Chemistry Question Bank

Career Endeavor - Chem Academy - Saraswati Dham

CSIR-UGC NET-JRF Chemistry

IIT-JAM Chemistry

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SP Sharma

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INORGANIC CHEMISTRY

VOLUME - 1

IIT-JAM

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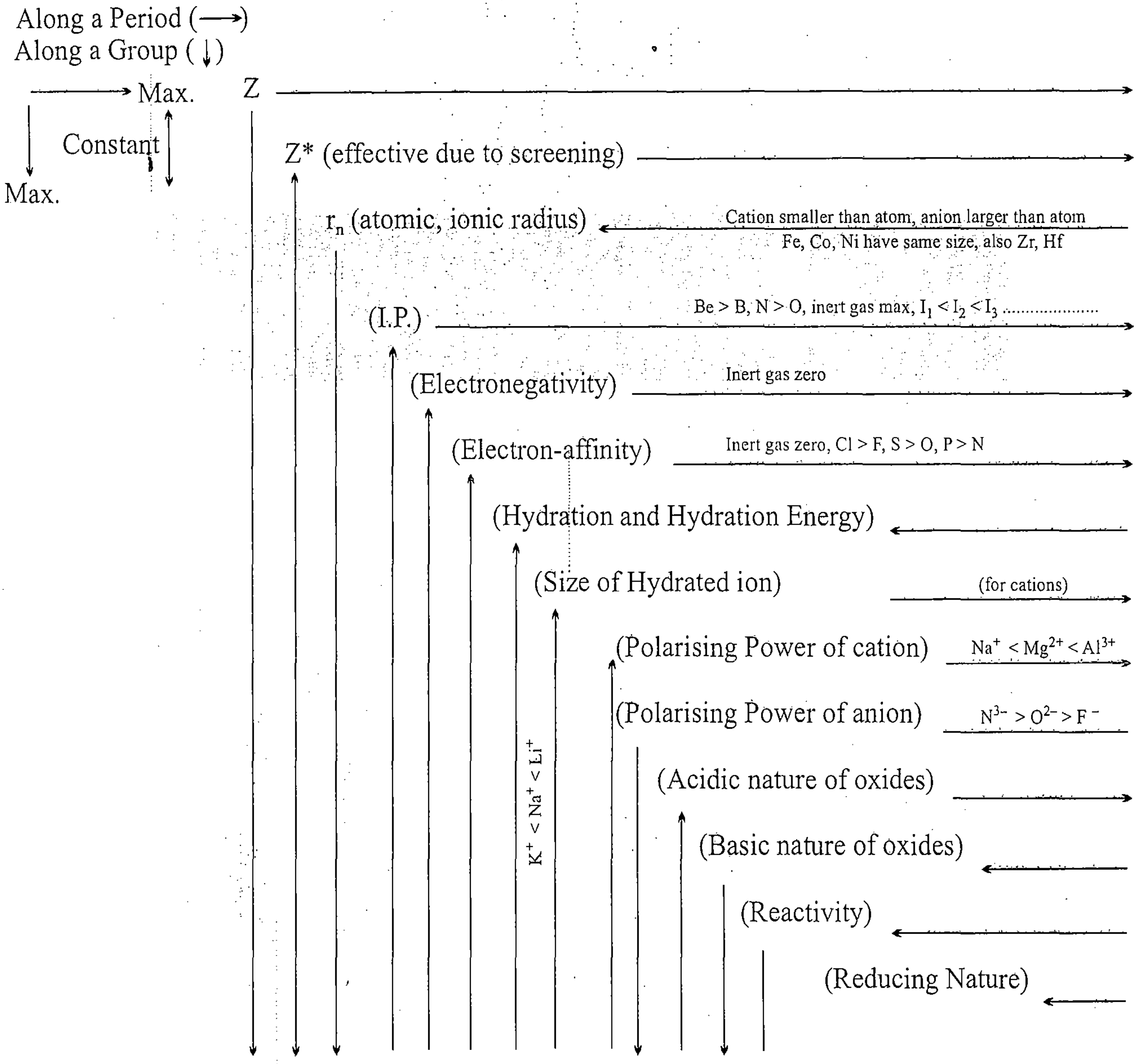
CHAPTER

1

PERIODIC PROPERTIES

SUMMARY OF PERIODICITY



Single Bond Covalent Radius, SBCR (bond length) -

(a) For homodiatomic molecules $d_{A-A} = r_A + r_A$ or $2r_A$ so, $r_A = \frac{d_{A-A}}{2}$

(b) For heterodiatomic molecules in which electronegativity remains approximately same.

$$d_{A-B} = r_A + r_B$$

- For heteronuclear diatomic molecule, A–B, where difference between the electronegativity values of atom A and atom B is relatively larger,

$$d_{A-B} = r_A + r_B - 0.09\,\Delta\chi \;(r = \text{Å})$$

This formula was given by **Stevenson & Schomaker**. Electronegativity values are given in Pauling units and radius in picometers.

$\Delta\chi = X_A - X_B$ where X_A and X_B are electronegativity values of high electronegative element A and less electronegative element B.

Later on modified and more accurate formula was proposed by **Porterfield** as given below;

$$d_{A-B} = r_A + r_B - 7.0\,(\Delta\chi)^2$$

(1) Pauling's Scale (1932):

The E.N. difference between two atoms is determined by the expression,

$$X_A - X_B = 0.208\left[E_{A-B} - (E_{A-A} \times E_{B-B})^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

X_A = E.N. of A

X_B = E.N. of B.

$\left.\begin{matrix} E_{A-A} \\ E_{B-B} \\ E_{A-B} \end{matrix}\right]$ Bond energies of A - A, B - B, A - B molecules.

Scale of measurement

(2) **Mulliken Scale (1934) :** According to this scale, EN. of an atom is the average sum of I E. and EA. of an atom.

$$E.N. = \frac{I.P. + E.A.}{2}$$

In Pauling Scale

$$E.N. = \frac{I.P. + E.A.}{5.6} \text{ (If I.P., E.A. are taken in eV)}$$

$$E.N. = \frac{I.P. + E.A.}{2 \times 62.8} \text{ (I.P., E.A. = Kcal mol}^{-1}\text{)}$$

Allred–Rochow's Electronegativity (χ_{AR}): Allred and Rochow defined electronegativity as the force exerted by the nucleus of an atom on its valence electrons :

$$\chi_{AR} = \frac{0.359\,Z_{effective}}{r^2} + 0.744$$

where $Z_{effective}$ is the effective nuclear charge and r the covalent radius in Å.

- According to the Allred-Rochow definition, elements with high electronegativity are those with high effective nuclear charge and the small covalent radius. Such elements lie close to fluorine.

Partial Ionic Character in Covalent bonds :

Partial ionic characters are generated in covalent compounds by the difference of electronegativities. **Hanney and Smith** calculated percentage of ionic character from the difference of electronegativity.

$$\text{Percentage of ionic character} = 16(X_A - X_B) + 3.5(X_A - X_B)^2$$

$$= 16\Delta + 3.5\Delta^2$$

$$= (0.16\Delta + 0.035\Delta^2) \times 100$$

X_A is electronegativity of element A (Higher)

X_B is electronegativity of element B (Lower)

$\Delta = X_A - X_B$

EXERCISE - I

Single Correct Type

Electronic Configuration

1. Choose the s-block element from the following:

(a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$
(b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
(d) all of the above

2. Pick out the isoelectronic species from the following:

I. $^+CH_3$ II. H_3O^+ III. NH_3 IV. CH_3^-

(a) I and II (b) III and IV (c) I and III (d) II, III and IV

3. If there were 10 periods in the periodic table then how many elements would this period can maximum comprise of.

(a) 50 (b) 72 (c) 32 (d) 98

4. If each orbital can hold a maximum of three electrons, the number of elements in 9th period of periodic table (long form) are

(a) 48 (b) 162 (c) 50 (d) 75

5. Which of the following element has highest metallic character .

	Element	IP
(a)	P	17 eV
(b)	Q	2 eV
(c)	R	10 eV
(d)	S	13 eV

CHEM ACADEMY

6. The electronic configuration of an element is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$. The atomic number and the group number of the element 'X' which is just below the above element in the periodic table are respectively.

(a) 24 & 6 (b) 24 & 15 (c) 34 & 16 (d) 34 & 8

7. Which of the following is the period number of the element whose atomic number is 98

(a) 4 (b) 7 (c) 5 (d) 6

8. Which of the following have same number of electrons in its outermost shell and penultuname shell

(a) Al^{3+} (b) Ca^{2+} (c) F^- (d) N^{3-}

9. According to IUPAC system of naming elements, the symbol of element of atomic number Z = 109 is

(a) unp (b) uns (c) uno (d) une

10. The screening effect of d electron

(a) less than p-electrons
(b) equal to p-electrons
(c) much more than p electrons
(d) equal to f

11. Correct order of size of ions is

(a) $H^- < F^- < Cl^- < Br^- < I^-$
(b) $F^- < Cl^- < Br^- < H^- < I^-$
(c) $F^- < H^- < Cl^- < Br^- < I^-$
(d) $F^- < Cl^- < Br^- < I^- < H^-$

12. Among alkali metals, the strongest reducing agent in aqueous solution is

(a) Li (b) Na (c) K (d) Cs

13. Which of the following sets of quantum number is correct for an electron in 4f-orbital
(a) $n = 4, l = 3, m = 4, s = 1/2$ (b) $n = 4, l = 4, m = -4, s = -1/2$
(c) $n = 4, l = 3, m = 1, s = 1/2$ (d) $n = 3, l = 2, m = -2, s = 1/2$

14. In multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electronic field
(i) $n = 1, l = 0, m = 0$ (ii) $n = 2, l = 0, m = 0$
(iii) $n = 2, l = 2, m = 0$ (iv) $n = 3, l = 2, m = 1$
(v) $n = 3, l = 2, m = 0$
(a) i and ii (b) ii and iii (c) iii and iv (d) iv and v

15. How many electrons are present in all subshells (fully filled) with $n + l = 5$
(a) 16 (b) 10 (c) 18 (d) 32

16. The maximum value of l for an electron in fourth energy level is
(a) 3 (b) 5 (c) 4 (d) 2

17. An element, M has an atomic mass 19 and atomic number 9, its stable ion is represented by
(a) M^+ (b) M^{2+} (c) M^- (d) M^{2-}

18. The electronic configuration of four elements are
(I) $[Kr]5s^1$ (II) $[Rn]5f^{14}6d^17s^2$ (III) $[Ar]3d^{10}4s^24p^5$ (IV) $[Ar]3d^64s^2$
Consider the following statements
(i) I shows variable oxidation state (ii) II is d block element
(iii) The compound formed between 1 and III are purely covalent
(iv) IV shows single oxidation state
Which statement is true (T) or false (F)
(a) FTFF (b) FTFT (c) FFTF (d) FFFF

19. Which of the following represent most electropositive element
(a) $[He]2s^1$ (b) $[Xe]6s^1$ (c) $[He]2s^2$ (d) $[Xe]6s^2$

20. Identify the group number of element having electronic configuration $1s^22s^22p^63s^23p^63d^54s^2$
(a) 8 (b) 7 (c) 17 (d) 5

21. An element X whose fourth shell contain two P electron. What is group of element
(a) 14 (b) 4 (c) 10 (d) 7

22. Which of following belong to Alkali metal series
(a) $3s^2\ 3p^5$ (b) $3d^{10}\ 4s^2$ (c) $3s^2\ 3p^6\ 4s^1$ (d) $1s^2\ 2s^2$

23. If an electron has spin quantum number of $+\frac{1}{2}$ and magnetic quantum number of -1 it cannot be present in
(a) f-orbital (b) d-orbital (c) p-orbital (d) s-orbital

24. When the quantum number n,l,m,s are represented by 3,3,2,+1/2, the symbolism for the electron is
(a) 3s (b) 3d
(c) 3f (d) impossible set of quantum number

25. Which one of the following sets of quantum numbers (n,*l*,m,s) represents an impossible arrangement?

(a) 3,2,–2,+1/2 (b) 4,0,0,+1/2 (c) 3,2,–3,+1/2 (d) 5,3,0,–1/2

26. What is a possible set of quantum numbers for the unpaired electron in the orbital box diagram below ?

[Ar] |↑↓|↑↓|↑↓|↑↓|↑↓| |↑↓| |↑↓|↑↓|↑|
3d 4s 4p

(a) $n = 1, \ell = 1, m_\ell = -1, m_s = +1/2$ (b) $n = 4, \ell = 1, m_\ell = -1, m_s = +1/2$

(c) $n = 4, \ell = 2, m_\ell = -2, m_s = +1/2$ (d) $n = 4, \ell = 0, m_\ell = 0, m_s = +1/2$

27. Total number of possible shells in uranium atom (atomic no. z = 92)

(a) 7 (b) 1 (c) 6 (d) None of these

28. Choose the incorrect statement.

(a) Be and Al are not in same group. (b) All the transition metal correspond to d-block.

(c) Be and Al are having lot of similarities in their properties.

(d) The atomic radius gradually decreases from Sc to Zn.

29. Choose the s-block element from the following:

(a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$ (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ (d) all of the above

Atomic Size

30. Arrange following isoelectronic species in decreasing order of their size

$O^{2-}, N^{3-}, Ne, F^-, Mg^{2+}, Na^+$

(a) $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$ (b) $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Ne$

(c) $Ne > N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+}$ (d) $N^{3-} > O^{2-} > F^- > Mg^{2+} > Na^+ > Ne$

31. The size of the following species increases in the order:

(a) $Mg^{2+} < Na^+ < F^-$ (b) $F^- < Na^+ < Mg^{2+}$ (c) $Mg^{2+} < F^- < Na^+$ (d) $Na^+ < F^- < Mg^{2+}$

32. Highest size will be of

(a) Br^- (b) I (c) I^- (d) I^+

33. Element Hg has two oxidation states Hg^{+1} & Hg^{+2}. the right order of radii of these ions.

(a) $Hg^{+1} > Hg^{+2}$ (b) $Hg^{+2} > Hg^{+1}$ (c) $Hg^{+1} = Hg^{+2}$ (d) $Hg^{+2} \geq Hg^{+1}$

34. The correct order of increasing atomic size of element N,F, Si & P.

(a) N < F < Si < P (b) F > N < P < Si (c) F < N < P < Si (d) F < N < Si < P

35. The correct order of atomic or ionic size

(a) N < Li < B (b) Cl < Mg < Ca (c) $Ca^{+2} < S^{-2} < Cl^-$ (d) $Na^+ < Mg^{+2} < Cl^-$

36. The ions O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+} are isoelectronic. Their ionic radii show

(a) a significance decrease from O^{2-} to Al^{3+}

(b) an increase from O^{2-} to F^- and then decrease from Na^+ to Al^{3+}

(c) a decrease from O^{2-} to F^- and then increase from Na^+ to Al^{3+}

(d) a significant increase from O^{2-} to Al^{3+}

37. The ions which are arranged in increasing order of ~~increasing~~ radii

(a) K^+, Ca^{2+}, Se^{2+} (b) Be^{2+}, Mg^{2+}, Na^+ (c) O^{2-}, F^-, N^{3-} (d) S^{2-}, O^{2-}, As^{3-}

38. If the ionic radii of K^+ and F^- are about 1.34 Å each, the expected value of atomic radii of K and F should be

(a) 1.34 and 1.34 Å (b) 2.31 and 0.64 Å (c) 0.64 and 2.31 Å (d) 2.31 and 1.34 Å

39. Metallic radius and covalent radius of K and Na are given below

	Metallic Radii (P_m)	Covalent Radii (P_M)
K	x	y
Na	p	q

x is greater than

(a) y (b) p (c) q (d) all

40. In crystal of which of the following ionic compound, would you expect the maximum distance between centre of cation and anion.

(a) CsF (b) CsI (c) LiI (d) LiF

Ionization Energy

41. The correct order of second ionisation potential of C, N, O and F is:

(a) C > N > O > F (b) O > N > F > C (c) O > F > N > C (d) F > O > N > C

42. Decreasing ionization potential for K, Ca & Ba is

(a) Ba > K > Ca (b) Ca > Ba > K (c) K > Ba > Ca (d) K > Ca > Ba

43. The ionization energy will be maximum for the process.

(a) $Ba \rightarrow Ba^+$ (b) $Be \rightarrow Be^+$ (c) $Cs \rightarrow Cs^+$ (d) $Li \rightarrow Li^+$

44. Alkaline earth metals always form dipositive ions due to

(a) $IE_2 - IE_1 > 11$ eV (b) $IE_2 - IE_1 = 17$ eV (c) $IE_2 - IE_1 < 11$ eV (d) None of these

45. Amongst the following, the incorrect order is

(a) IE_1 (Al) < IE_1 (Mg) (b) IE_1 (Na) < IE_1(Mg)

(c) IE_2 (Mg) > IE_2 (Na) (d) IE_3 (Mg) > IE_3 (Al)

46. The correct order of decreasing first ionization energy is

(a) C > B > Be > Li (b) C > Be > B > Li (c) B > C > Be > Li (d) Be > Li>B>C

47. Which of the following configuration is expected to have maximum difference in second and third ionization energies

(a) $(1s)^2 (2s)^2 (2p)^2$ (b) $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^3$

(c) $(1s)^2 (2s)^2 (2p)^6 (3s)^2$ (d) $(1s)^2 (2s)^2 (2p)^1$

48. The screening effect of inner electrons causes

(a) decrease in ionization energy (b) Increase in ionization energy

(c) No effect on ionization energy (d) Increase in attraction of nucleus to electron

49. The IE_1 of an element M(g) is 6000 kJ mol^{-1} and ratio of IE_2 and IE_3 is 3 : 2. If ΔH for conversion, $M(g) \rightarrow M^{3+}(g)$ is 10,000 kJ mol^{-1}. Find its IE_3

(a) 2400 kJ mol^{-1} (b) 1600 kJ mol^{-1} (c) 10,000 kJ mol^{-1} (d) 4000 kJ mol^{-1}

50. Which of the following configuration is associated with biggest jump between second and third IE.
(a) $1s^22s^22p^2$ (b) $1s^22s^22p^63s^1$ (c) $1s^22s^22p^63s^2$ (d) $1s^22s^22p^1$

51. The ionization of hydrogen atom would give rise to
(a) Hydride ion (b) Hydronium ion (c) Proton (d) Hydroxyl ion

52. For any given element, the second ionization potential will be ______ the first ionization potential
(a) less than (b) Higher than (c) Same (d) depends on element

Good Ques.

