REASONING QUESTIONS IN P BLOCK ELEMENTS

1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Ans: Nitrogen valence electronic configuration ns^2np^3 due to absence empty d- orbitals, it can not extend its valence to 5

2. PH_3 has lower boiling point than NH_3. Why?

Ans: Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

3. Why are pentahalides more covalent than trihalides ?

Ans: Higher the positive oxidation state of central atom, more will be its Polarizing power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

4. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?

Ans: Among hidres of group 15 from NH_3 to BiH_3 as size of central atom Increases M—H bond strength decreases. Hence it act as strong reducing agent.

5. Write the reaction of thermal decomposition of sodium azide.

Ans: $2\ NaN_3 \rightarrow 2\ Na + 3\ N_2(g)$

6. Why is N_2 less reactive at room temperature?

Ans: Due to its high N≡N bond dissociation energy

7. Why does NH_3 act as a Lewis base?

Ans: Due to presence of one lone pair of electron present on Nitrogen

8. Mention the conditions required to maximize the yield of ammonia.

Ans: Optimum Pressure & Optimum Temperature & Removal of ammonia by cooling.

9. How does ammonia react with a solution of Cu^{2+}?

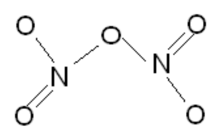
Ans: $Cu^{2+} + 4\ NH_3 \rightarrow [Cu(NH_3)_4]^{+2}$ and this is deep blue in color.

10. Why does NO_2 dimerise ?

Ans: Due to presence one odd electron on Nitrogen of NO_2

11. What is the covalence of nitrogen in N_2O_5 ?

Ans: Covalency is 4 because N is bonded with 4 bonds



12. In what way can it be proved that PH_3 is basic in nature?

Ans: Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g., $PH_3 + HBr \rightarrow PH_4Br$

Due to lone pair on phosphorus atom, PH3 is acting as a Lewis base in the above reaction.

13. Bond angle in PH_4^+ is higher than that in PH_3. Why?

Ans: Both are sp3 hybridized. In PH_4^+ all the four orbital are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone Pair-bond pair repulsion in PH_3 reducing the bond angle to less than 109° 28.

14. What happens when white phosphorus is heated with concentrated NaOH? Solution in an inert atmosphere of CO_2 ?

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$
(sodium hypophosphite)

15. Why does PCl_3 fume in moisture?
Ans: PCl_3 react with moisture and gives HCl vapours.
$$PCl_3 + 3 H_2O \rightarrow H_3PO_3 + 3 HCl$$
16. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.
Ans: PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.
17. What happens when PCl_5 is heated?
Ans: PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.
$$PCl_3 + 3 H_2O \rightarrow H_3PO_3 +3HCl$$
18. Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.
Ans: $PCl_5 + D_2O \rightarrow POCl_3 + 2DCl$
19. How do you account for the reducing behavior of H_3PO_2 on the basis of its structure ?
Ans: In H_3PO_2, two H atoms are bonded directly to P atom which imparts Reducing character to the acid.
20. What is the basicity of H_3PO_4?
Ans: Three P–OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.
21. Phosphorous in solid state is ionic, why?
Ans: In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$octahedral.
22. Elements of Group 16 generally show lower value of first ionization enthalpy compared to the corresponding periods of group 15. Why?
Ans: Due to extra stable half-filled *p* orbital electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.
23. H_2S is less acidic than H_2Te. Why?
Ans: Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.
24. List the important sources of sulphur.
Ans: Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.
25. Write the order of thermal stability of the hydrides of Group 16 elements.
Ans; $H_2O>H_2S>H_2Se>H_2Te>H_2Po$ As atomic size increases E—H bond strength decreases, Hence thermal stability decreases.
26. Why is H_2O a liquid and H_2S a gas ?
Ans: Because of small size and high electro negativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.
27. Which of the following does not react with oxygen directly?
Zn, Ti, Pt, Fe
Ans: Pt is a noble metal it do not react with any atmospheric gases.
28. Complete the following reactions:
(i) $C_2H_4 + O_2 \rightarrow 2 CO_2 + 2 H_2O$
(ii) $4Al + 3 O_2 \rightarrow 2 Al_2O_3$

29. Why does O_3 act as a powerful oxidizing agent?

Ans: Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent.

