16
p-Block Elements-II

Topic 1 Elements and Compounds of Group 15 and 16

Objective Questions I (Only one correct option)

1. The correct statement among the following is **(2019 Main, 12 April I)**

(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.

(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.

(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.

(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

2. The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are **(2019 Main, 10 April II)**

(a) 20 and 3 (b) 12 and 4

(c) 20 and 4 (d) 12 and 3

3. The oxoacid of sulphur that does not contain bond between sulphur atoms is **(2019 Main 10 April I)**

(a) $H_2S_2O_3$ (b) $H_2S_2O_4$

(c) $H_2S_2O_7$ (d) $H_2S_4O_6$

4. The correct order of the oxidation states of nitrogen in NO, NO_2, NO_2 and N_2O_3 is **(2019 Main, 9 April I)**

(a) NO_2 NO N_2O_3 N_2O (b) N_2O NO N_2O_3 NO_2

(c) O_2 N_2O_3 NO N_2O (d) N_2O N_2O_3 NO NO_2

5. The pair that contains two P H bonds in each of the oxoacids is **(2019 Main, 10 Jan II)**

(a) $H_4P_2O_5$ and $H_4P_2O_6$ (b) H_3PO_3 and H_3PO_2

(c) $H_4P_2O_5$ and H_3PO_3 (d) H_3PO_2 and $H_4P_2O_5$

6. When the first electron gain enthalpy $({}_{eg}H)$ of oxygen is 141 kJ/ mol, its second electron gain enthalpy is **(2019 Main, 9 Jan II)**

(a) a positive value

(b) a more negative value than the first

(c) almost the same as that of the first

(d) negative, but less negative than the first

7. Good reducing nature of H_3PO_2 is attributed to the presence of **(2019 Main, 9 Jan II)**

(a) two P H bonds (b) one P H bond

(c) two P OH bonds (d) one P OH bond

8. The compound that does not produce nitrogen gas by the thermal decomposition is **(2018 Main)**

(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$

(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

9. 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 **(2017 Adv.)**

(a) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$

(b) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$

(c) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

(d) $H_3PO_3 > H_3PO_2$ $H_3PO_4 > H_4P_2O_6$

10. The species in which the N-atom is in a state of *sp* hybridisation is **(2016 Main)**

(a) NO_2 (b) NO_3

(c) NO_2 (d) NO_2

11. The pair in which phosphorus atoms have a formal oxidation state of 3 is **(2016 Main)**

(a) pyrophosphorous and hypophosphoric acids

(b) orthophosphorous and hypophosphoric acids

(c) pyrophosphorous and pyrophosphoric acids

(d) orthophosphorous and pyrophosphorous acids

12. The product formed in the reaction of $SOCl_2$ with white phosphorus is **(2014 Adv.)**

(a) PCl_3 (b) SO_2Cl_2

(c) SCl_2 (d) $POCl_3$

13. Which of the following properties is not shown by NO? **(2014 Main)**

(a) It is paramagnetic in liquid state

(b) It is a neutral oxide

(c) It combines with oxygen to form nitrogen dioxide

(d) Its bond order is 2.5

14. Concentrated nitric acid upon long standing, turns yellow-brown due to the formation of **(2013 Main)**

(a) NO (b) NO_2

(c) N_2O (d) N_2O_4

15. Which of the following is the wrong statement? **(2013 Main)**
(a) ONCl and ONO are not isoelectronic
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas

16. The reaction of white phosphorus with aqueous NaOH gives phosphine alongwith another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product respectively are **(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

17. 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

18. 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) $Ba(N_3)_2$

19. The reaction of P_4 with *X* leads selectively to P_4O_6. The *X*, is
(a) dry O_2 **(2009)**
(b) a mixture of O_2 and N_2
(c) moist O_2
(d) O_2 in the presence of aqueous NaOH

20. The percentage of *p*-character in the orbitals forming P—P bonds in P_4 is **(2007, 3M)**
(a) 25 (b) 33 (c) 50 (d) 75

21. Which of the following is not oxidised by O_3? **(2005, 1M)**
(a) KI (b) $FeSO_4$
(c) $KMnO_4$ (d) K_2MnO_4

22. Which gas is evolved when PbO_2 is treated with concentrated HNO_3? **(2005)**
(a) NO_2 (b) O_2
(c) N_2 (d) N_2O

23. A pale blue liquid obtained by equimolar mixture of two gases at – 30°C is **(2005, 1M)**
(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5

24. Which of the following isomers of phosphorus is thermodynamically most stable? **(2005, 1M)**
(a) Red (b) White
(c) Black (d) Yellow

25. Which of the following has —O—O— linkage? **(2004, 3M)**
(a) $H_2S_2O_6$ (b) $H_2S_2O_8$
(c) $H_2S_2O_3$ (d) $H_2S_4O_6$

26. For H_3PO_3 and H_3PO_4, the correct choice is **(2003, 1M)**
(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

27. Polyphosphates are used as water softening agents because they **(2002, 3M)**
(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) form soluble complexes with cationic species
(d) precipitate cationic species

28. The number of S S bonds in sulphur trioxide trimer, (S_3O_9) is **(2001, 1M)**
(a) three (b) two
(c) one (d) zero

29. Ammonia can be dried by **(2000, 1M)**
(a) conc. H_2SO_4 (b) P_4O_{10}
(c) CaO (d) anhydrous $CaCl_2$

30. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is **(2000, 1M)**
(a) H_2O because of hydrogen bonding
(b) H_2Te because of higher molecular weight
(c) H_2S because of hydrogen bonding
(d) H_2Se because of lower molecular weight

31. The correct order of acidic strength is **(2000, 1M)**
(a) $Cl_2O_7 > SO_2 > P_4O_{10}$ (b) $CO_2 > N_2O_5 > SO_3$
(c) $Na_2O > MgO > Al_2O_3$ (d) $K_2O > CaO > MgO$

32. The number of P O P bonds in cyclic metaphosphoric acid is **(2000, 1M)**
(a) zero (b) two (c) three (d) four

33. One mole of calcium phosphide on reaction with excess water gives **(1999, 2M)**
(a) one mole of phosphine
(b) two moles of phosphoric acid
(c) two moles of phosphine
(d) one mole of phosphorus pentaoxide

34. Sodium thiosulphate is prepared by **(1996, 1M)**
(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

35. There is no S S bond in **(1991, 1M)**
(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$ (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$

36. Which one of the following is the strongest base? **(1989, 2M)**
(a) AsH_3 (b) NH_3 (c) PH_3 (d) SbH_3

37. Amongst the trihalides of nitrogen, which one is least basic?
(a) NF_3 (b) NCl_3 **(1987, 1M)**
(c) NBr_3 (d) NI_3

38. Which of the following oxides of nitrogen is a coloured gas ?
(a) N_2O (b) NO **(1987,1M)**
(c) N_2O_4 (d) NO_2

39. The bonds present in N_2O_5 are **(1986, 1M)**
(a) only ionic (b) covalent and coordinate
(c) only covalent (d) covalent and ionic

40. A gas that cannot be collected over water is **(1985, 1M)**
(a) N_2 (b) O_2 (c) SO_2 (d) PH_3

41. Ammonia gas can be dried by **(1978, 1M)**
(a) conc H_2SO_4 (b) P_2O_5
(c) $CaCl_2$ (d) quicklime

42. Which of the following is incorrect statement? **(1978, 1M)**
(a) NO is heavier than O_2
(b) The formula of heavy water is D_2O
(c) N_2 diffuses faster than oxygen through an orifice
(d) NH_3 can be used as a refrigerant

Objective Questions II
(One or more than one correct option)

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

44. Based on the compounds of group 15 elements, the correct statement(s) is (are) **(2018 Adv.)**
(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

45. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10} **(2016 Adv.)**
(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

46. The correct statement(s) about O_3 is/are **(2013 Adv.)**
(a) O—O bond lengths are equal
(b) thermal decomposition of O_3 is endothermic
(c) O_3 is diamagnetic in nature
(d) O_3 has a bent structure

47. 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) $_2$ $_5$

48. Ammonia, on reaction with hypochlorite anion, can form **(1999, 3M)**
(a) NO (b) NH_4Cl
(c) N_2H_4 (d) HNO_2

49. White phosphorus (P_4) has **(1998, 2M)**
(a) six P P single bonds
(b) four P P single bonds
(c) four lone pairs of electrons
(d) P P P angle of 60°

50. Nitrogen (I) oxide is produced by **(1989, 1M)**
(a) thermal decomposition of NH_4NO_3
(b) disproportionation of N_2O_4
(c) thermal decomposition of NH_4NO_2
(d) interaction of hydroxylamine and nitrous acid

Numerical Value

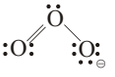
51. The total number of compounds having at least one bridging oxo group among the molecules given below is …… .
N_2O_3, N_2O_5, P_4O_6, P_4O_7, $H_4P_2O_5$, $H_5P_3O_{10}$, $H_2S_2O_3$, $H_2S_2O_5$
(2018 Adv.)

Assertion and Reason

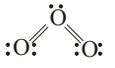
Read the following questions and answer as per the direction given below:
(a) Statement I is correct, Statement II is correct, Statement II is the correct explanation of Statement I
(b) Statement I is correct, Statement II is correct, Statement II is not the correct explanation of Statement I
(c) Statement I is correct, Statement II is incorrect
(d) Statement I is incorrect, Statement II is correct

52. **Statement I** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.
Statement II The reaction between nitrogen and oxygen requires high temperature. **(1998, 2M)**

53. **Statement I** The electronic structure of O_3 is



Statement II The following structure is not allowed because octet around O cannot be expanded.



