Colourless).

5. Explain why :

(i) No chemical compound of helium is known.

(ii) Bond dissociation energy of fluorine is less than that of chlorine.

(iii) Two S–O bonds in  $\text{SO}_2$  are identical.

6. Out of the following hydrides of group 16 elements, which will have :

(i)  $\text{H}_2\text{S}$  (ii)  $\text{H}_2\text{O}$  (iii)  $\text{H}_2\text{Te}$

(a) lowest boiling point

(b) highest bond angle

(c) highest electropositive hydrogen.

7. (i) How is  $\text{XeO}_3$  prepared from  $\text{XeF}_6$ ? Write the chemical equation for

the reaction.

(ii) Draw the structure of  $\text{XeF}_4$ .

8. (i) Thermal stability of hydrides of group 16 elements decreases down

the group. Why?

(ii) Compare the oxidising powers of  $\text{F}_2$  and  $\text{Cl}_2$  on the basis of bond dissociation enthalpy, electron gain enthalpy of halogens and hydration

enthalpy of halide ions.

(iii) Write the chemical equation for the reaction of copper metal with conc.  $\text{HNO}_3$ .

\*9. An unknown salt X reacts with hot conc.  $\text{H}_2\text{SO}_4$  to produce a brown coloured gas which intensifies on addition on copper turnings. On adding dilute ferrous sulphate solution to an aqueous solution of X and then carefully adding conc.  $\text{H}_2\text{SO}_4$  along the sides of the test tube, a brown complex Y is formed at the interface between the solution and  $\text{H}_2\text{SO}_4$ . Identify X and Y and write the chemical equation involved in the reaction.

**[Hint : X is  $\text{NO}_3$  – salt].**

10. Assign reason to the following :

(i) Noble gases have large positive values of electron gain enthalpy.

(ii) Helium is used by scuba divers.

11. Arrange the following in the order of the property indicated for each set–

(a)  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$  (Increasing bond dissociation energy).

(b)  $\text{HF}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  (decreasing acid strength).

(c)  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ ,  $\text{BiH}_3$  (decreasing base strength).

**[Hint :**

(a)  $\text{F}_2$  has exceptionally low bond dissociation enthalpy. Lone pairs in

$\text{F}_2$  molecule are much closer to each other than in  $\text{Cl}_2$  molecule. Larger electron–electron repulsions among the lone pairs in  $\text{F}_2$  molecule make its bond dissociation enthalpy exceptionally low.

(b) Depends upon H–X bond dissociation enthalpy as the size of atom

increases, bond dissociation enthalpy of H–X decreases.

(c) Electron availability on the central atom 'E' in  $\text{EH}_3$  decreases down the group.

\*12. A translucent white waxy solid (A) on heating in an inert atmosphere is converted to its allotropic form (B), Allotrope (A) on reaction with very dilute aqueous NaOH liberates a highly poisonous gas (C) having a rotten fish smell, with excess of chlorine forms D which hydrolyses to form compound (E). Identify the compounds (A) to (E).

A : White phosphorus, B : Red phosphorus, C :  $\text{PH}_3$ , D :  $\text{PCl}_3$ , E :  $\text{H}_3\text{PO}_4$

13. Write balanced equation for the following reactions :

(a) Zn is treated with dilute  $\text{HNO}_3$ .

(b) NaCl is heated with  $\text{H}_2\text{SO}_4$  in the presence of  $\text{MnO}_2$ .

(c) Iodine is treated with conc.  $\text{HNO}_3$ .

14.  $\text{X}_2$  is a greenish yellow gas with pungent offensive smell used in purification

of water. It partially dissolves in  $\text{H}_2\text{O}$  to give a solution which turns blue

litmus red. When  $\text{X}_2$  is passed through NaBr Solution,  $\text{Br}_2$  is obtained.

(a) Identify  $\text{X}_2$ , name the group to which it belongs.

(b) What are the products obtained when  $\text{X}_2$  reacts with  $\text{H}_2\text{O}$ ? Write chemical equation.

(c) What happens when  $\text{X}_2$  reacts with hot and conc. NaOH? Give equation.

16. Assign the appropriate reason for the following:

(a) Nitrogen exists as diatomic molecule and phosphorous as  $\text{P}_4$ , Why?

(b) Why does  $\text{R}_3\text{P} = \text{O}$  exist but  $\text{R}_3\text{N} = \text{O}$  does not ? (R = an alkyl group).