53. Value of IE_3 of Be, B and C are in order
(a) Be > B > C (b) B > C > Be (c) C > Be > B (d) Be > C > B

54. $M(g) \rightarrow M^+(g) + e^-$ $\Delta H = 100$ eV
$M(g) \rightarrow M^{2+}(g) + 2e^-$ $\Delta H = 300$ eV
Incorrect statement among the following
(a) IE_1 of M(g) is 100 eV (b) IE_1 of $M^+(g)$ is 200 eV
(c) IE_2 of M(g) is 200 eV (d) IE_2 of M(g) is 300 eV

55. Which configuration represent the atom having highest second ionization energy?
(a) $1s^22s^22p^4$ (b) $1s^22s^22p^63s^1$ (c) $1s^22s^22p^6$ (d) $1s^22s^22p^63s^2$

56. In which of the following electronic configuration ionisation energy will be maximum in
(a) [Ne] $3s^2\,3p^1$ (b) [Ne] $3s^2\,3p^2$ (c) [Ne] $3s^2\,3p^3$ (d) [Ar] $3d^{10}\,4s^2\,4p^3$

Electron Affinity

CHEM ACADEMY

57. The process requires absorption of energy is
(a) $F \rightarrow F^-$ (b) $Cl \rightarrow Cl^-$ (c) $O^- \rightarrow O^{2-}$ (d) $H \rightarrow H^-$

58. Of the following elements, which possess the highest electron affinity?
(a) As (b) O (c) S (d) Se

(S > Se > O > As)

59. Electron affinities of O,F,S and Cl are in the order.
(a) O < S < Cl < F (b) O < S < F < Cl (c) S < O < Cl < F (d) S < O < F < Cl

60. Highest electron affinity is shown by
(a) F^- (b) Cl^- (c) Li^+ (d) Na^+

61. Correct order of electron affinities is
(a) Cl > Na > Si > Ar (b) Cl > Si > Na > Ar
(c) Si > Cl > Ar > Na (d) Ar > Si > Cl > Na

Check electron affinity of Na and Ar

Good

62. A^+B^- is formed when
(a) $(IE)_A + (EA)_A < (IE)_B + (EA)_B$ (b) $(IE)_A + (EA)_B < (IE)_B + (EA)_A$
(c) $(IE)_B + (EA)_A < (IE)_A + (EA)_B$ (d) $(IE)_B + (EA)_B < (IE)_A + (EA)_A$

63. E.N. of element (a) is E_1 and IP is E_2. Hence EA will be
(a) $-E_2$ (b) $2E_1 - E_2$ (c) $\frac{E_1 - E_2}{2}$ (d) $\frac{E_1 + E_2}{2}$

64. Ionization energy of element X(g) is I and electron affinity of $X^+(g)$ is E, then
(a) I = E (b) I = –E (c) I = E/2 (d) I = –E/2

65. Which of the following is least stable
(a) Li^- (b) Be^- (c) O^- (d) Cl^-

Electronegativity

66. The outermost electronic configuration of most electronegative element is:
(a) $ns^2\ np$ (b) $ns^2\ np^4$ (c) $ns^2\ np^5$ (d) $ns^2\ np^6$

67. In the following which configuration of element has maximum electronegativity.
(a) $1s^2, 2s^2\ 2p^5$(b) $1s^2, 2s^2\ 2p^6$(c) $1s^2, 2s^2\ 2p^4$(d) $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^3$

68. On the Pauling's electronegativity scale, which element is next to F .
(a) Cl (b) O (c) Br (d) Ne

69. The increasing order of acidic nature of Li_2O, BeO, B_2O_3
(a) $Li_2O > BeO < B_2O_3$ (b) $Li_2O < BeO < B_2O_3$
(c) $Li_2O < BeO > B_2O_3$ (d) $Li_2O > BeO > B_2O_3$

70. Bond distance C–F in (CF_4) & Si–F in (SiF_4) are respective 1.33Å & 1.54 Å. C–Si bond is 1.87 Å. Calculation the covalent radius of F atom ignoring the electronegativity differences.
(a) 0.64 Å (b) $\frac{1.33+1.54+1.8}{3}$ Å (c) 0.5 Å (d) $\frac{1.54}{2}$ Å

71. Which of the following element is having highest electronegativity.
(a) $1s^2\ 2s^2\ 2p^1$ (b) [Ne] $3s^2\ 3p^1$ (c) [He] $2s^2\ 2p^4$ (d) [Ne] $3s^2\ 3p^5$

72. Which one is not correct order of electronegativity.
(a) F > Cl > Br > I (b) Si > Al > Mg > Na (c) Cl > S > P > Si (d) None of these

73. Calculate the bond length of C–X bond if C – C bond length is 1.54 Å and X–X bond length is 1.2 Å and electronegativities of C and X are 2.0 and 3.0 respectively.
(a) 2.74 Å (b) 1.37 Å (c) 1.46 Å (d) 1.28 Å

74. Covalent radius of oxygen is 0.74 Å and its electronegativity is 3.5. What is effective nuclear charge experienced by oxygen
(a) 5.20 (b) 4.20 (c) 0.655 (d) 3.8

75. Which of the following oxide is most basic
(a) Na_2O (b) MgO (c) Al_2O_3 (d) CuO

76. Correct order of acidic character are
(a) HF > HCl > HBr > HI (b) $HF > H_2O > NH_3$
(c) $H_3PO_4 > H_2SO_4 > HClO_4$ (d) $H_3PO_4 > H_3PO_3 > H_3PO_2$

77. Given oxides CO, BeO, Na_2O, N_2O_5, Cl_2O_7 frame code using P, N, B, A where
P = amphoteric oxides N = neutral oxide B = Basic oxide A = Acidic oxide
(a) NPBAA (b) NNABA (c) NPAAB (d) NABBA

78. Bond distance (C–H) in CH_4 is x and that of (Si – H) in SiH_4 is y. C–Si bond is Z Å. Calculate covalent radii of H atom ignoring the electronegativity difference
(a) $\frac{x+y+z}{2}$ (b) $\frac{x+y-z}{2}$ (c) $\frac{x-y-z}{2}$ (d) $\frac{x+y}{2}$

79. Which of the following is incorrect

(a) An element which has high electronegativity always has high electron gain enthalpy

(b) Electron gain enthalpy is the property of an isolated atom

(c) Electronegativity is the property of bonded atoms.

(d) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge.

80. Which of the following species of Mn has lowest electronegativity?

(a) Mn(II) (b) Mn(IV) (c) Mn(VI) (d) Mn(VII)

EXERCISE - II

Multiple Correct Type

1. Which of the following is correct order of EA.

(a) N < C < O < F (b) F > Cl > Br > I (c) Cl > F > Br > I (d) C < N < O < F

2. Select the correct statement(s).

(a) The value of electron gain enthalpy of an element can be -ve or +ve.

(b) In the periodic table, metallic character of the elements increases down the group and decreases across the period

(c) The Cl^- & S^{2-} are isoelectronic species but first one is not smaller in size than the second

(d) Ionization enthalpy of an atom is equal to electron gain enthalpy of corresponding cation

3. Which of the following statements is/are incorrect.

(a) Boron is diagonally related to magnesium.

(b) Bi^{5+} ion has smaller radius compared to Bi^{3+}.

(c) last number of the seventh period of periodic table will have atomic number of 124 if discovered.

(d) Al_2O_3 is an amphoteric oxide.

4. Which of the following are correct

(a) $IE_2(Mg) < IE_2(Na)$ (b) EA (N) < EA (P)

(c) Atomic size Mg^{+2} > Atomic size (Li^+) (d) IP of Na < Mg < Al

check once

5. If Hund's rule is not followed and energy of orbitals is governed by "n" only and not (n+l) rule then

(a) K would have been d–block element & paramagnetic.

(b) Cu would have been s–block element. (c) Cr would have been diamagnetic

(d) Fe^{+3} ion would have 5 unpaired electrons.

6. In halogen, which of the following properties increase from iodine to fluroine

(a) Ionisation energy (b) Electronegativity (c) Bond length (d) Electron affinity

Imp!

7. Which of the following pair have nearly the same atomic radii

(a) Al and Ga (b) Fe and Ni (c) Zr and Hf (d) Pt & Pd

8. In which of the following sets of elements 1st element is more metallic then second.

(a) Ba, Ca (b) Sb, Sn (c) Ge, S (d) Na, F

Ca Fe ≈ Co ≈ Ni

9. Amongst the following statements, which is / are correct?
   (a) Electronegtaivity of sulphur is greater than that of oxygen.
   (b) Electron affinity of oxygen is smaller than that of sulphur.
   (c) Electron gain enthalpy of fluorine is most negative
   (d) Electron gain enthalpy of chlorine is most negative

10. The ionic compound $A^+ B^-$ is formed when the
    (a) electron gain enthalpy of B is high (b) ionization energy of A is low
    (c) lattice energy of AB is high (d) lattice energy of AB is low

11. Which of the following is/are correct?
    (a) For $A(g) + e^- \longrightarrow A^-(g)$ ΔH may be negative
    (b) For $A^-(g) + e^- \longrightarrow A^{2-}(g)$ ΔH may be negative
    (c) For $A^-(g) + e^- \longrightarrow A^{2-}(g)$ ΔH must be positive
    (d) For $A^{+3}(g) + e^- \longrightarrow A^{+2}(g)$ ΔH must be negative

12. Select the correct order (s).
    (a) IE_1 of $F > IE_1$ of Cl (b) E A of $O >$ E A of S
    (c) Ionic radius of $Cl^- >$ Ionic radius of K^+ (d) None of these

13. The correct statement is
    (a) The second ionization energy of Se is greater than that of second ionization energy of As
    (b) The first ionization energy of C^{2+} ion is greater than that of first ionization energy of N^{2+} ion
    (c) The third ionization energy of F is greater than that of third ionization energy of O
    (d) Halogens have highest IE in respective period.

14. Which of the following represent correct order
    (a) $Be^{2+} < Mg^{2+} < Ca^{2+} < Ra^{2+}$: Ionic radii (b) $SiO_2 < Al_2O_3 < \overset{+6}{SO_3} < \overset{+5}{P_2O_5}$: Acidic
    (c) $AlH_3 < GaH_3 < InH_3 < TlH_3$: Basic character
    (d) None of these

15. Higher value of ionization energies of 5d transition elements are consistent with the
    (a) Relatively smaller screening effect (b) Relatively smaller size of their atoms
    (c) Relatively smaller effective nuclear charge
    (d) All above

16. Which of following is incorrect
    (a) $IE_1(Mg) > IE_1(Al)$ (b) $IE_2(Mg) > IE_2(Al)$
    (c) Order of IE_1 : $Cu < Zn < Ga$ (d) Order of IE_1 : $Zn > Cu > Ga$

17. Which of the following statement is incorrect
    (a) Energy is released when electron is added to an isolated gaseous atom
    (b) The oxides and hydroxides of alkali metals are strong base
    (c) Vander Waal's radius of chlorine is less than that of covalent radius
    (d) The reactivity of non-metallic elements in periodic table increases from top to bottom.

18. Consider the following reactions

(i) $O(g) + e^- \rightarrow O^-(g)\ \Delta H_1$ (ii) $F(g) + e^- \rightarrow F^-(g)\ \Delta H_2$

(iii) $Cl(g) + e^- \rightarrow Cl^-(g)\ \Delta H_3$ (iv) $O^-(g) + e^- \rightarrow O^{2-}(g)\ \Delta H_4$

Then according to given information, the correct statement is/are

(a) ΔH_3 is more negative than ΔH_1 and ΔH_2 (b) ΔH_1 is less negative than ΔH_2

(c) ΔH_1, ΔH_2, ΔH_3 are negative whereas ΔH_4 is positive

(d) ΔH_1 and ΔH_3 are negative whereas ΔH_2 and ΔH_4 are positive

19. Consider order $O^{2-} < F^- < Na^+ < Mg^{2+}$

Then correct statement is/are

(a) Increasing order of Zeff (b) Increasing order of size

(c) Increasing order of IE (d) Increasing order of EA

20. The value of four quantum number (n, *l*, m, s) for any electron of element X are 4, 3, –2, –1/2, then correct statement regarding element X is

(a) Element X may belong to lanthanide series

(b) It may belong to actinide series

(c) It may belong 2nd transition series (d) It may belong 3rd transition series

21. Which of the following ionisation energy order is/are correct.

(a) $Be^+ > B^{2+}$ (b) $C^{3+} > B^{2+}$ (c) $N^{4+} < O^{5+}$ (d) $F^{6+} < C^{3+}$

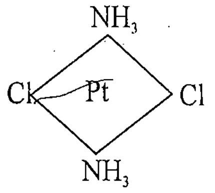
EXERCISE - III

Subjective and Numerical Answer Type

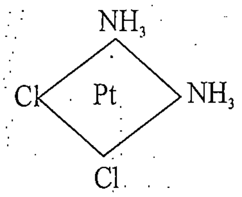
1. If internuclear distance between Cl atoms in Cl_2 is 10 Å & between H atoms in H_2 is 2 Å, then calculate internuclear distance between H & Cl (Electronegativity of H = 2.1 & Cl = 3.0).

2. The Pt-Cl distance has been found to be 2.32 Å in several crystalline compounds. If this value applies to both of the compounds shown in figure. What is Cl - Cl distance in (a) and (b)

(a)



(b)



3. Calculate E.N. of chlorine atom on Pauling scale if I.E. of Cl^- is 4eV & of E.A. of Cl^+ is + 13.0 eV.

4. Calculate the electronegativity of fluorine from the following data :

$E_{H-H} = 104.2$ kcal mol^{-1} $E_{F-F} = 36.2$ kcal mol^{-1}

$E_{H-F} = 134.6$ kcal mol^{-1} $X_H = 2.1$

5. How many chlorine atoms will be ionised $Cl \longrightarrow Cl^+ + e^-$ by the energy released from the process $Cl + e^- \longrightarrow Cl^-$ for 6.02×10^{23} atoms (I.P. for Cl = 1250 kJ mol^{-1} and E.A. = 350 kJ mole^{-1})

6. Calculate E.N. of flourine if $(r_F)_{covalent} = 0.72$ Å.

7. Calculate the screening constant of Ca . (atomic number 20)

8. The maximum number of electron that can have principal quantum number n = 3 and spin quantum number, $m_s = -\frac{1}{2}$ is

9. What is maximum number of electrons that may be present in all atomic orbital with principal quantum number 3 and azumuthal quantum number 2

10. If an electron has 3 spin values $\left(-\frac{1}{2}, 0, +\frac{1}{2}\right)$ then what will be maximum number of elements in 6th period?

EXERCISE - IV

Previous Year Questions

IIT-JAM Previous Year

1. Among the following, the isoelectronic pair is:
   (a) NO and CO (b) O_2^- (superoxide anion) and NO^-
   (c) NO^+ and CO (d) O_2^- (superoxide anion) and NO^+

2. Among lithium, nitrogen, carbon and oxygen which element has the highest first ionization potential?
   (a) lithium (b) nitrogen (c) carbon (d) oxygen

3. Identify the correct option:
   In the Periodic Table, on moving from left to right among a period,
   (a) the atomic size of the element increases
   (b) the first ionization potential of the element decreases
   (c) the oxide of the element becomes less basic
   (d) the oxide of the element becomes more basic

4. The decreasing order of the first ionization energy of the following elements is
   (a) He > H > Be > B (b) Be > B > H > He (c) H > He > Be > B (d) B > Be > He > H

5. The degree of hydration is expected to be maximum for
   (a) Mg^{2+} (b) Na^+ (c) Ba^{2+} (d) K^-

6. The decreasing order of the first ionization energy of the following elements is
   (a) Xe > Be > As > Al (b) Xe > As > Al > Be
   (c) Xe > As > Be > Al (d) Xe > Be > Al > As

Net & Gate Previous year Questions

7. The size of the d orbitals in Si, P, S and Cl follows the order
   (a) Cl > S > P > Si (b) Cl > P > S > Si (c) P > S > Si > Cl (d) Si > P > S > Cl

8. The electronegativity differences is the highest for the pair
   (a) Li, Cl (b) K, F (c) Na, Cl (d) Li, F

9. The correct order of decreasing electronegativity of the following atoms is
   (a) As > Al > Ca > S (b) S > As > Al > Ca (c) Al > Ca > S > As (d) S > Ca > As > Al

10. The correct order of the size of S, S^{2-}, S^{2+} and S^{4+} species is
(a) $S > S^{2+} > S^{4+} > S^{2-}$ (b) $S^{2+} > S^{4+} > S^{2-} > S$
(c) $S^{2-} > S > S^{2+} > S^{4+}$ (d) $S^{4+} > S^{2-} > S > S^{2+}$

11. The series with correct order of decreasing ionic size is
(a) $K^+ > Ca^{2+} > S^{2-} > Cl^-$ (b) $S^{2-} > Cl^- > K^+ > Ca^{2+}$
(c) $K^+ > Cl^- > Ca^{2+} > S^{2-}$ (d) $Cl^- > K^+ > S^{2-} > Ca^{2+}$

IIT-JEE Previous Year Questions

Single Choice

12. The correct order of second ionization potential of carbon, nitrogen, oxygen and fluorine is
(a) C > N > O > F (b) O > N > F > C (c) O > F > N > C (d) F > O > N > C

13. The element with the highest first ionization potential is
(a) boron (b) carbon (c) nitrogen (d) oxygen

14. The hydration energy of Mg^{2+} is larger than that of
(a) Al^{3+} (b) Na^+ (c) Be^{2+} (d) Mg^{3+}

15. The first ionization potential in electron volts of nitrogen and oxygen atoms are respectively given by
(a) 14.6, 13.6 (b) 13.6, 14.6 (c) 13.6, 13.6 (d) 14.6, 14.6

16. Atomic radii of fluorine and neon in Angstrom units are respectively given by
(a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) None of these

Imp 17. The electronegativity of the following elements increases in the order
(a) C, N, Si, P (b) N, Si, C, P (c) Si, P, C, N (d) P, Si, N, C

18. The first ionization potential of Na, Mg, Al and Si are in the order
(a) Na < Mg > Al < Si (b) Na > Mg > Al > Si
(c) Na < Mg < Al > Si (d) Na > Mg > Al < Si

19. Which one of the following is the smallest in size?
(a) N^{3-} (b) O^{2-} (c) F^- (d) Na^+

20. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is
(a) [Ne] $3s^2 3p^1$ (b) [Ne] $3s^2 3p^3$ (c) [Ne] $3s^2 3p^2$ (d) [Ar] $3d^{10} 4s^2 4p^3$

Check 21. The statement that is not correct for the periodic classification of elements, is
(a) The properties of elements are the periodic functions of their atomic numbers
(b) Non-metallic elements are lesser in number than metallic elements.
(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements the d-subshells are filled with electrons monotonically with increase in atomic number.