30. How is O_3 estimated quantitatively?

Ans: When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O3 gas.

31. Which form of sulphur shows paramagnetic behavior ?

Ans: In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

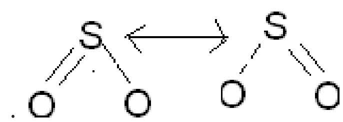
32. What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

Ans: When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions.

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

33. Comment on the nature of two S–O bonds formed in SO2 molecule. Are the two S–O bonds in this molecule equal ?

Ans: Both the S–O bonds are covalent and have equal strength due to resonating Structures.



34. How is the presence of SO_2 detected ?

Ans: It is a suffocating odor gas, when SO_2 gas passed into lime water it gives Milky white ppt $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

35. Mention three areas in which H_2SO_4 plays an important role.

Ans: The bulk of sulphuric acid produced is used in the manufacture of fertilizers (e.g., ammonium sulphate, super phosphate). Other uses are in:
(a) petroleum refining (b) manufacture of pigments, paints and dyestuff Intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanizing
(e) storage batteries

36. Write the conditions to maximize the yield of H_2SO_4 by Contact process.

Ans: $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta_r H^\ominus = -196.6\ kJmol^{-1}$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

37. Why is $K_{a2} << K_{a1}$ for H_2SO_4 in water ?

Ans: H_2SO_4 is a very strong acid in water largely because of its first ionization to H_3O^+ and HSO_4^-. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. That is why $K_{a1} << K_{a2}$.

38. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Ans: Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

39. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidizing agent than chlorine. Why?

Ans: It is due to (i) low enthalpy of dissociation of F-F bond
(ii) high hydration enthalpy of F^-

40. Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.

Ans: Fluorine is the most electronegative element and cannot exhibit any Positive oxidation state. Other halogens have *d* orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

41. Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidizing power of F_2 andCl_2.

Ans: Oxidizing power depends on bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy out of these Fluorine has more hydration Enthalpy and less bond dissociation energy that can compensate high negative enthalpy of Chlorine .

42. Give two examples to show the anomalous behavior of fluorine.

Ans: Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

43. Sea is the greatest source of some halogens. Comment.

Ans: Various minerals of halogens from soil are soluble in river water hence sea gets large amount of halogens in the dissolved form.

44. Write the balanced chemical equation for the reaction of Cl_2 with hot and Concentrated NaOH. Is this reaction a disproportionate reaction? Justify.

Ans: $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

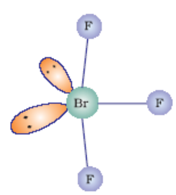
45. When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Ans: Its reaction with iron produces H_2.

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

46. Deduce the molecular shape of BrF_3 on the basis of VSEPR theory.



2 lp and 3 bp as VSPER theory it has trigonal bipyramydal shape.

47. Why is ICl more reactive than I_2?

Ans: In general, interhalogen compounds are more reactive than halogens due to weaker $X–X^1$ bonding than X–X bond. Thus, ICl is more reactive than I_2.

48. Why are the elements of Group 18 known as noble gases ?

Ans: The elements present in Group 18 have their valence shell orbital completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

49. Noble gases have very low boiling points. Why?

Ans: Noble gases being monatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low Temperatures. Hence, they have low boiling points.

50. Does the hydrolysis of XeF_6 lead to a redox reaction?

Ans: No, the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

51. Why is helium used in diving apparatus?

Ans: It is used as a diluent for oxygen in modern diving apparatus because of its Very low solubility in blood.

52. Balance the following equation: $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$

Ans: $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

53. Why has it been difficult to study the chemistry of radon?

Ans: Radon is radioactive with very short half-life which makes the study of Chemistry of radon difficult.

54. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Ans: Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations.

