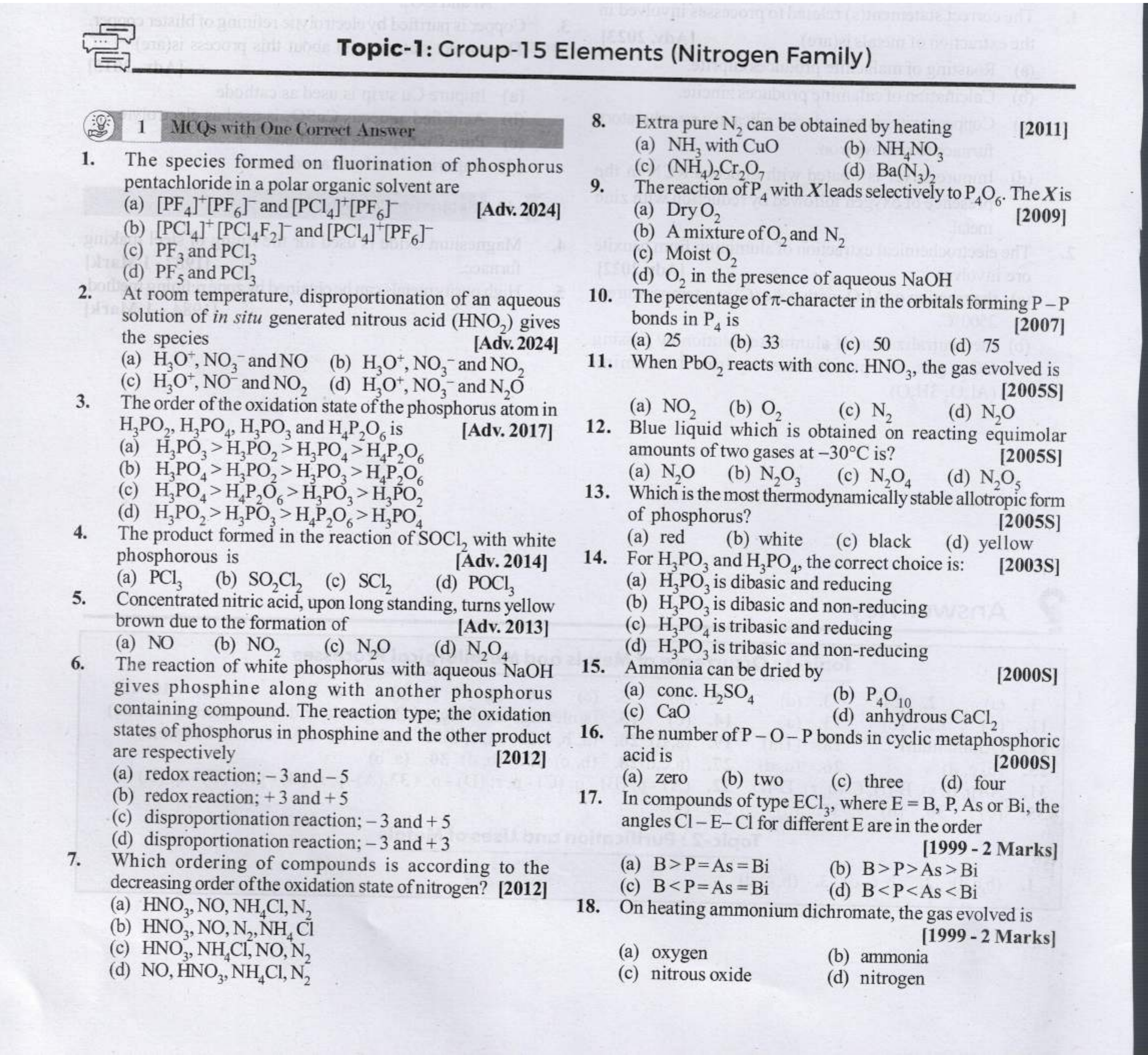
Chapter
The p-Block Elements
(Group 15,16,17,18)



Topic-1: Group-15 Elements (Nitrogen Family)

1 MCQs with One Correct Answer

1. The species formed on fluorination of phosphorus pentachloride in a polar organic solvent are **[Adv. 2024]**
   (a) $[PF_4]^+[PF_6]^-$ and $[PCl_4]^+[PF_6]^-$
   (b) $[PCl_4]^+[PCl_4F_2]^-$ and $[PCl_4]^+[PF_6]^-$
   (c) PF_3 and PCl_3
   (d) PF_5 and PCl_3
2. At room temperature, disproportionation of an aqueous solution of *in situ* generated nitrous acid (HNO_2) gives the species **[Adv. 2024]**
   (a) H_3O^+, NO_3^- and NO (b) H_3O^+, NO_3^- and NO_2
   (c) H_3O^+, NO^- and NO_2 (d) H_3O^+, NO_3^- and N_2O
3. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ is **[Adv. 2017]**
   (a) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$
   (b) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$
   (c) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$
   (d) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$
4. The product formed in the reaction of $SOCl_2$ with white phosphorous is **[Adv. 2014]**
   (a) PCl_3 (b) SO_2Cl_2 (c) SCl_2 (d) $POCl_3$
5. Concentrated nitric acid, upon long standing, turns yellow brown due to the formation of **[Adv. 2013]**
   (a) NO (b) NO_2 (c) N_2O (d) N_2O_4
6. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively **[2012]**
   (a) redox reaction; – 3 and – 5
   (b) redox reaction; + 3 and + 5
   (c) disproportionation reaction; – 3 and + 5
   (d) disproportionation reaction; – 3 and + 3
7. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? **[2012]**
   (a) HNO_3, NO, NH_4Cl, N_2
   (b) HNO_3, NO, N_2, NH_4Cl
   (c) HNO_3, NH_4Cl, NO, N_2
   (d) NO, HNO_3, NH_4Cl, N_2
8. Extra pure N_2 can be obtained by heating **[2011]**
   (a) NH_3 with CuO (b) NH_4NO_3
   (c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$
9. The reaction of P_4 with *X* leads selectively to P_4O_6. The *X* is **[2009]**
   (a) Dry O_2
   (b) A mixture of O_2 and N_2
   (c) Moist O_2
   (d) O_2 in the presence of aqueous NaOH
10. The percentage of π-character in the orbitals forming P – P bonds in P_4 is **[2007]**
    (a) 25 (b) 33 (c) 50 (d) 75
11. When PbO_2 reacts with conc. HNO_3, the gas evolved is **[2005S]**
    (a) NO_2 (b) O_2 (c) N_2 (d) N_2O
12. Blue liquid which is obtained on reacting equimolar amounts of two gases at –30°C is? **[2005S]**
    (a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5
13. Which is the most thermodynamically stable allotropic form of phosphorus? **[2005S]**
    (a) red (b) white (c) black (d) yellow
14. For H_3PO_3 and H_3PO_4, the correct choice is: **[2003S]**
    (a) H_3PO_3 is dibasic and reducing
    (b) H_3PO_3 is dibasic and non-reducing
    (c) H_3PO_4 is tribasic and reducing
    (d) H_3PO_3 is tribasic and non-reducing
15. Ammonia can be dried by **[2000S]**
    (a) conc. H_2SO_4 (b) P_4O_{10}
    (c) CaO (d) anhydrous $CaCl_2$
16. The number of P – O – P bonds in cyclic metaphosphoric acid is **[2000S]**
    (a) zero (b) two (c) three (d) four
17. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl – E– Cl for different E are in the order **[1999 - 2 Marks]**
    (a) $B > P = As = Bi$ (b) $B > P > As > Bi$
    (c) $B < P = As = Bi$ (d) $B < P < As < Bi$
18. On heating ammonium dichromate, the gas evolved is **[1999 - 2 Marks]**
    (a) oxygen (b) ammonia
    (c) nitrous oxide (d) nitrogen

19. One mole of calcium phosphide on reaction with excess water gives **[1999 - 2 Marks]**
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentoxide

20. Amongst the trihalides of nitrogen which one is least basic? **[1987 - 1 Mark]**
(a) NF_3 (b) NCl_3
(c) NBr_3 (d) NI_3

21. Which of the following oxides of nitrogen is a coloured gas? **[1987 - 1 Mark]**
(a) N_2O (b) NO (c) N_2O_5 (d) NO_2

22. The bonds present in N_2O_5 are : *(1986 - 1 Mark)*
(a) only ionic (b) covalent and coordinate
(c) only covalent (d) covalent and ionic

23. Nitrogen dioxide cannot be obtained by heating : **[1985 - 1 Mark]**
(a) KNO_3 (b) $Pb(NO_3)_2$ (c) $Cu(NO_3)_2$ (d) $AgNO_3$

24. Ammonia can be dried by **[1980]**
(a) Conc. H_2SO_4 (b) P_2O_5
(c) Anhydrous $CuSO_4$ (d) none

25. The reddish brown coloured gas formed when nitric oxide is oxidised by air is **[1979]**
(a) N_2O_5 (b) N_2O_4 (c) NO_2 (d) N_2O_3

2 Integer Value Answer

26. The total number of lone pairs of electrons in N_2O_3 is **[Adv. 2015]**

27. Among the following, the number of compounds than can react with PCl_5 to give $POCl_3$ is **[2011]**
$O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}$

3 Numeric / New Stem Based Questions

28. Dissolving 1.24 g of white phosphorous in boiling NaOH solution in an inert atmosphere gives a gas **Q**. The amount of $CuSO_4$ (in g) required to completely consume the gas **Q** is______. **[Adv. 2022]**
[Given: Atomic mass of H = 1, O = 16, Na = 23, P = 31, S = 32, Cu = 63]

4 Fill in the Blanks

29. In P_4O_{10}, the number of oxygen atoms bonded to each phosphorus atom is .... **[1992 - 1 Mark]**

30. The basicity of phosphorous acid (H_3PO_3) is .... **[1990 - 1 Mark]**

31. .... phosphorus is reactive because of its highly strained tetrahedral structure. **[1987 - 1 Mark]**

32. The lowest possible oxidation state of nitrogen is **[1980]**

5 True / False

33. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. **[1991 - 1 Mark]**

34. The H-N-H bond angle in NH_3 is greater than the H-As-H bond angle is AsH_3. **[1984 - 1 Mark]**

35. Red phosphorus is less volatile than white phosphorus because the former has a tetrahedral structure. **[1982 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

36. The correct statement(s) related to oxoacids of phosphorous is(are) **[Adv. 2021]**
(a) Upon heating, H_3PO_3 undergoes disproportionation reaction to produce H_3PO_4 and PH_3.
(b) While H_3PO_3 can act as reducing agent, H_3PO_4 cannot.
(c) H_3PO_3 is a monobasic acid.
(d) The H atom of P–H bond in H_3PO_3 is not ionizable in water.