22. Which has most stable +2 oxidation state?
(a) Sn (b) Pb (c) Fe (d) Ag

23. Which of the following has the maximum number of unpaired electrons?
(a) Mg^{2+} (b) Ti^{3+} (c) V^{3+} (d) Fe^{2+}

24. The incorrect statement among the following is
(a) The first ionization potential of Al is less than the first ionization potential of Mg
(b) The second ionization potential of Mg is greater than the second ionization potential of Na
(c) The first ionization potential of Na is less than the first ionization potential of Mg
(d) The third ionization potential of Mg is greater than third ionization potential of Na

25. The correct order of radii is
(a) $N < Be < B$ (b) $F^- < O^{2-} < N^{3-}$ (c) $Na < Li < K$ (d) $Fe^{3+} < Fe^{2+} < Fe^{4+}$

26. The set representing the correct order of first ionization potential is
(a) $K > Na > Li$ (b) $Be > Mg > Ca$ (c) $B > C > N$ (d) $Ge > Si > C$

27. Identify the least stable ion amongst the following
(a) Li^+ (b) Be^- (c) B^- (d) C^-

One or more than one correct option

28. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because
(a) the hydration energy of sodium sulphate is more than its lattice energy
(b) the lattice energy of barium sulphate is more than its hydration energy
(c) the lattice energy has no role to play in solubility
(d) the hydration energy of sodium sulphate is less than its lattice energy

29. Ionic radii of
(a) $Ti^{4+} < Mn^{7+}$ (b) $^{35}Cl^- < {}^{37}Cl^-$ (c) $K^+ > Cl^-$ (d) $P^{3+} > P^{5+}$

ANSWER KEY

EXERCISE - I

1. c	2. d	3. b	4. d	5. b	6. c	7. b
8. b	9. d	10. a	11. b	12. a	13. c	14. d
15. c	16. a	17. c	18. d	19. b	20. b	21. a
22. c	23. d	24. d	25. c	26. b	27. a	28. d
29. c	30. a	31. a	32. c	33. a	34. c	35. b
36. a	37. b	38. b	39. d	40. b	41. c	42. b
43. b	44. c	45. c	46. b	47. c	48. a	49. b
50. c	51. c	52. b	53. d	54. d	55. b	56. c
57. c	58. c	59. b	60. c	61. b	62. a	63. b
64. a	65. b	66. c	67. a	68. b	69. b	70. c
71. c	72. d	73. d	74. b	75. a	76. b	77. a
78. b	79. a	80. a				

EXERCISE - II

1. a,c	2. a,b,d	3. a,c	4. a,b	5. a,b,d	6. a,b	7. b,c,d
8. a,c,d	9. b,d	10. a,b,c	11. a,c,d	12. a,c	13. a,b,c	14. a,c
15. a,b	16. b,c	17. c,d	18. a,b,c	19. a,c,d	20. a,b,c,d	21. b,c

EXERCISE - III

1. 5.919 Å	2. (a) 4.64 (b) 3.28
3. 3.03	4. 3.8752
5. 1.686×10^{23} atoms	6. 4.1
7. 17.15	8. 9
9. 10	10. 48

EXERCISE - IV

1. c	2. b	3. c	4. a	5. a	6. c	7. d
8. b	9. b	10. c	11. b	12. c	13. c	14. b
15. a	16. a	17. c	18. a	19. d	20. b	21. d
22. b	23. d	24. b	25. b	26. b	27. b	28. a,b
29. d						

CHAPTER 2

CHEMICAL BONDING

RULES FOR LEWIS STRUCTURE DRAWING

(1) Calculate n_1 = no. of valence shell electrons of all atoms + no. of negative charge (if any) – no. of positive charge (if any)

(2) Calculate n_2 = (no. of H-atom × 2) + (no. of atoms other than H-atoms × 8)

(3) Calculate $n_3 = n_2 - n_1 \Rightarrow$ no. of shared electrons;

i.e. number of bonds $= \frac{n_3}{2}$ ...(a)

(4) Calculate $n_4 = n_1 - n_3 \Rightarrow$ no. of unshared electrons;

i.e. no. of lone pairs $= \frac{n_4}{2}$ ....(b)

Using the informations (a) & (b) the structure is to be assigned as follows :

(i) Find out the central atom first (i.e. either least in number or more electro positive)

(ii) Allocate the surrounding atoms around the central atom with the help of bonds available in (a).

(iii)To fulfill the octet of each atom, utilise the lone pairs available in (b).

(iv)Finally calculate the formal charge for each atom and assign the atoms according to the formula given

F.C. (on an atom) = Valence shell electron of that atom – no. of bonds associated with it – no. of unshared electrons on it.

Important points in resonance

(i) The canonical forms should have the same number of unpaired electrons.

(ii) In the case of charge separation, if the adjacent atoms bear the same charge then the electrostatic repulsion will destabilise the structure.

(ii) Placement of opposite charge on the adjacent atoms stabilises the system through an electrostatic interaction.

(iv)The canonical forms in which the negative charge resides on the electronegative atoms contribute more.

FORMAL CHARGE

The formal charge is the charge which an atom would have if electron pairs were shared equally; **Lewis structures with low formal charges typically have the lowest energy.**

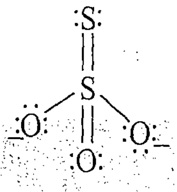
Formal charge of an atom is the difference between the number of valence electrons in an isolated atom (i.e. free atom) and the number of electrons assigned to that atom in a Lewis structure.

$$\begin{bmatrix}\text{Formal}\\ \text{charge on}\\ \text{atom in}\\ \text{Lewis structure}\end{bmatrix} = \begin{bmatrix}\text{Total number}\\ \text{of valence}\\ \text{electrons on free}\\ \text{atoms}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{Total number}\\ \text{of shared}\\ \text{electrons}\end{bmatrix} - \begin{bmatrix}\text{Total number}\\ \text{of unshared}\\ \text{valence electrons}\end{bmatrix}$$

$$\boxed{q_F = n_A - \frac{1}{2}n_{bp} - n_{lp}}$$

Example:

$S_2O_3^{2-}$:



$$q_F(S_{centre}) = 6 - 0 - \frac{1}{2}\times 12 = 0$$

$$q_F(S_{terminal}) = 6 - 4 - \frac{1}{2}\times 4 = 0$$

$$q_F(O) = 6 - 4 - \frac{1}{2}\times 4 = 0$$

$$q_F(O^-) = 6 - 6 - \frac{1}{2}\times 2 = -1$$

Calculation of Hybridisation:

Steric no. = 1/2 [V + M ± Q]

V = volume shell electron of central atom

M = No. of monovalent atoms (H, X)

Q = Charge on species (+ for anionic species; – for cationic species)

Table: Types of Hybridisation

S.N.	Hybridisation	s-character	p-character	d-character	Shape
2	sp	50%	P_z along the axis 50%	-	Linear
3	sp^2	33.33%	Along the axis P_z, P_x or P_y : 66.67%	-	Trigonal Planar
4	sp^3	25%	P_x, P_y, P_z : 75%	-	Tetrahedral
5	sp^3d	33.33%	$P_{x,y}$: 66.67%, P_z :50%	d_{z^2} 50%	Trigonal bipyramidal
6	sp^3d^2	16.67%	P_x, P_y, P_z : 50%	$d_{x^2-y^2}$ & d_{z^2} : 33.33%	Octahedral

Orbital analysis of hybridisation

$$\cos\theta = \frac{-1}{i} \text{ where, } \theta = \text{bond angle; } i = \frac{\%\text{P character}}{\%\text{S character}}$$

knowing the value of i, we can determine hybridisation which is equal to **sp^i**

$$\cos\theta = \frac{S}{S-1} = \frac{P-1}{P}$$

Table: Idealised orientation of the electron pairs leading to the minimum repulsion around the central atom.

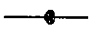
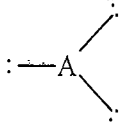
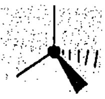
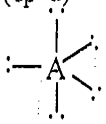
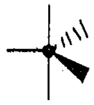
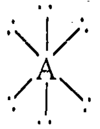
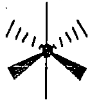
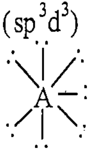
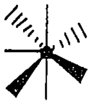
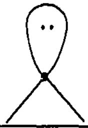
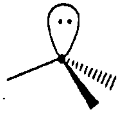
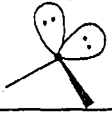
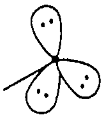
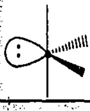
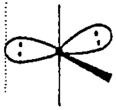
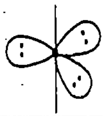
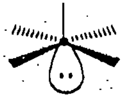
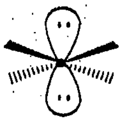
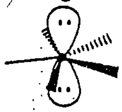
No. of σ-bonding pairs (considering no non-bonding pair)	Geometrical position of the σ-bonding pairs	Bond angle $X\hat{A}X$	Shape	Examples
(i) 2	Linear (sp); :—A—:	180°		NO_2^+, N_2O, CO_2, CdI_2, $HgCl_2$, $Ag(CN)_2^-$, etc.
(ii) 3	Trigonal planar (sp^2); 	120°		BX_3(X = F, Cl, Br, R), O = CCl_2, SO_3, NO_3^-, CO_3^{2-}, CH_3^+ etc.
(iii) 4	Tetrahedron (sp^3) 	109°28'		CH_4, NH_4^+, BF_4, AsH_4^+, PH_4^+, SnX_4, SO_4^{2-}, O = PF_3, ClO_4^-, PCl_4^+, XeO_4, $S_2O_3^{2-}$, PO_4^{3-}, SiO_4^{4-}, BH_4^-, SO_2Cl_2 etc.
(iv) 5	Trigonal bipyramid (sp^{3}d) 	90 ($X_{ax}\hat{A}X_{eq}$) 120° ($X_{eq}\hat{A}X_{eq}$)		XeO_3F_2, PCl_5, $SbCl_5$, VF_5, etc.
(v) 6	Octahedron (sp^{3}d^2) 	90°		SeF_6, TeF_6, SF_6, PX_6^-, SiF_6^{2-}, S_2F_{10}, XeO_6^{4-} etc.
(vi) 7	Pentagonal bipyramid (sp^{3}d^3)  Capped octahedron Capped trigonal prism	90 ($X_{ax}\hat{A}X_{eq}$) 72° ($X_{eq}\hat{A}X_{eq}$)		IF_7, ReF_7, etc.

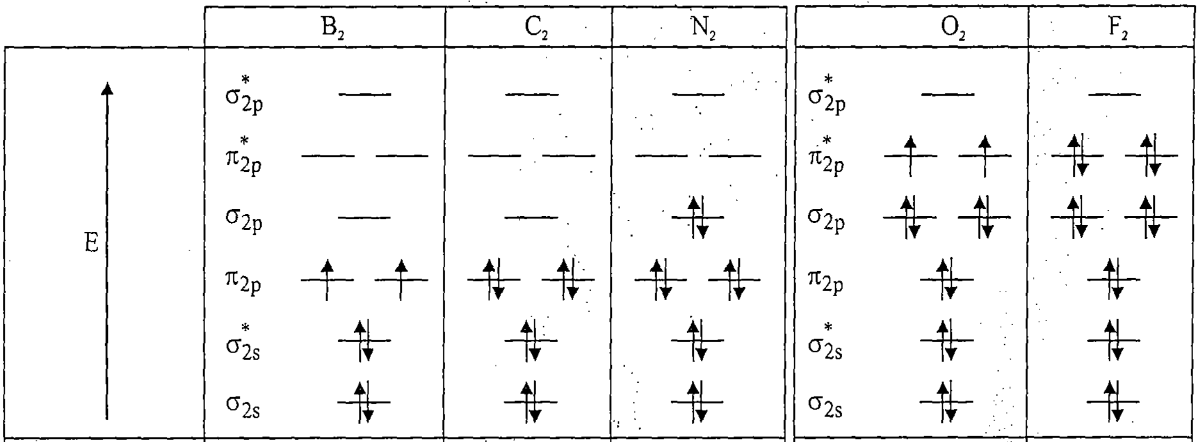
Table: Shape of some molecules having stereochemically active lone pairs according to VSEPR theory

Number of *l*p + bp	Geometry for the distribution of electron pair domains	Types of electron pairs	Configuration shape	Examples
3	Triangular (sp^2)	2 bp + 1 *l*p	V-shaped 	$SnCl_2$, $PbCl_2$, SO_2, GeF_2, NO_2^-
4	Tetrahedral (sp^3)	3 bp + 1 *l*p	Trigonal pyramidal 	NH_3, NR_3, H_3O^+, PX_3, XeO_3, NF_3, XO_3^- (X = Cl, Br, I), SO_3^{2-}, CH_3^-
		2bp + 2 *l*p	V-shaped 	H_2O, F_2O, Cl_2O, SCl_2, XO_2^- (X = Cl, Br, I)
		1 bp + 3 *l*p	Linear 	HX, OX^- (X = Cl, Br, I)
5	Trigonal bipyramidal (sp^3d)	4 bp + 1 *l*p	Distorted tetrahedral 	$TeBr_4$, SF_4, $TeCl_4$, XeO_2F_2
		3 bp + 2 *l*p	T-shaped 	ClF_3, BrF_3, XeF_3^+, $XeOF_2$
		2 bp + 3 *l*p	Linear 	XeF_2, ICl_2^-, I_3^-
6	Octahedral (sp^3d^2)	5 bp + 1 lp	Square pyramidal 	BrF_5, IF_5, TeF_5^-, $XeOF_4$, XeF_5^+
		4 bp + 2 *l*p	Square planar 	ICl_4^-, BrF_4^-, XeF_4
7	Pentagonal bipyramid (sp^3d^3)	6 bp + 1 *l*p	Distorted octahedraon	XeF_6, $XeOF_5^-$
		5 bp + 2 *l*p	Pentagonal planar 	XeF_5^-

Summary of Electronic Configurations of Molecular Orbitals of 1st and 2nd row diatomic Molecules

Molecule	E.C.	Unpaired e⁻	Bond order
H_2^+	$\sigma 1s^1$	1	0.5
H_2	$\sigma 1s^2$	0	1
H_2^-	$\sigma 1s^2 \sigma^* 1s^1$	1	0.5
He_2^+	$\sigma 1s^2 \sigma^* 1s^1$	1	0.5
He_2	$\sigma 1s^2 \sigma^* 1s^2$	0	0
He_2^-	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^1$	1	0.5
Li_2^+	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^1$	1	0.5
Li_2	$KK\sigma 2s^2$	0	1
Li_2^-	$KK\sigma 2s^2 \sigma^* 2s^1$	1	0.5
Be_2	$KK\sigma 2s^2 \sigma^* 2s^2$	0	0
B_2	$KK\sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^1 \pi 2p_z^1$	2	1
C_2	$KK\sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^2 \pi 2p_z^2$	0	2
N_2	$KK\sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^2 \pi 2p_z^2 \sigma 2p_x^2$	0	3
N_2^+	$KK\ LL\ \pi 2p_y^2 \pi 2p_z^2 \sigma 2p_x^1$	1	2.5
N_2^-	$KK\ LL\ \pi 2p_y^2 \pi 2p_z^2 \sigma 2p_x^2 \pi^* 2p_y^1$	1	2.5
O_2^+	$KK\ LL\ \sigma 2p_x^2 \pi 2p_y^2 \sigma 2p_2^2 \pi^* 2p_y^1$	1	2.5
O_2	$KK, LL\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^1 \pi^* 2p_z^1$	2	2
O_2^-	$KK, LL\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^1$	1	1.5
O_2^{2-}	$KK, LL\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^2$	0	1.0
F_2	$KK, LL\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^2$	0	1
Ne_2	$KK, LL\ \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^2 \sigma^* 2p_x^2$	0	0

Table. Molecular Orbital Summary of Second Row Diatomic Molecules



	B_2	C_2	N_2	O_2	F_2
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

EXERCISE - I

(Single Correct Type)

Hybridization

1. A sigma bond may be formed by the overlap of 2 atomic orbitals of atoms A and B. If the bond is formed along the x-axis, which of the following overlaps is acceptable ?

(a) s orbital of A and p_z orbital of B (b) p_x orbital of A and p_y orbital of B

(c) p_z orbital of A and p_x orbital of B (d) p_x orbital of A and s orbital of B

2. Which of the following statements is/are true?

(a) Covalent bonds are directional (b) Ionic bonds are directional

(c) A polar bond is formed between two atoms which have the same electronegativity value.

(d) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment

3. Which of the following species are hypervalent?

1. ClO_4^-, 2. BF_3, 3. SO_4^{2-}, 4. CO_3^{2-}

(a) 1, 2, 3 (b) 1, 3 (c) 3, 4 (d) 1, 2

4. The types of bond present in N_2O_5 are

(a) only covalent (b) only ionic (c) ionic and covalent (d) covalent & coordinate

5. Which of the following molecules does not have coordinate bonds?

(a) $CH_3–NC$ (b) CO (c) O_3 (d) CO_3^{2-}

6. The strength of bonds by $s-s, p-p, s-p$ overlap is in the order in which shell :

(a) $s-s<s-p<p-p$ (b) $s-s<p-p<s-p$

(c) $s-p<s-s<p-p$ (d) $p-p<s-s<s-p$

7. Which of the following has a geometry different from the other three species?

(a) BF_4^- (b) SO_4^{2-} (c) XeF_4 (d) PH_4^+

8. Number and type of bonds between two carbon atoms in CaC_2 are :

(a) one sigma (σ) and one pi (π) bond (b) one σ and two π bonds

(c) one σ and one and a half π bond (d) one σ bond

9. If $C-C$ bond in C_2H_6 undergoes heterolytic fission, the hybridisation of two resulting carbon atoms is/are

(a) sp^2 both (b) sp^3 both (c) sp^2, sp^3 (d) sp, sp^2

10. In the context of carbon, which of the following is arranged in the correct order of electronegativity:

(a) $sp > sp^2 > sp^3$ (b) $sp^3 > sp^2 > sp$ (c) $sp^2 > sp > sp^3$ (d) $sp^3 > sp > sp^2$

11. Carbon atoms in $C_2(CN)_4$ are :

(a) sp-hybridized (b) sp^2-hybridized

(c) sp- and sp^2 hybridized (d) sp, sp^2 and sp^3 - hybridized

12. There is change in the type of hybridisation when:

(a) NH_3 combines with H^+ (b) AlH_3 combines with H^-

(c) NH_3 forms NH_2^- (d) SiF_4 forms $Si(OH)_4$

13. The bond angle in PH_3 is :

(a) Much lesser than NH_3 (b) Equal to that in NH_3

(c) Much greater than in NH_3 (d) Slightly more than in NH_3

14. Which one of the following compounds has bond angle as nearly 90° ?

(a) NH_3 (b) H_2S (c) H_2O (d) CH_4

15. The compound which contains ionic as well as covalent bonds is

(a) $C_2H_4Cl_2$ (b) CH_3I (c) KCN (d) H_2O_2

16. 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

17. In which of the following C–H bond has the highest 's' character ?

(a) acetylene (b) ethylene (c) methane (d) CH radical

18. The correct order of d_{C-H} in the following option is

(a) $CHF_3 = CH_2F_2 = CH_3F$ (b) $CHF_3 > CH_2F_2 > CH_3F$

(c) $CH_2F_2 > CH_3F > CHF_3$ (d) $CH_3F > CH_2F_2 > CHF_3$

19. The strongest $P-O$ bond is found in the molecule.

(a) F_3PO (b) Cl_3PO (c) Br_3PO (d) $(CH_3)_3PO$

VSEPR/NBEPR

20. CO_2 has the same geometry as :

(I) $HgCl_2$ (II) NO_2 (III) $SnCl_4$ (IV) C_2H_2

(a) I and III (b) II and IV (c) I and IV (d) III and IV

21. Which of the following pairs is isostructural?

(a) SF_4 and SiF_4 (b) SF_6 and SiF_6^{2-} (c) SiF_6^{2-} and SeF_6^{2-} (d) XeO_6^{4-} and TeF_6^{2-}

22. The correct order of increasing $X-O-X$ bond angle is ($X = H, F$ or Cl) :

(a) $H_2O > Cl_2O > F_2O$ (b) $Cl_2O > H_2O > F_2O$

(c) $F_2O > Cl_2O > H_2O$ (d) $F_2O > H_2O > Cl_2O$

23. $H-B-H$ bond angle in BH_4^- is :

(a) 180° (b) 120° (c) 109° (d) 90°

24. The correct order of the bond angles is

(a) $NH_3 > H_2O > PH_3 > H_2S$ (b) $NH_3 > PH_3 > H_2O > H_2S$

(c) $NH_3 > H_2S > PH_3 > H_2O$ (d) $PH_3 > H_2S > NH_3 > H_2O$

25. Which of the following species has linear shape?

(a) O_3 (b) NO_2^- (c) SO_2 (d) NO_2^+

26. The molecular shapes of SF_4, CF_4 and XeF_4 are

(a) different with 1, 0 and 2 lone pairs on central atom

(b) different with 0, 1, 2 lone pairs on central atom.