(1998, 2M)

54. **Statement I** HNO_3 is a stronger acid than HNO_2.
Statement II In HNO_3, there are two nitrogen to oxygen bonds whereas in HNO_2 there is only one. **(1998, 2M)**

55. **Statement I** Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.
Statement II Phosphorus has lower electronegativity than nitrogen. **(1994, 2M)**

Passage Based Questions

Passage

Upon heating $KClO_3$ in 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*. **(2017 Adv.)**

56. *Y* and *Z* are, respectively
(a) N_2O_4 and HPO_3 (b) N_2O_4 and H_3PO_3
(c) N_2O_3 and H_3PO_4 (d) N_2O_5 and HPO_3

57. *W* and *X* are, respectively
(a) O_2 and P_4O_{10} (b) O_2 and P_4O_6
(c) O_3 and P_4O_6 (d) O_3 and P_4O_{10}

Passage

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. Hybridisation easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus. **(2008, 3 4M = 12M)**

58. 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

59. 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

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

Match the Columns

61. The unbalanced chemical reactions given in Column I show missing reagent or condition (?) which are provided in Column II. Match Column I with Column II and select the correct answer using the codes given below the Columns. **(2013 Adv.)**

	Column I	Column II
P.	$PbO_2 \quad H_2SO_4 \quad ? \quad PbSO_4 \quad O_2$ other product	1. NO
Q.	$Na_2S_2O_3 \quad H_2O \quad ? \quad NaHSO_4$ other product	2. I_2
R.	$N_2H_4 \quad ? \quad N_2$ other product	3. Warm
S.	$XeF_2 \quad ? \quad Xe$ other product	4. Cl_2

Codes

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

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

Fill in the Blanks

62. The lead chamber process involves oxidation of SO_2 by atomic oxygen under the influence of ……as catalyst. **(1992, 1M)**

63. In P_4O_{10}, the number of oxygen atoms bonded to each phosphorus atom is …… . **(1992, 1M)**

64. The basicity of phosphorus acid (H_3PO_3) is …… **(1990, 1M)**

65. …… phosphorus is reactive because of its highly strained tetrahedral structure. **(1987, 1M)**

True/False

66. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. **(1991, 1M)**

67. The H N H bond angle in NH_3 is greater than the H As H bond angle in AsH_3. **(1984, 1M)**

68. In aqueous solution, chlorine is a stronger oxidising agent than fluorine. **(1984, 1M)**

69. Dilute HCl oxidises metallic Fe to Fe^2 . **(1983, 1M)**

Integer Answer Type Question

70. The total number of lone pair of electrons in N_2O_3 is **(2015 Adv.)**

71. Among the following, the number of compounds that can react with PCl_5 to give $POCl_3$ is $O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}$. **(2011)**

72. The total number of diprotic acids among the following is

H_3PO_4	H_2SO_4	H_3PO_3
H_2CO_3	$H_2S_2O_7$	H_3BO_3
H_3PO_2	H_2CrO_4	H_2SO_3 **(2010)**

Subjective Questions

73. Draw the structure of P_4O_{10}. **(2005)**

74. Arrange the following oxides in the increasing order of Bronsted basicity.
Cl_2O_7, BaO, SO_3, CO_2, B_2O_3 **(2004)**

75. Identify the compounds *A, B, C, D*

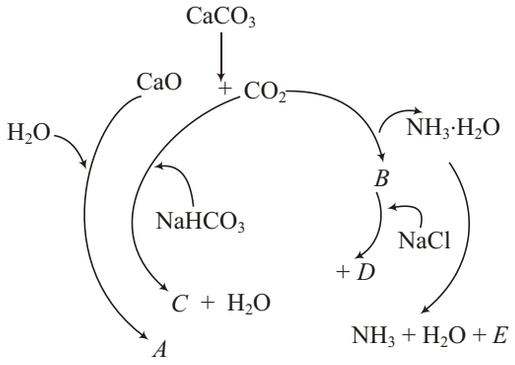
$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow{\text{Elemental S}} C \xrightarrow{I_2} D$

and give oxidation state of sulphur in each compounds. **(2003, 4M)**

76. Write the balanced equations for the reactions of the following compounds with water:
(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4 **(2002, 5M)**

77. Give reason(s), why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule? **(2000, 2M)**

78. The Haber's process can be represented by the following scheme.



Identify *A, B, C, D* and *E* . **(1999, 5M)**

79 (a) In the following equation

$$A \quad 2B \quad H_2O \qquad C \quad 2D$$

($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$).

Identify *D*. Draw the structures of *A*, *B*, *C* and *D*.

(b) 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, 10M)**

80. Complete and balance the following chemical equations.

(i) $P_4O_{10} + PCl_5$

(ii) $SnCl_4 + C_2H_5Cl + Na$ **(1998, 1M 2 2M)**

81. (a) Thionyl chloride can be synthesised 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.

(b) Reaction of phosphoric acid with $Ca_3(PO_4)_2$ yields a fertiliser "triple superphosphate" represent the same through balanced chemical equation. **(1998, 5M)**

82. 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, 2M)**

83. Write balanced equations for the following.

(i) Phosphorus is treated with concentrated nitric acid.

(ii) Oxidation of hydrogen peroxide with potassium permanganate in acidic medium.

(iii) Manufacture of phosphoric acid from phosphorus.

(iv) Reaction of aluminium with aqueous sodium hydroxide. **(1997, 1M 4 4M)**

84. Draw the structure of P_4O_{10} and identify the number of single and double P O bonds. **(1996, 3M)**

85. Account for the following. Write the answers in four or five sentences only.

(i) The experimentally determined N F bond lengths in NF_3 is greater than the sum of the single bond covalent radii of N and F.

(ii) Mg_3N_2 when reacted with water gives of NH_3 but HCl is not obtained from $MgCl_2$ on reaction with water at room temperature.

(iii) $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$. **(1995, 2M 3 = 6M)**

86. Complete and balance the following reactions. **(1994, 1M)**

$$Ca_5(PO_4)_3F + H_2SO_4 + H_2O \xrightarrow{\text{Heat}} \ldots + 5CaSO_4 \quad 2H_2O + \ldots$$

87. In the following reaction, identify the compounds *A* and *B*

$$PCl_5 + SO_2 \qquad A \quad B$$ **(1994, 1M)**

88. Complete and balance the following reaction.
Red phosphorus is reacted with iodine in the presence of water.

$$P + I_2 + H_2O \qquad \ldots + \ldots$$ **(1992, 1M)**

89. Give reasons in two or three sentences only.Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. **(1992, 2M)**

90. Draw the two resonance structures of ozone which satisfy the octet rule. **(1991, 1M)**

91. Give reasons in one or two sentences.

Ammonium chloride is acidic in liquid ammonia solvent. **(1991, 1M)**

92. Write the balanced chemical equations for the following.

(i) Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda.

(ii) Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate.

(iii) Elemental phosphorus reacts with concentrated HNO_3 to give phosphoric acid.

(iv) Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution.

(v) Carbon dioxide is passed through a suspension of limestone in water. **(1991, 1 5 5M)**

93. Write the balanced chemical equation for the following reactions.

(i) Aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution.

(ii) Sodium iodate is added to a solution of sodium bisulphite **(1990, 2M)**

94. Write the two resonance structures of N_2O that satisfy the octet rule. **(1990, 2M)**

95. Draw balanced equations for
(i) the preparation of phosphine from CaO and white phosphorus.
(ii) the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. **(1990, 2M)**

96. Explain the following **(1989, 2M)**
(i) H_3PO_3 is a dibasic acid.
(ii) Phosphine has lower boiling point than ammonia.

97. Write the balanced chemical equations for the following.
(i) Hypophosphorous acid is heated.
(ii) Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium.

98. Arrange the following as indicated. $CO_2, N_2O_5, SiO_2, SO_3$ in the order of increasing acidic character.

99. Give balanced equations for the following.
(i) Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide.
(ii) Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. **(1988, 3M)**

100. Give reason for "valency of oxygen is generally two, whereas sulphur shows valency of two, four and six." **(1988, 1M)**

101. Explain the following in one or two sentences.
(i) Magnesium oxide is used for the lining of steel making furnace.
(ii) The mixture of hydrazine and hydrogen peroxide with a copper (II) catalyst is used as a rocket fuel.
(iii) Orthophosphorous acid is not tribasic acid.
(iv) The molecule of magnesium chloride is linear, whereas that of stannous chloride is angular. **(1987, 4M)**

102. Write balanced equations for the following. **(1987, 2M)**
(i) Phosphorus is reacted with boiling aqueous solution of sodium hydroxide in an inert atmosphere.
(ii) Dilute nitric acid is slowly reacted with metallic tin.

103. Complete and balance the following reactions.
(i) $S + OH^- \quad S^{2-} + S_2O_3^{2-} + ...$
(ii) $ClO_3^- + I^- + H_2SO_4 \quad Cl^- + HSO_4^- + ... + ...$ **(1986, 2M)**

104. Write down the balanced equation for the reactions when
(i) calcium phosphate is heated with a mixture of sand and carbon.
(ii) ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. **(1985, 2M)**

105. Draw the resonance structures of nitrous oxide. **(1985, 90, 2M)**

106. Show with balanced chemical reaction what happens when following are mixed?
Aqueous solution of ferric sulphate and potassium iodide. **(1984, 1M)**

107. Write the matched set (of three) for each entry in Column *A*

A	*B*	*C*
Asbestos	Paramagnetic	Air pollutant
Lithium metal	Silicates of Ca and Mg	Electron donor
Nitric oxide	Reducing agent	

(1984, 2M)

108. Complete and balance the following reactions.
(i) $HNO_3 + HCl \quad NO + Cl_2$
(ii) $Ce^{3+} + S_2O_8^{2-} \quad SO_4^{2-} + Ce^{4+}$
(iii) $Cl_2 + OH^- \quad Cl^- + ClO^-$ **(1983, 3M)**

109. Explain, "orthophosphoric acid, H_3PO_4 is tribasic but phosphorous acid, H_3PO_3 is dibasic". **(1982, 1M)**

110. Give structural formula for the following.
(i) Phosphorous acid, H_3PO_3
(ii) Pyrophosphoric acid, $H_4P_2O_7$ **(1981, 2M)**

111. Sulphur melts to a clear mobile liquid at 119°C, but on further heating above 160° C, it becomes viscous, explain. **(1981, 1M)**

112. Explain the following in not more than two sentences .
(i) Conc. HNO_3 turns yellow in sunlight.
(ii) Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. **(1980, 2M)**

Topic 2 Elements and Compounds of Group 17 and 18

Objective Questions I (Only one correct option)

1. The noble gas that does not occur in the atmosphere is **(2019 Main, 10 April II)**
(a) Ra (b) Kr
(c) He (d) Ne

2. Chlorine on reaction with hot and concentrated sodium hydroxide gives **(2019 Main, 12 Jan II)**
(a) Cl and ClO (b) Cl and ClO_3
(c) ClO_3 and ClO_2 (d) Cl and ClO_2

3. Iodine reacts with concentrated HNO_3 to yield *Y* along with other products. The oxidation state of iodine in *Y*, is **(2019 Main, 12 Jan I)**
(a) 1 (b) 3
(c) 7 (d) 5

4. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is **(2019 Main, 10 Jan II)**
(a) $H_2 + Cl_2 \quad 2HCl$ (b) $H_2 + I_2 \quad 2HI$
(c) $H_2 + F_2 \quad 2HF$ (d) $H_2 + Br_2 \quad 2HBr$

5. The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are **(2019 Main, 10 Jan I)**

(a) sp^3d^2 and 1 (b) sp^3d and 2

(c) sp^3d and 1 (d) sp^3d^2 and 2

6. Which of the following reactions is an example of a redox reaction? **(2017 Main)**

(a) $XeF_4 \quad O_2F_2 \quad XeF_6 \quad O_2$

(b) $XeF_2 \quad PF_5 \quad [XeF]^+ PF_6$

(c) $XeF_6 \quad H_2O \quad XeOF_4 \quad 2HF$

(d) $XeF_6 \quad 2H_2O \quad XeO_2F_2 \quad 4HF$

7. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are **(2017 Main)**

(a) ClO and ClO_3 (b) ClO_2 and ClO_3

(c) Cl and ClO (d) Cl and ClO_2

8. Which among the following is the most reactive? **(2015 Main)**

(a) Cl_2 (b) Br_2 (c) I_2 (d) ICl

9. Which one has highest boiling point? **(2015 Main)**

(a) He (b) Ne (c) Kr (d) Xe

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

$XeF_6 \xrightarrow{\text{Complete hydrolysis}} P + \text{Other product}$

$P \xrightarrow{HO^-/H_2O} Q$

$Q \xrightarrow{\text{Slow disproportionation in } HO^-/H_2O} \text{Products}$

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

11. Among the following oxoacids, the correct decreasing order of acidic strength is **(2014 Main)**

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$

(b) $HClO_4 > HOCl > HClO_2 > HClO_3$

(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$

(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

12. The shape of XeO_2F_2 molecule is **(2012)**

(a) trigonal bipyramidal (b) square planar

(c) tetrahedral (d) *see-saw*

13. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives **(2008, 3M)**

(a) $Na_2S_4O_6$ (b) $NaHSO_4$

(c) NaCl (d) NaOH

14. When I is oxidised by $KMnO_4$ in alkaline medium, I converts into **(2004, 1M)**

(a) IO_3 (b) I_2

(c) IO_4 (d) IO

15. The set with correct order of acidic strength is **(2001, 1M)**

(a) $HClO < HClO_2 < HClO_3 < HClO_4$

(b) $HClO_4 < HClO_3 < HClO_2 < HClO$

(c) $HClO < HClO_4 < HClO_3 < HClO_2$

(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

16. Which one of the following species is not a pseudo halide? **(1997, 1M)**

(a) CNO^- (b) *R*COO (c) OCN (d) NNN

17. The following acids have been arranged in the order of decreasing acidic strength. Identify the correct order.

ClOH (I), BrOH (II), IOH (III) **(1996, 1M)**

(a) I > II > III (b) II > I > III

(c) III > II > I (d) I > III > II

18. KF combines with HF to form KHF_2. The compound contains the species **(1996, 1M)**

(a) K^+, F and H^+ (b) K^+, F^- and HF

(c) K and $[HF_2]^-$ (d) $[KHF]^+$ and F^-

19. Bromine can be liberated from potassium bromide solution by the action of **(1987, 1M)**

(a) iodine solution (b) chlorine water

(c) sodium chloride (d) potassium iodide

20. Chlorine acts as a bleaching agent only in the presence of **(1983, 1M)**

(a) dry air (b) moisture

(c) sunlight (d) pure oxygen

21. HBr and HI reduce sulphuric acid, HCl can reduce $KMnO_4$ and HF can reduce **(1981, 1M)**

(a) H_2SO_4 (b) $KMnO_4$

(c) $K_2Cr_2O_7$ (d) None of these

Objective Questions II

(One or more than one correct option)

22. The correct statement(s) about the oxoacids, $HClO_4$ and HClO, is (are) **(2017 Adv.)**

(a) The central atom in both $HClO_4$ and HClO is sp^3-hybridised

(b) $HClO_4$ is formed in the reaction between Cl_2 and H_2O

(c) The conjugate base of $HClO_4$ is weaker base than H_2O

(d) $HClO_4$ is more acidic than HClO because of the resonance stabilisation of its anion

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 **(2017 Adv.)**

(a) decrease in * * gap down the group

(b) decrease in ionisation energy down the group

(c) the physical state of X_2 at room temperature changes from gas to solid down the group

(d) decreases in HOMO-LUMO gap down the group

24. The compound(s) with two lone pairs of electrons on the central atom is (are) **(2016 Adv.)**

(a) BrF_5 (b) ClF_3

(c) XeF_4 (d) SF_4

25. The correct statement(s) regarding,

(i) $HClO$, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$ is (are)

(a) the number of Cl O bonds in (ii) and (iii) together is two

(b) the number of lone pair of electrons on Cl in (ii) and (iii) together is three

(c) the hybridisation of Cl in (iv) is sp^3

(d) amongst (i) to (iv), the strongest acid is (i)

Passage Based Questions

Passage 1

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 the 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*. **(2013 Adv.)**

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

(a) hypochlorous and chloric acids

(b) hypochlorous and chlorous acids

(c) chloric and perchloric acids

(d) chloric and hypochlorous acids

27. *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

Passage 2

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)**

28. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N 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

29. 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

Passage 3

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 give 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. **(2007, 3 4M = 12M)**

30. Argon is used in arc welding because of its

(a) low reactivity with metal

(b) ability to lower the melting point of metal

(c) flammability

(d) high calorific value

31. The structure of XeO_3 is

(a) linear (b) planar

(c) pyramidal (d) T-shaped

32. XeF_4 and XeF_6 are expected to be

(a) oxidising (b) reducing

(c) unreactive (d) strongly basic

Match the Columns

33. 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.	Polymerisation
		t.	O_2 formation

Fill in the Blanks

34. The increase in solubility of iodine in aqueous solution of KI is due to the formation of ….. **(1982, 94, 1M)**

True/False

35. HBr is a stronger acid than HI because of hydrogen bonding. **(1993, 1M)**

Integer Answer Type Questions

36. 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)**

Subjective Questions

37. Write the balanced equation for the reaction of the following compound with water.

XeF_4 **(2002, 5M)**

38. Draw molecular structures of XeF_2, XeF_4 and XeO_2F_2, indicating the locations of lone pair(s) of electrons. **(2000, 3M)**

39. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. **(2000, 2M)**

40. Work out the following using chemical equations

"Chlorination of calcium hydroxide produces bleaching powder." **(1998, 2M)**

41. Complete the following chemical equations:
(i) $KI + Cl_2$ (ii) $KClO_3 + I_2$ **(1996, 2M)**

42. Give reasons in two or three sentences only for
(i) Bond dissociation energy of F_2 is less than that of Cl_2.
(ii) Sulphur dioxide is a more powerful reducing agent in the alkaline medium than in acidic medium. **(1992, 2M)**

43. Write the balanced chemical equation for the following:
Sodium bromate reacts with fluorine in the presence of alkali.

44. Arrange the following as indicated. HOCl, $HOClO_2$, $HOClO_3$, HOClO in increasing order of thermal stability **(1988, 2M)**

45. Give balanced equation for the following:
Iodate ion reacts with bisulphite ion to liberate iodine. **(1988, 3M)**

46. Mention the products formed in the following
"Chlorine gas is bubbled through a solution of ferrous bromide." **(1986, 2M)**

47. Complete and balance the following reaction:
ClO_3^- I^- H_2SO_4 Cl^- HSO_4^- .... **(1986, 2M)**

48. Arrange the following in the order of
(i) increasing bond strength HCl, HBr, HF, HI
(ii) increasing oxidation number of iodine
I_2, HI, HIO_4, ICl **(1986, 2M)**

49. Give reason in one or two sentences.
Fluorine cannot be prepared from fluorides by chemical reduction method. **(1985, 1M)**

50. Complete and balance the following reaction.
Cl_2 OH^- Cl^- ClO^- **(1983, 3M)**

51. Explain the following in not more than two sentences.
Bleaching powder loses its bleaching properties when it is kept in an open bottle for a long time. **(1980, 2M)**

52. Give reasons for the following in one or two sentences.
(i) Hydrogen bromide cannot be prepared by the action of conc. sulphuric acid on 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, 2M)**

53. Write the balanced equations involved in the preparation of
(i) bleaching powder from slaked lime **(1979, 10M)**
(ii) nitric oxide from nitric acid
(iii) chlorine from sodium chloride
(iv) anhydrous aluminium chloride from alumina

Answers

Topic 1

1. (a) **2.** (b) **3.** (c) **4.** (b)
5. (d) **6.** (a) **7.** (a) **8.** (d)
9. (b) **10.** (d) **11.** (d) **12.** (a)
13. (a) **14.** (b) **15.** (c) **16.** (c)
17. (b) **18.** (d) **19.** (b) **20.** (d)
21. (c) **22.** (b) **23.** (b) **24.** (c)
25. (b) **26.** (a) **27.** (c) **28.** (d)
29. (c) **30.** (a) **31.** (a) **32.** (c)
33. (c) **34.** (b) **35.** (d) **36.** (b)
37. (a) **38.** (d) **39.** (b) **40.** (c)
41. (d) **42.** (a) **43.** (b,c) **44.** (a,b,c)
45. (b, d) **46.** (a, c, d) **47.** (a, b, c) **48.** (c)
49. (a, c, d) **50.** (a, d) **51.** (6) **52.** (a)
53. (a) **54.** (a) **55.** (b) **56.** (a)
57. (b) **58.** (c) **59.** (c) **60.** (b)
61. (d) **62.** NO_2 **63.** Four **64.** Two
65. white **66.** T **67.** T **68.** F
69. T **70.** (8) **71.** 4 **72.** 6

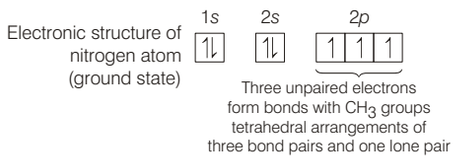
Topic 2

1. (a) **2.** (b) **3.** (d) **4.** (b)
5. (a) **6.** (a) **7.** (c) **8.** (d)
9. (d) **10.** (c) **11.** (c) **12.** (a)
13. (a) **14.** (a) **15.** (a) **16.** (b)
17. (a) **18.** (c) **19.** (b) **20.** (b)
21. (d) **22.** (a, c, d) **23.** (b, c) **24.** (b, c)
25. (b, c) **26.** (a) **27.** (a) **28.** (c)
29. (a) **30.** (a) **31.** (c) **32.** (a)
33. A p, s B p, q, r, t C p, q, t D p
34. KI_3 **35.** F **36.** 5

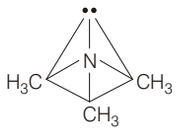
Hints & Solutions

Topic 1 Elements and Compounds of Group 15 and 16

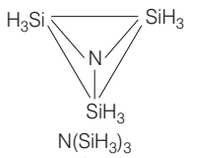
1. The correct statement is that $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae, but have totally different structures. In trimethylamine the arrangement of electrons is as follows :



In trisilylamine, three sp^2 orbitals are used for -bonding, giving a plane triangular structure.