37. Based on the compounds of group 15 elements, the correct statement(s) is (are) **[Adv. 2018]**
(a) Bi_2O_5 is more basic than N_2O_5
(b) NF_3 is more covalent than BiF_3
(c) PH_3 boils at lower temperature than NH_3
(d) The N–N single bond is stronger than the P–P single bond

38. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300 °C is (are) **[Adv. 2018]**
(a) NH_4NO_3 (b) $(NH_4)_2Cr_2O_7$
(c) $Ba(N_3)_2$ (d) Mg_3N_2

39. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} **[Adv. 2016]**
(a) can also be prepared by reaction of P_4 and HNO_3
(b) is diamagnetic
(c) contains one N-N bond
(d) reacts with Na metal producing a brown gas

40. The nitrogen oxide(s) that contain(s) N-N bond(s) is(are) **[2009]**
(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

41. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt (s) H is (are) **[2008]**
(a) NH_4NO_3 (b) NH_4NO_2 (c) NH_4Cl (d) $(NH_4)_2SO_4$

42. Ammonia, on reaction with hypochlorite anion, can form **[1999 - 3 Marks]**
(a) NO (b) NH_4Cl (c) N_2H_4 (d) HNO_2

43. White phosphorus (P_4) has **[1998 - 2 Marks]**
(a) six P-P single bonds
(b) four P-P single bonds
(c) four lone pairs of electrons
(d) PPP angle of 60°

44. Sodium nitrate decomposes above 800° C to give **[1998 - 2 Marks]**
(a) N_2 (b) O_2
(c) NO_2 (d) Na_2O

45. Nitrogen(I) oxide is produced by : **[1989 - 1 Mark]**
(a) thermal decomposition of ammonium nitrate
(b) disproportionation of N_2O_4
(c) thermal decomposition of ammonium nitrite
(d) interaction of hydroxylamine and nitrous acid.

7 Match the Following

46. Match the reactions (in the given stoichiometry of the reactants) in List-I with one of their products given in List-II and choose the correct option. **[Adv. 2023]**

List-I	List-II
(P) $P_2O_3 + 3H_2O \rightarrow$	(1) $P(O)(OCH_3)Cl_2$
(Q) $P_4 + 3NaOH + 3H_2O \rightarrow$	(2) H_3PO_3

(R) $PCl_5 + CH_3COOH \rightarrow$ (3) PH_3
(S) $H_3PO_2 + 2H_2O + 4AgNO_3 \rightarrow$ (4) $POCl_3$
(5) H_3PO_4

(a) $P \rightarrow 2; Q \rightarrow 3; R \rightarrow 1; S \rightarrow 5$
(b) $P \rightarrow 3; Q \rightarrow 5; R \rightarrow 4; S \rightarrow 2$
(c) $P \rightarrow 5; Q \rightarrow 2; R \rightarrow 1; S \rightarrow 3$
(d) $P \rightarrow 2; Q \rightarrow 3; R \rightarrow 4; S \rightarrow 5$

47. Match the following, choosing one item from column **X** and the appropriate item from column **Y**. **[1983 - 2 Marks]**

X	Y
(i) Haber	(a) Activation energy
(ii) Graham	(b) Diffusion of gases
(iii) Arrhenius	(c) Octet rule
(iv) Lewis	(d) Ammonia synthesis

8 Comprehension/Passage Based Questions

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous. **[2008]**

48. Among the following, the correct statement is
(a) Phosphates have no biological significance in humans
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
(d) Oxidation of nitrates is possible in soil

49. Among the following, the correct statement is
(a) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical *s*-orbital and is less directional
(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical *s*-orbital and is less directional

50. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(a) dimerization reaction
(b) disproportionation reaction
(c) condensation reaction
(d) precipitation reaction

9 Assertion and Reason/Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as
(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

51. **Statement-1 :** Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed
Statement-2 : Phosphorus has lower electronegativity than nitrogen. **[1994 - 2 Marks]**

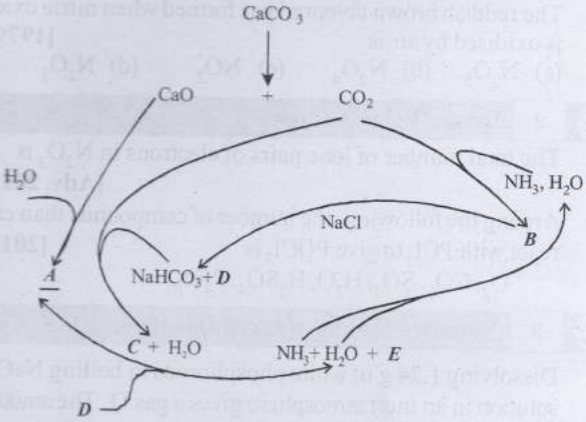
10 Subjective Problems

52. Write the structures of $(CH_3)_3N$ and $(Me_3Si)_3N$. Are they isostructural? Justify your answer. **[2005 - 2 Marks]**

53. How many grams of CaO are required to neutralize 852 g of P_4O_{10}? Draw structure of P_4O_{10} molecule. **[2005 - 2 Marks]**

54. Give reason(s) why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus as a tetraatomic molecule. **[2000 - 2 Marks]**

55. The Haber process can be represented by the following scheme;



Identify *A*, *B*, *C*, *D* and *E*. **[1999 - 5 Marks]**

56. Reaction of phosphoric acid with $Ca_5(PO_4)_3F$ yields a fertilizer "triple superphosphate". Represent the same through balanced chemical equation. **[1998 - 2 Marks]**

57. A soluble compound of a poisonous element *M*, when heated with Zn/H_2SO_4, gives a colourless and extremely poisonous gaseous compound *N*, which on passing through a heated tube gives a silvery mirror of element *M*. Identify *M* and *N*. **[1997 - 2 Marks]**

58. Draw the structure of P_4O_{10} and identify the number of single and double P—O bonds. **[1996 - 3 Marks]**

59. Complete and balance the following chemical reactions :
(*i*) Red phosphorus is reacted with iodine in presence of water. **[1992 - 1 Mark]**
$P + I_2 + H_2O \rightarrow .... + ...$
(*ii*) Anhydrous potassium nitrate is heated with excess of metallic potassium. **[1992 - 1 Mark]**
$KNO_3(s) + K(s) \rightarrow .... + ...$

60. Arrange the following in : **[1991 - 1 Mark]**
Increasing order of extent of hydrolysis :
$CCl_4, MgCl_2, AlCl_3, PCl_5, SiCl_4$

61. Write down the balanced equations for the reactions when:
- (*i*) a mixture of potassium chlorate, oxalic acid and sulphuric acid is heated; **[1985 - 1 Mark]**
- (*ii*) ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. **[1985 - 1 Mark]**

62. Write down the resonance structures of nitrous oxide. **[1985 - 2 Marks]**

OR

Write the two resonance structures of N_2O that satisfy the octet rule. **[1990 - 1 Mark]**

63. State with balanced equations what happens when :
- (*i*) $P_4O_{10} + PCl_5 \rightarrow$ **[1998 - 1 Mark]**
- (*ii*) Phosphorus is treated with concentrated nitric acid. **[1997 - 1 Mark]**

  OR

  Manufacture of phosphoric acid from phosphorus. **[1997 - 1 Mark]**
- (*iii*) Elemental phosphorus reacts with conc. HNO_3 to give phosphoric acid. **[1991 - 1 Mark]**
- (*iv*) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. **[1991 - 1 Mark]**
- (*v*) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. **[1991 - 1 Mark]**
- (*vi*) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution. **[1990 - 1 Mark]**
- (*vii*) Write balanced equations for the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. **[1990 - 1 Mark]**
- (*viii*) Write balanced equations for the preparation of phosphine from CaO and white phosphorus. **[1990 - 2 Marks]**
- (*ix*) Hypophosphorous acid is heated. **[1989 - 1 Mark]**
- (*x*) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. **[1988 - 1 Mark]**
- (*xi*) Dilute nitric acid is slowly reacted with metallic tin. **[1987 - 1 Mark]**
- (*xii*) White phosphorous (P_4) is boiled with a strong solution of sodium hydroxide in an inert atmosphere. **[1982/87 - 1 Mark]**

64. Give reasons for the following :
- (*i*) The experimentally determined N – F bond length in NF_3 is greater than the sum of the single covalent bond radii of N and F. **[1995 - 2 Marks]**
- (*ii*) Ammonium chloride is acidic in liquid ammonia solvent. **[1991 - 1 Mark]**
- (*iii*) Phosphine has lower boiling point than ammonia. **[1989 - 1 Mark]**
- (*iv*) H_3PO_3 is a dibasic acid. **[1989 - 1 Mark]**
- (*v*) Orthophosphorus acid is not tribasic acid. **[1987 - 1 Mark]**
- (*vi*) A bottle of liquor ammonia should be cooled before opening the stopper. **[1983 - 1 Mark]**
- (*vii*) Orthophosphoric acid, H_3PO_4, is tribasic, but phosphorous acid, H_3PO_3, is dibasic. **[1982 - 1 Mark]**

65. Give structural formula for the following :
- (*i*) Phosphorous acid, H_3PO_3 **[1981 - 1 Mark]**
- (*ii*) Pyrophosphoric acid, $H_4P_2O_7$ **[1981 - 1 Mark]**

Topic-2: Group-16 Elements (Oxygen Family)

1 MCQs with One Correct Answer

1. In the following reaction sequence in aqueous solution, the species *X*, *Y* and *Z*, respectively, are **[Adv. 2016]**

$$S_2O_3{}^{2-} \xrightarrow{Ag^+} \underset{\substack{\text{clear}\\\text{solution}}}{X} \xrightarrow{Ag^+} \underset{\substack{\text{white}\\\text{precipitate}}}{Y}$$

$$\xrightarrow{\text{with time}} \underset{\text{black precipitate}}{Z}$$

(a) $[Ag(S_2O_3)_2]^{3-}, Ag_2S_2O_3, Ag_2S$
(b) $[Ag(S_2O_3)_3]^{5-}, Ag_2SO_3, Ag_2S$
(c) $[Ag(SO_3)_2]^{3-}, Ag_2S_2O_3, Ag$
(d) $[Ag(SO_3)_3]^{3-}, Ag_2SO_4, Ag$

2. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives– **[2008]**
(a) $Na_2S_4O_6$ (b) $NaHSO_4$
(c) NaCl (d) NaOH

3. Which of the following is not oxidized by O_3 ? **[2005S]**
(a) KI (b) $FeSO_4$ (c) $KMnO_4$ (d) K_2MnO_4

4. The acid having O – O bond is **[2004S]**
(a) $H_2S_2O_3$ (b) $H_2S_2O_6$ (c) $H_2S_2O_8$ (d) $H_2S_4O_6$

5. The number of S – S bonds in sulphur trioxide trimer (S_3O_9) is **[2001S]**
(a) three (b) two (c) one (d) zero

6. Sodium thiosulphate is prepared by **[1996 - 1 Mark]**
(a) reducing Na_2SO_4 solution with H_2S
(b) boiling Na_2SO_3 solution with S in alkaline medium
(c) neutralising $H_2S_2O_3$ solution with NaOH
(d) boiling Na_2SO_3 solution with S in acidic medium

7. Hydrolysis of one mole of peroxodisulphuric acid produces **[1996 - 1 Mark]**
(a) two moles of sulphuric acid
(b) two moles of peroxomonosulphuric acid
(c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
(d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide.