(c) same with 1, 1, 1 lone pairs on central atom.

(d) same with 2, 0, 1 lone pairs on central atom.

27. The shape of $[BrF_4]^+$ ion is

(a) Regular tetrahedron (b) Square planar

(c) Trigonal pyramidal (d) See-saw OR irregular tetrahedron

28. Specify the co-ordination geometry around and hybridization of N and B atoms in 1 : 1 complex of BF_3 and NH_3.

(a) N : tetrahedral, sp^3; B : tetrahedral, sp^3 (b) N : pyramidal, sp^3; B : pyramidal, sp^3

(c) N : pyramidal, sp^3 ; B : planar, sp^2 (d) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

29. The shape of O_2F_2 is similar to that of :

(a) C_2F_2 (b) H_2O_2 (c) H_2F_2 (d) C_2H_2

30. Arrange the following in order of decreasing $N-O$ bond length : NO_2^+, NO_2^-, NO_3^-

(a) $NO_3^- > NO_2^+ > NO_2^-$ (b) $NO_3^- > NO_2^- > NO_2^+$

(c) $NO_2^+ > NO_3^- > NO_2^-$ (d) $NO_2^- > NO_3^- > NO_2^+$

31. Identify isostructural pairs from NF_3(I), NO_3^-(II), BF_3(III), H_3O^+(IV), HN_3(V)

(a) I & II, III & IV (b) I & V, II & III (c) I & IV, II & III (d) I & IV, III & V

32. Match list I with list II and select the correct answer:

	List I (species)		List II (O–N–O angle)
A.	NO_2^+	1.	180°
B.	NO_2	2.	134°
C.	NO_2^-	3.	120°
D.	NO_3^-	4.	115°
		5.	109°

	A	B	C	D		A	B	C	D
(a)	5	4	3	2	(b)	5	2	4	3
(c)	1	2	4	3	(d)	1	4	3	2

33. Among the following species identify the isostructural pairs.

$$NF_3, NO_3^-, BF_3, H_3O^+, N_3H$$

(a) [NF_3, NO_3^-] and [BF_3, H_3O^+] (b) [NF_3, N_3H] and [NO_3^-, BF_3]

(c) [NF_3, H_3O^+] and [NO_3^-, BF_3] (d) [NF_3, H_3O^+] and [N_3H, BF_3]

34. Which of the following molecule has a planar geometry ?

(a) $Ni(CO)_4$ (b) SF_4 (c) $CoCl_4^{2-}$ (d) XeF_4

35. The xenon compounds that are isotructural with IBr_2^- and BrO_3^- respectively are :

(a) linear XeF_2 and pyramidal XeO_3 (b) bent XeF_2 and pyramidal XeO_3

(c) bent XeF_2 and planar XeO_3 (d) linear XeF_2 and tetrahedral XeO_3

36. The correct order of hybridization of the central atom in the following species

$$NH_3, XeO_2F_2, SeF_4, NO_2^+$$

(a) sp^3, sp^3, sp^3d, sp (b) sp^3, sp^3d, sp^3d, sp

(c) $sp^3, sp^3d^2, sp^3d, sp^2$ (d) sp^3, sp^3d, sp^3d^2, sp

37. Which of the following pairs of species have identical shapes?

(a) NO_2^+ and NO_2^- (b) PCl_5 and BrF_5 (c) XeF_4 and ICl_4^- (d) $TeCl_4$ and XeO_4

38. The structure of O_3 and N_3^- are

(a) Both linear (b) Linear and bent respectively.

(c) Both bent (d) Bent and linear respectively.

d-Orbital Participation

39. The shapes of IF_5 and IF_7 are respectively :

(a) square pyramidal and pentagonal bipyramidal

(b) octahedral and pyramidal

(c) trigonal bipyramidal and square antiprismatic

(d) distorted square planar and distorted octahedral

40. Which of the following has not octahedral geometry :

(a) $SbCl_6^-$ (b) $SnCl_6^{2-}$ (c) XeF_6 (d) IO_6^{5-}

41. The structure of XeF_6 is :

(a) pentagonal bipyramidal (b) octahedral (c) capped octahedral (d) square pyramidal

42. In which of the following molecule are all the bonds not equal?

(a) NF_3 (b) ClF_3 (c) BF_3 (d) AlF_3

43. In $ICl_4^{\ominus}$, the shape is square planar. The number of bond pair-lone pair repulsion at 90° are:

(a) 6 (b) 8 (c) 12 (d) 4

44. The cationic part of solid Cl_2O_6 is having the "__________" shape.

(a) linear (b) angular (c) Tetrahedron (d) undefined

45. In case of PF_5, the ground state trigonal bipyramidal (TBP) structure converts into transition state and back to a new TBP structure. The hybridisation of central atom phosphorus in the transition state is.

(a) $sp^3d_{z^2}$ (b) $sp^3d_{x^2-y^2}$ (c) sp^2 (d) $sp^3d_{x^2-y^2}d_{z^2}$

46. Which of the following statement is correct regarding BrF_5 and $BrCl_5$?

(a) Both have equal X – Br – X bond angle (b) $\angle F - Br - F = \angle Cl - Br - Cl$

(c) $\angle F - Br - F > \angle Cl - Br - Cl$ (d) Both are isostructural

47. According to VSEPR theory, the geometry (with lone pair) around the central iodine in I_3^+ and I_3^- ions respectively are

(a) tetrahedral and tetrahedral (b) trigonal bipyramidal and trigonal bipyramidal

(c) tetrahedral and trigonal bipyramidal (d) tetrahedral and octahedral

48. Which of the following sets of orbitals has/have same geometry?

(a) $sp_z, p_zd_{z^2}$ (b) sp^3, d^3s (c) Both (d) None of these

49. F-As-F bond angle in AsF_3Cl_2 can be

(a) 90° & 180° only (b) 120° only (c) 90° & 120° only (d) 90° only

50. Which of the following shape can not be obtained from sp^3d^2 hybridisation.

(a) Square planar (b) Square pyramidal (c) Tetrahedral (d) Octahedral

51. Which of the following set of species have planar structures

(a) $I_3^-, \dot{C}H_3, ClO_3^-, SiF_6^{2-}$ (b) $I_3^+, ICl_4^-, TeCl_4, CCl_4$

(c) $SCl_2, N_2O_5, SF_4, XeOF_4$ (d) $H_2O, XeF_2, BrF_4^-, BF_3$

MOT

52. Which of the following is diamagnetic –

(a) O_2^+ (b) O_2 (c) O_2^- (d) O_2^{2-}

53. The bond energy order of He_2^+ and HeH^+ is

(a) $He_2^+ > HeH^+$ (b) $HeH^+ = He_2^+$ (c) $HeH^+ > He_2^+$ (d) Can't be predicted

54. In the cyanide ion the negative charge is on

(a) *C* (b) *N* (c) Both *C* and *N* (d) Resonate between *C* and *N*

55. Mg_2C_3 reacts with water forming propyne, C_3^{4-} has:

(a) two sigma and two pi bonds (b) three sigma and one pi bonds

(c) two sigma and one pi bonds (d) two sigma and three pi bonds

56. During the formation of a molecular orbital from atomic orbitals, probability of electron density is:

(a) minimum in the nodal plane (b) maximum in the nodal plane

(c) zero in the nodal plane (d) zero on the surface of the lobe

57. Pick out the incorrect statement?

(a) N_2 has greater dissociation energy than N_2^+

(b) O_2 has lower dissociation energy than O_2^+

(c) Bond length in N_2^+ is less than N_2

(d) Bond length in NO^+ is less than in NO.

58. A simplified application of *MO* theory to the hypothetical 'molecule' *OF* would give its bond order as:

(a) 2 (b) 1.5 (c) 1.0 (d) 0.5

59. In the formation of N_2^+ from N_2, the electron is removed from :

(a) σ orbital (b) π orbital (c) σ^* orbital (d) π^* orbital

60. Which of the following is true?

(a) $\text{Bond order} \propto \frac{1}{\text{bond length}} \propto \text{bond energy}$ (b) $\text{Bond order} \propto \text{bond length} \propto \frac{1}{\text{bond energy}}$

(c) $\text{Bond order} \propto \frac{1}{\text{bond length}} \propto \frac{1}{\text{bond energy}}$ (d) $\text{Bond order} \propto \text{bond length} \propto \text{bond energy}$

Structures

61. Which of the following oxyacid of sulphur does not contain $S-S$ bonds ?

(a) $H_2S_2O_8$ (b) $H_2S_2O_6$ (c) $H_2S_2O_4$ (d) $H_2S_2O_5$

62. Which has higher bond energy :

(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

63. Most ionic compounds does not have :

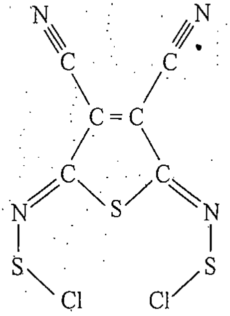
(a) high melting points and low boiling points

(b) high melting points and nondirectional bonds

(c) high solubilities in polar solvents and low solubilities in nonpolar solvents

(d) three-dimensional network structures, and are good conductors of electricity in the molten state

64. Write the maximum number of atoms having same hybridisation in 2, 5-di-N-chloridothioimino-3, 4-diazonothiophene as shown below :



(a) 4 (b) 5 (c) 6 (d) 8

65. Borax is actually made of two tetrahedra and two triangular units joined together and should be written as: $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$

Consider the following statements about borax:

a. Each boron atom has four B–O bonds

b. Each boron atom has three B–O bonds

c. Two boron atoms have four B–O bonds while other two have three B–O bonds

d. Each boron atom has one –OH groups

Select correct statement(s):

(a) a, b (b) b, c (c) c, d (d) a, c

66. Hybridization of carbon in C_3O_2 is :

(a) sp (b) sp^2 (c) sp^3 (d) sp^3d

67. The number of σ-bond and π-bond in HCP are respectively

(a) 2 and 2 (b) 1 and 3 (c) 2 and 1 (d) None

68. The hybridisation of C-atoms in tetracyanomethane is

(a) sp, sp^2 (b) sp^3, sp (c) sp^3, sp^3 (d) sp^3, sp^2

Hydrogen Bonding / Weak Forces

69. The hydration of ionic compounds involves :

(a) Evolution of heat (b) Weakening of attractive forces

(c) Dissociation into ions (d) All of these

70. Which of the following, when dissolved in water forms a solution, which shows Non-conductivity?

(a) Green Vitriol (b) Indian salt Petre (c) Alcohol (d) Potash alum

71. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :

(a) resonance (b) coordinate bonding

(c) hydrogen bonding (d) ionic bonding

72. Arrange the following in order of decreasing boiling point :

(I) *n*-Butane (II) *n*-Butanol (III) *n*-Butyl chloride (IV) Isobutane

(a) $IV > III > II > I$ (b) $IV > II > III > I$ (c) $I > II > III > IV$ (d) $II > III > I > IV$

73. Which of the following compounds would have significant intermolecular hydrogen bonding ?

HF, CH_3OH, N_2O_4, CH_4

(a) HF, N_2O_4 (b) HF, CH_4, CH_3OH (c) HF, CH_3OH (d) CH_3OH, CH_4

74. Which of the following molecules are expected to exhibit intermolecular H–bonding

I. Acetic acid II. o-nitrophenol III. m–nitrophenol IV. o–boric acid

(a) I, II, III (b) I, II, IV (c) I, III, IV (d) II, III, IV

75. Intramolecular hydrogen bonding is found in :

(a) Salicylaldehyde (b) Water (c) Acetaldehyde (d) Phenol

76. The volatility of HF is low because of :

(a) its low polarizability

(b) the weak dispersion interaction between the molecules

(c) its small molecular mass (d) its strong hydrogen bonding

77. Which one of the following does not have intermolecular H-bonding?

(a) H_2O (b) *o*-nitro phenol (c) HF (d) CH_3COOH

78. Which of the following exhibit/s H-bonding?

(a) CH_4 (b) H_2Se (c) N_2H_4 (d) H_2S

79. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :

(a) van der Waal's forces (b) Covalent attraction

(c) Hydrogen bond formation (d) Dipole-dipole attraction

Dipole Moment

80. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atm. no. < 21) are :

(a) pure p (b) sp hybrid (c) sp^2 hybrid (d) sp^3 hybrid.

81. Among the following compounds, the one that is polar and has the central atom with sp^2 hybridisation is.

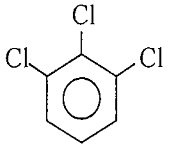
(a) H_2CO_3 (b) SiF_4 (c) BF_3 (d) $HClO_2$

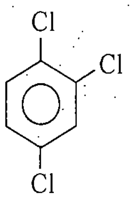
82. Which of the set of isomers of $C_6H_4Cl_2$ is having equal dipole moment with C_6H_5Cl and C_6H_6 respectively

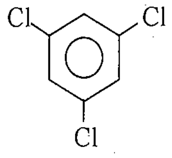
(a) ortho and meta (b) meta and para

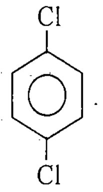
(c) ortho and para (d) para and ortho

83. Which has maximum dipole moment?

(a) 

(b) 

(c) 

(d) 

84. Which of the following has been arranged in order of decreasing dipole moment ?

(a) $CH_3Cl > CH_3F > CH_3Br > CH_3I$
(b) $CH_3F > CH_3Cl > CH_3Br > CH_3I$
(c) $CH_3Cl > CH_3Br > CH_3I > CH_3F$
(d) $CH_3F > CH_3Cl > CH_3I > CH_3Br$

85. The experimental value of the dipole moment of HCl is 1.03 D. The length of the $H-Cl$ bond is $1.275\mathring{A}$. The percentage of ionic character in HCl is :

(a) 43 (b) 21 (c) 17 (d) 7

Fajan's Rule

86. Amongst $LiCl, RbCl, BeCl_2$ and $MgCl_2$, the compounds with the greatest and the least ionic character, respectively are :

(a) $LiCl$ and $RbCl$ (b) $RbCl$ and $BeCl_2$ (c) $RbCl$ and $MgCl_2$ (d) $MgCl_2$ and $BeCl_2$

87. Compound with maximum ionic character is formed from :

(a) Na and Cl (b) Cs and F (c) Cs and I (d) Na and F

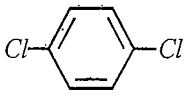
EXERCISE - II

Multiple Answer Type

1. Which have fractional bond order?

(a) O_2^+ (b) O_2^- (c) NO (d) H_2^+

2. Which (have) zero value of dipole moment?

(a) XeF_4 (b) $CHCl_3$ (c) CO_2 (d) 

3. Which of the following have planar structure?

(a) I_3^- (b) H_2O (c) PCl_5 (d) XeF_4

4. Which of the following have dipole moment ?

(a) nitrobenzene
(b) *p*-chloronitrobenzene
(c) *m*-dichlorobenzene
(d) *o*-dichlorobenzene

5. Resonance occurs due to the

(a) delocalization of a lone pair of electrons
(b) delocalization of sigma electrons
(c) delocalization of pi electrons
(d) migration of protons

6. Which of the following have unpaired electron(s)

(a) O_2^+ (b) O_2^- (c) NO (d) H_2^+

7. What is the state of hybridisation of Xe in cationic part of solid XeF_6.

(a) sp^3d^3 (b) sp^3d^2 (c) sp^3d (d) sp^3

8. According to MOT (Molecular Orbital Theory), the molecular orbitals are formed by mixing of atomic orbitals through LCAO (linear combination of atomic orbitals). The correct statement(s) about molecular orbitals is/are

Statement (a) :bonding molecular orbitals are formed by addition of wave-functions of atomic orbitals of same phase

Statement (b) : anti-bonding molecular orbitals are formed by subtraction of wave-functions of atomic orbitals of same phase

Statement (c) : non-bonding molecular orbitals do not take part in bond formation because they belong to inner shells

Statement (d) : anti-bonding molecular orbitals provide stability to molecules while bonding molecular orbitals make the molecules unstable.