55. AgCl is soluble in water, where as it is soluble in aqueous ammonia solution.

Ans: Ammonia react with AgCl forms $[Ag(NH_3)_2]Cl$ complex which is soluble in water.

56. Give the reason for bleaching action of Cl_2.

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

57. Name two poisonous gases which can be prepared from chlorine gas.

Ans: poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

58. Why does the reactivity of nitrogen differ from phosphorus?

Ans: Nitrogen can form multiple bonds and has more bond dissociation energy due to which it is less reactive. Phosphorous can not form multiple bonds.

59. Why does NH_3 form hydrogen bond but PH_3 does not?

Ans: Electronegetivity of N is more than P.

60. The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

Ans: Due to more electronegative nature of Nitrogen it causes more repulsion, hence bond angle is more.

61. Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

Ans: Nitrogen can not form $d\pi$-$p\pi$ multiple bond due absence of empty d - orbitals.

62. Explain why NH_3 is basic while BiH_3 is only feebly basic.

Ans: Due to small size of ‘N’ it has more electron density and act as strong base.

63. Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Ans: ‘N’ can form multiple bonds where as P can not hence its tri valency it utilized in tetrahedron structure.

64. Give the disproportionate reaction of H_3PO_3.

Ans: phosphorous acid on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

65. Can PCl_5 act as an oxidizing as well as a reducing agent? Justify.

Ans: In PCl_5 oxidation state of P is +5, it can not increase its oxidation state more than it hence it can not act as reducing agent. But it can change its oxidation state to +3 and act as oxidizing agent.

66. Why is dioxygen a gas but sulphur a solid?

Ans: Due to small size Oxygen can form multiple bonds where as S can't hence S bond with S_8 molecule and exist in solid.

67. Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 And 702 kJ mol–1 respectively, how can you account for the formation of a Large number of oxides having O^{-2} species and not O^-?

Ans: Higher second electron gain enthalpy is compensated by high hydration energy and more lattice energy.

68. Why are halogens strong oxidizing agents?

Ans: Since halogens are having high electron gain enthalpy they act as strong oxidizing agents.

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

Ans: 'F' can form only -1 oxidation state, due to small size and absence of empty d – orbitals , hence it forms only one oxoacid HOF

70. Explain why in spite of nearly the same electro negativity, oxygen forms Hydrogen bonding while chlorine does not.

Ans: Due to small size of Oxygen as compared to Sulphur.

71. Why are halogens colored?

Ans: All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2 , greenish yellow, Br_2, red and I_2, violet colour.

72. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?

Ans: 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 ionization enthalpy of molecular oxygen (1175 kJmol–1) was almost identical with that of xenon (1170 kJ mol–1). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour
compound $Xe^+PtF_6^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

73. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Ans: ClF is isoelectronic with ClO^- and it has lone pairs hence act as Lewis base.

74. Arrange the following in the order of property indicated for each set:

(i) F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI - increasing acid strength.

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 – increasing base strength.

Ans: (i) $Cl_2 > Br_2 > F_2 > I_2$ As atomic size increases bond dissociation energy Decreases and since F is extremely small size and cause repulsion Between lone pairs of two F atoms of F_2 molecule.

(ii) HF<HBr<HCl<HI as atomic size increases from F to I bond strength decreases and acidity increases.

(iii) $BiH_3<SbH_3<AsH_3<PH_3<NH_3$ as size increases from N to Bi electron density decreases and basesity decreases.

75. Give the formula and describe the structure of a noble gas species which is isostructural with:

(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-

Ans: (i) $XeCl_4$ (2lp + 4 bp =6, sp^3d^2occupied with 2 lone pairs over all geometry is square planar)

(ii) $XeBr_2$ (2bp+4lp=6, sp^3d^2occupied with 2 lone pairs over all geometry is linear)

(iii) XeO_3 (3bp+ 1lp=4, sp^3 occupied by one lone pair, pyramidal shape.

76. Why do noble gases have comparatively large atomic sizes?

Ans: Noble gases exist as mono atomic gases, there is no overlapping of atomic orbitals like in other compounds. Here atomic radius is considered as vandrwaal's radii. Hence atomic radii are comparatively large.