8. H_2SO_4 cannot be used to prepare HBr from NaBr as it : **[1995S]**
(a) reacts slowly with NaBr (b) oxidises HBr
(c) reduces HBr (d) disproportionates HBr

9. The compound which gives off oxygen on moderate heating is : **[1986 - 1 Mark]**
(a) cupric oxide (b) mercuric oxide
(c) zinc oxide (d) aluminium oxide

10. A gas that cannot be collected over water is : **[1985 - 1 Mark]**
(a) N_2 (b) O_2
(c) SO_2 (d) PH_3

11. Which of the following is coloured **[1980]**

(a) NO (b) N_2O (c) SO_3 (d) None

2 Integer Value Answer

12. The total number of compounds having at least one bridging oxo group among the molecules given below is _____. N_2O_3, N_2O_5, P_4O_6, P_4O_7, $H_4P_2O_5$, $H_5P_3O_{10}$, $H_2S_2O_3$, $H_2S_2O_5$ **[Adv. 2018]**

3 Numeric / New Stem Based Questions

13. The amount of water produced (in g) in the oxidation of 1 mole of rhombic sulphur by conc.HNO_3 to a compound with the highest oxidation state of sulphur is ____ (Given data : Molar mass of water = 18g mol^{-1}) **[Adv. 2019]**

4 Fill in the Blanks

14. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence of .... as catalyst. **[1992 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

15. The compound(s) having peroxide linkage is(are) **[Adv. 2024]**

(a) $H_2S_2O_7$ (b) $H_2S_2O_8$
(c) $H_2S_2O_5$ (d) H_2SO_5

16. The correct statement(s) about O_3 is(are)

(a) O—O bond lengths are equal **[Adv. 2013-II]**
(b) Thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure

17. Which of the following halides react(s) with $AgNO_3$(aq) to give a precipitate that dissolves in $Na_2S_2O_3$(aq)?

(a) HCl (b) HF **[2012]**
(c) HBr (d) HI

8 Comprehension/Passage Based Questions

Passage-1

Upon heating $KClO_3$ in the presence of catalytic amount of MnO_2, a gas *W* is formed. Excess amount of *W* reacts with white phosphorus to give *X*. The reaction of *X* with pure HNO_3 gives *Y* and *Z*. **[Adv. 2017]**

18. *W* and *X* are, respectively

(a) O_3 and P_4O_6 (b) O_2 and P_4O_6
(c) O_2 and P_4O_{10} (d) O_3 and P_4O_{10}

19. *Y* and *Z* are, respectively

(a) N_2O_3 and H_3PO_4 (b) N_2O_5 and HPO_3
(c) N_2O_4 and HPO_3 (d) N_2O_4 and H_3PO_3

Passage-2

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, *P* and *Q*, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product *R*. *R* reacts with white phosphorus to give a compound *S*. On hydrolysis, *S* gives an oxoacid of phosphorus, *T*. **[Adv. 2013]**

20. *P* and *Q*, respectively, are the sodium salts of

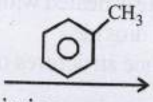
(a) Hypochlorus and chloric acids
(b) Hypochlorus and chlorus acids
(c) Chloric and perchloric acids
(d) Chloric and hypochlorus acids

21. *R*, *S* and *T* respectively, are

(a) SO_2Cl_2, PCl_5 and H_3PO_4 (b) SO_2Cl_2, PCl_3 and H_3PO_3
(c) $SOCl_2$, PCl_3 and H_3PO_2 (d) $SOCl_2$, PCl_5 and H_3PO_4

10 Subjective Problems

22. $(B) \xleftarrow{NaBr+MnO_2} (A) \xrightarrow{Conc.HNO_3} (C)$



(*D*) (explosive product)

Identify the missing compounds. Give the equation from *A* to *B* and *A* to *C*. **[2005 - 4 Marks]**

23. Identify the following: **[2003 - 4 Marks]**

$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{Elemental S}} C \xrightarrow{I_2} D$$

Also mention the oxidation state of S in all the compounds.

24. In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2? **[1999 - 4 Marks]**

25. In the following equation, **[1999 - 6 Marks]**

$A + 2B + H_2O \rightarrow C + 2D$

($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$). Identify *D*. Draw the structures of *A*, *B*, *C* and *D*.

26. Thionyl chloride can be synthesized by chlorinating SO_2 using PCl_5. Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2, 2 – dimethoxypropane. Discuss all this using balanced chemical equations. **[1998 - 6 Marks]**

27. $PbS \xrightarrow[\text{air}]{\text{heat in}} A + PbS \xrightarrow{B} Pb + SO_2$; Identify *A* and *B*. **[1991 - 2 Marks]**

28. Write the two resonance structures of ozone which satisfy the octet rule. **[1991 - 1 Mark]**

29. Mention the products formed in the following :
Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. **[1986 - 1 Mark]**

30. Arrange the following in :
CO_2, N_2O_5, SiO_2, SO_3 in the order of increasing acidic character. **[1988 - 1 Mark]**

31. What happens when :

(*i*) hydrogen sulphide is bubled through an aqueous solution of sulphur dioxide. **[1985 - 1 Mark]**

(*ii*) tin is treated with concentrated nitric acid. **[1985 - 1 Mark]**

(*iii*) Pb_3O_4 is treated with nitric acid. **[1985 - 1 Mark]**

32. Show with equations, how the following compound is prepared (equations need not be balanced) : sodium thiosulphate from sodium sulphite. **[1982 - 1 Mark]**

33. State with balanced equations what happens when :
Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. **[1991 - 1 Mark]**

34. Give reasons for the following :

(*i*) Sulphur dioxide is a more powerful reducing agent in an alkaline medium than in acidic medium. **[1992 - 1 Mark]**

(*ii*) Valency of oxygen is generally two whereas sulphur shows valency of two, four and six. **[1988 - 1 Mark]**

(*iii*) Sulphur melts to a clear mobile liquid at 119ºC, but on further heating above 160ºC, it becomes viscous. **[1981 - 1 Mark]**

Topic-3: Group-17 Elements (Halogen Family)

1 MCQs with One Correct Answer

1. The reaction of $HClO_3$ with HCl gives a paramagnetic gas, which upon reaction with O_3 produces **[Adv. 2022]**
(a) Cl_2O (b) ClO_2 (c) Cl_2O_6 (d) Cl_2O_7

2. A colorless aqueous solution contains nitrates of two metals, **X** and **Y**. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue **P** and a solution **Q**. The residue **P** was soluble in aq. NH_3 and also in excess sodium thiosulfate. The hot solution **Q** gave a yellow precipitate with KI. The metals **X** and **Y**, respectively, are **[Adv. 2020]**
(a) Ag and Pb (b) Ag and Cd
(c) Cd and Pb (d) Cd and Zn

3. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are : **[2017]**
(a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-
(c) Cl^- and ClO^- (d) Cl^- and ClO_2^-

4. Which one of the following species is not a pseudohalide? **[1997 - 1 Mark]**
(a) CNO^- (b) $RCOO^-$ (c) OCN^- (d) NNN^-

5. KF combines with HF to form KHF_2. The compound contains the species. **[1996 - 1 Mark]**
(a) K^+, F^- and H^+ (b) K^+, F^- and HF
(c) K^+ and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

6. Which of the following statements is correct for $CsBr_3$? **[1996 - 1 Mark]**
(a) It is a covalent compound.
(b) It contains Cs^{3+} and Br^- ions.
(c) It contains Cs^+ and Br_3^- ions
(d) It contains Cs^+, and Br^- and lattice Br_2 molecule

7. Bromine can be liberated from potassium bromide solution by the action of **[1987 - 1 Mark]**
(a) Iodine solution (b) Chlorine water
(c) Sodium chloride (d) Potassium iodide

8. Chlorine acts as a bleaching agent only in presence of **[1983 - 1 Mark]**
(a) dry air (b) moisture
(c) sunlight (d) pure oxygen

9. HBr and HI reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce **[1981 - 1 Mark]**
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) none of the above

10. A solution of KBr is treated with each of the following. Which one would liberate bromine **[1980]**
(a) Cl_2 (b) HI (c) I_2 (d) SO_2

11. Which of the following is most stable to heat **[1980]**
(a) HCl (b) HOCl (c) HBr (d) HI

2 Integer Value Answer

12. Ozonolysis of ClO_2 produces an oxide of chlorine. The average oxidation state of chlorine in this oxide is ____. **[Adv. 2021]**

13. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is **[2011]**

4 Fill in the Blanks

14. Solubility of iodine in water is greatly increased by the addition of iodide ions because of the formation of........ **[1994 - 1 Mark]**

15. .... acid gives hypo .... ion. **[1988 - 1 Mark]**
(hydrobromic, hypobromous, perbromic, bromide, bromite, perbromate)

16. The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of .... **[1982 - 1 Mark]**

17. .... is a weak acid. (HF, HCl, HI) **[1981 - 1 Mark]**

18. Iodine reacts with hot NaOH solution. The products are NaI and .... **[1980]**

5 True / False

19. HBr is a stronger acid than HI because of hydrogen bonding. **[1993 - 1 Mark]**

20. In aqueous solution, chlorine is a stronger oxidizing agent than fluorine. **[1984 - 1 Mark]**

21. Dil. HCl oxidizes metallic Fe to Fe^{2+}. **[1983 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

22. With respect to hypochlorite, chlorate and perchlorate ions, choose the correct statement(s).
(a) The hypochlorite ion is the strongest conjugate base.
(b) The molecular shape of only chlorate ion is influenced by the lone pair of electrons of Cl.
(c) The hypochlorite and chlorate ions disproportionate to give rise to identical set of ions.
(d) The hypochlorite ion oxidizes the sulfite ion.

23. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to **[Adv. 2017]**
(a) The physical state of X_2 at room temperature changes from gas to solid down the group
(b) Decrease in ionization energy down the group
(c) Decrease in π^* - σ^* gap down the group
(d) Decrease in HOMO-LUMO gap down the group

24. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is (are) **[Adv. 2017]**
(a) The central atom in both $HClO_4$ and HClO is sp^3 hybridized
(b) $HClO_4$ is more acidic than HClO because of the resonance stabilization of its anion
(c) $HClO_4$ is formed in the reaction between Cl_2 and H_2O
(d) The conjugate base of $HClO_4$ is weaker base than H_2O

25. The compounds used as refrigerant are **[1990 - 1 Mark]**
(a) NH_3 (b) CCl_4 (c) CF_4 (d) CF_2Cl_2
(e) CH_2F_2

8 Comprehension/Passage Based Questions

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. **[2012 - II]**

26. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

(a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

27. 25 mL of household solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

9 Assertion and Reason/Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

28. **Statement-1:** F atom has less electron affinity than Cl atom.
Statement-2: Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F atom. **[1998 - 2 Marks]**

10 Subjective Problems

29. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. **[2000 - 2 Marks]**

30. Complete the following chemical equations :

(a) $KI + Cl_2 \rightarrow$ (b) $KClO_3 + I_2 \rightarrow$

Justify the formation of the products in the above reactions. **[1996 - 2 Marks]**

31. Gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. **[1996 - 2 Marks]**

32. Complete and balance the following chemical reactions :

(iii) $NH_3 + NaOCl \rightarrow$ .... + ... **[1993 - 1 Mark]**

33. Mention the products formed in the following :

(*i*) Chlorine gas is bubbled through a solution of ferrous bromide. **[1986 - 1 Mark]**
(*ii*) Iodine is added to a solution of stannous chloride. **[1986 - 1 Mark]**

34. Arrange the following in :

(*i*) HOCl, $HOClO_2$, $HOClO_3$, HOClO in increasing order of thermal stability. **[1988 - 1 Mark]**
(*ii*) increasing bond strength **[1986 - 1 Mark]**
HCl, HBr, HF, HI

35. State with balanced equations what happens when :

(*i*) Sodium iodate is added to a solution of sodium bisulphite. **[1990 - 1 Marks]**
(*ii*) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. **[1989 - 1 Mark]**
(*iii*) Sodium bromate reacts with fluorine in presence of alkali. **[1989 - 1 Mark]**
(*iv*) Iodate ion reacts with bisulphite ion to liberate iodine. **[1988 - 1 Mark]**
(*v*) Sodium iodate is treated with sodium bisulphite solution. **[1982 - 1 Mark]**

36. Give reasons for the following :

(*i*) Bond dissociation energy of F_2 is less than that of Cl_2. **[1992 - 1 Mark]**
(*ii*) Fluorine cannot be prepared from fluorides by chemical oxidation. **[1985 - 1 Mark]**
(*iii*) Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor; **[1985 - 1 Mark]**
(*iv*) In the preparation of hydrogen iodide from alkali iodides, phosphoric acid is preferred to sulphuric acid **[1982 - 1 Mark]**