(a) Statement a, d (b) Statement a, b, c (c) Statement a, b, d (d) Statement a, b

9. No $X-X$ bond exists in which of the following compounds having general form of X_2H_6?

(a) B_2H_6 (b) C_2H_6 (c) Al_2H_6 (d) Si_2H_6

10. Which of the following species is (are) isostructural with XeF_4 ?

(a) ICl_4^- (b) I_5^- (c) BrF_4^- (d) XeO_4

11. Which one of the following compounds has bond angle as nearly 90° ?

(a) NH_3 (b) H_2S (c) H_2O (d) SF_6

12. The linear structure is assumed by :

(a) $SnCl_2$ (b) NCO^- (c) CS_2 (d) NO_2^+

13. Which of the following statements is/are correct ?

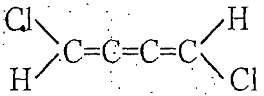
(a) NH_2^+ shows sp^2 – hybridisation whereas NH_2^- shows sp^3 – hybridisation

(b) $Al(OH)_4^-$ has a regular tetrahedral geometry

(c) sp^2 – hybridized orbitals have equal s- and p- character

(d) Usually hybridized orbitals form σ - bonds

14. Choose the correct option for the following molecule in view of chemical bonding



(a) non-planar (b) $\mu \neq 0$ (c) A & B both (d) $\mu = 0$

15. Shape of NH_3 is very similar to :

(a) SeO_3^{2-} (b) CH_3^- (c) BH_3 (d) CH_3^+

16. Polarization may be called the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is/are incorrect:

(a) Minimum polarization is brought about by a cation of low radius

(b) A large cation is likely to bring about a large degree of polarization

(c) Maximum polarization is brought about by a cation of high charge

(d) A small anion is likely to undergo a large degree of polarization

17. Pick out among the following species isoelectronic with CO_2 :

(a) N_3^- (b) $(CNO)^-$ (c) $(NCN)^{2-}$ (d) NO_2^-

18. Which is correct statement?

As the s-character of a hybrid orbital decreases

(I) The bond angle decreases (II) The bond strength increases

(III) The bond length increases (IV) Size of orbital increases

(a) (I), (III) and (IV) (b) (II), (III) and (IV)

(c) (I) and (II) (d) All are correct

19. Which of the following conditions apply to resonating structures ?

(a) The contributing structures should have nearly similar energies

(b) The contributing structures should be represented such that like charges reside on atoms that are far apart

(c) The more electropositive element should preferably have positive charge and the more electronegative element have negative charge

(d) The contributing structures must have the same number of unpaired electrons

20. A π-bond may between two p_x orbitals containing one unpaired electron each when they approach each other appropriately along :

(a) x - axis (b) y - axis (c) z - axis (d) any direction

21. During the complete combustion of methane CH_4, what change in hybridisation does the carbon atom undergo?

(a) sp^3 to sp (b) sp^3 to sp^2 (c) sp^2 to sp (d) sp^2 to sp^3

22. The octet rule is not obeyed in :

(a) CO_2 (b) BCl_3 (c) PCl_5 (d) SiF_4

23. A, B, C are three substances. A does not conduct electricity in the soild, molten state and aqueous solution. B conducts electricity both in the fused and aqueous states, while C conducts electricity only in the aqueous state. In solid state neither B nor C conducts electricity. Which of the following statements is/are true regarding A, B and C ?

(a) A has polar covalent linkage (b) A has nonpolar covalent linkage

(c) B is ionic in nature (d) Cation formed by C is highy polarizing

24. Three centre – two electron bonds exist in :

(a) B_2H_6 (b) $Al_2(CH_3)_6$ (c) $BeH_2(s)$ (d) $BeCl_2(s)$

25. Which of the following have a three dimentional network structure ?

(a) SiO_2 (b) $(BN)_x$ (c) P_4(white) (d) CCl_4

26. To which of the following species octet rule is not applicable :

(a) BrF_5 (b) SF_6 (c) IF_7 (d) CO

27. Which of the following do not exists ?

(a) SH_6 (b) HFO_4 (c) FeI_3 (d) $HClO_3$

28. Which of the following species contain coordinate bond :

(a) $AlCl_3$ (b) CO (c) $[Fe(CN)_6]^{4-}$ (d) N_3^-

29. Which of the following factors are responsible for origination of van der Waals forces ?

(a) Instantaneous dipole-induced dipole interaction

(b) Dipole-induced dipole interaction and ion-induced dipole interaction

(c) Dipole-dipole interaction and ion-induced dipole interaction

(d) Small size of molecule

30. Which of the following are true ?

(a) Van der Waals forces are responsible for the formation of molecular crystals

(b) Branching lowers the boiling points of isomeric organic compounds due to decrease in van der Waals forces of attraction

(c) In graphite, van der Waals forces act between the carbon layers

(d) In diamond, van der Waals forces act between the carbon layers

31. Which of the following species have a bond order of 3 ?

(a) CO (b) CN^- (c) NO^+ (d) O_2^+

32. Among the following, the species with one unpaired electron are :

(a) O_2^+ (b) NO (c) O_2^- (d) B_2

33. Which of the following pairs have identical values of bond order ?

(a) N_2^+ and O_2^+ (b) F_2 and Ne_2 (c) O_2^{2-} and B_2 (d) C_2 and N_2

34. Which of the following is correct ?

(a) During N_2^+ formation, one electron is removed from the bonding molecular orbitals

(b) During O_2^+ formation, one electron is removed from the antibonding molecular orbitals

(c) During O_2^- formation, one electron is added to the bonding molecular orbitals

(d) During CN^- formation, one electron is added to the bonding molecular orbitals

EXERCISE - III

Subjective and Numerical Answer Type

1. Write the number of ∠ FIF angles which are less than 90° in IF_5.
2. The number of corner or O-atom shared per tetrahedron in 2D-silicate is________.
3. The total number of bonding and antibonding electrons in O_2^+ are ".............." and "................" respectively. (If the answer is 14 and 7, then represent as 0147]
4. Find the number of plane of symmetry in CCl_4 molecule.
5. Find the maximum number of identical angle in CH_2F_2 molecule.
6. The ratio of lone pairs in XeF_2 molecule and the lone pairs on its central atom is ....
7. Count the total number of X–O bonds are having equal length in HSO_4^- and $S_3O_6^{2-}$ respectively. (If the answer is 5 and 3 then represent as 53)
8. Ratio of sp^3 and sp^2 hybridized atoms in the anionic part of Borax is _________.
   (if ans is 12 : 4 then represent as 124)
9. The number of molecules having planar structure.
   (i) BFCl Br (ii) $F_2B–C≡C–BF_2$ (iii) $(SiH_3)_3N$ (with restpect to N) (iv) $H_2N–NH_2$
10. It has been observed that % 's' character in Sb-H bond in SbH_3 is 0.5%. Predict the % 's' character in the orbital occupied by the lone pair.
11. Total number of the compounds with reason in which hybridisation do not takes place :
    $NH_3, H_2O, H_2S, ASH_3, PCl_3, SF_4, CH_4, SiH_4, PH_3, XeH_4$.

EXERCISE - IV

Previous Year Questions

1. Among the following, the linear molecule is :
   (a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2
2. Which one of the following molecules is planar ?
   (a) NF_3 (b) NCl_3 (c) PH_3 (d) BF_3
3. Among the following species identify the isostructural pairs.
   $NF_3, NO_3^-, BF_3, H_3O^+, N_3H$
   (a) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$ (b) $[NF_3, N_3H]$ and $[NO_3^-, BF_3]$
   (c) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$ (d) $[NF_3, H_3O^+]$ and $[N_3H, BF_3]$
4. In compounds of type ECl_3, where E = B, P, As or Bi, the angle Cl—E—Cl
   (a) B > P = As > Bi (b) B > P > As > Bi (c) B < P = As = Bi (d) B < P < As < Bi
5. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are :
   (a) sp, sp^3 and sp^2 respectively (b) sp, sp^2 and sp^3 respectively
   (c) sp^2, sp and sp^3 respectively (d) sp^2, sp^3 and sp respectively
6. Which of the following are isoelectronic and isostructural ?
   $NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$
   (a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^- (c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, O_3

7. Which of the following contains maximum number of lone pairs on the central atom ?

(a) ClO_3^- (b) XeF_4 (c) SF_4 (d) I_3^-

8. The species having pyramidal shape is :

(a) SO_3 (b) BrF_3 (c) SiO_3^{2-} (d) OSF_2

9. The shape of BrF_3 is :

(a) Trigonal pyramidal (b) Trigonal planar

(c) Trigonal bipyramidal (d) T-shaped

10. Which one of the following statements is correct for XeO_2F_2 ?

(a) It has a square planar structure (b) It has a trigonal bipyramid based structure

(c) It is isostructural with XeF_4 (d) It has a tetrahedral structure

11. Which of the following species has two non bonded electron pairs on the central atom ?

(a) $TeCl_4$ (b) ClF_3 (c) ICl_2^- (d) PCl_3

12. The structures of O_3 and N_3^- are :

(a) linear and bent, respectively (b) both linear

(c) both bent (d) bent and linear, respectively

13. The xenon compounds that are isotructural with IBr_2^- and BrO_3^- respectively are :

(a) linear XeF_2 and pyramidal XeO_3 (b) bent XeF_2 and pyramidal XeO_3

(c) bent XeF_2 and planar XeO_3 (d) linear XeF_2 and tetrahedral XeO_3

14. The bond angle of Cl_2O is :

(a) smaller than that of F_2O (b) greater than that of H_2O

(c) smaller than that of H_2O (d) same as that of F_2O

15. $[XeO_6]^{4-}$ is octahedral whereas XeF_6 is a distorted one, because :

(a) fluorine is more electronegative than oxygen

(b) Xe has a lone-pair in XeF_6

(c) XeF_6 is neutral whereas $[XeO_6]^{4-}$ is anionic

(d) Xe-F bond has more ionic character

16. The minimum number of electrons needed to form a chemical bond between two atoms is :

(a) 1 (b) 2 (c) 3 (d) 4

17. In which of the following C–H bond has the highest 's' character ?

(a) acetylene (b) ethylene (c) methane (d) CH radical

18. Which one of the following is an electron-deficient molecule according to the octet rule ?

(a) CH_4 (b) $H_3N \rightarrow BH_3$ (c) AlH_3 (d) GeH_4

19 The number P = O bonds present in the tetrabasic acid $H_4P_2O_7$ is :

(a) three (b) two (c) one (d) none

20. The shape of CH_3^- ion is :

(a) trigonal planar (b) tetrahedral (c) trigonal pyramidal (d) linear

ANSWER KEY

EXERCISE I

1. d	2. a	3. b	4. d	5. d	6. a	7. c
8. b	9. c	10. a	11. c	12. b	13. a	14. b
15. c	16. c	17. a	18. d	19. a	20. c	21. b
22. b	23. c	24. a	25. d	26. a	27. d	28. a
29. b	30. b	31. c	32. c	33. c	34. d	35. a
36. b	37. c	38. d	39. a	40. c	41. c	42. b
43. b	44. b	45. b	46. d	47. c	48. c	49. a
50. c	51. d	52. d	53. c	54. a	55. a	56. c
57. c	58. b	59. a	60. a	61. a	62. b	63. a
64. c	65. c	66. a	67. a	68. b	69. d	70. c
71. c	72. d	73. c	74. c	75. a	76. d	77. b
78. c	79. c	80. c	81. a	82. b	83. a	84. a
85. c	86. b	87. b				

EXERCISE II

1. a,b,c,d	2. a,c,d	3. a,b,d	4. a,b,c,d	5. a,c	6. a,c	7. b
8. d	9. a,c	10. a,c	11. b,d	12. b,c,d	13. a,b,d	14. d
15. a,b	16. a,b,d	17. a,b,c	18. a	19. a,b,c,d	20. b,c	21. a
22. b,c	23. b,c,d	24. a,b,c	25. a,b	26. a,b,c	27. a,b,c	28. b,c,d
29. a,b,c	30. a,b,c	31. a,b,c	32. a,b,c	33. a,c	34. a,b,d	

EXERCISE III

1. 8	2. 3	3. 0105	4. 0006	5. 0004	6. 3	7. 36
8. 0112	9. 3	10. 98.5	11. 4			

EXERCISE IV

1. a	2. d	3. c	4. b	5. b	6. a	7. d
8. d	9. d	10. b	11. b	12. d	13. a	14. b
15. b	16. a	17. a	18. c	19. b	20. c	

CHAPTER 3

S-BLOCK

Main Group elements (s) Block

1. **Electronic Configuration**

Elements	At. No.		Electronic Configuration	Configuration of the valenc shell
Li	3	2, 1	$1s^2, 2s^1$	$2s^1$
Na	11	2, 8, 1	$1s^2, 2s^2 2p^6, 3s^1$	$3s^1$
K	19	2, 8, 8, 1	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$	$4s^1$
Rb	37	2, 8, 18, 8, 1	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^1$	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^6, 6s^1$	$6s^1$
Fr	87	2, 8, 18, 32, 18, 8, 1	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^6, 7s^1$	$7s^1$

(a) Metallic Lustre: The silvery lustre of alkali metals is due to the presence of highly mobile electrons of the metallic lattice.

(b) Softness: There being only a single electron per atom, the metallic bonding is not so strong. As a result of this, these metals are soft in nature. However, the softness increases with increase of atomic number because there is continuous decrease of metallic bond strength on account of increase in atomic size.

✶ **Bigger is the size of metal kernel weaker is the metallic bonding.**

2. **Atomic and ionic radii**

	Li	Na	K	Rb	Cs
At radii (Å)	1.23	1.57	2.03	2.16	2.35

Atomic volume also increases as the atomic number increases

3. **Density**

All are light metals. The densities of metals Li, Na & K are lesser than water. Density gradually increases in moving down from Li to Cs. Potassium is however, lighter than sodium.

Sequence of densities: Li < K < Na < Rb <Cs

The reason for the low values is that these metals have high atomic volumes. The abnormal value of potassium is due to unusual increase in atomic size, i.e., atomic volume.

4. Structures of the metals, hardness and cohesive energy

- At normal temperatures all the Group 1 metals adopt a body-centred cubic-type of lattice with a coordination number of 8. However, at very low temperatures lithium forms a hexagonal close-packed structure with a coordination number of 12.
- The cohesive energy is the force holding the atoms or ions together in the solid.
- The atoms become larger on descending the group from lithium to caesium, so the bonds are weaker, the cohesive energy decreases and the softness of the metals increases.

✶ **The crystal sturcutures of Li_2O, Na_2O, K_2O and Rb_2O are anitfluorite structures, Cs_2O has an anti $CdCl_2$ layer structure.**

5. Melting and boiling points

- **The cohesive energy decreases down the group, and the melting points decrease correspondingly.**

The energy binding the atoms in the crystal lattices of these metals is relatively low on account of a single electron in the valency shell. Consequently, the metals have low metling and boiling points. These decrease in moving down from Li to Cs as the metallic bond strength decreases or cohesive force decreases.

6. Ionisation energies and electropositive character

Due to their large size, the outermost electron is far from the nucleus and can easily be removed. Their ionisation energies or ionisation potentials are relatively low. Thus, the metals have a great tendency to lose the ns^1 electron to change into M^+ ions. These metals are highly electropositive in nature. As the ionisation potential decreases from Li to Cs, the electropositive character increases, i.e. metallic character increases. The reactivity of these metals increases from Li to Cs.

	Li	Na	K	Rb	Cs
Ionisation Potential(ev)	5.4	5.1	4.3	4.2	3.9

$\longrightarrow$ Decreases

Electropositive or metallic nature $\longrightarrow$ Increases

Reactivity $\longrightarrow$ Increases

✶ **The ns^1 electron is so loosely held that even the low energy photons (light) can eject this electron from the metal surface. This property is termed as photoelectric effect. K and Cs are used in photoelectric cells which are sensitive to blue light.**

7. Oxidation States

The alkali metals can lose their ns^1 electron quite easily to form univalent positive ion, M^+. The ion has a stable configuration of an inert gas

These metals are univalent in nature and show electrovalency, i.e. form electrovalent compounds.

✶ **Since the electron configuration of M^+ ions are similar to those of inert gases, these ions have no unpaired electrons and consequently are colourless and diamagnetic in nature.**

8. Hydration of Ions, hydrated radii and hydration energy

The salts of alkali metals are ionic and soluble in water. The solubility is due to the test that cations get hydrated by water molecules $M^+ + aq \longrightarrow [M(aq)]^+$ Hydrated Cation

- **The smaller the cation, the greater is the degree of its hydration of M^+ ions & decrease from Li^+ to Cs^+.**
- Consequently the radii of the hydrated ion decreases from Li^+ to Cs^+.
- The ionic conductance of these hydrated ions increases from $[Li(aq)]^+$ to $[Cs(aq)]^+$.
- Hydration of ions is an exothermic process.
- The energy released when one gram mole of an ion is dissolved in water to get it hydrated is called hydration energy. Since the degree of hydration decreases from Li^+ to Cs^+, the hydration energy of alkali metal ion also decreases from Li^+ to Cs^+.
- **Some water molecules touch the metal ion and bond to it, forming a complex. These water molecules consititute the primary shell of water. Thus Li^+ is tetrahedrally surrounded by four water molecules (sp^3 hybridisation).**
- **With the heavier ions, particularly Rb^+ and Cs^+, the number of water molecules increases to six. VSEPR theory predicts an octahedral structure (d^2sp^3 hybridisation).**
- **A secondary layer of water molecules further hydrates the ions, though these are only held by weak ion-dipole attractive forces.**

9. **Solubility**

All the simple salts dissolve in water, producing ions, and consequently the solutions conduct electricity. Since Li^+ ions are small, it might be expected that solutions of lithium salts would conduct electricity better than solutions of the same concentration of sodium, potassium, rubidium or caesium salts. The small ions should migrate more easily towards the cathode, and thus conduct more than the larger ions. However, ionic mobility or conductivity measurements in aqueous solution give results in the opposite order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The reason for this apparent anomaly is that the ions are hydrated in solution. Since Li^+ is very small, it is heavily hydrated. This makes the radius of the hydrated ion large, and hence it moves only slowly. In contrast, Cs^+ is the least hydrated, and the radius of the hydrated Cs^+ ion is smaller than the radius of hydrated Li^+, and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Some water molecules touch the metal ion and bond to it, forming a complex. These water molecules constitute the primary shell of water. Thus Li^+ tetrahedrally surrounded by four water molecules. This may be explained by the oxygen atoms of the four water molecules using a lone pair to form a coordinate bond to the metal ion. With four electron pairs in the valence shell the VSEPR theory predicts a tetrahedral structure. Alternatively, using valence bond theory, the 2s orbital and the three 2p orbitals form four sp^3 hybrid orbitals which are filled by the lone pairs from the oxygen atoms.

A secondary layer of waer molecules further hydrates the ions, though these are only held by weak ion-dipole attractive forces. The strength of such forces is inversely proportional to the distance, that is to the size of the metal ion. Thus the secondary hydration decreases from lithium to caesium, and accounts for Li^+ being the most heavily hydrated.

10. **Electronegativity**

The tendency to attract electrons is low as the alkali metals are electropositive. The electronegativity, thus decreases from Li to Cs as the electropositive character increases.

11. Conductivity

The alkali metals are good conductors of heat and electricity. This is due to the presence of loosely held valency electrons which are free to move throughout the metal structure.

12. Heat of atomisation

- Heat of atomisation decreases from Li to Cs.
- This is due to the decrease in the metallic bond strength from Li to Cs.

13. Flame colours & spectra

The alkali metals and their salts impart a characteristic colour to flame.

The colour actually arises from electronic transitions in short-lived species which are formed momentarily in the flame.