77. Why does the reactivity of nitrogen differ from phosphorus?

Ans: Due to small size, multiple bond formation, absence of empty d- orbitals.

78. The increase in the atomic size from As to Bi is small as compare from N to P, justify your answer.

Ans: There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

78. Why N differs in its properties as compare with rest of elements of goup 15.

Ans: Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, high ionisation enthalpy and non-availability of *d* orbitals.

79. Except N other elements of group 15 don't form pπ- pπ multiple bond. Explain?

Ans: Heavier elements of this group do not form pπ- pπ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

80. Why N–N bond is weaker than the single P–P bond?

Ans: N–N bond is weaker than the single P–P bond because of high inter electronic repulsion of the non-bonding electrons, owing to the small bond length.

81. N has low catenation as compare with C. Comment.

Ans: Due to its weak N-N single bond energy.

82. Based on what property white phosphorous is used in Holmes signals & smoke screens?

Ans: It under goes spontaneous combustion.

83. Red P is chemically less reactive compare with White P. Give reason.

Ans: Due to its polymeric structure it will have more bonds to break in chemical reactin.

84. oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8). Give reason.

Ans: oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8) because due to large size of S it cannot form multiple bonds.

84. Why oxygen shows anomalous behavior as compare with its congeners ?

Ans: It is due to its small size, High Electro negativity, More Ionization Enthalpy and absence of empty d- orbitals.

85. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increase in group 16, Explain.

Ans: It is due to inert pair effect.

85. Al_2O_3 is amphoteric explain with chemical reactions.

Ans:
$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$
$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$

86. During dilution of sulphuric acid it must be added to water but water should not be added to acid. Explain?

Ans: It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

87. Oxidising ability of halogens is $F_2 > Cl_2 > Br_2 > I_2$ give reason.

Ans: The decreasing oxidising ability of the halogens in aqueous solution Down the group is evident from their standard electrode potentials which are dependent on the parameters indicated below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\,\Delta_{diss}H^\ominus} X(g) \xrightarrow{\Delta_{eg}H^\ominus} X^-(g) \xrightarrow{\Delta_{hyd}H^\ominus} X^-(aq)$$

88. Ionic character of metal halides decreases from MF to MI. Give reason.

Ans: The ionic character of the halides decreases in the order MF >MCl > MBr > MI where M is a monovalent metal.
As electronegetivity/Electron gain enthalpy decreases Ionic character increases.

89. Ionic character of Metal chlorides decreases as oxidation state increases, Explain.

Ans: As oxidation state increases Ionization energy increases hence ionic Character decreases.
the halides in higher oxidation state will be more covalent than the one in lower oxidation state .For e.g., $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

90. What is the maximum valence of Elements of Group 15.
Maxmum valency = group No. – 10=15-10=5

- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,
  $$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$
- In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.
  $$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$
- It can also be obtained by the thermal decomposition of ammonium dichromate.
  $$(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$$
- Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.
  $$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

- At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

- It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g) + 3H_2(g) \underset{}{\overset{773\ k}{\rightleftharpoons}} 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1\ kJmol^{-1}$$

- Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$N_2 + O_2(g) \overset{Heat}{\rightleftharpoons} 2NO(g)$$

- Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

- On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or lime.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2\ SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

- On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1\ kJ\ mol^{-1}$$

- It forms ammonium salts with acids, e.g., NH_4Cl, $(NH4)_2\ SO_4$, etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,

$$2FeCl_3(aq) + 3NH_4OH(aq) \rightarrow \underset{(brown\ ppt)}{Fe_2O_3.xH_2O(s)} + 3NH_4Cl(aq)$$

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow \underset{(white\ ppt)}{Zn(OH)_2(s)} + (NH_4)_2\ SO_4(aq)$$

- Ammonia donate lone pair to the metal ions and form different complex compounds, by this metals ions can be detected.