37. Write balanced equation involved in the preparation of

(i) Anhydrous aluminium chloride from alumina.
(ii) Bleaching powder from slaked lime.
(iii) Tin metal from cassiterite
(iv) Chlorine from sodium chloride. **[1979]**

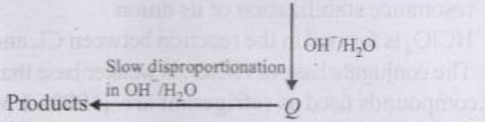
38. Account for the following. Limit your answer to two sentences

(*i*) Hydrogen bromide cannot be prepared by action of concentrated sulphuric acid or sodium bromide.
(*ii*) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised. **[1979]**

Topic-4: Group-18 Elements (Noble Gases)

1 MCQs with One Correct Answer

1. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is **[Adv. 2014]**



(a) 0 (b) 1 (c) 2 (d) 3

2. The shape of XeO_2F_2 molecule is **[2012]**

(a) trigonal bipyramidal (b) square planar
(c) tetrahedral (d) see-saw

3. Total number of lone pair of electrons with central atom in $XeOF_4$ is **[2004S]**

(a) 0 (b) 1 (c) 2 (d) 3

3 Numeric / New Stem Based Questions

4. At 143 K, the reaction of XeF_4 with O_2F_2, produces a xenon compound Y. The total number of lone pair(s) of electron present on the whole molecule of Y is ____ **[Adv. 2019]**

7 Match the Following

5. The unbalanced chemical reactions given in **List-I** show missing reagent or condition (?) which are provided in **List-II**. Match **List-I** with **List-II** and select the correct answer using the code given below the lists **[Adv. 2013-II]**

	List-I		List-II
P.	$PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2$ + other product	1.	NO
Q.	$Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4$ + other product	2.	I_2
R.	$N_2H_4 \xrightarrow{?} N_2$ + other product	3.	Warm
S.	$XeF_2 \xrightarrow{?} Xe$ + other product	4.	Cl_2

Codes :

	P	Q	R	S
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

6. All the compounds listed in **Column I** react with water. Match the result of the respective reactions with the appropriate options listed in **Column II**. **[2010]**

Column-I	Column-II
(A) $(CH_3)_2SiCl_2$	(p) Hydrogen halide formation
(B) XeF_4	(q) Redox reaction
(C) Cl_2	(r) Reacts with glass
(D) VCl_5	(s) Polymerization
	(t) O_2 formation

8 Comprehension/Passage Based Questions

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to given XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

7. Argon is used in arc welding because of its **[2007]**
(a) low reactivity with metal
(b) ability to lower the melting point of metal
(c) flammability
(d) high calorific value

8. The structure of XeO_3 is **[2007]**
(a) linear (b) planar
(c) pyramidal (d) T-shaped

9. XeF_4 and XeF_6 are expected to be **[2007]**
(a) oxidizing (b) reducing
(c) unreactive (d) strongly basic

10 Subjective Problems

10. Write balanced equations for the reactions of the following compounds with water : **[2002 - 5 Marks]**
(i) Al_4C_3 (ii) CaNCN
(iii) BF_3 (iv) NCl_3
(v) XeF_4

11. Draw the molecular structures of XeF_2, XeF_4 and XeO_2F_2 indicating the location of lone pair(s) of electrons. **[2000 - 3 Marks]**

Answer Key

Topic-1 : Group-15 Elements (Nitrogen Family)

1. (b) **2.** (a) **3.** (c) **4.** (a) **5.** (b) **6.** (c) **7.** (b) **8.** (d) **9.** (b) **10.** (d)
11. (b) **12.** (b) **13.** (c) **14.** (a) **15.** (c) **16.** (c) **17.** (b) **18.** (d) **19.** (c) **20.** (a)
21. (d) **22.** (b) **23.** (a) **24.** (d) **25.** (c) **26.** (8) **27.** (4) **28.** (2.38) **29.** (four) **30.** (two)
31. (white/yellow) **32.** (–3) **33.** True **34.** True **35.** False **36.** (a,b,d) **37.** (a,b,c) **38.** (b,c) **39.** (b,d)
40. (a,b,c) **41.** (a,b) **42.** (c) **43.** (a,c,d) **44.** (a,b,d) **45.** (a,d) **46.** (d) **47.** (i) (d) (ii) (b) (iii) (a) (iv) (c)
48. (c) **49.** (c) **50.** (b) **51.** (b)

Topic-2 : Group-16 Elements (Oxygen Family)

1. (a) **2.** (b) **3.** (c) **4.** (c) **5.** (d) **6.** (b) **7.** (c) **8.** (b) **9.** (b) **10.** (c)
11. (d) **12.** (6) **13.** (288) **14.** Nitric oxide. [NO] **15.** **(b,d)** **16.** (a,c,d) **17.** (a,c,d) **18.** (c) **19.** (b)
20. (a) **21.** (a)

Topic-3 : Group-17 Elements (Halogen Family)

1. (c) **2.** (a) **3.** (c) **4.** (b) **5.** (c) **6.** (c) **7.** (b) **8.** (b) **9.** (d) **10.** (a)
11. (a) **12.** (6) **13.** (5) **14.** I_3 complex ion **15.** Hypobromous; bromite **16.** KI_3 **17.** HF
18. $NaIO_3$ **19.** False **20.** False **21.** True **22.** (a,b,d) **23.** (c,d) **24.** (a,b,d) **25.** (a,d) **26.** (a) **27.** (c)
28. (c)

Topic-4 : Group-18 Elements (Noble Gases)

1. (c) **2.** (d) **3.** (b) **4.** (19) **5.** (d)
6. (A)–(p), (s); (B)–(p), (q), (r), (t); (C)–(p), (q); (D)–(p), (q) **7.** (a) **8.** (c) **9.** (a)

Hints & Solutions

Topic-1: Group-15 Elements (Nitrogen Family)

1. **(b)** If PCl_5 is fluorinated in a polar solvent, ionic isomers are formed e.g.:-
$[PCl_4]^+[PCl_4F_2]^-$ (colourless crystals)
and $[PCl_4]^+[PF_6]^-$ (white crystals)

2. **(a)** Disproporationation of HNO_2 in aqueous solution takes place as:

$$3\overset{+3}{HNO_2} \rightleftharpoons \overset{+5}{HNO_3} + 2\overset{+2}{NO} + H_2O$$

Hence, the products formed are H_3O^+, NO_3^- and NO.

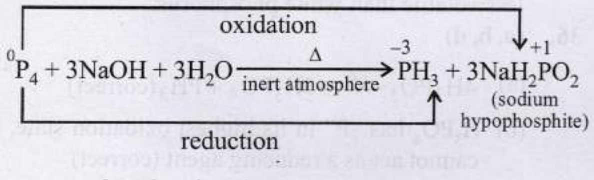
3. **(c)** Let oxidation states of phosphorus in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ be w, x, y and z respectively.
Thus, in H_3PO_2:
$3\times(+1)+w+2\times(-2)=0 \quad \therefore w=+1$
In H_3PO_4:
$3\times(+1)+x+4\times(-2)=0 \quad \therefore x=+5$
In H_3PO_3:
$3\times(+1)+y+3\times(-2)=0 \quad \therefore y=+3$
In $H_4P_2O_6$:
$4\times(+1)+2z+6\times(-2)=0 \quad \therefore z=+4$
Thus, the order of oxidation state is :
$H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$

4. **(a)** $\underset{\text{white phosphorus}}{P_4} + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

5. **(b)** The slow decomposition of HNO_3 is represented by the eqn.

$$4HNO_3 \rightarrow \underset{\text{(yellow-brown)}}{4NO_2} + 2H_2O + O_2$$

6. **(c)**



$$\overset{0}{P_4} + 3NaOH + 3H_2O \xrightarrow[\text{inert atmosphere}]{\Delta} \overset{-3}{PH_3} + 3Na\overset{+1}{H_2PO_2}$$

7. **(b)** $\overset{+5}{HNO_3}, \overset{+2}{NO}, \overset{0}{N_2}, \overset{-3}{NH_4Cl}$

8. **(d)** $Ba(N_3)_2 \longrightarrow Ba + 3N_2$

9. **(b)** $P_4 + 3O_2 \xrightarrow{\text{in presence of } N_2} P_4O_6$
Here N_2 acts as a diluent and thus retards further oxidation. Reaction of P_4 under other three conditions.
(a) $P_4 + 3O_2 \longrightarrow P_4O_6 \xrightarrow{2O_2} P_4O_{10}$
(c) In moist air, P_4O_6 is hydrolysed to form H_3PO_3
$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$
(d) In presence of NaOH,
$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$

10. **(d)** In P_4, the P–P linkage is formed by sp^3–sp^3 hybridised orbital overlapping. So, the percentage of π-character will be 75%.

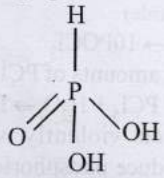
11. **(b)** PbO_2 is a powerful oxidizing agent and liberate O_2 when treated with acids.

$$2PbO_2 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + 2H_2O + O_2\uparrow$$

12. **(b)** $NO\,(g) + NO_2\,(g) \xrightarrow{-30°C} \underset{\text{(blue liquid)}}{N_2O_3}$

13. **(c)** The ignition temperature of black phosphorus is highest among all its allotropes, hence is most stable.

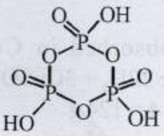
14. **(a)** The structure of H_3PO_3 is as follows: There are only two –OH groups and hence **dibasic**. The oxidation number of P in this acid is +3. Whereas P can have +5 oxidation state also. Therefore, H_3PO_3 can be oxidised which means H_3PO_3 is a **reducing agent**.



15. **(c)** NH_3 does not react with basic oxide, CaO, while other reacts with NH_3

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$
$$P_4O_{10} + 12NH_3 \rightarrow 4(NH_4)_3PO_4 + 6H_2O$$
$$CaCl_2 + 8NH_3 \rightarrow CaCl_2.8NH_3$$

16. **(c)** In cyclic metaphosporic acid number of P–O–P bonds is three.



17. **(b)** In BCl_3, $H = \frac{1}{2}(3+3+0-0) = 3$; sp^2 hybridization (bond angle = 120°). Similarly PCl_3, $AsCl_3$ and $BiCl_3$ are found to have sp^3 hybridized central atom with one lone pair of electrons on the central atom. The bond angle ≤ 109°28′, since the central atoms belong to the same group. The bond

angle of the chlorides decreases as we go down the group. Thus, the order of bond angle is, $BCl_3 > PCl_3 > AsCl_3 > BiCl_3$.

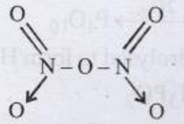
18. **(d)** $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$

19. **(c)** $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$; *i.e.* 2 moles of phosphine are produced.

20. **(a)** Least basic trihalogen of nitrogen is NF_3 because of the highest electronegativity of fluorine.

21. **(d)** NO_2 is reddish brown coloured gas. Rest of the oxides are colourless.

22. **(b)**



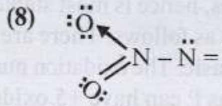
The structure clearly shows the presence of covalent and co-ordinate bonds.

23. **(a)** Only nitrates of heavy metals and lithium decompose on heating to produce NO_2.

24. **(d)** None; it reacts with all given compounds. It forms addition compounds with them because it is basic in nature and given compounds are acidic in nature.
It can be dried over any metal oxide.