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Pale violet	Violet	Violet

- The reason for flame colouration is that the energy of the flame causes an excitation of the outermost electrons which on return to their original position give out the energy so absorbed in the visible region. The energy released is minimum in the case of Li^+ and increases from Li^+ to Cs^+. Thus the frequency of the light emitted increases in accordance with the formula $E = h\nu$. The frequency of light in lithium is minimum which corresponds to red region of the spectra.
- Compounds of Group 1 metals are typically white, except those where the anion is coloured, for example sodium chromate $Na_2[CrO_4]$ (yellow), potassium dichromate $K_2[Cr_2O_7]$ (orange), and potassium permanganate $K[MnO_4]$ (deep purple).

14. Reducing nature

An element, which acts as a reducing agent, must have low ionisation energy. Alkali metals act as strong reducing agents as their ionisation energy values are low. Since ionisation energy decreases on moving down from Li to Cs, the reducing property should increases in the same order but from E°_{ox} values it is observed that Li is the strongest reducing agent amongst alkali metals in solution as E°_{ox} value of Li is maximum.

It is due to high hydration energy of Li^+ in aquous solutions.

	Li	Na	K	Rb	Cs
Oxidation potential (V)	+3.05	+2.71	+2.93	+2.99	+2.99

CHEMICAL PROPERTIES

1. Action with Air

On exposure to moist air, all alkali metals except lithium tarnish quickly. The effect of atmosphere increases from Li to Cs. These are, therefore always kept under kerosene oil to protect them from air.

$$\underset{\text{Alkali metal}}{M} \xrightarrow{O_2} \underset{\text{Oxide}}{M_2O} \xrightarrow{H_2O} \underset{\text{Hydroxide}}{MOH} \xrightarrow{CO_2} \underset{\text{Carbonate}}{M_2CO_3}$$

- Lithium when heated in air combines with nitrogen to form nitride, it is due to diagonal relationship with magnesium.

2. Action with Water

Alkali metals decompose water with the evolution of hydrogen gas.

$$2M + 2H_2O \longrightarrow 2MOH + H_2 \uparrow$$

3. Action with hydrogen

The alkali metals combine directly with hydrogen to form crystalline hydrides of the formula MH. These hydrides are ionic and contain the hydrides ion. H^-

$$2M + H_2 \longrightarrow 2MH$$

The ionic character of the bonds in these hydride increases from LiH to CsH and the stability decreases in the same order. They are powerful reducing agents especially at high temperatures.

$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$

4. Action with Oxygen (Oxides and Hydroxides)

- Down the group affinity towards oxygen increases.
- The metals all burn in air to form oxides, though the product varies depending on the metal. Lithium forms the monoxide Li_2O (and some peroxide Li_2O_2), sodium forms the peroxide Na_2O_2 (and some monoxide Na_2O), and the others form superoxides of the type MO_2.

$$M \xrightarrow{O_2} \underset{\substack{\text{Normal Oxide} \\ (Li_2O)}}{M_2O} \xrightarrow{O_2} \underset{\substack{\text{Peroxide} \\ (Na_2O_2)}}{M_2O_2} \xrightarrow{O_2} \underset{\substack{\text{Super oxide} \\ (KO_2, RbO_2, CsO_2)}}{MO_2}$$

The normal oxides 'M_2O' react with water to form hydroxides.

$$M_2O + H_2O \longrightarrow 2MOH$$

The basic nature of the oxides (M_2O) increases gradually on moving down in the group. The hydroxides (MOH) are colourless, strong alkaline and corrosive compounds. These are soluble in water and dissolve with evolution of heat. The hydroxides are thermally stable except LiOH. The relative strength of the hydroxides increases from LiOH to CsOH.

$$CsOH > RbOH > KOH > NaOH > LiOH$$

5. Action with halogens

The alkali metals directly react with halogens forming the halides of the type MX.

$2M + X_2 \rightarrow 2MX$

With the exception of certain lithium halides, the alkali metal halides are ionic compounds ($M^+ X^-$). ~~The halides are crystalline and have high melting and~~ boiling points. The fused halides are good conductors of electricity and are used for the preparation of alkali metals. All haldies except LiF dissolve in water.

- The alkali metal halides react with the halogens and interhalogen compounds forming ionic polyhalide compounds:

$$KI + I_2 \rightarrow K[I_3], \qquad KBr + ICl \rightarrow K[BrICl], \qquad KF + BrF_3 \rightarrow K[BrF_4]$$

6. Nature of Oxysalts

Alkali metals readily react with oxyacids forming corresponding salts with evolution of hydrogen. Lithium salts behave abnormally due to polarising power of Li^+ ion (small size) and lattice energy effects.

7. Nature of carbonates and bicarbonates

As the electropositive character increases from Li to Cs, the stability of the carbonates increases in the same order.

$$Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$$

Li_2CO_3 decomposes on heating and is insoluble in water. The aqueous solution of carbonates are alkaline. This is due to hydrolysis as carbonates are salts of strong bases and weak acid (H_2CO_3 carbonic acid).

$$M_2CO_3 + 2H_2O \rightleftharpoons \underset{\text{Strong alkali}}{2MOH} + \underset{\text{Weak acid}}{H_2CO_3}$$

The bicarbonates, $MHCO_3$, of the alkali metals, with the exception of lithium, are known in solid state. The bicarbonates are soluble in water. On heating, bicarbonates decompose into carbonates with evolution of CO_2.

$$2MHCO_3 \longrightarrow M_2CO_3 + H_2O + CO_2$$

The abnormal behaviour of Li_2CO_3 towards heat can be explained in the following manner.

The Li^+ ion exerts a strong polarising action and distorts the electron cloud of the nearby atom the large CO_3^{2-} ion. This results in the weakening of the C-O bond and strengthening of the Li-O bond. This ultimately facilitates the decomposition of Li_2CO_3 into Li_2O and CO_2. The lattice energy Li_2O is higher than the lattice energy of carbonate. This also favours the decomposition of Li_2CO_3.

✶ **Lithium due to its less electropositive nature, does not form solid bicarbonate and $LiHCO_3$ exists in solutions only.**

8. **Nature of nitrates**

Nitrates of the type, MNO_3, are known. These are colourless, soluble in water and electrovalent in nature. The nitrates do not undergo hydrolysis. With the exception of $LiNO_3$, the other nitrates decompose to nitrites and oxygen.

$$2MNO_3 \longrightarrow 2MNO_2 + O_2$$

Lithium nitrate decomposes to oxide on heating, it is due to diagonal relationship with magnesium.

$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$$

9. **Nature of Sulphates**

Sulphates of the type M_2SO_4 are known. With the exception of Li_2SO_4, other sulphates are soluble in water. The sulphates when fused with carbon form sulphides.

$$M_2SO_4 + 4C \longrightarrow M_2S + 4CO$$

The sulphates of alkali metals form double salts with the sulphates of the trivalent metals like Fe, Al, Cr, etc. The double sulphates crystallise with large number of water molecules as potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ consists of 24 water molecules. Sulphate of lithium are not known to form alum.

10. **Action of liquid ammonia**

The alkali metals dissolve in liquid ammonia without the evolution of hydrogen. The colour of the dilute solutions is blue. The metal atom loses electron and it combines with ammonia molecule.

$M \rightarrow M^+$ (in liquid ammonia) + e (ammoniated)

$M + (x + y)\,NH_3 \rightarrow [M(NH_3)_x]^+ + e(NH_3)_y$ solvated electron

On heating its blue colour changes to bronze. It is ammoniated electron which is responsible for colour.

The solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature.

When dry ammonia is passed over hot metal, amides are formed

$$2M + 2NH_3 \longrightarrow \underset{\text{Amide}}{2MNH_2} + H_2 \uparrow$$

The amides are decomposed by cold water with evolution of NH_3.

$$MNH_2 + H_2O \longrightarrow MOH + NH_3$$

Recent studies proved the existence of $Li(NH_3)_4$, a golden yellow solid.

11. **Formation of alloys**

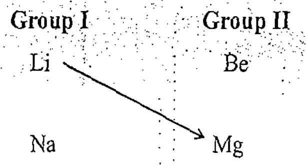
The alkali metals form alloys amongst themselves and with other metals. These combine with mercury readily forming amalgams.

12. **Complex formation**

Alkali metals have a very little tendency to form complexes, Lithium being small in size forms certain complexes but this tendency decreases as the size increases.

DIAGONAL RELATIONSHIP: SIMILARITIES WITH MAGNESIUM

Lithium shows resemblance with magnesium, an element of group IIA. This resemblance is termed as diagonal relationship.



Reason for the diagonal relationship are the following :

(i) Electronegativities of Li and Mg are quite comparable (Li = 1.00 Mg = 1.20)

(ii) Atomic radii and ionic radii of Li and Mg are not very much different.

Atomic radii (Å) Li – 1.23, Mg – 1.36

Ionic radii (Å) Li^+ – 00.60, Mg^{2+} – 0.65

(iii) Atomic volumes of Li and Mg are go to similar Li – 12.97 mL, Mg – 13.97 mL

(iv) Both have high polarising power (ionic potenital) Polarising power $(\phi) = \frac{\text{Ionic charge}}{(\text{Ionic radius})}$

Cations with large ionic potentials have a tendency to polarize the anions and to give partial covalent character to compounds.

Lithium resembles magnesium in the following respects.

(a) Both Li and Mg are harder and have higher melting points than the other metals in their respective groups.

(b) Li Like Mg decomposes water slowly to liberate hydrogen.

$2Li + 2H_2O \longrightarrow 2LiOH + H_2$; $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$

(c) Both elements combine with nitrogen on heating.

$6Li + N_2 \longrightarrow 2Li_3N$; $3Mg + N_2 \longrightarrow Mg_3N_2$

Both the nitrides are decomposed by water with evolution of ammonia (NH_3)

$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$; $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$

(d) Both Li and Mg combine with carbon on heating

$2Li + 2C \longrightarrow Li_2C_2$; $Mg + 2C \longrightarrow MgC_2$

Both the carbides yield C_2H_2 with water.

(e) Lithium forms only monoxide when heated in oxygen.

Mg also forms the monoxide

$4Li + O_2 \longrightarrow 2Li_2O$; $2Mg + O_2 \longrightarrow 2MgO$

Both the are less soluble in water.

(f) Hydroxides of Li and Mg are weak bases and are slightly soluble in water. Both decomposes on heating

$2LiOH \longrightarrow Li_2O + H_2O$; $Mg(OH)_2 \longrightarrow MgO + H_2O$

(g) Lithium fluoride, phosphate, oxalate and carbonate like the corresponding salts of Mg, are sparingly soluble in water.

(h) Carbonates of Li and Mg decomposes on heating.

$Li_2CO_3 \longrightarrow Li_2O + CO_2$; $MgCO_3 \longrightarrow MgO + CO_2$

(i) Nitrates of Li and Mg decompose on heating giving mixture of nitrogen dioxide and oxygen.

$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$; $2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$

COMPOUNDS OF SODIUM

1. Sodium Oxide, Na_2O

$2NaNO_3 + 10Na \longrightarrow 6Na_2O + N_2$; $2NaNO_2 + 6Na \longrightarrow 4Na_2O + N_2$

Properties

$Na_2O + H_2O \longrightarrow 2NaOH$

2. Sodium Peroxide, Na_2O_2

It is formed by heating sodium in excess of air free from moisture and carbon dioxide or in excess of pure oxygen.

$2Na + O_2(\text{excess}) \xrightarrow{350°C} Na_2O_2$

Properites

$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$; $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

3. Sodium Hydroxide (Caustic Soda), NaOH

It is one of the important chemicals and manufactured on a very large scale forming an important chemical industry. It is most conveniently manufactured by one of the following processes :

(a) **Methods involving sodium carbonate as a starting material :** Two methods are used. These are

(i) Causticisation process (Gossage process)

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH$$

(ii) **Lowig's process :**

$$Na_2CO_3 + Fe_2O_3 \longrightarrow 2NaFeO_2 + CO_2; \quad 2Na_2FeO_2 + H_2O \longrightarrow 2NaOH + Fe_2O_3$$

(b) **Methods inolving sodium chloride as starting material (electrolysis of brine)**

At cathode $2H_2O + 2e \rightleftharpoons H_2 + 2OH^-; \quad Na^+ + OH^- \rightleftharpoons NaOH$

At anode $2Cl^- \rightarrow Cl_2 + 2e$

Properties:

1. **Strong alkali:** $NaOH \rightleftharpoons Na^+ + OH^-$

(i) $NaOH + HCl \longrightarrow NaCl + H_2O;$ (ii) $2NaOH + CO_2 \longrightarrow \underset{\text{Sodium Carbonate}}{Na_2CO_3} + H_2O$

(iii) $Al_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium meta alu min ate}}{2NaAlO_2} + H_2O$

2. **Action on non-metals**

(i) **Halogens**

$$Cl_2 + \underset{\text{(cold \& dilute)}}{2NaOH} \longrightarrow NaCl + \underset{\text{Sodium hypochlorite}}{NaClO} + H_2O$$

$$3Cl_2 + \underset{\text{(hot \& conc.)}}{6NaOH} \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

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

3. **Action on Metals**

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2;$$

4. **Action on Salts**

(i) $Ni(NO_3)_2 + 2NaOH \longrightarrow Ni(OH)_2 + 2NaNO_3$

(ii) Insoluble hydroxides which dissolve in excess of NaOH

$$ZnSO_4 + 2NaOH \longrightarrow \underset{\text{White (inso lub le)}}{Zn(OH)_2} + Na_2SO_4$$

(iii) **Unstable hydroxides**

$$2AgNO_3 + 2NaOH \longrightarrow 2AgOH + 2NaNO_3$$

$$2AgOH \longrightarrow \underset{\text{(Brown)}}{Ag_2O} + H_2O$$

SODIUM CARBONATE OR WASHING SODA ($Na_2CO_3.10\ H_2O$)

(a) **Le-Blanc Process**

(i) **Conversion of NaCl into Na_2SO_4**

$$NaCl + H_2SO_4 \longrightarrow \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + HCl$$

$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$

(b) **Solvay ammonia soda process**

$$NH_3 + H_2O + CO_2 \longrightarrow \underset{\text{Ammonium bicarbonate}}{NH_4HCO_3}$$

$$NaCl + NH_4HCO_3 \longrightarrow \underset{\text{Sodium bicarbonate}}{NaHCO_3} + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

CHEMICAL PROPERTIES

1. **Action of Acids**

$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$; $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

2. **Action of CO_2**

$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$

3. **Action of silica**

When the mixture of sodium carbonate and silica is fused, sodium silicate is formed.

$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$

Sodium silicate is called soluble glass or water glass as it is soluble in water.

4. **Action on salts of non-alkali metals**

Solution of carbonates reacts with metal salts (except alkai metal Salt) to form insoluble normal or basic carbonates.

$$2MgCl_2 + 2Na_2CO_3 + H_2O \longrightarrow \underset{\text{Basic magnesium carbonate}}{MgCO_3{\cdot}Mg(OH)_2} + 4NaCl + CO_2$$

SODIUM BICARBONATES ($NaHCO_3$)

$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$ (Sparingly soluble)

Properties

$NaHCO_3 + H_2O \longrightarrow NaOH + H_2CO_3$; $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$

SODIUM THIOSULPHATE ($Na_2S_2O_3.5H_2O$)

(i) **Spring's reaction**

$Na_2S + I_2 + Na_2SO_3 \longrightarrow Na_2S_2O_3 + 2NaI$

Properties:

(i) **Oxidation**

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6}$$

SODIUM AMMONIUM HYDROGEN PHOSPHATE ($NaNH_4HPO_4$)

Preparation

$$NH_4Cl + Na_2HPO_4 + 4H_2O \longrightarrow NaNH_4HPO_4.4H_2O + NaCl$$

Properties

(i) $$Na(NH_4)HPO_4 \longrightarrow \underset{\text{Sodium metaphosphate}}{NaPO_3} + NH_3 + H_2O$$

SODIUM CYANIDE (NaCN)

(i) From sodium

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2\uparrow$$

$$2NaNH_2 + C \longrightarrow Na_2CN_2 + 2H_2$$

$$Na_2CN_2 + C \longrightarrow 2NaCN$$

$$2NaNH_2 + 2C \longrightarrow 2NaCN + 2H_2$$

(ii) From calcium cyanide

$$Ca(CN)_2 + C + Na_2CO_3 \longrightarrow 2NaCN + CaCO_3$$

Properties:

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

It forms complex cyanides with the salts of copper cadmium, zinc, iron, cobalt, nicked etc. Some examples are given below :

(i) $AgNO_3 + NaCN \longrightarrow AgCN + NaNO_3$; $AgCN + NaCN \longrightarrow Na[Ag(CN)_2]$

POTASSIUM

Carnalite	$KCl\ MgCl_2\ 6H_2O$
Kainite	$KCl.MgSO_4.MgCl_2.3H_2O$
Indian Saltpetre	KNO_3
Felspar	$K_2O.Al_2O_3.6SiO_2$ (caly)
Polyhalite	$K_2SO_4MgSO_4.\ CaSO_4.6H_2O$
Sylvine	KCl

POTASSIUM IODIDE (KI)

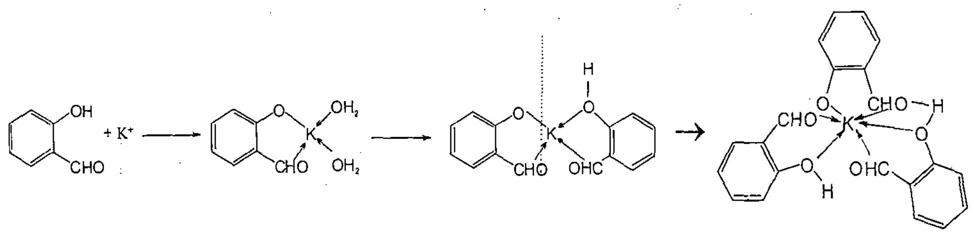
Preparation

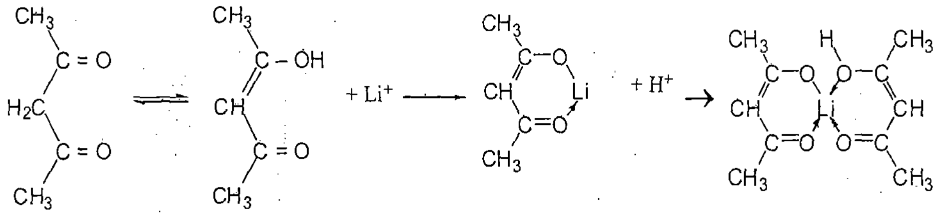
(i) $KOH + HI \longrightarrow KI + H_2O$

(ii) $3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 3H_2O$

(iii) $KI + I_2 \longrightarrow KI_3 \rightleftharpoons KI + I_2$

COMPLEX FORMATIONS





★ **An unusual compound $[Na(Cryptand\text{-}222)]^+ Na^-$ having interesting feature is that it contains Na^-, the sodide ion (Negative charge on metal).**

Group 2 Elements (Alkaline Earth metals)

Electronic Configuration

The arrangement of the distribution of electrons on various subshells in the atoms of alkaline earth metals is given below :

Elements	At. No.		Electronic Configuration	Configuration of the valence shell
Be	4	2, 2	$1s^2, 2s^2$	$[He]\ 2s^2$
Mg	12	2, 8, 2	$1s^2, 2s^2 2p^6, 3s^2$	$[Ne]\ 3s^2$
Ca	20	2, 8, 8, 2	$1s^2, 2s^2, 2p^6, 3s^2 3p^6, 4s^2$	$[Ar]\ 4s^2$
Sr	38	2, 8, 18, 8, 2	$1s^2, 2s^2 2p^6, 3s^2, 3p^6 3d^{10}, 4s^2 4p^6, 5s^2$	$[Kr]\ 5s^2$
Ba	56	2, 8, 18, 18, 8, 2	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^6, 6s^2$	$[Xe]\ 6s^2$
Ra	88	2, 8, 18, 32, 18, 8, 2	$1s^2, 2s^2 sp^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14},$ $5s^2 5p^6 5d^{10}, 6s^2 6p^6 7s^2$	$[Rn]\ 7s^2$

PHYSICAL PROPERTIES

1. **Physical State**

   They are all silvery white metals. They have greyish white lustre when freshly cut, but tarnish soon after their exposure in air due to surface oxidation.