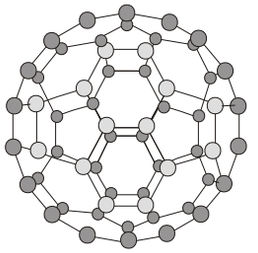


$N(CH_3)_3$ molecule

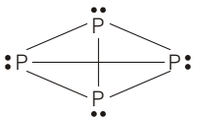


$N(SiH_3)_3$ molecule

2. In C_{60} (Buckminster fullerene) twenty hexagons and twelve pentagons are present which are interlocked resulting a shape of soccer ball. Every ring in this structure is aromatic.

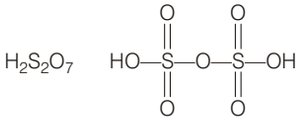


Phosphorus has large atomic size and less electronegativity, so it forms single bond instead of p -p multiple bond. So, it consists of discrete tetrahedral P_4 molecule as shown below :



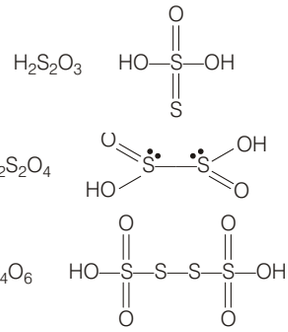
Number of trigons (triangles) 4

3. S S bond is not present in $H_2S_2O_7$ (pyrosulphuric acid or oleum).



While the other given oxoacids of sulphur, i.e.

$H_2S_2O_3$ (thiosulphuric acid), $H_2S_2O_4$ (hyposulphurous or dithionous acid) and $H_2S_4O_6$ (tetrathionic acid) contains S S bonds.



4. The correct increasing order of oxidation state of nitrogen for nitrogen oxides is

$$\overset{1}{N_2}O < \overset{+2}{N}O < \overset{+3}{N_2}O_3 \quad \overset{4}{N}O_2$$

- Oxidation state of N in N_2O is

$$2(x) \quad 2 \quad 0$$
$$x \quad \frac{2}{2} \quad 1$$

- Oxidation state of N in NO is

$$x \quad 2 \quad 0$$
$$x \quad 2$$

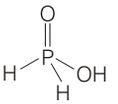
- Oxidation state of N in N_2O_3 is

$$2x \quad 3(\ 2) \quad 0$$
$$x \quad \frac{6}{2} \quad 3$$

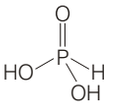
- Oxidation state of N in NO_2 is

$$x \quad 2(\ 2) \quad 0$$
$$x \quad 4 \quad 0$$
$$x \quad 4$$

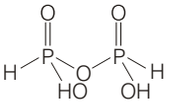
5. Let us consider the structure of the phosphorus oxyacids,



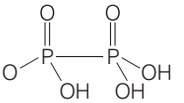
H_3PO_2
Hypophosphorus acid
(P H bonds=2)



H_3PO_3
Orthophosphorus acid
(P H bond=1)



$H_4P_2O_5$
Pyrophosphorus acid
(P H bonds=2)



$H_4P_2O_6$
Hypophousphoric acid
(P H bond=0)

6. As given, the first electron gain enthalpy of oxygen can be shown as,

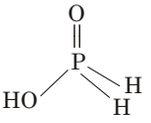
$$O(g) + e \qquad O\ (g), \quad {}_eH_1 \qquad 141\text{kJ/mol}$$

The expression of second electron gain enthalpy of oxygen will be,

$$O(g) + e \quad O^{2}(g), \quad e_g H_2 \quad \text{ve}$$

$e_g H_2$ of oxygen is positive, i.e. endothermic, because a strong electrostatic repulsion will be observed between highy negative O and the incoming electron (e). A very high amount of energy will be consumed (endothermic) by the system to overcome the electrostatic repulsion.

7. The structure of H_3PO_2 (hypophosphorous) acid is



Due to the presence of two P H bonds, H_3PO_2 acts a strong reducing agent. e.g.

$$4\overset{+1}{Ag}NO_3 \quad \overset{+1}{H_3}PO_2 \quad 2H_2O \quad 4\overset{0}{Ag} \quad \overset{+5}{H_3}PO_4 \quad 4HNO_3$$

8. The thermal decomposition of given compounds is shown below

$$(NH_4)_2Cr_2O_7 \quad N_2 + 4H_2O + Cr_2O_3$$

$$NH_4NO_2 \quad N_2 + 2H_2O$$

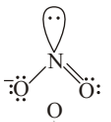
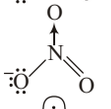
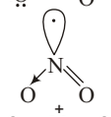
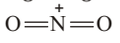
$$(NH_4)_2SO_4 \quad 2NH_3 + H_2SO_4$$

$$Ba(N_3)_2 \quad Ba + 3N_2$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating (It give NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

9. $\overset{5}{H_3}PO_4 \quad \overset{4}{H_4}P_2O_6 \quad \overset{3}{H_3}PO_3 \quad \overset{1}{H_3}PO_2$

10.

Species	Hybridisation
	sp^2
	sp^2
	sp^2
	sp

11. Orthophosphorous acid, H_3PO_3 : HO P OH

H

$\overset{x}{H_3}PO_3 = 3 \quad x \quad 3(\ 2) \quad 0$ or $x \quad 3$

Pyrophosphorous acid, $H_4P_2O_5$:

O O

HO P O P OH

H H

$\overset{x}{H_4}P_2O_5 \quad 4 \quad 2x \quad 5(\ 2) \quad 0$

$4 \quad 2x \quad 10 \quad 0, \ x \quad 3$

12. **PLAN** This problem is based on chemical properties of phosphorus.

White phosphorus on reaction with thionyl chloride ($SOCl_2$) produces phosphorus trichloride.

$$P_4(s) \quad 8SOCl_2(l) \quad 4PCl_3(l) \quad 4SO_2(g) \quad 2S_2Cl_2(g)$$

But if amount of thionyl chloride ($SOCl_2$) is in excess then it produces phosphorus pentachloride.

$$P_4 + 10SOCl_2(l) \quad 4PCl_5 + 10SO_2$$

13. NO is paramagnetic in gaseous state because in gaseous state, it has one unpaired electron.

Total number of electrons present $7 \quad 8 \quad 15e$

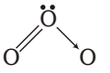
Hence, there must be the presence of unpaired electron in gaseous state while in liquid state, it dimerises due to unpaired electron.

14. NO_2 is a brown coloured gas and imparts this colour to concentrated HNO_3 during long standing.

$$4HNO_3 \quad 2H_2O \quad 2NO_2 \quad 3O_2$$

15. (a) ONCl $8 \quad 7 \quad 17 \quad 32e$

ONO $8 \quad 7 \quad 8 \quad 1 \quad 24e$ (correct)

(b) 

Central O-atom is sp^2-hybridised with 1 lone pair, so bent shape (correct).

(c) In solid state, ozone is violet-black. Ozone does not exist in solid state, thus incorrect.

(d) O_3 has no unpaired electrons, so diamagnetic (correct).

Hence, (c) is the correct.

16. The reaction of white phosphorus with aqueous alkali is

$$P_4 + 3NaOH + 3H_2O \quad PH_3 + NaH_2PO_2$$

In the above reaction, phosphorus is simultaneously oxidised [$P_4(0) \quad NaH_2\overset{+1}{P}O_2$] as well as reduced [$P_4(0) \quad \overset{3}{P}H_3$]. Therefore, this is an example of disproportionation reaction. Oxidation number of phosphorus in PH_3 is 3 and in NaH_2PO_2 is 1. However, 1 oxidation number is not given in any option, one might think that NaH_2PO_2 has gone to further decomposition on heating.

$$2NaH_2PO_2 \quad Na_2H\overset{+5}{P}O_4 + PH_3$$

17. Let oxidation number of N be x.

In HNO_3, $1 \quad x \quad 3(\ 2) \quad 0 \quad x \quad 5$

In NO, $x \quad 2 \quad 0 \quad x \quad 2$

In N_2, $x \quad 0$

In NH_4Cl, $x \quad 4 \quad 1 \quad 0 \quad x \quad 3$

18. $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be obtained in purest form as well as the decomposition product contain solid Ba as by product

alongwith gaseous nitrogen, hence no additional step of separation is required.
Other reactions are

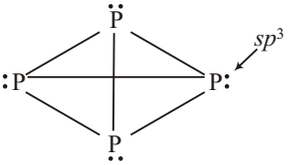
$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$$

$$2NH_3 \quad 3CuO \xrightarrow{\text{Heat}} 3Cu + 3H_2O + N_2$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} Cr_2O_3 \quad 4H_2O + N_2$$

19. In limited supply of oxygen, phosphorus is oxidised to its lower oxide P_4O_6 while excess of oxygen gives P_4O_{10}. A mixture of O_2 and N_2 is used for controlled oxidation of phosphorus into P_4O_6.

20. In P_4, all phosphorus are sp^3-hybridised and has 75% *p*-character.



21. In $KMnO_4$, Mn is already in its highest oxidation state (+7), cannot be oxidised by any oxidising agent.

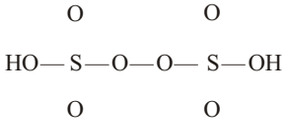
22. $PbO_2 + HNO_3 \quad Pb(NO_3)_2 + H_2O + O_2$

23. Equimolar amounts of NO and NO_2 at –30°C gives $N_2O_3(l)$ which is a blue liquid.

$$NO(g) + NO_2(g) \xrightarrow{30\ C} N_2O_3(l)$$
(Blue)

24. Black phosphorus is thermodynamically most stable allotrope of phosphorus.
It is due to three dimensional, network structure of polymeric black phosphorus.