25. **(c)** $\underset{\substack{\text{Nitric oxide}\\\text{(colourless)}}}{2NO} + O_2 \longrightarrow \underset{\substack{\text{Nitrogen dioxide}\\\text{(reddish brown coloured)}}}{2NO_2}$

26. **(8)**



Number of lone pairs = 8

27. **(4)** $PCl_5 + SO_2 \longrightarrow POCl_3 + \underset{\text{(Thionyl chloride)}}{SOCl_2}$

$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$

When equimolar amounts of PCl_5 and H_2O are used, the reaction is gentle: $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

[**Note:** PCl_5 reacts violently with H_2O on complete hydrolysis to produce phosphoric acid.
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$]

$2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + \underset{\text{(sulphuryl chloride)}}{SO_2Cl_2} + 2HCl$

28. **(2.38)** $\underset{\text{(White phosphorous)}}{P_4} + 3NaOH + 3H_2O \xrightarrow[\text{atmosphere}]{\text{Inert}} \underset{\text{Phosphine}}{PH_3\uparrow} + 3NaH_2PO_2$

PH_3 : a non-inflammable gas in its pure form; slightly soluble in water.

When PH_3 is absorbed in $CuSO_4$ solution cupric phosphide forms: $2PH_3 + 3CuSO_4 \longrightarrow CuP_2 + 3H_2SO_4$

1 mol of $P_4 = 31 \times 4 = 124$ g

$\therefore$ 1.24 g of white phosphorous = 0.01 mol

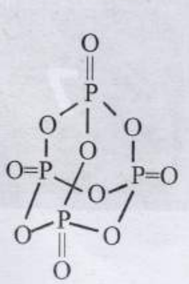
$\therefore$ 0.01 mol of P_4 forms 0.01 mol of PH_3

No. of moles of $CuSO_4$ is required for complete consumption of 0.01 mol $= 0.01 \times \dfrac{3}{2} = 15 \times 10^{-3}$

M.W. of $CuSO_4$ = 159 g/mol

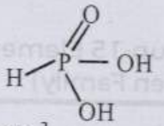
$\therefore$ Amount of $CuSO_4$ required $= 15 \times 10^{-3} \times 159 = 2.38$g

29. **four.**



Each 'P' atom is linked to 4 'O' atoms as confirmed by its structure. It is linked to three 'O' atoms by single bond and one 'O' atom by double bond.
Each P atom is linked to 4 oxygen atoms

30. **two;**



[It contains two replaceable hydrogens.]

31. **white/ yellow; :** In white phosphorus, each phosphorus atom is linked to the other three atoms by covelent bonds. PPP bond angle is 60°, due to which the molecule remains under strain and hence is active in nature.

32. **–3;** Nitrogen has 5 electrons in its valence shell. Thus, it can accept maximum 3 electrons.

33. **True :** The molecule of NO has eleven valence electrons (5 due to N and 6 due to O). It is impossible for all of them to be paired, hence the nitric oxide molecule contains an *odd electron* which makes gaseous nitric oxide *paramagnetic*.

$:N \overset{\cdot}{\equiv} O:$

In the liquid and solid states, nitric oxide is polymerised to a dimer which is *diamagnetic*.

34. **True :**

The central element in the metal hydrides of group 15 elements is although in sp^3 hybrid state, the H – M – H bond angle is less than the normal tetrahedral bond angle of 109° 28'; *e.g.* the bond angle, H – N – H in NH_3 is 106° 45'. This is due to greater repulsion between a lone pair and a bond pair of electrons than between the two bond pairs of electrons.

The decrease in bond angle from 107.8° in ammonia to about 90° in AsH_3 can be explained by the fact that in the latter case sp^3 hybridisation becomes less and less distinct with the increasing size of their electron clouds, *i.e.*, pure *p* orbitals (instaed of sp^3 hybrid orbitals) are used for M – H bonding and the lone pair of electrons is present in spherical *s*-orbital.

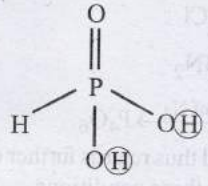
35. **False :** Red phosphorus is ***polymeric substance***. It exist as chains of P_4 tetrahedra linked together. Therefore, it is less volatile than white phosphorus.

36. **(a, b, d)**

(a) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (correct)

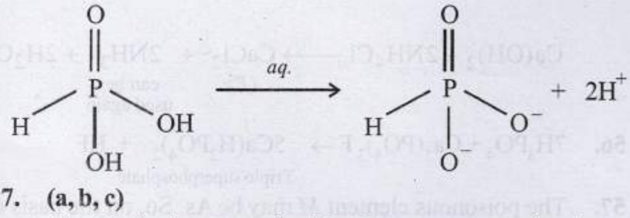
(b) H_3PO_4 has "P" in its highest oxidation state, hence cannot act as a reducing agent (correct)

(c)



So, it is dibasic acid (incorrect)

(d) The hydrogen which is directly attached to phosphorous does not ionized in water.



37. **(a, b, c)**

(a) Basic character of oxides increases on moving down the group therefore, Bi_2O_5 is more basic than N_2O_5.

(b) Covalent nature depends on electronegativity difference between bonded atoms. In NF_3, N and F are non-metals but in BiF_3, Bi is metal while F is non metal therefore, NF_3 is more covalent than BiF_3.

(c) In PH_3, hydrogen bonding is absent but in NH_3, hydrogen bonding is present, therefore PH_3 boils at lower temperature than NH_3.

(d) Due to small size in N–N single bond, l.p. – l.p. repulsion is more than P–P single bond therefore, N–N single bond is weaker than the P–P single bond.

38. **(b, c)**

(a) $NH_4NO_3 \xrightarrow[\text{below 300°C}]{} N_2O + 2H_2O$

$2N_2O \xrightarrow[\text{above 600°C}]{} 2N_2 + O_2$

(b) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} \underset{\text{(colourless}}{N_2} + \underset{\text{(Green colour)}}{Cr_2O_3} + 4H_2O$

(c) $Ba(N_3)_2 \xrightarrow[180°C]{\Delta} Ba + 3N_2$

(d) $Mg_3N_2 \xrightarrow[\text{above 700°C}]{} 3Mg + N_2$

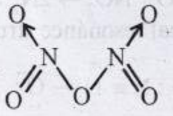
Hence, only $(NH_4)_2Cr_2O_7$ and $Ba(N_3)_2$ can provide N_2 gas on heating below 300°C

39. **(b, d)**

$$P_4O_{10} + 4HNO_3 \xrightarrow{\text{dehydration of } HNO_3} 4(HPO_3) + \underset{\text{(required product)}}{2N_2O_5}$$

(a) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2\uparrow + 4H_2O$

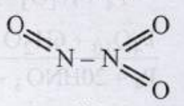
(b) N_2O_5 is diamagnetic in nature

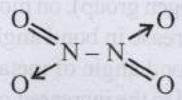
(c) $N_2O_5 \rightarrow$ 

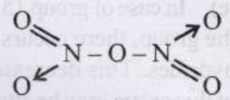
N_2O_5 contains one N–O–N bond but not N–N bond.

(d) $Na + N_2O_5 \rightarrow NaNO_3 + \underset{\text{(Brown gas)}}{NO_2\uparrow}$

40. **(a, b, c)** $N \equiv N \rightarrow O$
(a)


(b)


(c)


(d)

41. **(a,b)** When ammonium salt NH_4NO_3 or NH_4NO_2 (ammonium salts are colourless) is boiled with excess of NaOH, ammonia (NH_3) gas is evolved as follows:

$$NH_4NO_2 + NaOH \longrightarrow NaNO_2 + NH_3 + H_2O$$
$$NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$$

The NH_3 gas evolved is non-flammable gas.

When the gas evolution ceases we are left with $NaNO_2$ or $NaNO_3$ in solution.

These salts get reduced when Zn is added to this solution containing salt ($NaNO_2$ or $NaNO_3$). Again NH_3 gas evolves.

$$NaNO_2 + 6(H) \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$$

$$NaNO_3 + 8(H) \xrightarrow{Zn/NaOH} NaOH + NH_3 + 2H_2O$$

Thus, the colourless salt [H] is either NH_4NO_2 or NH_4NO_3. Thus, (a) and (b) are correct answers.

42. **(c)** $2NH_3 + OCl^- \rightarrow NH_2.NH_2 + H_2O + Cl^-$

43. **(a, c, d)** The four atoms in a P_4 molecule are situated at the corners of a tetrahedron. There are six P - P single bonds with PPP bond angle equal to 60°. Each phosphorus has a lone pair of electrons.

44. **(a, b, d)** Sodium nitrate on decomposition upto 500°C gives $NaNO_2$ and oxygen.

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$$

While at higher temperature (*i.e.* above 800°C), $NaNO_2$ further decomposes into Na_2O, N_2 and O_2.

$$2NaNO_2 \xrightarrow{800°C} Na_2O + 3/2O_2\uparrow + N_2\uparrow$$

45. **(a, d)** $NH_4NO_3 \longrightarrow N_2O + 2H_2O$
$NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$

46. **(d)** (P) $P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$
(Q) $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$
(R) $PCl_5 + CH_3COOH \rightarrow CH_3COCl + POCl_3 + HCl$
(S) $H_3PO_2 + 2H_2O + 4AgNO_3 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$

47. **(i) (d) (ii) (b) (iii) (a) (iv) (c)**

48. **(c)** We know that phosphates have a biological significance in human, therefore statement (a) is not correct. Since nitrates are more soluble in water so they are less abundant in earth's crust where as phosphates are less soluble in water and so they are more abundant in earth's crust. Thus, statement (b) is False and statement (c) is correct.

In nitrates (NO_3^-) nitrogen is in + 5 oxidation state which is the highest oxidation state exhibited by nitrogen. Because of this, nitrates can not be oxidized (oxidation means increase in oxidation state). Hence, statement (d) is not correct.
The correct answer is (c).

49. **(c)** In case of group 15 (nitrogen group), on moving down the group, there occurs a decrease in bond angle of metal hydrides. This decrease in bond angle of metal hydrides of this group may be attributed to the increased *p*- character in the bond pair which results in more *s*- character in lone pair orbital.
The directional character is more for sp^3 hybrid orbital than on *s*- orbital.
Thus, the correct answer is (c).

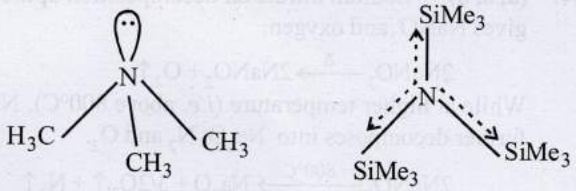
50. **(b)** The reaction between NaOH and white phosphorus (P_4) can be represented as follows:

$$\underset{\text{(white Phosphorus)}}{\overset{0}{P_4}} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \underset{\text{(Phosphine)}}{\overset{-3}{P}H_3}$$

In this reaction, Phosphorus is oxidised as well as reduced, so it is a disproportionation reaction.
∴ The correct answer is (b).

51. **(b)** Nitrogen cannot form pentahalides because it cannot expand its octet due to non-availability of *d*-orbitals. So E is not correct explanation of S.

52. $(CH_3)_3N$ and $(Me_3Si)_3N$ are not isostructural, the former is pyramidal while the latter is trigonal planar. Silicon has vacant *d* orbitals which can accommodate lone pair of electrons from N (back bonding) leading to planar shape.