2. **Atomic and ionic radii**

   The size of the atom increases gradually from Be to Ra, on account of the presence of an extra energy shell at each step.

3. **Density**

   These metals are denser than alkali metals in the same period because these can be packed more tightly due to their greater nuclear charge and smaller size. The density decreases slightly upto calcium and then increases considerably upto radium. Irregular trend is due to the difference in the crystals structure of these elements.

4. **Melting and boiling points**

The melting and boiling points of these elements are higher than corresponding alkali metals. This is due to the presence of two electrons in the valency shell and thus, strongly bonded in the solid state. However, melting and boiling points do not show any regular trend because atoms adopt different crystal structures. Be > Mg > Ca > Sr > Ba > Ra

5. **Ionisation energies and electropositive character**

The first and second ionisation energies of these metals decrease from Be to Ba. The second ionisation energy in each case is higher than the first, nearly double the first ionisation energy.

$$\xrightarrow{\text{Be} \quad \text{Mg} \quad \text{Ca} \quad \text{Sr} \quad \text{Ba} \quad \text{Ra}}$$

Electropositive nature increases
Metallic character increases
Reacitivity of the metals increases

6. **Oxidation States**

All show a stable oxidation state +2 in their compounds. The second ionisation energy is nearly double the first ionisation energy for all these elements. This should cause these elements to exhibit a stable +1 oxidation state and form compounds like BaCl, SrBr, CaI, etc., instead of $BaCl_2$, $SrBr_2$, CaI_2, etc.

- Amongst alkaline earth metals, berylium has the highest ionisation energy, i.e., least electropositive in nature.
- Thus, berylium has minimum tendency to form Be^{2+} ion and hence a number of compounds of beryllium are covalent in nature.

7. **Hydration of ions and hydration energy**

The M^{2+} ions of alkaline earth metals are extensively hydrated to form hydrated ions $[M(H_2O)_x]^{2+}$ and during hydration a huge amount of energy, called hydration energy, is released.

$$M^{2+} + xH_2O \longrightarrow [M(H_2O)_x]^{2+} + \text{Energy}$$

The degree of hydration and the amount of hydration energy decreases as the size of the ion increases from Be^{2+} to Ba^{2+}

The hydration energies of alkaline earth metal ions are higher than those of alkali metal ions and thus the compounds of alkaline earth metals are more extensively hydrated than alkali metals, Magnesium chloride and calcium chloirde exist as $MgCl_2.6H_2O$ and $CaCl_2$. $6H_2O$, respectively, while sodium chloride and potassium chloride exists as NaCl and KCl.

- The ionic mobilities or ionic conductance of these ions increase from $[Be(H_2O)_x]^{2+}$ due to high degree to hydration.

8. **Flame colouration**

In berylium and magnesium, the electrons are tightly held and hence excitation is rather difficult, thus do not show flame colouration. Ca, Sr, Ba and Ra impart a characteristic colour to the flame.

Ca-brick red Sr - crimson Ba - green Ra-crimson

9. Reducing nature

The alkaline earth metals have the tendency to lose electrons and change into bivalent cation :

$$M \longrightarrow M^{2+} + 2e$$

Hence, they act as strong reducing agents. The reducing nature increases as the atomic number increases. Strength of a reducing agent is linked with the value of oxidation potential. The values of the oxidation potentials increases from Be to Ba, hence the strength as a reducing agent increases in the same order.

	Be	Mg	Ca	Sr	Ba
Oxidation potential (volt)	1.85	2.37	2.87	2.89	2.90

The oxidation potentials are lower than those of the alkali metals, hence, the allkaline earth metals are weaker reducing agents than alkali metals.

- The reason for the lower values of oxidation ~~potentials~~ is due to high heats of atomisation (sublimiation) and ionisation energies.

10. Colour and magnetic porperty

Since, the divalent ions have noble gas configuration with no unpaired electrons, their compounds are diamagnetic and colourless unless the anion is coloured. The metals are also diamagnetic in nature as all the orbitals are fully filled with spin paired electrons, e.g.

$$Mg = 2, 8$$
$$= 1s^2, 2s^2\ 2p^6$$
$$= \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \uparrow\downarrow}$$

CHEMICAL PROPERTIES

The following are important minerals of these elements.

1.	**Berylium**	—	Beryl	$3BeO, Al_2O_3, 6SiO_2$
2.	**Magnesium**	—	Magnetic	$MgCO_3$
			Dolomite	$MgCO_3, CaCO_3$
			Carnallite	$KCl.MgCl_2.6H_2O$
			Epsomite or Epsom salt	$MgSO_4.7H_2O$
			Asbestos	$CaMg_3(SiO_3)_4$
3.	**Calcium**	—	Lime, stone, chalk	$CaCO_3$
			Calcite, marble	$CaCO_3$
			and iceland spar	$CaCO_3$
			Gypsum	$CaSO_4.2H_2O$
			Fluorspar	CaF_2
4.	**Strontium**	—	Celestine	$SrSO_4$
			Strontianite	$SrCO_3$
5.	**Barium**	—	Barytes or heavy spar	$BaSO_4$
			Witherite	$BaCO_3$

6.	**Radium**	—	Pitchblende, Carnotite	Minerals of uranium consisting minutes quantites of radium.

1. **Action of water**

Calcium, strontium, barium and radium decompose cold water readily with evolution of hydrogen

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2$$

2. **Action of atmosphere**

Except beryllium, these metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect of atmosphere increases as the atomic number increases. Barium in powdered form bursts into flame on exposure to air.

3. **Action of acids**

Like alkali metals, the alkaline earth metals freely react with acids and displace hydrogen.

$$M + H_2SO_4 \longrightarrow MSO_4 + H_2$$

Beryllium behaves differently as it dissolves in caustic alkalies also with liberation of hydrogen. It is due to diagonal relationship with aluminium.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

4. **Reaction with hydrogen**

Except berylium, all combine with hydrogen directly to form hydrides of the type MH_2 when heated with hydrogen.

$$M + H_2 \longrightarrow MH_2$$

BeH_2 and MgH_2 are covalent in nature while other hydrides are ionic in nature. Calcium, strontium and barium hydrides liberate hydrogen at anode on electrolysis in the fused state. Ionic hydrides are violently decomposed by water evolving hydrogen. CaH_2 is technically called hydrolith and used on large scale for the production of hydrogen.

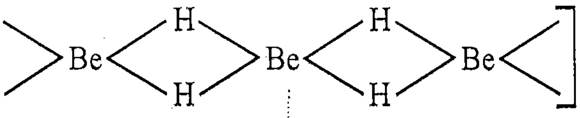
$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

[BeH_2 is not obtained by direct combination of beryllium and hydrogen. It is formed by reacting beryllium chloride with lithium aluminium hydride.

$$2BeCl_2 + LiAH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

It is polymeric $(BeH_2)_n$ and possesses hydrogen bridges.

Three centre bonds are present in which a banana shaped molecular orbital covers three atoms Be----H----Be and contains two electrons. Hydrogen atoms lie in the plane prependicular to the plane of molecule containing beryllium atoms.



The stability of the hydrides decreases with increasing atomic number because the metallic nature of the elements increases.

5. **Reaction with oxygen (Oxides and Hydroxides)**

Except Ba and Ra, these elements when burnt in oxygen form oxides of the type MO.

$$2M + O_2 \longrightarrow 2MO$$

Berylium metal is relatively unreactive and does not react burns brilliantly. The element, Mg burns with dazzling brilliance evolving a lot of heat.

Barium and radium, being highly electropositive, form peroxides.

$$\underset{\text{Barium}}{Ba} \xrightarrow{O_2} \underset{\text{Barium oxide}}{BaO} \xrightarrow[\text{High temp.}]{O_2} \underset{\text{Barium peroxide}}{BaO_2}$$

Thus, the affinity for oxygen increases on moving down the group.

BeO is usually formed by ignition of the metal but the other metal oxides (MO type) are usually obtained by thermal decomposition of the carbonates, MCO_3.

$$MCO_3 \xrightarrow{\text{Heat}} MO + CO$$

The oxides are very stable compounds (BeO and MgO are used as refractory materals) and white crystalline solids.

BeO is covalent and has a 4 : 4 zinc sulphide (wurtzite) structure. All the other oxides are ionic and possess 6 : 6 NaCl structure (face centred cubic). The reason for high stability is due to high lattice energy values which, however, decrease as the size of the metal ion increases.

Except BeO, which is amphoteric in nature, other MO oxides are basic in nature as they combine with water to form basic hydroxides. This reaction is highly exothermic.

$$MO + Heat \longrightarrow M(OH)_2 + Heat$$

(where, M = Ca^{2+}, Sr^{2+} or Ba^{2+})

Basic nature of the oxides increases gradually from BeO to BaO

$$\underset{\text{Amphoteric}}{BeO} \quad \underset{\text{Weakly Basic}}{MgO} \quad \underset{\text{Basic}}{CaO} \quad \underbrace{SrO \quad BaO}_{\text{Strongly Basic}}$$

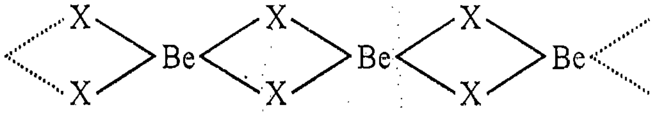
[BeO and MgO are insoluble in water as these are tightly held together in the solid state]

6. **Reaction with halogens (Halides)**

The alkaline earth metals directly combine with halogens, when heated with them.

$$M + X_2 \xrightarrow{\text{heated}} MX_2$$

Beryllium halides are covalent in nature. This is due to small size and high charge of Be^{2+} ion, i.e. it has high polarising power. The glassy forms of halides are known to have chains of ------ X_2BeX_2 Be -----



7. **Action with nitrogen**

All the alkaline earth metals burn in nitrogen to form nitrides of the type M_3N_2.

$$3M + N_2 \longrightarrow M_3N_2$$

The ease of formation of nitrides decreases from Be to Ba.

8. **Action with carbon (Carbides)**

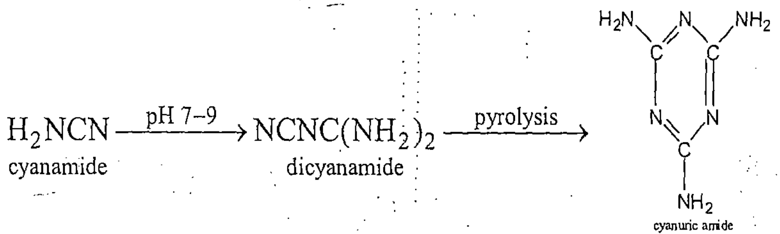
With the exception of Be, other metals when heated with carbon in an electric furnace or when their oxides are heated with carbon form carbides of the type MC_2. These carbides are called acetylides as on hydrolysis they evolve acetylene.

$$M + 2C \longrightarrow MC_2$$

$$MC_2 + 2H_2O \longrightarrow M(OH)_2 + C_2H_2 \text{ Acetylene}$$

- CaC_2 is an important chemical intermediate. When CaC_2 is heated in an electric furnace with atmospheric dinitrogen at 1100°C, calcium cyanamide CaNCN is formed.
- The cyanamide ion $[N=C=N]^{2-}$ is isoelectronic with CO_2, and has the same linear structure.

$$CaNCN + H_2SO_4 \rightarrow H_2NCN + CaSO_4$$



9. **Nature of oxy salts**

(i) **Bicarbonates and carbonates**

Bicarbonates of alkaline earth metals do not exist in solid state but are known in solutions only. When such solutions are heated, bicarbonates are decomposed with evolution of carbon dioxide.

$$\underset{\text{Solution}}{M(HCO_3)_2} \xrightarrow{\text{Heated}} MCO_3 + CO_2 + H_2O$$

Carbonates of alkaline earth metals (MCO_3) are insoluble in water. These dissolve in water in presence of carbon dixoide.

$$MCO_3 + H_2O + CO_2 \longrightarrow M(HCO_3)_2$$

Solubility of carbonates decreases on moving down the group, while stability increases. This is evident from the values of decomposition temperatures of various carbonates which increase gradually.

Increasing stability can be explained on the basis of polarisation and covalent character. Be^{2+} is smallest in size hence show high polarising power. $BeCO_3$ is least ionic and has least stability.

$$\xrightarrow[\text{Increasing ionic character and stability}]{BeCO_3 < MgCO_3 < CaCO_3 < SiCO_3 < BaCO_3}$$

✶ **The carbonates are all ionic, but $BeCO_3$ is unusual because it contains hydrated ion $[Be(H_2O)_4]^{2+}$, rather than Be^{2+}**

(ii) **Sulphates**

Alkaline earth metals form sulphates of the type MSO_4. These are prepared by the action of sulphuric acid on oxides, hydroxides or carbonates.

$$MO + H_2SO_4 \longrightarrow MSO_4 + H_2O$$

The solubility of sulphates decreases on moving down the group. $CaSO_4$ is springly soluble, while $SrSO_4$, BaS_4 and $RaSO_4$ are almost insoluble. The solubilities of $BeSO_4$ and $MgSO_4$ are due to high energy of solvation of smaller Be^{2+} and Mg^{2+} ions.

The sulphates decomposes on heating to give the corresponding oxide (MO).

$$2MSO_4 \xrightarrow{\text{Heat}} 2MO + 2SO_2 + O_2$$

The stability increases as the basic nature of the metal increases.

Difference Between Alkaline Earth Metals and Alkali Metals

Properties		Alkaline earth metals	Alkali metals
(i)	Electronic configuration	Two electrons are present in the valence shell. The configuration is ns^2	One electron is present in the valence shell. The configuration is ns^1
(ii)	Valency	Bivalent	Monovalent
(iii)	Electropositive nature	Less electropositive	More electropositive
(iv)	Hydroxides	Weak bases, less soluble and decompose on heating	Strong bases, highly soluble and stable towards heat.
(v)	Bicarbonates	These are not known in free state. Exist only in solution	These are known in solid state.
(vi)	Carbonates	Insoluble in water. Decompose on heating	Soluble in water. Do not decompose on heating (Li_2CO_3 is an exception).
(vii)	Action of carbon	Directly combine will carbon and form carbides.	Do not directly combine with carbon.
(viii)	Action of nitrogen	Directly combine with nitrogen and form nitrides.	Do not directly combine with nitrogen.
(ix)	Nitrates	Decomposes on heating evolving a mixture of NO_2 and oxygen.	Decompose on heating evolving only oxygen.
(x)	Solubility of salts	Sulphates, Phosphates, fluorides, Chromates, oxalates etc. are insoluble in water	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.
(xi)	Physical properties	Comparatively harder, High melting points, Diamagnetic	Soft, low melting points, Paramagnetic.
(xii)	Hydration of Compounds	The compounds are extensively hydrated. $MgCl_2.6H_2O$, $CaCl_2.\ 6H_2O$, $BaCl_2.2H_2O$ are hydrated chlorides.	The compounds are less hydrated. NaCl, KCl, RbCl, form non-hydrated chlorides.
(xiii)	Reducing power	Weaker, as ionization potential values are high and oxidation potential values are low.	Stronger, as ionization potential values are low and oxidation potential values are high.

Anomalous Behaviour of Beryllium

Be differs from the rest of the group for three reason.

(i) It is extremely small, and Fajans rules state that small highly charged ions tend to form covalent compounds.

(ii) Be has comparatively high electronegativity. Thus when beryllium reacts with another atom, the difference in electronegativity is seldom large, which again favours the formation of covalent compounds. Even BeF_2 (electronegativity difference 2.5) and BeO (electronegativity difference 2.0) show evidence of covalent character.

(iii) Be is in the second row of the periodic table, and the outer shell can hold a maximum of eight electrons. (The orbitals available for bonding are one 2s and three 2p orbitals). Thus Be can form a maximum of four conventional electron pair bonds, and in many compounds the maximum coordination number of Be is 4. The later elements can have more than eight outer electrons, and may attain a coordination number of 6 using one s, three p and two d orbitals for bonding. Exceptions occur if multi-centre bonding occurs, as for example in basic beryllium acetate, when higher coordination number are obtained.

Thus we should expect Be to form mainly covalent compounds, and commonly have a coordination number of 4. Anhydrous compounds of Be are predominantly two-covalent, and BeX_2 molecules should be linear.

In fact linear molecules exist only in the gas phase, as this electronic arrangement has not filled the outer shell of electrons. In the solid state four-fold coordination is always achieved. There are several ways by which this can be achieved:

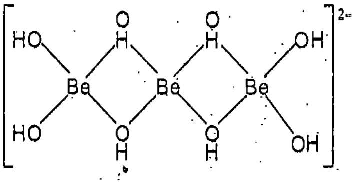
(i) Two ligands that have a lone pair of electrons may form coordinate bonds using the two unfilled orbitals in the valence shell of Be. Thus two F^- ions might coordinate to BeF_2, forming $[BeF_4]^{2-}$ Similarly diethyl ether can coordinate to Be(+II) in $BeCl_2$, forming $[BeCl_2(OEt_2)_2]$.

(ii) The BeX_2 molecules may polymerize to form chains, containing bridging halogen groups, for example $(BeF_2)_n$, $(BeCl_2)_n$. Each halogen forms one normal covalent bond, and uses a lone pair to form a coordinate bond.