25. $H_2S_2O_8$ is a peroxy acid, has—O—O—linkage



Peroxodisulphuric acid

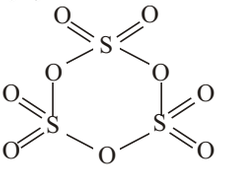
26. H_3PO_3 is a dibasic, reducing acid. H_3PO_4 is tribasic, non-reducing acid.

Dibasic, reducing Tribasic, non-reducing

27. Polyphosphates are used as water softening agents because they form soluble complexes with cationic species of hard water.

$Na_2[Na_4(PO_3)_6] + CaSO_4 \quad Na_2[(Ca_2(PO_3)_6] + Na_2SO_4$
Soluble complex

28. The structure of S_3O_9 is



It has no S—S linkage.

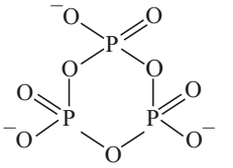
29. CaO, a basic oxide, is most suitable for drying of basic ammonia.

30. H_2O, due to its ability to form intermolecular H-bonds.

31. Corresponding acids are $HClO_4$, H_2SO_3 and H_3PO_4. Hence, the order of acidic strength is

$$Cl_2O_7 > SO_2 > P_4O_{10}$$

32. The structure of cyclic metaphosphate is

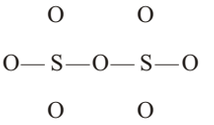


There is three P—O—P bonds.

33. $Ca_3P_2 \quad 6H_2O \quad 3Ca(OH)_2 \quad 2PH_3$

34. $Na_2SO_3 + S \xrightarrow{OH} Na_2S_2O_3$

35. $S_2O_7^{2-}$ has no S—S linkage.



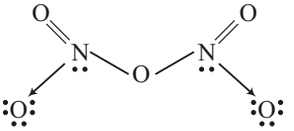
All others have atleast one S—S linkage.

36. Amongst XH_3 where '*X*' is group-15 elements, basic strength decreases from top to bottom. Hence, NH_3 is strongest base.

37. The electron withdrawing inductive effect of halogen decreases electron density on nitrogen, lowers basic strength. Since, fluorine is most electronegative, NF_3 is least basic.

38. $NO_2(g)$ is deep brown coloured.

39. In N_2O_5, there are (sigma) covalent bonds, (pi) bonds and coordinate covalent bonds as



40. SO_2 cannot be collected over water because it reacts with water forming H_2SO_3.

$$SO_2 + H_2O \quad H_2SO_3$$

41. Quicklime (CaO) is used for drying NH_3 gas because both are basic, do not react. On the other hand, H_2SO_4 and P_2O_5 are acidic, reacts with ammonia forming salts. $CaCl_2$ forms complex with ammonia.

42. NO is lighter than O_2.

D_2O is commonly known as heavy water.

N_2 is lighter than O_2, effuse at faster rate under identical experimental conditions. NH_3 liquefies at very low temperature. Therefore, liquid NH_3 is used as a refrigerant.

43. Among the given compounds, those which generate N_2 on thermal decomposition below 300°C are **ammonium dichromate** i.e., $(NH_4)_2Cr_2O_7$ and **barium azide** or nitride i.e., $Ba(N_3)_2$. Reactions of their thermal decomposition are given below

(i) $(NH_4)_2Cr_2O_7 \xrightarrow{\text{Below 300 C}} N_2 \quad Cr_2O_3 \quad 4H_2O$

It is an exothemic reaction with

$H \quad 429.1 \quad 3 \text{ kcal/mol.}$

(ii) $Ba(N_3)_2 \xrightarrow{\text{Around 160 and above}} Ba \quad 3N_2$

Ammonium nitrate (NH_4NO_3) on heating below 300°C gives N_2O as

$$NH_4NO_3 \xrightarrow{\text{below 300 C}} N_2O \quad 2H_2O$$

However, on rapid heating or explosion

(i.e. above 300°C) it gives off nitrogen as

$$2NH_4NO_3 \xrightarrow[\text{or explosion}]{\text{Rapid heating}} 2N_2 \quad O_2 \quad 4H_2O$$

Magnesium nitride (Mg_3N_2) does not decompose at lower temperatures being comparatively more stable. Its thermal decomposition requires a minimum temperature of 700°C and proceeds as

$$Mg_3N_2 \xrightarrow{700\ 1500\ C} 3Mg \quad N_2$$

44. Statement wise explanation is

(i) **Statement (a)** Bi_2O_5 is a metallic oxide while N_2O_5 is a non-metallic oxide.

Metallic oxides being **ionic** are **basic in nature** while non metallic oxides being **covalent** are **acidic in nature**. This confirms more basic nature of Bi_2O_5 in comparison to N_2O_5. Hence, this is a correct statement.

(ii) **Statement (b)** The electronegativity difference between N(3) and F(4) is less as compared to the electronegativity difference between Bi (1.7) and F(4). More electronegativity difference leads to ionic compounds. Thus, NF_3 must be more covalent in nature as compared to BiF_3. Hence, this statement is also correct.

(iii) **Statement (c)** In NH_3 intermolecular hydrogen bonding is present, which is altogether absent in PH_3. Thus, PH_3 boils at lower temperature than NH_3.

Hence, this is also a correct statement.

(iv) **Statement (d)** Due to smaller size of N the lone pair-lone pair repulsion is more in N—N single bond as compared to O—P single bond. This results to weaker N—N single bond as compared to P—P single bond. Hence, this statement is incorrect.

45. P_4O_{10} is a dehydrating agent and converts HNO_3 into N_2O_5

$$2HNO_3 \quad N_2O_5 + H_2O$$

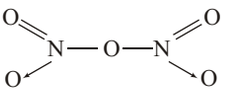
$$P_4O_{10} + 6H_2O \quad 4H_3PO_4$$

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

Thus, (a) is incorrect.

(b) N_2O_5 has no unpaired electron and is thus, diamagnetic thus, (b) is correct.

(c)



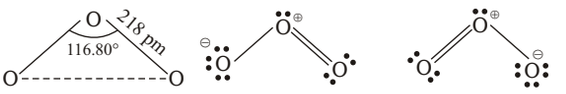
There is no N—N bond, thus, (c) is incorrect.

(d) $N_2O_5 + Na \quad NaNO_3 + NO_2$

N_2O_5 vapours are of brownish colour. Thus, (d) is correct.

46. **Plan** Due to resonance, bond lengths between two atoms are equal. Species is said to be diamagnetic if all electrons are paired.

Process is endothermic if it takes place with absorption of heat.



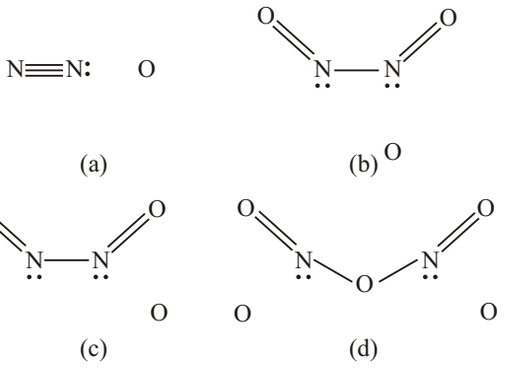
bent molecule all electrons paired thus, diamagnetic

$2O_3 \quad 3O_2 \quad H \quad 142 \text{ kJ mol}^{-1}$

Exothermic

Thus, (b) is incorrect. (a, c, d) are correct.

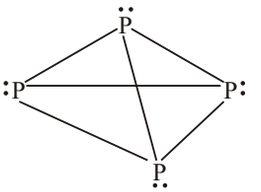
47. The structures of these oxides are



(a), (b), (c) have N—N bonds.

48. $2NH_3 + OCl \quad H_2N—NH_2 + H_2O + Cl$

49. The structure of P_4 is



It has six P—P single bonds.

There are four lone pairs on four phosphorus. P—P—P bond angles are of 60°.

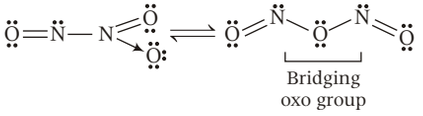
50. $NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$

$NH_2OH \ HCl + NaNO_2 \quad NaCl + 2H_2O + N_2O$

However, NH_4NO_2 on heating gives N_2.

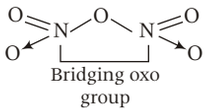
51. The structures of various molecules given in problem are discussed below—

1. **N_2O_3** It is the tautomeric mixture of following two structures—



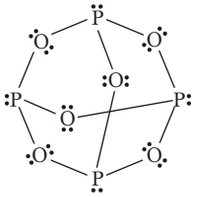
Conclusion 1 bridging oxo group is present in the compound.

2. **N_2O_5** It has following structure.



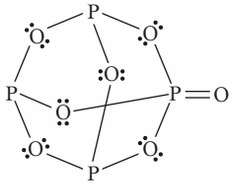
Conclusion 1 bridging oxo group is present in the compound.

3. **P_4O_6**



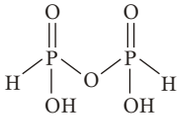
Conclusion 6 bridging oxo groups are present in the compound.

4. **P_4O_7**



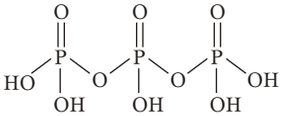
Conclusion 6 bridging oxo groups are present in the compound.

5. **$H_4P_2O_5$**



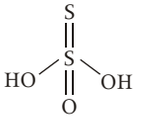
Conclusion 1 bridging oxo group is present in the compound.

6. $H_5P_3O_{10}$



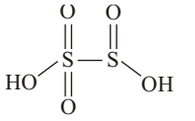
Conclusion 2 bridging oxo groups are present in the compound.

7. **$H_2S_2O_3$**



Conclusion This compound does not contain any bridging oxo group.

8. **$H_2S_2O_5$**

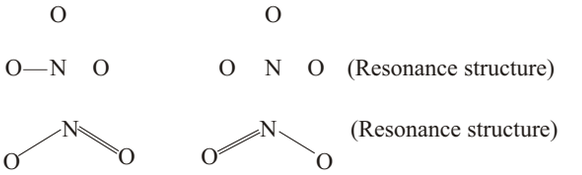


Conclusion This compound also does not contain any bridging oxo group.

52. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

53. Both Statement I and Statement II are true and Statement II is correct explanation of Statement I.

54. Both Statement I and Statement II are true and Statement II explains the Statement I appropriately. Nitrate ion (NO_3) is more stable than nitrite ion :



55. Both Statement I and Statement II are independently correct but reason is not the correct explanation of Statement I. Nitrogen does not has any vacant *d*-orbitals, it cannot expand its valence shell beyond eight electrons, i.e. it cannot violate octet. Therefore, nitrogen forms only trihalides (NX_3 with eight electrons in valence shell of N).