53. $6\,CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$

Moles of $P_4O_{10} = \dfrac{852}{284} = 3$

Moles of CaO = 3 × 6 = 18; wt. of CaO = 18 × 56 = 1008 g
For structure of P_4O_{10} : [See previous question].

54. Elemental nitrogen exists as a diatomic molecule because nitrogen can form $p\pi$ - $p\pi$ multiple bonds which is not possible in case of phosphorus due to repulsion between non-bonded electrons of the inner core. There is no such repulsion in case of smaller nitrogen atoms as they have only $1s^2$ electrons in their inner core.

55. In such a case :
$A = Ca(OH)_2$, $B = NH_4HCO_3$, $C = Na_2CO_3$, $D = NH_4Cl$ and $E = CaCl_2$

$$CaO + H_2O \longrightarrow \underset{(A)}{Ca(OH)_2}$$

$$NH_3 + CO_2 + H_2O \longrightarrow \underset{\text{Sod. Bicarbonate}(B)}{NH_4HCO_3}$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + \underset{\text{Amm. chloride}(D)}{NH_4Cl}$$

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{Sod. carbonate }(C)}{Na_2CO_3} + H_2O + CO_2$$

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow \underset{(E)}{CaCl_2} + \underset{\substack{\text{can be}\\ \text{used again}}}{2NH_3} + 2H_2O$$

56. $7H_3PO_4 + Ca_5(PO_4)_3F \rightarrow \underset{\text{Triple superphosphate}}{5Ca(H_2PO_4)_2} + HF$

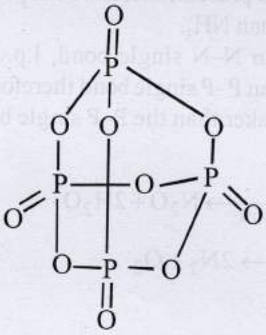
57. The poisonous element *M* may be As. So, on the basis of the given facts,

$$AsCl_3 + 6H \xrightarrow{Zn/H_2SO_4} \underset{(N)}{AsH_3} + 3HCl$$

$$2AsH_3 \xrightarrow{\Delta} \underset{(M)}{2As} + 3H_2\uparrow$$

Hence, $M = As$; $N = As\,H_3$

58.



No. of P – O single bonds = 12
No. of P – O double bonds = 4

59. (*i*) $2P + 3I_2 + 6H_2O \rightarrow 2H_3PO_4 + 6HI$
(*ii*) $2KNO_3 + 10K \rightarrow 6K_2O + N_2$

60. Since *carbon* has no *d*-orbital, it cannot extend its coordination number beyond four, its halides are not attacked (hydrolysed) by water. On the other hand, silicon have vacant *d*-orbitals to which water molecules can coordinate and hence their halides are hydrolysed by water. As the charge on central atom increases, the tendency of attack of a nucleophile (OH^-) increases.
Increasing order of extent of hydrolysis
$CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$

61. (*i*) $KClO_3 + 2H_2C_2O_4 + H_2SO_4 \rightarrow KHSO_4 + HCl + 6CO_2 + 3H_2O$
(*ii*) $(NH_4)_2SO_4 + NO + NO_2 \rightarrow 2N_2 + 3H_2O + H_2SO_4$

62. N_2O has two principal resonance structures :

$$\overset{-}{\ddot{:N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow :N \equiv \overset{+}{N} - \overset{-}{\underset{..}{\ddot{O}}}:$$

63. (*i*) $P_4O_{10} + 6PCl_5 \rightarrow 10\,POCl_3$
(*ii*) $[2HNO_3 \rightarrow H_2O + 2NO_2 + [O]] \times 10$

$$P_4 + 10[O] \rightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

$$\overline{P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O}$$

(*iii*) $P_4 + 20HNO_3 \xrightarrow[\text{catalyst}]{I_2\text{ as}} 4H_3PO_4 + 20NO_2 + 4H_2O$

(*iv*) $2KMnO_4 + 2NH_4OH \rightarrow 2MnO_2 + N_2 + 2KOH + 4H_2O$

(*v*) $Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$

(*vi*) $NaNO_2 + 6H \xrightarrow{Zn/NaOH} NaOH + NH_3 + H_2O$

(*vii*) $CaSO_4 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$

(*viii*)
$$15CaO + 4P_4 \xrightarrow{\Delta} 5Ca_3P_2 + 3P_2O_5 \uparrow$$
$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3 \uparrow] \times 5$$
$$\overline{15CaO + 4P_4 + 30H_2O \rightarrow 15Ca(OH)_2 + 3P_2O_5 \uparrow + 10PH_3 \uparrow}$$

(*ix*) $2H_3PO_2 \xrightarrow{\text{Heat}} \underset{\text{Phosphine}}{PH_3} + H_3PO_4$

(*x*) $4P + 10HNO_3 + H_2O \rightarrow 5NO + 5NO_2 + 4H_3PO_4$

(*xi*) $4Sn + \underset{\text{(dilute)}}{10HNO_3} \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

(*i*) Phosphine gas (PH_3) is evolved when white phosphorous is boiled with aqueous NaOH or alcoholic solution of potassium hydroxide.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Sod. Hypophosphite}}{NaH_2PO_2} + PH_3 \uparrow$$

64. (*i*) Nitrogen and fluorine both are small and have high electron density, they repel the bonded pair of electrons leading to larger bond length than expected.

(*ii*) It is due to self ionization of NH_3, the reaction is

$$2NH_3 \rightarrow NH_4^+ + NH_2^-$$

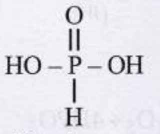
Thus, on addition of NH_4Cl the concentration of NH_4^+ radical increases and therefore, NH_4Cl acts as an acid in liquid NH_3.

(*iii*) As compared to P, N atom has higher electronegativity and small size and shows H-bonding. Thus, ammonia molecule show association where as phosphine does not.

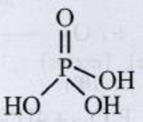
(*iv*) H_3PO_3 is a dibasic acid because it contains two OH groups in its molecule.

In the two P–OH bonds, the hydrogen is ionisable.

(*v*) Orthophosphorus acid is a dibasic acid as it has 2–OH groups in its formula : whereas orthophoric acid has 3 – OH groups.



Phosphorous acid

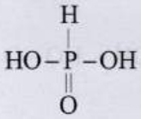


Orthophosphoric acid

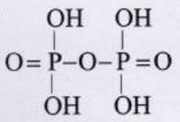
(*vi*) Liquor ammonia possesses high vapour pressure at room temperature and thus before opening a bottle of liquor ammonia, it should be cooled to lower the pressure of NH_3 inside the bottle, otherwise NH_3 will bump out of the bottle.

(*vii*) In H_3PO_4 and H_3PO_3, the P atom is attached to 3 and 2 OH groups respectively. The H atom of these P – OH bonds are ionisable. This clearly shows that H_3PO_4 is tribasic and H_3PO_3 is dibasic.

65. (*i*)



(*ii*)



Topic-2: Group-16 Elements (Oxygen Family

1. **(a)**

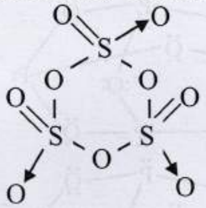
$$S_2O_3^{2-} \xrightarrow{Ag^+} \underset{\substack{(X)\\ \text{clear solution}}}{\left[Ag(S_2O_3)_2\right]^{3-}} \xrightarrow{Ag^+} \underset{\substack{(Y)\\ \text{white precipitate}}}{Ag_2S_2O_3 \downarrow}$$
$$\xrightarrow{\text{on standing}} \underset{\substack{(Z)\\ \text{black precipitate}}}{Ag_2S \downarrow}$$

2. **(b)** The following reaction occurs
$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2\,NaHSO_4 + 8HCl.$

3. **(c)** In $KMnO_4$, manganese is already present in its highest possible oxidation state *i.e.* +7. So, no further oxidation is possible.

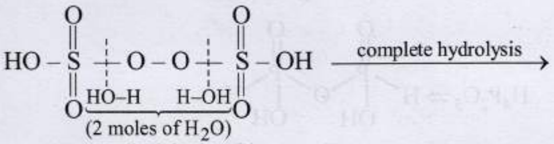
4. **(c)** Among oxyacids of sulphur, only Caro's acid (H_2SO_5) and Marshall's acid ($H_2S_2O_8$) have the O – O linkage.

5. **(d)** In sulphur trioxide trimer S_3O_9 (also called γ–sulphur trioxide), two sulphur atoms are linked to each other via O atoms, hence there is no S –S bond.

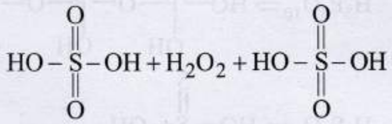


6. **(b)** $Na_2SO_3 + S \xrightarrow[\text{medium}]{\text{In alkaline}} Na_2S_2O_3$

7. **(c)**

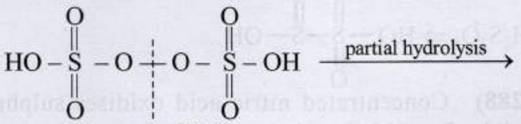


(2 moles of H_2O)
Peroxodisulphuric acid



(2 moles of sulphuric acid and 1 mole of H_2O_2)

But this is not one of the options.



(one mole of H_2O)
Peroxodisulphuric acid

21. (a) $\underset{}{SO_2 + Cl_2} \xrightarrow[\text{Catalyst}]{\text{Charcoal}} \underset{(R)}{SO_2Cl_2}$

$\underset{(R)}{10SO_2Cl_2} + P_4 \rightarrow \underset{(S)}{4PCl_5} + 10SO_2$

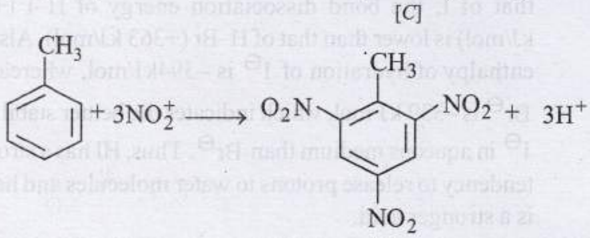
$\underset{(S)}{PCl_5} + 4H_2O \rightarrow \underset{(T)}{H_3PO_4} + 5HCl$

22. $2NaBr + 2H_2SO_4 + \underset{[A]}{MnO_2}$

$\longrightarrow Na_2SO_4 + MnSO_4 + \underset{[B]}{Br_2} \uparrow + 2H_2O$

Brown fumes and pungent smell

$2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + \underset{[C]}{NO_2^+} + H_3O^+$



[*D*]
Trinitrotoluene (TNT)
(Explosive)

23. $Na_2CO_3 + 2SO_2 + H_2O \rightarrow \underset{(A)}{2NaH\overset{+4}{S}O_3} + CO_2$;

$2NaHSO_3 + Na_2CO_3 \rightarrow \underset{(B)}{2Na_2\overset{+4}{S}O_3} + H_2O + CO_2$

$Na_2SO_3 + S \rightarrow \underset{(C)}{2Na_2\overset{+2}{S_2}O_3}$

$2Na_2S_2O_3 + I_2 \rightarrow \underset{(D)}{2Na_2\overset{+2.5}{S_4}O_6} + 2NaI$

Oxidation states of 'S' are : +4 in (A), (+4) in B and +2 in (C), +2.5 in (D)

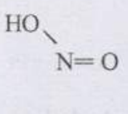
24. Sulphur trioxide produced in the contact process is passed into 98% sulphuric acid forming $H_2S_2O_7$. It is not dissolved in water as the reaction is violent and it gives a dense chemical mist of sulphuric acid particles.

The catalyst used in the contact process is vanadium pentoxide.