$$\underset{(blue)}{Cu^{2+}(aq)} + 4\ NH_3(aq) \rightleftharpoons \underset{(deep\ blue)}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{(colourless)}{Ag^+(aq)} + Cl^-(aq) \rightarrow \underset{(white\ ppt)}{AgCl(s)}$$

$$\underset{(white\ ppt)}{AgCl(s)} + 2NH_3(aq) \rightarrow \underset{(colourless)}{[Ag(NH_3)_2]Cl(aq)}$$

- Nitrogen (I) Oxide [Nitrous Oxide] $NH_4\ NO_3 \xrightarrow{Heat} N_2O + 2\ H_2O$
- Nitrogen (II) Oxide [Nitric Oxide]
  $2NaNO_2 + 2\ FeSO_4 + 3H_2\ SO_4 \rightarrow Fe_2\ (SO_4)_3 + 2NaHSO_4 + 2H_2\ O + 2NO$
- Nitrogen (III) Oxide [di Nitrogen Tri Oxide} $2\ NO + N_2\ O_4 \xrightarrow{250K} 2N_2\ O_3$
- Nitrogen di Oxide [Nitrogen (IV) Oxide]
  $2Pb\ (NO_3)_2 \xrightarrow{673K} 4NO_2 + 2\ PbO$

- Nitrogen (IV) Oxide [di Nitrogen tetroxide] $2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$
- Nitrogen (V) Oxide [di Nitrogen pentoxide] $4HNO_3 + P_4O_{10} \rightarrow 4H_3PO_3 + 2N_2O_5$
- In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.
$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
- On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.
$$\underset{\text{(from air)}}{4NH_3(g) + 5O_2(g)} \xrightarrow[500\,K,\ 9\,bar]{Pt/Rh\ gauge\ catalyst} 4NO(g) + 6H_2O(g)$$
- Nitric oxide thus formed combines with oxygen giving NO_2.
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
- Nitrogen dioxide so formed, dissolves in water to give HNO_3.
$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$
- Concentrated nitric acid is a strong oxidizing agent and attacks most metals except noble metals such as gold and platinum.
$$3Cu + 8\ HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
- Zinc reacts with dilute nitric acid to give N2O and with concentrated acid to give NO_2.
$$4Zn + 10HNO_3(dilute) \rightarrow 4\ Zn\ (NO_3)_2 + 5H_2O + N_2O$$
$$Zn + 4HNO_3(conc.) \rightarrow Zn\ (NO_3)_2 + 2H_2O + 2NO_2$$
- Concentrated nitric acid also oxidises non–metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4, and phosphorus to phosphoric acid.
$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10\ NO_2 + 4H_2O$$
$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$
$$S_8 + 48HNO_3(conc.) \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$
$$P_4 + 20HNO_3(conc.) \rightarrow 4H_3PO_4 + 20\ NO_2 + 4H_2O$$
- *Brown Ring Test*: The familiar brown ring test for nitrates depends on the ability of Fe2+ to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex.
$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe\,(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe\ (H_2O)_5\,(NO)]^{2+}} + H_2O$$
- It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.
$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$
- It readily catches fire in air to give dense white fumes of P_4O_{10}.
$P_4 + 5O_2 \rightarrow P_4O_{10}$
- Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.
$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

- In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

- it is absorbed in HI to form phosphonium iodide (PH4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

- When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$$

- Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$$PH_3 + HBr \rightarrow PH_4Br$$

- It is obtained by passing dry chlorine over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

- It is also obtained by the action of thionyl chloride with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

- It is a colourless oily liquid and hydrolyses in the presence of moisture.

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

- It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

- Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

- PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

- When heated, it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

- It reacts with organic compounds containing –OH group converting them to chloro derivatives.