Phosphorus has vacant 3*d*-orbitals, it can expand its valence shell beyond eight electrons, its both trihalides and pentahalides exist.

Passage

$$KClO_3 \xrightarrow{MnO_2} \underset{W}{KCl} + O_2$$

$$O_2 + P_4 \longrightarrow \underset{X}{P_4O_{10}} \xrightarrow{HNO_3} \underset{Y}{N_2O_5} + \underset{Z}{HPO_3}$$

56. (a)

57. (b)

Passage

58. Due to greater solubility in water and prone to microbial attack, nitrates are less abundant in earth's crust.

59. NH_3 is stronger Lewis base than PH_3. In a group of hydrides, basic strength decreases down the group.

60. White phosphorus undergo disproportionation in alkaline medium.

$$P_4 + NaOH \longrightarrow PH_3 + NaH_2PO_2$$

61. (P) $2PbO_2 \quad 2H_2SO_4 \xrightarrow{\text{Warm (3)}} 2PbSO_4 \quad O_2 \quad 2H_2O$

(Q) $Na_2S_2O_3 \quad H_2O \xrightarrow{Cl_2(4)} NaHSO_4 \quad HCl$

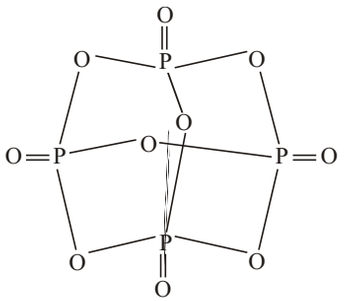
(R) $N_2H_4 \xrightarrow{I_2(2)} N_2 \quad HI$

(S) $XeF_2 \xrightarrow{NO(l)}$ Xe NOF

Thus, P—(3), Q—(4), R—(2), S—(1)

62. NO_2 : $2SO_2(g) + O_2(g) \xrightarrow[(NO_2)]{\text{Oxides of } N_2} 2SO_3(g)$

63.



Here four oxygen atoms are bonded to each phosphorus atom.

64. H_3PO_3 $[O{=}PH(OH)_2]$ is a dibasic acid.

65. White phosphorus has highly strained, tetrahedral structure, therefore highly reactive.

66. In liquid state, nitric oxide (NO) dimerises into $(NO)_2$ and odd electrons disappear giving diamagnetic property.

$\underset{\text{Paramagnetic}}{2NO} \qquad \underset{\text{Diamagnetic}}{O{=}N{-}N{=}O\ (l)}$

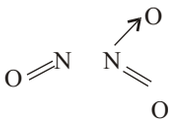
67. Both 'N' and 'As' in corresponding hydrides are sp^3-hybridised. If central atoms are from same group, bond angle decreases from top to bottom if all other things are similar. Hence, H—N—H bond angle in NH_3 is greater than H—As—H bond angle in AsH_3.

68. Halogens are all good oxidising agent and their oxidising power decreases from top to bottom (F_2 to I_2) in group. Any halogen above in group oxidises halides down in group from their aqueous solution. Hence, Cl_2 can oxidise Br to Br_2, I to I_2 but cannot oxidise F to F_2 rather F_2 can oxidise Cl to Cl_2.

69. Fe is more electropositive than hydrogen, displaces H ions from acid solution as :

$Fe + 2HCl \qquad FeCl_2 + H_2$

70. N_2O_3 has two proposed structures.

O N O N O and 

In both cases, number of lone pair of electrons are eight.

71. PCl_5 produces $POCl_3$ with the following reagents

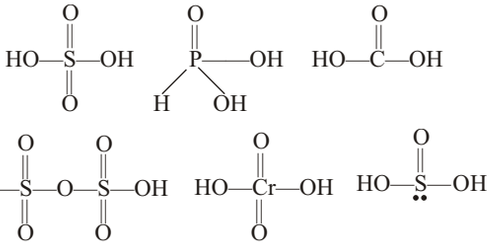
$PCl_5 + SO_2 \qquad POCl_3 + SOCl_2$

$PCl_5 + H_2O \qquad POCl_3 + 2HCl$

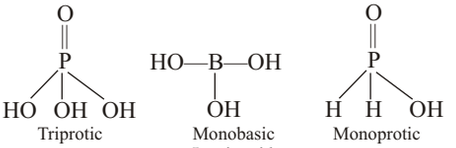
$2PCl_5 + H_2SO_4 \qquad SO_2Cl_2 + 2POCl_3 + 2HCl$

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

72. Diprotic acids 6

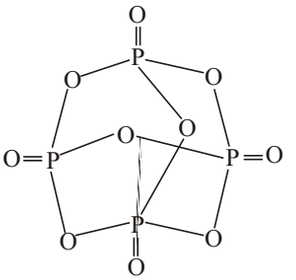


Others are



Triprotic Monobasic Lewis acid Monoprotic

73.



(P_4O_{10})

74. $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$

75. $A = \overset{+4}{NaH}SO_3$; $B = Na_2\overset{+4}{S}O_3$; $C = Na_2\overset{+2}{S_2}O_3$; $D = Na_2\overset{+2.5}{S_4}O_6$

76. (i) $Al_4C_3 + 12H_2O \qquad 4Al(OH)_3 + 3CH_4$

(ii) $CaNCN + 5H_2O \qquad CaCO_3 + 2NH_4OH$

(iii) $4BF_3 + 3H_2O \qquad H_3BO_3 + 3HBF_4$

(iv) $NCl_3 + 3H_2O \qquad NH_3 + 3HOCl$

(v) $2XeF_4 + 3H_2O \qquad Xe + XeO_3 + F_2 + 6HF$

77. Nitrogen in N_2 are bonded by one sigma and two pi bonds. Phosphorus and other elements of this period, due to larger size, are very less likely to form pi bonds, hence P_4 is formed in which there is no pi bonds.

78. In given scheme : A $Ca(OH)_2$

B NH_4HCO_3, C Na_2CO_3

D NH_4Cl and E $CaCl_2$

79. (a) $\underset{A}{HNO_2} + \underset{B}{2H_2SO_3} + H_2O \qquad \underset{C}{NH_2OH} + \underset{D}{2H_2SO_4}$

(b) In $SO_3 + H_2O$ H_2SO_4, sulphuric acid is obtained in misty form and the reaction is explosive. By adding H_2SO_4, above reaction is prevented :

$H_2SO_4 + SO_3 \qquad H_2S_2O_7$ (oleum)

$H_2S_2O_7 + H_2O \qquad 2H_2SO_4$

In the contact process, V_2O_5 is used as catalyst.

80. (i) $P_4O_{10} + 6PCl_5 \qquad 10\ POCl_3$

(ii) $SnCl_4 + 2C_2H_5Cl + 2Na \qquad Na_2SnCl_4 + C_4H_{10}$

81. (a) $PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$

(b) $Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$
triple superphosphate

82. The poisonous element *M* may be As. On the basis of given information

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

$$2AsH_3 \rightarrow \underset{M}{2As} + 3H_2$$

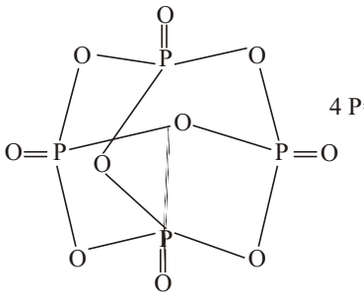
83. (i) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(ii) $3KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$

(iii) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$

84.



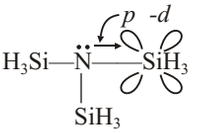
4 P═O bonds

85. (i) The size of both nitrogen and fluorine are very small as well as they have very high electron density. Thus in NF_3, N and F repel each other stretching the N—F bond. Hence, in NF_3, N—F bond lengths are greater than the sum of their single bond covalent radii.

(ii) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

$MgCl_2$ is a salt of strong acid HCl and strong base $Mg(OH)_2$ and therefore, not hydrolysed in aqueous solution.

(iii) In $(SiH_3)_3N$, the lone pair of nitrogen is involved in p - d bonding, less available on nitrogen for donation to a Lewis acid, a weaker Lewis base



Carbon does not have any vacant *d*-orbitals, no such p - d bonding occur in trimethyl amine, lone pair of nitrogen is available for donation to Lewis acid, hence a stronger Lewis base.

86. $Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \xrightarrow{Heat} 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF$

87. $PCl_5 + SO_2 \rightarrow \underset{A}{POCl_3} + \underset{B}{SOCl_2}$

88. Red phosphorus reacts with iodine in the presence of water to form H_3PO_3 and HI as–

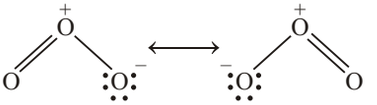
$$2P + 3I_2 + 6H_2O \rightarrow 2H_3PO_3 + 6HI$$

89. SO_2 acts as reducing agent on account of following reaction :

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

Hence, the above reaction proceeds in forward direction on increasing concentration of HO ion. H^+ is on product side, adding H^+ retards the reaction by sending it in backward direction.

90.



91. Ammonia, in liquid state undergo self-ionisation as :

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

Thus, addition of NH_4Cl to liquid ammonia increases concentration of NH_4^+ in solution and NH_4Cl act as acid.

92. (i) $Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$

(ii) $2KMnO_4 + 2NH_3 \rightarrow 2MnO_2 + 2KOH + 2H_2O + N_2$

(iii) $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $2H_2S + NaHSO_3 \xrightarrow{H^+} 3S + 3H_2O + Na^+$

(v) $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

93. (i) $NaNO_2 + Zn + NaOH \rightarrow 3Na_2ZnO_2 + NH_3 + H_2O$

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

94. N N—O N═N═O

95. (i) $15CaO + 4P_4 \rightarrow 5Ca_3P_2 + 3P_2O_5$

$[Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3\ ]\ 5$

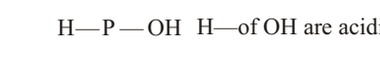
$15CaO + 4P_4 + 30H_2O \rightarrow 15Ca(OH)_2 + 3P_2O_5 + 10PH_3$

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

$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4$
gypsum

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

96. (i) In H_3PO_3, there is only two replaceable H, hence dibasic



H—of OH are acidic, dibasic.

(ii) NH_3 molecules are associated by intermolecular H—bonds.