25. The reaction is

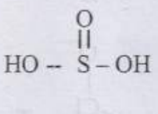
$\underset{(A)}{HNO_2} + \underset{(B)}{2H_2SO_3} + H_2O \rightarrow \underset{(C)}{NH_2OH} + \underset{(D)}{2H_2SO_4}$

The structures of *A*, *B*, *C* and *D* are as follows.



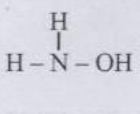
$HO-N=O$

(*A*)



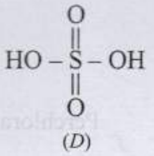
$HO-\overset{\overset{O}{\|}}{S}-OH$

(*B*)



$H-\overset{\overset{H}{|}}{N}-OH$

(*C*)



$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$

(*D*)

26. $SO_2 + PCl_5 \rightarrow \underset{\text{Thionyl chloride}}{SOCl_2} + POCl_3$

$FeCl_3 . 6H_2O + 6SOCl_2 \rightarrow FeCl_3 + 12HCl + 6SO_2$

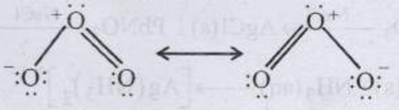
$FeCl_3 . 6H_2O + 6CH_3-C(OCH_3)_2-CH_3$

$\rightarrow FeCl_3 + 12CH_3OH + 6CH_3COCH_3$

27. $3PbS \xrightarrow[\text{air}]{\text{heat in}} \underset{(A)}{2PbO} + PbS$

$\xrightarrow{\text{heat in the absence of air } (B)} 3Pb + SO_2$

28. The two resonating structures of ozone are :



29. $SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$

$H_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2HCl$

30. $SiO_2 < CO_2 < N_2O_5 < SO_3$.

Among oxides of the non-metals, the acidic strength increases with oxidation state. Hence SO_3 (O.S. of S = +6) is most acidic followed by N_2O_5 (O.S. of N = +5) and CO_2 and SiO_2 (O.S. of C and Si = +4). Further CO_2 is more acidic than SiO_2 because of small size of C-atom.

31. (*i*) H_2S oxidises into S,

$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$

(*ii*) $Sn + \underset{\text{conc.}}{4HNO_3} \rightarrow \underset{\text{meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

(*iii*) $Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + PbO_2 \downarrow$

32. By boiling Na_2SO_3 solution with powder of sulphur in absence of air, sodium thiosulphate is prepared. Unreacted S is removed, filtrate is evaporated to give crystals of sod. thiosulphate.

$Na_2SO_3 + S \rightarrow Na_2S_2O_3$

33. $2H_2S + NaHSO_3 + H^+ \rightarrow 3S \downarrow + 3H_2O + Na^+$

34. (*i*) The reducing nature of SO_2 is represented as

$SO_2 + 2OH^- \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

Hence, with the increase of OH^- (alkalinity) the forward reaction is favoured.

(*ii*) Oxygen is the 2nd most electronegative element after the fluorine and thus invariably show negative oxidation state. Furthermore, it has $2s^22p^4$ configuration and thus requires only two electrons to complete its octet to show −2 oxidation state. Although sulphur also possess $3s^23p^4$ configuration but due to availability of *d*-orbitals in their outermost shell −2, +2, +4, +6 oxidation state are also shown. Oxygen, however, cannot exceed −2 oxidation state due to non-availability of *d*-orbitals in its outermost shell.

(*iii*) Sulphur consists of S_8 rings held together by weak van der Waal's forces. As sulphur melts at 119°C, these van der Waal's forces are overcome and S_8 rings slip and roll over one another giving rise to a clear mobile liquid. Above 160°C, the S_8 rings begin to open up and form long chains which gets tangled with each other, thereby gradually increasing the viscosity.

Topic-3: Group-17 Elements (Halogen Family)

1. (c) $2HClO_3 + 2HCl \longrightarrow \underset{\text{(paramegnetic)}}{2ClO_2} + Cl_2 + 2H_2O$

$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$

2. (a) X : Ag , Y : Pb

$AgNO_3 \xrightarrow{NaCl} AgCl(s)$; $PbNO_3 \xrightarrow{NaCl} PbCl_2(s)$

$\underset{(P)}{AgCl(s)} + NH_3(aq) \longrightarrow \underset{\text{soluble}}{\left[Ag(NH_3)_2\right]^+}$

$\underset{(Q)}{PbCl_2(s)} + KI \longrightarrow \underset{\text{yellow ppt.}}{PbI_2}$

$AgCl(s) + Na_2S_2O_3 \longrightarrow Na_3\left[Ag(S_2O_3)_2\right] + NaCl$

3. (c) $Cl_2 + \underset{\text{[cold and dilute]}}{NaOH} \longrightarrow NaCl + NaClO + H_2O$

4. (b) The ions consisting of two or more atoms of which at least one is 'N' atom is known as pseudohalide ions. These are univalent, have properties similar to those of halide ions. They combine to form dimers comparable with halogen molecules, X_2. These dimers are known as pseudohalogens.

5. (c) $KF + HF \rightarrow KHF_2 \rightleftharpoons K^+ + (HF_2)^-$

6. (c) $CsBr_3$ may be represented as $Cs^+Br_3^-$

7. (b) Chlorine is stronger oxidising agent than bromine therefore, chlorine water will liberate bromine from KBr solution.

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$

8. (b) Bleaching action of chlorine is only in presence of moisture where nascent oxygen is displaced from H_2O.

$Cl_2 + H_2O \rightarrow HCl + HClO$ (unstable)

$HClO \rightarrow HCl + |O|$

9. (d) HI and HBr (in that order) are the strongest reducing hydracids and hence they reduce H_2SO_4. HCl is quite stable and hence is oxidised by strong oxidising agent like $KMnO_4$. HF is not a reducing agent. In the smallest F^- ion, the electron which is to be removed during oxidation is closest to the nucleus and therefore most difficult to be removed. Therefore, HF is a poor reducing agent.

10. (a) $\because$ Cl_2 is more reactive than bromine.

11. (a) Due to highest bond dissociation energy.

12. (6) $2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$

$Cl_2O_6 \Rightarrow 2x + 6(-2) = 0$

$x = +6$

Average oxidation state of Cl in Cl_2O_6 is (+6).

13. (5) $3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$

14. I_3^- **complex ion;** $I_2 + I^- \longrightarrow I_3^-$

15. **Hypobromous; bromite.** $HBrO \rightleftharpoons H^+ + BrO^-$

16. **KI_3;** complexes are more soluble in water as compared to normal salts. $[KI + I_2 \longrightarrow KI_3]$

17. **HF;** HF is the weakest of the three, because the ionisation (*i.e.* acidic character) of *HX* is a multistep process and when its ΔH, heat of ionisation, is calculated it comes out to be the minimum. This is due to the strong H – F bond, large heat of hydration (because of H-bonding) and low value of electron affinity of F-atom.

18. **$NaIO_3$**

$3I_2 + \underset{\text{(hot)}}{6NaOH} \longrightarrow 5NaI + NaIO_3 + 3H_2O$

19. **False :** None amongst HBr and HI, exhibit hydrogen bonding. HI is a stronger acid than HBr. Although the electronegativity and electron affinity of Br is greater than that of I, the bond dissociation energy of H–I (+295 kJ/mol) is lower than that of H–Br (+363 kJ/mol). Also the enthalpy of hydration of $I^{\ominus}$ is –394kJ/mol, whereas for $Br^{\ominus}$ is –339 kJ/mol, which indicates the bettter stability of $I^{\ominus}$ in aqueous medium than $Br^{\ominus}$. Thus, HI has a stronger tendency to release protons to water molecules and hence, is a stronger acid.

20. **False :** The reason of accepting electrons by fluorine more readily than chlorine is as follows:

(i) F_2 has lower enthalpy of dissociation (+159 kJ mol^{-1}) due to weak F–F bond than Cl_2(+243 kJ mol^{-1}).

(ii) F_2 has higher enthalpy of hydration due to the smaller size of F^- ion (–513 kJ/mol) than that of Cl^- ion (–370 kJ mol^{-1}). Thus, F_2 is stronger reductant than Cl_2 both in solution and when dry.

Similarly, Cl_2 will displace Br^- and I^- ions from their solutions and Br_2 will displace I^- ions.

In general, *a halogen of low atomic number will oxidise the halide ion of higher atomic number.*

21. **True :** $Fe + 2HCl \rightarrow \overset{+2}{Fe}Cl_2 + H_2$; $E^{\circ}_{Fe^2/Fe} = -044V$

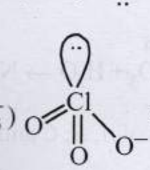
22. **(a, b, d)**

(a) Acidic order : $\overset{+1}{HClO} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$

Conjugate base order : $ClO^- > ClO_3^- > ClO_4^-$

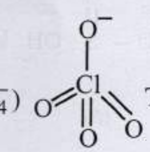
(b) Hypochlorite ion (ClO^-) : $:\underset{..}{\ddot{Cl}} - \underset{..}{\overset{=}{O}}:$ Linear

Chlorate ion : (ClO_3^-)



Trigonal pyramidal

Perchlorate ion : (ClO_4^-)



Tetrahedral

In chlorate ion bond angle changes due to presence of lone pair on chlorine atom. While there is no effect of lone pair on hypochlorite ion and perchlorate ion.

(c) Disproportionation reaction of

Hypochlorite ion : $3\overset{+1}{\mathrm{Cl}}\mathrm{O}^- \rightarrow 2\overset{-1}{\mathrm{Cl}}^- + \overset{+5}{\mathrm{Cl}}\mathrm{O}_3^-$

Chlorate ion : $4\overset{+5}{\mathrm{Cl}}\mathrm{O}_3^- \rightarrow 3\overset{+7}{\mathrm{Cl}}\mathrm{O}_4^- + \overset{-1}{\mathrm{Cl}}^-$

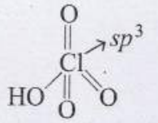
(d) $\mathrm{ClO}^- + \overset{+4}{\mathrm{S}}\mathrm{O}_3^{2-} \rightarrow \overset{+6}{\mathrm{S}}\mathrm{O}_4^{2-} + \mathrm{Cl}^-$

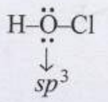
23. **(c, d)** Energy, $E = \frac{hc}{\lambda}$

On moving down the group, the colour of the X_2 molecule of group 17 elements changes gradually from yellow to violet. This happens because the amount of energy required for the excitation of the halogen atom decreases down the group. HOMO (π^*)- LUMO (σ^*) gap decreases down the group that makes π^* to σ^* excitation easier. Lesser the energy gap, more is the wavelength of light absorbed and hence, lesser is the wavelength of light emitted.

24. **(a, b, d)**

(a) In both the acids central atom is sp^3 hybridized.





(b) $HClO_4$ is more acidic than HClO because ClO_4^- is more stable than ClO^- due to resonance.

(c) $Cl_2 + H_2O \longrightarrow HCl + HClO$

(d) $HClO_4$ is a stronger acid than H_3O^+, hence conjugate base of $HClO_4$, *i.e.* ClO_4^- is weaker base than H_2O.

25. **(a, d)** NH_3 and CF_2Cl_2 (freon-12) are used as refrigerants.