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

- Finely divided metals on heating with PCl5 give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

- phosphorous acid on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

- The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, for example, AgNO3 to metallic silver.

  $$4\,AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

- These dimeric halides undergo disproportionation as given below:

  $$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

- Dioxygen can be obtained in the laboratory by the following ways:

  (i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

  $$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

  (iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

  $$2H_2O_2(aq) \xrightarrow[MnO_2]{} 2H_2O(1) + O_2(g)$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \qquad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g); \qquad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:

$$2Ca + O_2 \rightarrow 2CaO$$
$$4Al + 3O_2 \rightarrow 2Al_2O_3$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$C + O_2 \rightarrow CO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Some compounds are catalytically oxidised. For e.g.,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$
$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

- SO_2 combines with water to give H_2SO_3, an acid.

  $$SO_2 + H_2O \rightarrow H_2SO_3$$

- Al_2O_3 reacts with acids as well as alkalies.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(1) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$
$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(1) \rightarrow 2Na_3[Al(OH)_6](aq)$$

- When a slow dry stream of oxygen is passed through a silent electricaldischarge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

  $$3O_2 \rightarrow 2O_3 \quad \Delta H^\ominus (298\ K) = +142\ kJ\ mol^{-1}$$

- it oxidizes lead sulphide to lead sulphate and iodide ions to iodine.

  $$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$
  $$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

- Nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$$

Industrially, it is produced as a by-product of the roasting of sulphide ores.

- $$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

- When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolorizes acidified potassium permanganate(VII) solution

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

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

- The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta_r H^\ominus = -196.6\,\text{kJmol}^{-1}$$

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

- Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

$$2\,MX + H_2SO_4 \rightarrow 2\,HX + M_2SO_4 \; (X = F, Cl, NO_3)$$

(M = Metal)

- Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

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

- metals and non-metals are oxidized by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2\,H_2SO_4(\text{conc.}) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + 2H_2SO_4(\text{conc.}) \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(\text{conc.}) \rightarrow CO_2 + 2\,SO_2 + 2\,H_2O$$

- In general, a halogen oxidizes halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \; (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \; (X = Br \text{ or } I)$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

- I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$$

(where X = Cl or Br)

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

- Preparation of Chlorine:

By heating manganese dioxide with concentrated hydrochloric acid.

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

$$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Deacon's process: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$2Na + Cl_2 \rightarrow 2NaCl$; $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$;

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$H_2S + Cl_2 \rightarrow 2HCl + S$$

$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; $NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$
(cold and dilute)

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

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temp.}} \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

Coloured substance + O → Colourless substance

In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$$

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

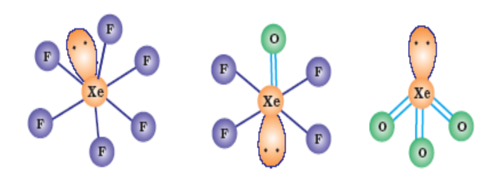
$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437K} 2ClF; \qquad I_2 + \underset{\text{(excess)}}{3Cl_2} \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573K} 2ClF_3; \qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

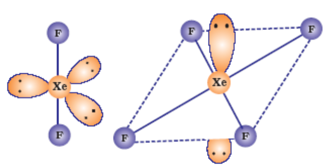
$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl; \qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

$$XX' + H_2O \rightarrow HX' + HOX$$

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



(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal



(a) Linear (b) Square planar

$$\underset{\text{(xenon in excess)}}{Xe\ (g) + F_2\ (g)} \xrightarrow{673K,\ 1bar} XeF_2(s)$$

$$\underset{\text{(1:5 ratio)}}{Xe\ (g) + 2F_2\ (g)} \xrightarrow{873\ K,\ 7\ bar} XeF_4(s)$$

$$\underset{\text{(1:20 ratio)}}{Xe\ (g) + 3F_2\ (g)} \xrightarrow{573\ K,\ 60-70bar} XeF_6(s)$$

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

$$2XeF_2\ (s) + 2H_2O(l) \rightarrow 2Xe\ (g) + 4\ HF(aq) + O_2(g)$$

$$XeF_2 + PF_5 \rightarrow [XeF]^+\ [PF_6]^-; \quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+\ [SbF_6]^-$$

$$XeF_6 + MF \rightarrow M^+\ [XeF_7]^-\ (M = Na,\ K,\ Rb\ or\ Cs)$$

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

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

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

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