97. (i) $\underset{\text{hypophosphorus acid}}{2H_3PO_2} \rightarrow PH_3 + H_3PO_4$ (Disproportionation)

(ii) $NaClO_3 + SO_2 \xrightarrow{10H} NaCl + S + 5H_2O$

98. $SiO_2 < CO_2 < N_2O_5 < SO_3$

99. (i) $4P + 10HNO_3 + H_2O \rightarrow 5NO + 5NO_2 + 4H_3PO_4$

(ii) $NaCl + NH_4OH + CO_2 \rightarrow NH_4Cl + NaHCO_3$

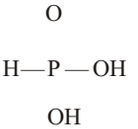
100. Oxygen lacks empty *d*-orbitals in its valence shell, cannot violate octet rule, hence in most of its compound it show only divalency. On the other hand, sulphur has vacant 3*d*-orbitals in its valence shell, can violate octet rule, show di, tetra and hexa valency.

101. (i) MgO is used for the lining of steel making furnace because it forms slag with impurities, and thus helps in removing them from iron.

(ii) The mixture of N_2H_4 and H_2O_2 (in presence of Cu(II) catalyst) is used as a rocket propellant because the reaction is highly exothermic and large volumes of gases is evolved.

$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(g)$$

(iii) In orthophosphorus acid (H_3PO_3) only two of the three H are replaceable as



(Only H of —OH are acidic)

(iv) In $MgCl_2$, Mg is *sp*-hybridised while in $SnCl_2$, Sn is sp^2-hybridised with a lone pair at Sn. Hence, $MgCl_2$ is linear while $SnCl_2$ is angular.

102. (i) $P_4 + 3NaOH + 3H_2O \xrightarrow{\text{Inert atm.}} 3NaH_2PO_2 + PH_3$ (phosphine)

(ii) $4Sn + 10HNO_3 \xrightarrow{\text{dil}} 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

103. (i) $4S + 6OH^- \longrightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(ii) $ClO_3^- + 6I^- + 6H_2SO_4 \longrightarrow Cl^- + 6HSO_4^- + 3I_2 + 3H_2O$

104. (i) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$ (white)

(ii) $(NH_4)_2SO_4 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O + H_2SO_4$

105. N N—O N=N=O

106. $Fe_2(SO_4)_3 + 2KI \longrightarrow 2FeSO_4 + K_2SO_4 + I_2$

In the above reaction, strong reducing agent, iodide, reducing ferric salt into ferrous salt.

107.

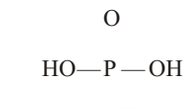
A	*B*	*C*
Asbestos	Silicates of Ca and Mg	Donar
Lithium metal	Reducing agent	Electron donor
Nitric oxide	Paramagnetic	Air pollutant

108. (i) $2HNO_3 + 6HCl \longrightarrow 2NO + 3Cl_2 + 4H_2O$

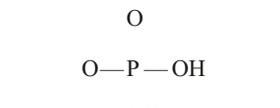
(ii) $2Ce^{3+} + S_2O_8^{2-} \longrightarrow 2SO_4^{2-} + 2Ce^{4+}$

(iii) $Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$

109. Orthophosphoric acid (H_3PO_4) has three replaceable (acidic) hydrogen while orthophosphorus acid (H_3PO_3) has only two replaceable hydrogen.

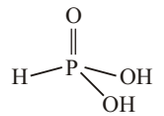


orthophosphoric acid
(it has three acidic H)



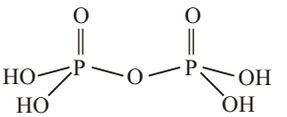
orthophosphorus acid
(only two acidic H, H directly bonded to P is not acidic)

110. (i)



phosphorus acid
(P is sp^3-hybridised)

(ii)



(pyrosphosphoric acid)

111. Rhombic sulphur has a eight membered puckered ring structure.

On heating ring tends to break and linear chain sulphur is formed. When sulphur melts, the S_8 rings slip and roll over one another very easily. It gives rise to a clear mobile liquid.

When liquid sulphur is further heated to higher temperature, rings are broken giving long chain sulphur molecules. This long chain molecules of sulphur gets entangled into one another increasing viscosity of melt.

112. (i) In the presence of sunlight, concentrated nitric acid decomposes partially as

$$\text{Conc. } HNO_3 \xrightarrow{h} NO_2 + H^+ + O_2$$

It is the NO_2 which impart yellow colouration to nitric acid.

(ii) The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

Topic 2 Element and Compound of Group 17 and 18

1. Radium (Ra) is a radioactive element. Ra belongs to group 2 (alkaline earth metals), it is not a noble gas.

Note In question noble gas which does not exist in the atmosphere is asked and answer is Ra. But Ra (radium) is an alkaline earth metal and not noble gas. It can be Rn (radon) and is misprint in JEE Main Paper.

2. Halogens form halates and halides with hot and concentrated solution of NaOH as :

$$3X_2 + 6NaOH \longrightarrow 5NaX + NaXO_3 + 3H_2O$$

So, Cl_2 will also give Cl (as NaCl) and ClO_3 ($NaClO_3$) in the above reaction.

Thus, option (b) is correct.

Note When halogens react with cold and dilute solution of NaOH, hypohalites and halides are produced as:

$$X_2 + 2NaOH \longrightarrow NaX + NaXO + H_2O$$

3. Iodine reacts with concentrated HNO_3 to yield HIO_3 along with NO_2 and H_2O. The reaction involved in as follows :

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

The oxidation state of 'I' in HIO_3 is 5 as calculated below :

$$1 \quad x \quad 3(-2) \quad 0$$

$$x - 5 = 0, \; x = +5$$

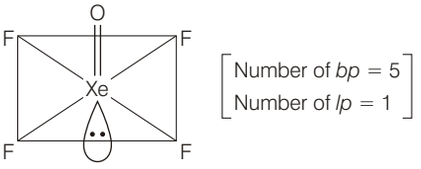
4. Chemical reactivity of halogens decreases down the group.
The chemical reactivity follows the order.

$$F_2 > Cl_2 > Br_2 > I_2.$$

The highest reactivity of fluorine is attributed to two factors:
(i) The low dissociation energy of F F bond (which results in low attraction energy for the reaction).
(ii) Very strong bonds which are formed. Both properties arise from, small size of fluorine. I_2 is being the least reactive halogen, it requires a catalyst for the reaction.

$$H_2 + I_2 \quad 2HI$$

5. In $XeOF_4$, Xe is sp^3d^2-hybridised. Geometry of the molecule is octahedral, but shape of the molecule is square pyramidal.
According to VSEPR, theory it has one bond. Remaining six electron pairs form an octahedron with one position occupied by a lone pair.



Here, Xe contains one lone pair of electrons.

6. The reaction in which oxidation and reduction occur simultaneously are termed as redox reaction.

$$\overset{+4}{Xe}F_4 \quad \overset{1}{O}_2 \ (\ F_2) \qquad \overset{6}{X}eF_6 \quad \overset{0}{O}_2$$

Since, Xe undergoes oxidation while O undergoes reduction. So, it is an example of redox reaction.

7. Cl_2, Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalies while a mixture of halides and haloate when react with concentrated cold alkalies.

$$Cl_2 \quad 2NaOH \qquad NaCl \quad NaClO \quad H_2O$$

Cold and dilute

Cl and ClO are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

8. Interhalogen compounds are generally more reactive than halogens (except fluorine).

9. Xe has highest boiling point.

10. **PLAN** This problem can be solved by using concept involved in chemical properties of xenon oxide and xenon fluoride.
XeF_6 on complete hydrolysis produces XeO_3.
XeO_3 on reaction with OH produces $HXeO_4$ which on further treatment with OH undergo slow disproportionation reaction and produces XeO_6^4 along with Xe(g), $H_2O(l)$ and $O_2(g)$ as a by-product.
Oxidation half-cell in basic aqueous solution

$$HXeO_4 \quad 5OH \qquad XeO_6^4 \quad 3H_2O \quad 2e^-$$

Reduction half-cell in basic aqueous solution

$$HXeO_4 \quad 3H_2O \quad 6e \qquad Xe \quad 7OH$$

Balanced overall disproportionation reaction is

$$4HXeO_4 \quad 8OH \qquad \underbrace{3XeO_6^4 \qquad Xe}_{\text{2 products}} + 6H_2O$$

Complete sequence of reaction can be shown as

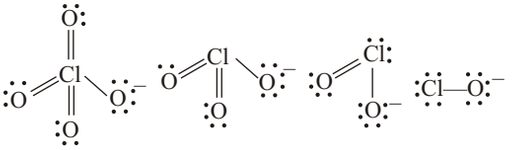
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 3H_2F_2$$
$$\downarrow OH^-$$
$$HXeO_4^-$$
$$\downarrow OH^-/H_2O \text{ (disproportionation)}$$
$$XeO_6^{4-}(s) + Xe(g) + H_2O(l) + O_2(g)$$

Thus, (c) is the correct answer.

11. Decreasing order of strength of oxoacids

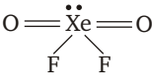
$$HClO_4 > HClO_3 > HClO_2 > HOCl$$

Reason Consider the structures of conjugate bases of each oxyacids of chlorine.

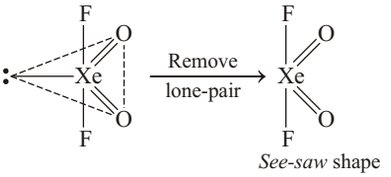


Negative charge is more delocalised on ClO_4 due to resonance, hence, ClO_4 is more stable (and less basic).
Hence, we can say as the number of oxygen atom(s) around Cl-atom increases as oxidation number of Cl-atom increases and thus, the ability of loose the H increases.

12. In XeO_2F_2, the bonding arrangement around the central atom Xe is



4 bonds 1.0 1 p 5
Hybridisation of Xe sp^3d
sp^3d-hybridisation corresponds to trigonal bipyramidal geometry.
Also, in trigonal bipyramidal geometry, lone pairs remain present on equatorial positions in order to give less electronic repulsion.



See-saw shape

NOTE According to Bent's rule, the more electronegative atoms must be present on axial position. Hence, F are kept on axial positions.

13. Sodium thiosulphate, $Na_2S_2O_3$ gets oxidised by chlorine water as $Na_2S_2O_3 \quad 4Cl_2 \quad 5H_2O \qquad 2NaHSO_4 \quad 8HCl$
$FeCl_3$ oxidises $Na_2S_2O_3$ to $Na_2S_4O_6$.