26. **(a)** $Ca(OCl)Cl \longrightarrow Ca^{2+} + {}^-OCl + Cl^-$

${}^-OCl$ (Hypochlorite ion) is anion of the acid HOCl which on dehydration gives Cl_2O.

$$2HOCl \longrightarrow H_2O + Cl_2O$$

27. **(c)** Bleach + 2KI $\longrightarrow$ I_2 + Products

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

Number of millimole of hypo $= 0.25 \times 48$

$= 2 \times$ millimole of I_2

$\therefore$ Number of millimole of $I_2 = \frac{0.25 \times 48}{2} = 6$

millimole of I_2 = millimole of bleach

Molarity of bleaching solution

$$\frac{\text{Millimoles of bleach}}{\text{Vol. (in mL) of bleach}} = \frac{6}{25} = 0.24$$

28. **(c)** F has slightly less electron affinity than chlorine because F has very small atomic size (only two shells). Hence, there is a tendency of electron-electron repulsion, which results in less evolution of energy in the formation of F^- ion. Assertion is correct but reason is incorrect.

29. More electronegative halogen displaces lesser electronegative halogen from its halide. Thus,

$$Cl_2 + 2KBr\ (\text{or } 2KI) \longrightarrow 2KCl + Br_2\ (\text{or } I_2)$$

30. **(a)** $2KI + Cl_2 \rightarrow 2KCl + I_2$

Since, Cl_2 is more powerful oxidising agent than I_2, Cl_2 is able to displace I^- to form I_2.

$2I^- \rightarrow I_2 + 2e^-, \quad E° = +0.54\,V \quad ...(i)$

$Cl_2 + 2e^- \rightarrow 2Cl^- \quad E° = 1.36V \quad ...(ii)$

On subtracting eq. (i) from eq. (ii), we get

$$Cl_2(g) + 2I^-(aq) + \rightarrow 2Cl^-(aq) + I_2(s), \quad E° = 0.82V$$

(b) $2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$.

Here, ClO_3^- is more powerful oxidising agent than IO_3^-, so Cl is displaced by I.

$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O,\ E° = 1.195V \quad ...(i)$

$2ClO_3^- + 12H^+ + 10e^- \rightarrow Cl_2 + 6H_2O, E° = 1.47V ..(ii)$

On subtracting eq. (i) from eq. (ii), we get

$$2ClO_3^- + I_2 \rightarrow 2IO_3^- + Cl_2,\ E° = 0.275V$$

31. At first, $Bi(NO_3)_3$ hydrolyses to give nitric acid which being an oxidising agent, oxidises potassium iodide liberating free iodine responsible for dark brown precipitate. Iodine dissolves in excess of potassium iodide forming soluble KI_3 imparting yellow colour to solution.

$$\begin{array}{l} Bi(NO_3)_3 + H_2O \longrightarrow [Bi(OH)(NO_3)_2] + HNO_3 \\ NO_3^- + 4H^+ + 3e^- \longrightarrow NO_2 + 2H_2O\,] \times 2 \\ \qquad 2I^- \longrightarrow I_2 + 2e^-\,] \times 3 \\ \hline 2NO_3^- + 8H^+ + 6I^- \longrightarrow 2NO_2 + 4H_2O + \underset{\text{(dark brown ppt)}}{3I_2 \downarrow} \end{array}$$

$$KI + I_2 \longrightarrow \underset{\text{(Yellow solution)}}{KI_3}$$

32. $2NH_3 + NaOCl \rightarrow \underset{\text{Hydrazine}}{H_2N.NH_2} + NaCl + H_2O$

33. (*i*) $2\overset{+2}{\mathrm{Fe}}\overset{-1}{\mathrm{Br}}_2 + 3\overset{0}{\mathrm{Cl}}_2 \rightarrow 2\overset{+3}{\mathrm{Fe}}\overset{-1}{\mathrm{C}}_3 + 2\overset{0}{\mathrm{Br}}_2$

(*ii*) $2SnCl_2 + 2I_2 \rightarrow SnCl_4 + SnI_4$

34. (*i*) $HOCl < HOClO < HOClO_2 < HOClO_3$

As the number of oxygen atoms increase, the -ve charge dispersal becomes more and more from Cl atom due to more electronegativity of oxygen atom. Due to more double bond character between Cl and O atoms, the bond length decreases and thus, bond strength increases. Hence, thermal stability increases.

(*ii*) $HI < HBr < HCl < HF$

The strength of H–*X* bond decreases from HF to HI. The larger is H–*X* bond length, lower is the bond energy, lesser is the bond strength.

35. (*i*) This is a method used to prepare I_2.

$$5NaHSO_3 + 2NaIO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + I_2 + H_2O$$

(*ii*) $NaClO_3 + SO_2 + 10H^+ \rightarrow NaCl + S + 5H_2O$

(*iii*) $NaBrO_3 + F_2 + 2NaOH \rightarrow NaBrO_4 + 2NaF + H_2O$

(*iv*) $2IO_3^- + 5HSO_3^- \rightarrow I_2 + H_2O + 3HSO_4^- + 2SO_4^{2-}$

36. (*i*) The repulsive forces between fluorine atoms are high due to its small size and high electronegativity. It makes dissociation of F – F bond easy. So, bond dissociation energy of F_2 is less than Cl_2

(*ii*) The standard reduction potential of fluorine is highest and thus, it cannot be oxidized by any reagent.

$$\left(\frac{1}{2}\right) F_2 + e^- \longrightarrow F^-;\ E^\circ_{RP} = \text{maximum}$$

(*iii*) Anhydrous HCl, being a covalent compound, is a bad conductor however, an aqueous solution of HCl is ionised to give H^+ and Cl^- ions and is a good conductor.

(*iii*) HI cannot be prepared by heating hydrogen iodide with conc. H_2SO_4 because it is a strong oxidising agent and oxidises HI to I_2.

$$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$$

Hence, HI is prepared by heating iodides with conc. phosphoric acid.

$$3KI + H_3PO_4 \rightarrow K_3PO_4 + 3HI$$

H_3PO_4 is not a strong oxidising agent.

37. (*i*) $\underset{\text{Alumina}}{Al_2O_3} + 3C + 3Cl_2 \longrightarrow \underset{\text{Aluminium chloride}}{2AlCl_3} + 3CO$

(*ii*) $\underset{\text{slaked lime}}{3Ca(OH)_2} + 2Cl_2 \longrightarrow \underset{\text{bleaching powder}}{Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O}$

(*iii*) $\underset{\text{Cassiterite}}{SnO_2} + 2C \longrightarrow \underset{\text{Tin}}{Sn} + 2CO$

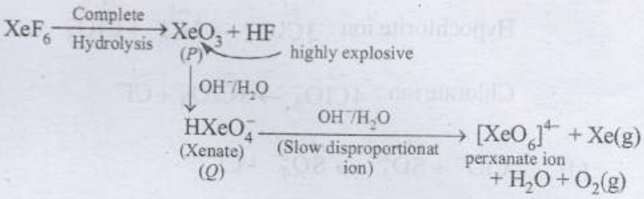
(*iv*) $\underset{\text{Sodium chloride}}{2NaCl} + MnO_2 + 2H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

38. (*i*) HBr is a reducing agent and it reduces H_2SO_4 to SO_2.

(*ii*) Acids turn blue litmus red, so HClO also turns blue litmus red. The colour of litmus is decolourised because HClO is also a strong oxidising agent.

Topic-4: Group-18 Elements (Noble Gases)

1. (c)

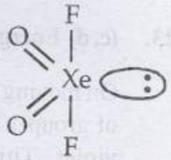


$$XeF_6 \xrightarrow[\text{Hydrolysis}]{\text{Complete}} \underset{(P)}{XeO_3} + HF$$

highly explosive

$$\underset{(P)}{XeO_3} \xrightarrow{OH^-/H_2O} \underset{\substack{\text{(Xenate)}\\(Q)}}{HXeO_4^-} \xrightarrow[\text{(Slow disproportionation)}]{OH^-/H_2O} \underset{\text{perxanate ion}}{[XeO_6]^{4-}} + Xe(g) + H_2O + O_2(g)$$

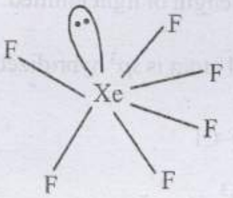
2. (d) XeO_2F_2 has trigonal bipyramidal geometry, but due to presence of lone pair of electrons on equitorial position, its shape is *see-saw.*



3. (b) In $XeOF_4$, Xenon is sp^3d^2 hybridised and has one lone pair.

4. (19)

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



Shape of XeF_6 is distorted octahedral contains one lone pair e^-s on central atom 3 lone pair e^- s on each F atom surrounded by Xe.

Total no. of lone pairs: 1 + 18 = 19

5. (d) (P)

$$2PbO_2 + 2H_2SO_4 \xrightarrow{\text{Warm}} 2PbSO_4 + 2H_2O + O_2$$

(Q)

$$Na_2S_2O_3 + 5H_2O + 4Cl_2 \longrightarrow 2NaHSO_4 + 8HCl$$

(R) $N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$

(S) $XeF_2 + 2NO \longrightarrow Xe + 2NOF$

6. **(A) – (p), (s)** $(CH_3)_2SiCl_2 + 2H_2O \xrightarrow[-2HCl]{} (CH_3)_2Si(OH)_2 \xrightarrow{\text{Polymerisation}} [(CH_3)_2Si\text{–}O]_n.$

(B) – (p), (q), (r), (t) $XeF_4 + H_2O \longrightarrow Xe + XeO_3 + H_2F_2 + O_2$

$\underset{\text{glass}}{SiO_2} + 4HF \longrightarrow SiF_4 + 2H_2O$

$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$

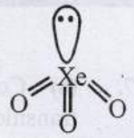
Soluble hexafluorosilicic(IV) acid

(C) – (p), (q) $Cl_2 + H_2O \longrightarrow HCl + HOCl$

(D) – (p), (q) $VCl_5 + 7H_2O \longrightarrow [V(H_2O)_6]^{3+} + 3Cl^- + HCl + HOCl$

7 **(a)** Argon, being a noble gas, will not react with the metals, thus, can be used in arc welding.

8. **(c)** In XeO_3 there are total of 4 electron pairs around central atom. Out of which 3 are bonding electron pair and one is non-bonding electron pair. This combination provides sp^3-hybridization and pyramidal shape.



9. **(a)** All xenon fluorides are strongly oxidizing, XeF_4 can act as reducing agent (with F_2) as well as oxidizing agent but XeF_6 can only function as an oxidizing agent.

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

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

10. (*i*) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow$

(*ii*) $CaNCN + 3H_2O \longrightarrow CaCO_3 \downarrow + 2NH_3$

Ammonia formed dissolves in water to form NH_4OH

$CaNCN + 5H_2O \longrightarrow 2NH_4OH + CaCO_3 \downarrow$

(*iii*) $4BF_3 + 3H_2O \longrightarrow 3HBF_4 + B(OH)_3$

(*iv*) $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

(*v*) $3XeF_4 + 6H_2O \longrightarrow XeO_3 + 2Xe + \frac{3}{2}O_2 + 12HF$

11. Use the formula

H (hydridisation), $H = \frac{1}{2}(V + M - C + A)$ where

V = number of electron in valence shell of central atom
M = number of monovalent atoms surrounding the central atom
C = Charge on cation
A = Charge on anion

XeF_2 : $H = \frac{1}{2}(8 + 2 - 0 + 0) = 5$ Hence, hybridisation is sp^3d, and thus its shape is linear.

XeF_4 : $H = \frac{1}{2}(8 + 4 - 0 + 0) = 6$, Hence, hybridisation is sp^3d^2. and thus its shape is square planar.

XeO_2F_2 : $H = \frac{1}{2}(8 + 2 - 0 + 0) = 5$, Hence, hybridisation is sp^3d. and shape is see saw.