(c) Explain why fluorine forms only one oxoacid, HOF.

**[Hint :**

(a) Due to its small size and high electronegativity N forms  $p^2 - p^2$  multiple bond ( $N \equiv N$ ). whereas P does not form  $p^2 - p^2$  bonds but forms P - P single bond.

(b) Due to the absence of d-orbitals, N cannot expand its covalence beyond four.

In  $R_3N = O$ , N should have a covalence of 5 so the compound  $R_3N = O$  does not exist since maximum covalence shown by N cannot exceed 4.

(c) F does not form oxoacids in which the oxidation state of F would be

+3, +5, +7, it forms one oxoacid, because of unavailability of d orbitals in its valence shell.

**LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)**

1. How is  $PH_3$  prepared in the laboratory? How is it purified? How does the

solution of  $PH_3$  in water react on irradiation with light and on absorption

in  $CuSO_4$ ? How can you prove that  $PH_3$  is basic in nature?

Write the chemical equations for all the reactions involved.

2. Assign a possible reason for the following :

(a) Stability of +5 oxidation state decreases and that of +3 oxidation state increases down the group 15 elements.

(b)  $H_2O$  is less acidic than  $H_2S$ .

(c)  $SF_6$  is inert while  $SF_4$  is highly reactive towards hydrolysis.

(d)  $H_3PO_2$  and  $H_3PO_3$  act as good reducing agents while  $H_3PO_4$  does

not.

(e) Noble gases have comparatively large size in their respective periods.

3. (a) How is  $XeF_6$  prepared from the  $XeF_4$ ? Write the chemical equation

for the reaction.

- (b) Deduce the structure of  $\text{XeF}_6$  using VSEPR theory.
- (c) How does  $\text{XeF}_2$  react with  $\text{PF}_5$ ?
- (d) Give one use each of helium and neon.
- (e) Write the chemical equation for the hydrolysis of  $\text{XeF}_4$ .
4. (a) Why does nitrogen show anomalous behaviour? Discuss the trend of chemical reactivity of group 15 elements with.
- (a) oxygen (b) halogens (c) metals
- (b)  $\text{H}_3\text{PO}_3$  is a dibasic acid. Why?
5. (a) Arrange the following in the order of their increasing acid strength.
- (a)  $\text{Cl}_2\text{O}_7$ ,  $\text{SO}_2$ ,  $\text{P}_4\text{O}_{10}$
- (b) How is  $\text{N}_2\text{O}$  gas prepared? And draw its structure.
- (c) Give one chemical reaction to show  $\text{O}_3$  is an oxidising agent.

\*6. Identify A, B, C, D and E in the following sequence of reactions  
Complete the reactions of the above mentioned sequence.

[Hint : A is  $\text{P}_4$ ].

- \*7. A white waxy, translucent solid, M, insoluble in water but soluble in  $\text{CS}_2$ , glows in dark. M dissolves in  $\text{NaOH}$  in an inert atmosphere giving a poisonous gas (N). Also M catches fire to give dense white fumes of Q :
- (a) Identify M, N and Q and write the chemical equations of the reactions involved.
- (b) M exists in the form of discrete tetrahedral molecules. Draw its structure.
- (c) M on heating at 573 K is changed into other less reactive form, Q, which is non-poisonous, insoluble in water as well as in  $\text{CS}_2$  and does not glow in dark, Identify Q and draw its structure.
8. Write the structure of A, B, C, D and E in the following sequence of reactions :  
Complete reactions of the above mentioned sequence and name the

process by which 'C' is obtained.

[**Hint.** : A is NO and Ostwald process for the manufacture of HNO<sub>3</sub>].

9. Give reason for each of the following :

(a) NH<sub>3</sub> is more basic than PH<sub>3</sub>.

(b) Ammonia is a good complexing agent.

(c) Bleaching by SO<sub>2</sub> is temporary.

(d) PCl<sub>5</sub> is ionic in solid state.

(e) Sulphur in vapour state exhibits paramagnetism.

10. Knowing the electrons gain enthalpy value for O → O<sup>-</sup> and O<sup>-</sup> → O<sup>2-</sup> as

-141 and 720 kJ mol<sup>-1</sup> respectively, how can you account for the formation

of large number of oxides having O<sup>2-</sup> species and not O<sup>-</sup>?

[**Hint** : Latice enthalpy of formation of oxides having O<sup>2-</sup> more than compensates the second ·<sub>eg</sub>H of oxygen.