14. I^- is oxidised by MnO_4^- in alkaline medium to form IO_3^-
$2KMnO_4 \quad KI \quad H_2O \qquad 2KOH \quad 2MnO_2 \quad KIO_3$

15. Amongst oxyacids of a given halogen, higher the oxidation number of halogen, stronger the acid. Hence,

$$HOCl < HClO_2 < HClO_3 < HClO_4.$$

16. Pseudo halides must contain atleast one nitrogen atom.

17. Among oxyacids of halogens, if there are same number of oxygens bonded to central atom, higher the electronegativity of halogen, stronger the acid. Hence,

$$IOH < BrOH < ClOH$$

18. All others has at least one S-S linkage.

$$KF + HF \qquad K^+ + HF_2$$

19. Among halogens, oxidising power decreases from top to bottom. Hence, the upper halogen oxidises lower halides from aqueous solution. Chlorine will oxidise bromide into bromine.

20. Moist chlorine gives nascent oxygen, act as oxidising agent :

$$Cl_2 + H_2O \qquad HCl + HOCl$$

$$HOCl \qquad HCl + [O]$$

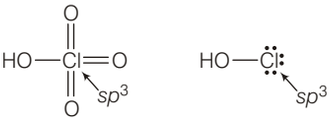
nascent oxygen (bleaching action)

21. Fluorine, being the most electronegative, its size is very small. Therefore, it does not have a tendency to loose electrons. Hence, HF does not act as a reducing agent.

22. (a) ClO_4 is more stable than ClO .

(b) Incorrect : $Cl_2 \quad H_2O \qquad HCl \quad HOCl$

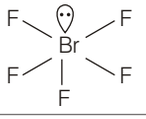
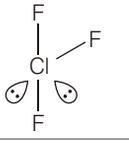
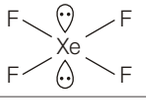
(c)



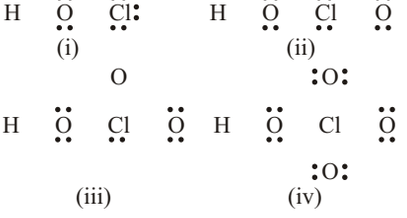
(d) $HClO_4$ is stronger acid than H_2O.

23. Colour of halogen arises due to transition from HOMO to LUMO in the visible region. On moving down a group, the difference in energy between HOMO and LUMO decreases electronic transition occur more easily and colour intensity increases.

24.

Compounds	Hydridisation	Structures	Lone pair on central atom
BrF_5	sp^3d^2		1
ClF_3	sp^3d		2
XeF_4	sp^3d^2		2
SF_4	sp^3d		1

25.



(*a*) Number of Cl = O bonds in (ii) and (iii) together is three. Hence, wrong.

(*b*) Number of Lone Pair on Cl in (ii) and (iii) together is three. Hence, correct.

(*c*) In (iv), Cl is sp^3-hybridised. Hence, correct.

(*d*) Amongst (i) to (iv), the strongest acid is (iv). Hence, wrong.

Passage 1 Q. Nos. (**26-27**)

$$2NaOH \quad Cl_2 \xrightarrow{\text{Cold}} NaCl \quad \underset{P}{NaOCl} \quad H_2O$$

$$6NaOH \quad 3Cl_2 \xrightarrow{\text{hot}} 5NaCl \quad \underset{Q}{NaClO_3} \quad 3H_2O$$

$$\underset{\text{hypochlorous acid}}{HOCl} \xrightarrow{NaOH} \underset{P}{NaOCl}$$

$$\underset{\text{chloric acid}}{HClO_3} \xrightarrow{NaOH} \underset{Q}{NaClO_3}$$

$$Cl_2 \quad SO_2 \qquad \underset{R}{SO_2Cl_2}$$

$$10\ \underset{R}{SO_2Cl_2} \quad P_4 \qquad \underset{S}{4PCl_5} \quad 10\ SO_2$$

$$PCl_5 \quad 4H_2O \qquad \underset{T}{H_3PO_4} \quad 5\ HCl$$

Passage 2 Q.Nos. **(28-29)**

28. The involved redox reactions are :

$$2H^+ + OCl^- + 2I^- \qquad Cl^- + I_2 + H_2O \qquad \ldots(i)$$

$$I_2 + 2S_2O_3^{2-} \qquad 2I^- + S_4O_6^{2-} \qquad \ldots(ii)$$

Also the *n*-factor of $S_2O_3^{2-}$ is one as

$$2S_2O_3^{2-} \qquad S_4O_6^{2-} \quad 2e^-$$

[one '*e*' is produced per unit of $S_2O_3^{2-}$]

Molarity of $Na_2S_2O_3 = 0.25$ N $\quad 1 = 0.25$ M

m mol of $Na_2S_2O_3$ used up $\quad 0.25 \quad 48 \quad 12$

Now from stoichiometry of reaction (ii)

12 m mol of $S_2O_3^{2-}$ would have reduced 6 m mol of I_2.

From stoichiometry of reaction (i)

m mol of OCl^- reduced = m mol in I_2 produced $\quad 6$

Molarity of household bleach solution $\quad \frac{6}{25} \quad 0.24$ M

Shortcut Method

Milliequivalent of $Na_2S_2O_3$ = milliequivalent of OCl^-

$$= 0.25 \quad 48 = 12$$

Also *n*-factor of $OCl^- \quad 2$ [$Cl^- \qquad Cl$, gain of $2e^-$]

m mol of $OCl^- \quad \frac{12}{2} \quad 6$ m mol. Remaining part is solved in the same manner.

29. Bleaching powder is Ca(OCl)Cl. Therefore, the oxoacid whose salt is present in bleaching powder is HOCl. Anhydride of HOCl is Cl_2O as

$$2\ HOCl \qquad Cl_2O + H_2O$$

NOTE The oxidation number of element in anhydride and oxoacid remains the same.

Passage 3 Q.Nos. **(30-32)**

30. Ar, being inert, provide inert atmosphere in arc welding, and prevent from undesired oxidation.

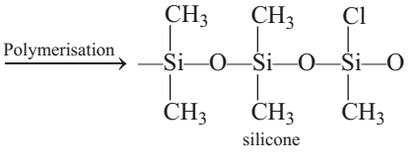
31. O Xe O

O

Xe is sp^3-hybridised with one lone pair. Hence, molecule of XeO_3 has pyramidal shape.

32. Both XeF_4 and XeF_6 are strong oxidising agent.

33. $(CH_3)_2SiCl_2 + H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$



silicone

$3XeF_4 + 6H_2O \rightarrow XeO_3 + 2Xe + 12HF + \frac{3}{2}O_2$

$Cl_2 + H_2O \rightarrow HCl + HOCl \rightarrow HCl + \frac{1}{2}O_2$

$VCl_5 + H_2O \rightarrow VOCl_3 + 2HCl$

34. $KI + I_2 \rightarrow KI_3$

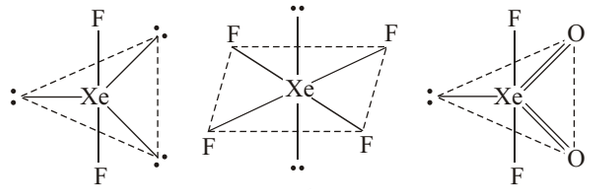
35. Among H*X*, acidic strength increases from HF to HI.

36. Br_2 is disproportionated in basic medium as

$3Br_2 + 3Na_2CO_3 \rightarrow 5NaBr + NaBrO_3 + 3CO_2$

37. $2XeF_4 + 3H_2O \rightarrow Xe + XeO_3 + F_2 + 6HF$

38.



39. Halogen above in the group oxidises halide below to it from their aqueous solution, e.g.

$Cl_2 + 2I^-(aq) \rightarrow 2Cl^- + I_2$

40. $Ca(OH)_2 + Cl_2 \xrightarrow{40\ ^\circ C} CaOCl_2 + H_2O$

41. (i) $2KI + Cl_2 \rightarrow 2KCl + I_2$

(ii) $2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$

42. (i) Due to small size and high electron density of fluorine atom, there exist a significant repulsions between fluorine atoms in F_2, they have greater tendency to get apart. Hence, bond energy of F_2 is less than that of Cl_2. This is against to bond-length bond-energy relationship,.

(ii) Sulphur dioxide is a more powerful reducing agent in alkaline medium because nascent hydrogen is produced in the presence of moisture

i.e. $SO_2 \quad 2H_2O \rightarrow H_2SO_4 \quad 2H$

And alkaline solution neutralises the acid i.e. H_2SO_4 and shift the equilibrium in the forward direction producing more nascent hydrogen. But in acidic medium the equilibrium will suppressed resulting in a lesser amount of nascent hydrogen.

43. $NaBrO_3 + 3F_2 \rightarrow 3F_2O + NaBr$

44. $HOCl < HOClO < HOClO_2 < HOClO_3$

45. $2IO_3^- + 5HSO_3^- \rightarrow I_2 + H_2O + 3HSO_4^- + 2SO_4^{2-}$

46. $Cl_2 + FeBr_2 \rightarrow FeCl_3 + Br_2$

47. $ClO_3^- + 6I^- + 6H_2SO_4 \rightarrow Cl^- + 6HSO_4^- + 3I_2 + 3H_2O$

48. (i) Bond strength is inversely related to bond length. Hence, bond energy : $HI < HBr < HCl < HF$

(ii) $HI(-1) < I_2(0) < ICl(+1) < HIO_4\ (+7)$

49. F_2 itself, is the strongest oxidising agent. Therefore, chemical reagent cannot oxidise fluoride to fluorine.

50. Complete and balance the following reactions

$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

51. The bleaching action of bleaching powder is due to presence of available chlorine, but in contact of moisture, it releases chlorine decreasing the amount of available chlorine. Hence, bleaching property decreases gradually as bleaching powder is kept in open container for long time.

52. (i) HBr is a stronger reducing agent, reduces cencentrated H_2SO_4 to SO_2. Hence, HBr cannot be prepared by heating bromide salts with concentrated H_2SO_4.

(ii) Hypochlorous acid is acidic in nature, therefore it turns blue litmus paper into red. However, HOCl is also an oxidising acid (bleaching), it bleaches red colour to finally colourless.

53. (i) $Ca(OH)_2 + Cl_2 \xrightarrow{40\ ^\circ C} CaOCl_2 + H_2O$

(ii) $3Cu + 8HNO_3\ (dil) \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(iii) $2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$

(iv) $Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$