(iii) $(BeMe_2)_n$ has essentially the same structure as $(BeCl_2)_n$, but the bonding in the methyl compound is best regarded as three-centre two electron bonds covering one Me and two Be atoms.

(iv) A covalent lattice may be formed with a zinc blende or wurtzite structure (coordination number 4). for example by BeO and BeS.

In water beryllium salts are extensively hydrolysed to give a series of hydroxo complexes of unknown structure. They may be polymeric and of the type:



If alkali is added to these solutions the polymers break down to give the simple mononuclear beryllate ion $[Be(OH)_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+} and the hydrated ion too is a tetrahedral complex ion. Note that the coordination number is 4. Forming a hydrated complex increases the effective size of the beryllium ion, thus spreading the charge over a larger area. Stable ionic salts such as $[Be(H_2O)_4]SO_4$, $[Be(H_2O)_4](NO_3)_2$ and $[Be(H_2O)_4]Cl_2$ are known.

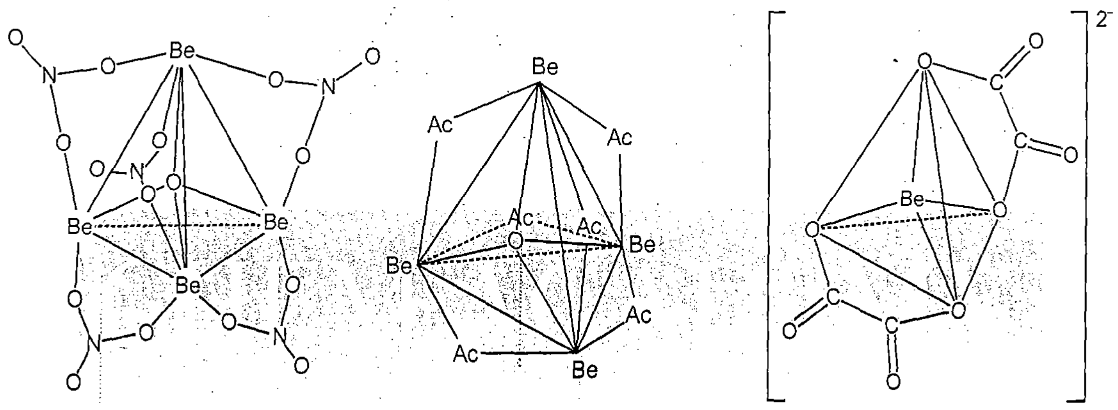
Beryllium salts are acidic when dissolved in pure water because the hydrated ion hydrolyses, producing H_3O^+. This happens because the Be—O bond is very strong, and so in the hydrated ion this weakens the O—H bonds, and hence there is a tendency to lose protons. The initial reaction is

$$H_2O + [Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^{+} + H_3O^{+}$$

but this may be followed by further polymerization, involving hydroxobridged structures $[Be_2OH]^{3+}$, $[Be_3(OH)_4]^{3+}$. In alkaline solutions $[Be(OH)_4]^{2-}$ is formed. The other Group 2 salts do not interact so strongly with water, and do not hydrolyse appreciably.

Beryllium salts rarely have more than four molecules of water of crystallization associated with the metal ion, because there are only four orbitals available in the second shell of electrons, whereas magnesium can have a coordination number of 6 by using some 3d orbitals as well as 3s and 3p orbitals.

✶ Beryllium is unique in forming a series of stable covalent molecules of formula $[Be_4O(R_6)]$ where R may be NO_3^-, $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_6H_5COO^-$.



(a) (b) (c)

SIMILARITIES (DIAGONAL RELATIONSHIP) BETWEEN BERYLLIUM AND ALUMINIUM

Beryllium shows some similarities in properties with aluminium, the second typical element of group IIIA (next group in Mendeleefs periodic table) of the next higher period. This type of relationship between diagonally placed elements is called diagonal relationship

	Group II A		Group III A
Second period	Be	↘	B
Third period	Mg		Al

EXERCISE - I

Single Correct Type

1. The compound(s) of alkaline earth metals, which are amphoteric in nature is/are

(a) BeO (b) MgO (c) $Be(OH)_2$ (d) $Mg(OH)_2$

2. The hydroxide of alkaline earth metal, which has the lowest value of solubility product (K_{sp}) at normal temperature (25°C) is

(a) $Ca(OH)_2$ (b) $Mg(OH)_2$ (c) $Sr(OH)_2$ (d) $Be(OH)_2$

3. The incorrect statement is/are

(a) $BeCl_2$ is a covalent compound (b) $BeCl_2$ is an electron deficient molecule

(c) $BeCl_2$ can form dimer (d) the hybrid state of Be in $BeCl_2$ is sp^2

Imp..

4. Which of the following carbonate of alkali metals has the least thermal stability?

(a) Li_2CO_3 (b) K_2CO_3 (c) Cs_2CO_3 (d) Na_2CO_3

5. The alkali metals which form normal oxide, peroxide as well as super oxides are

(a) Na, Li (b) K, Li (c) Li, Cs (d) K, Rb

6. The order of solubility of lithium halides in non-polar solvents follows the order

(a) LiI > LiBr > LiCl > LiF (b) LiF > LiI > LiBr > LiCl

(c) LiCl > LiF > LiI > LiBr (d) LiBr > LiCl > LiF > LiI

7. $CsBr_3$ contains

(a) Cs–Br covalent bonds (b) Cs^{3+} and Br^- ions

(c) Cs^+ and Br_3^- ions (d) Cs^{3+} and Br_3^{3-} ions

8. The compound(s) which do not have –O–O– bond(s) is

(a) BaO_2 (b) Na_2O_2 (c) CrO_5 (d) Fe_2O_3

Bicarbonates solubility increases down the group

9. The correct order of solubility is

(a) $CaCO_3 < KHCO_3 < NaHCO_3$ (b) $KHCO_3 < CaCO_3 < NaHCO_3$

(c) $NaHCO_3 < CaCO_3 < KHCO_3$ (d) $CaCO_3 < NaHCO_3 < KHCO_3$

10. The complex formation tendency of alkaline earth metals decreases down the group because

(a) atomic size increases (b) availability of empty d and f-orbitals increases

(c) nuclear charge to volume ratio increases (d) all the above

11. $Y \xleftarrow{\Delta, 205°C} CaSO_4 \cdot 2H_2O \xrightarrow{\Delta, 120°C} X$. X and Y are respectively

(a) plaster of paris, dead burnt plaster (b) dead burnt plaster, plaster of paris

(c) CaO and plaster of paris (d) plaster of paris, mixture of gases

12. Which of the following compounds are paramagnetic in nature?

(a) KO_2 (b) K_2O_2 (c) Na_2O_2 (d) Rb_2O_2

13. $X \xrightarrow{N_2,\Delta} Y \xrightarrow{H_2O} Z(\text{colourless gas}) \xrightarrow[CuSO_4]{} T(\text{blue colour})$

Then, substances Y and T are

(a) $Y = Mg_3N_2$ and $T = CuSO_4 \cdot 5H_2O$ (b) $Y = Mg_3N_2$ and $T = CuSO_4 \cdot 4NH_3$

(c) $Y = Mg(NO_3)_2$ and $T = CuO$ (d) $Y = MgO$ and $T = CuSO_4 \cdot 4NH_3$

14. $X + C + Cl_2 \xrightarrow[\text{of about} 1000K]{\text{High temperature}} Y + CO$; $Y + 2H_2O \rightarrow Z + 2HCl$

Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be

(a) BeO (b) $BeCl_2$ (c) BeH_2 (d) $AlCl_3$

15. Which of the following is not a ionic carbides?

(a) CaC_2 (b) Al_4C_3 (c) SiC (d) Be_2C

16. The reaction between NH_4Br and Na metal in liquid ammonia (solvent) results in the products.

(a) NaBr, HBr (b) NaBr, H_2 (c) H_2, HBr (d) NBr_3, H_2

17. Among the nitrates of alkaline earth metals, whose nitrate has highest solubility

(a) Be (b) Mg (c) Ca (d) Sr

18. Which of the following metal will not give any blue colour in NH_3 ?

(a) Be (b) Li (c) Na (d) Cs

19. (Milky cloud) $C \xleftarrow{CO_2} A + Na_2CO_3 \longrightarrow B + C$

The chemical formulae of A and B are

(a) NaOH and $Ca(OH)_2$ (b) $Ca(OH)_2$ and NaOH

(c) NaOH and CaO (d) CaO and $Ca(OH)_2$

Imp.

20. What is the change in the O – O bond length of O_2 when it is treated with a solution of metal in liquid NH_3 ?

(a) increases (b) decreases (c) remains same (d) can't be measured

21. When solution of Mg in liquid ammonia is evaporated, initially an ammoniated complex $Mg(NH_3)_x$ is obtained. What is the value of x ?

(a) 4 (b) 6 (c) 10 (d) 2

22. Calgon used for water softening is $Na_2[Na_4(PO_3)_6]$ and it is prepard by heating microcosmic salt. The microcosmic salt is

(a) Na_2HPO_3 (b) NaH_2PO_4 (c) Na_2HPO_4 (d) $Na(NH_4)HPO_4$

EXERCISE - II

One or More Than One Correct Type

1. The hydration energy of Mg^{2+} ion is higher than that of :

(a) Al^{3+} (b) Ca^{2+} (c) Na^{+} (d) None of these

2. Peroxide ion is present in :

(a) K_2O_2 (b) CaO (c) Li_2O (d) BaO_2

3. Which of the following metal carbonate is/are thermally stable ?

(a) Na_2CO_3 (b) $MgCO_3$ (c) K_2CO_3 (d) Rb_2CO_3

4. Which is/are not correct configuration of s–block elements :

(a) $[Ar]\ 3d^{10}\ 4s^2$ (b) $[Ar]\ 3d^{10}\ 4s^1$ (c) $[Ar]\ 4s^2$ (d) $[Ar]\ 4s^1$

5. Alkali metals are characterised by their :

(a) high electropositive character (b) high reduction potentials

(c) low melting points (d) high solubility in liquid ammonia at –33°C.

6. Which of the following statements is/are true ?

(a) All alkali metals are soft and can be cut with knife.

(b) Alkali metals do not occur in free state in nature.

(c) Alkali metals are highly electropositive elements.

(d) Alkali metal hydrides are covalent and low melting solids.

7. Select correct statement(s) :

(a) Li_2CO_3 is only sparingly soluble in water and no $LiHCO_3$ has been isolated.

(b) K_2CO_3 cannot be made by a method similar to the ammonia – soda (Solvay) process.

(c) Li_2CO_3 and $MgCO_3$ both are thermally stable.

(d) $Na_2CO_3 . NaHCO_3 . 2H_2O$ is a mineral called trona.

8. Select correct statement(s) :

(a) Stability of peroxides and superoxides of alkali metals increases with increase in size of the cation.

(b) Increase in stability in (a) is due to stabilisation of large anions by larger cations through lattice energy effects.

(c) The low solubility of LiF is due to its high lattice energy whereas low solubility of CsI is due to smaller hydration energy .

(d) NaOH does not form hydrated salt.

9. Which of the following statement(s) is/are correct ?

(a) Sodium bicarbonate is more soluble than sodium carbonate.

(b) Sodium hydroxide is used in the purification of bauxite.

(c) Sodium bicarbonate is used as antacid and for making baking powder.

(d) Potassium hydroxide is used in the manufacture of soft soaps.

10. Flame test is not given by

(a) Be (b) Mg (c) Ca (d) Sr

11. Going down in II A group, following properties decrease :

(a) solubility of sulphates in H_2O (b) hydration energy

(c) thermal stability of carbonates (d) ionic radius

Alkaline earthmeta carbonates are
thermelly unstable.

12. Which is/are true statements?
(a) The heats of hydration of the dipositive alkaline earth metal ions decrease with an increase in their ionic size.
(b) Hydration of alkali metal ion is less than that of II A.
(c) Alkaline earth metal ions, because of their much larger charge to radius ratio, exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.
(d) None.

13. In water :
(a) temporary hardness is due to the bicarbonates of Ca^{2+} and Mg^{2+}
(b) permanent hardness is due to chlorides and sulphates of Ca^{2+} and Mg^{2+}
(c) hardness can be removed by adding phosphates.
(d) none is correct.

14. Sodium sulphate is soluble in water but barium sulphate is sparingly soluble because :
(a) the hydration energy of Na_2SO_4 is more than its lattice energy
(b) the lattice energy of $BaSO_4$ is more than its hydration energy
(c) the lattice energy has no role to play in solubility
(d) the lattice energy of Na_2SO_4 is more than its hydration energy

15. Nitrate can be converted into metal oxide on heating not above 500°C in case of :
(a) Li (b) Na (c) Mg (d) None of these.

16. Be and Al have following resemblance due to diagonal relationship :
(a) have nearly equal electronegativity (b) form amphoteric oxides
(c) have same charge/radius ratio (d) both form dimeric halides

17. Be and Al resemble in :
(a) both become passive on reaction with HNO_3 due to formation of oxide layer.
(b) their chlorides are Lewis acids.
(c) chlorides exist in polymeric form.
(d) hydroxides are soluble in alkali as well as in acid.

18. What is are the correct order of thermal stability ?
(a) $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Cs_2CO_3$ (b) $Cs_2CO_3 < K_2CO_3 < Na_2CO_3 < Li_2CO_3$
(c) $LiF > NaF > KF > RbF$ (d) $Li_3N > Na_3N > K_3N > Rb_3N$

19. The characteristics of the blue solution of sodium in liquid NH_3 is/are
(a) diamagnetic (b) paramagnetic (c) reducing in nature (d) conducts electricity

20. Select the correct statement(s) about the formation of a blue coloured solution when an alkali metal is dropped in NH_3 solution,
(a) The blue colour of the sol. is due to ammoniated electrons
(b) There is a change in colour from blue to bronze if concentration of the metal increases
(c) There is a change in colour from blue to bronze if conc. of the metal decreases
(d) The solution is oxidising in nature

23. Ammonia can be dried by :

(a) conc. H_2SO_4 (b) P_4O_{10} (c) CaO (d) anhydrous $CaCl_2$

EXERCISE - III

Previous Year Questions

IIT-JAM Previous Year Questions

1. Which one of the following order of the carbonates is CORRECT for their decomposition temperature ?

(a) $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$ (b) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

(c) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$ (d) $MgCO_3 > CaCO_3 > BaCO_3 > SrSO_3$

2. Which one of the following has the highest lattice energy ?

(a) LiCl (b) $CaCl_2$ (c) LiF (d) KCl

3. Draw the structure of anionic Ca(II)-EDTA chelate. How many rings are formed in the chelate and specify the number of atoms in each ring ?

4. The correct order of the ionic radii is

(a) $In^{3+} > Sn^{4+} > Sr^{2+} > Rb^+$ (b) $Sn^{4+} > In^{3+} > Sr^{2+} > Rb^+$

(c) $Rb^+ > In^{3+} > Sr^{2+} > Rb^+$ (d) $Rb^+ > Sr^{2+} > In^{3+} > Sn^{4+}$

5. If the values of Madelung constants of the following compounds ware equal, then their lattice energy values decrease in the order

(a) $KCl > NaF > CaO > Al_2O_3$ (b) $Al_2O_3 > CaO > NaF > KCl$

(c) $NaF > KCl > CaO > Al_2O_3$ (d) $Al_2O_3 > CaO > KCl > NaF$

6. The decreasing order of the ionic nature of the following compounds is

(a) LiI > NaBr > KCl > CsF (b) LiI > KCl > NaBr > CsF

(c) CsF > NaBr > KCl > LiI (d) CsF > KCl > NaBr > LiI

7. The compound having the highest melting point is

(a) LiCl (b) LiF (c) LiI (d) LiBr

8. The degree of hydration is expected to be maximum for

(a) Mg^{2+} (b) Na^+ (c) Ba^{2+} (d) K^-

IIT-JEE Previous Year Questions

9. The temporary hardness of water is due to calcium bicarbonate can be removed by adding

(a) $CaCO_3$ (b) $Ca(OH)_2$ (c) $CaCl_2$ (d) HCl

10. A solution of sodium metal in liquid ammonia in strongly reducing due to the presence of

(a) sodium atoms (b) sodium hydride (c) sodium amide (d) solvated electrons

11. Heavy water is

(a) H_2O^{18} (b) water obtained by repeated distillation

(c) D_2O (d) Water at 4°C

12. The oxide that gives H_2O_2 on treatment with a dilute acid is

(a) PbO_2 (b) Na_2O_2 (c) MnO_2 (d) TiO_2

13. The metallic lustre exhibited by sodium metal is explained by

(a) diffusion of sodium ions (b) oscillation of loose electron

(c) excitation of free protons (d) existence of body centred cubic lattice

14. The oxidation state of the most electronegative element in the products of the reaction, BaO_2 with dil. H_2SO_4 are

(a) 0 and –1 (b) –1 and –2 (c) –2 and 0 (d) –2 and 0

15. The species that do not contain peroxide ions, is

(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2

16. The material used in solar cells contains

(a) Cs (b) Si (c) Sn (d) Ti

ANSWER KEY

EXERCISE - I

1. a 2. d 3. d 4. a 5. d 6. a 7. c
8. d 9. d 10. a 11. a 12. a 13. b 14. b
15. c 16. b 17. a 18. a 19. b 20. a 21. b
22. d

EXERCISE - II

1. b,c 2. a,d 3. a,c,d 4. a,b 5. a,c,d 6. a,b,c 7. a,b,d
8. a,b,c 9. b,c,d 10. a,b 11. a,b 12. a,b,c 13. a,b,c 14. a,b
15. a,c 16. a,b,c,d 17. a,b,c,d 18. a,c,d 19. b,c,d 20. a,b 21. c,d

EXERCISE - III

1. b 2. b 3. 5 4. d 5. b 6. d 7. b
8. a 9. b 10. d 11. c 12. b 13. b 14. b
15. a 16. b

CHAPTER 4

P-BLOCK

The elements in which the last electron enters the outer most p orbital are called p- block elements. As the maximum number of electrons that can be accommodated in a set of p-orbitals is six, therefore there are six groups of p - blocks in the periodic table.

B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn

INERT PAIR EFFECT

The inert pair effect shows itself increasingly in the heavier members of the group. There is a decrease in stability of the **maximum** oxidation state and an increase in the stability of the **(Maximum – 2)** state on descending the group. Ge(+II) is a strong reducing agent whereas Ge(+IV) is stable Sn(+II) exists as simple ions which are strongly reducing but Sn(+IV) is covalent and stable. Pb(+II) is ionic, stable and more common than Pb(+IV), which is oxidizing. The lower valencies are more ionic because the radius of M^{2+} is greater than that of M^{4+} and according to Fajans rules, the smaller the ion the greater the tendency to covalency

GROUP 13 ELEMENTS (BORON FAMILY)

The Elements are B (Non metal), Al, Ga, In, Tℓ (Metals)

General electronic configuration [Noble gas] $ns^2\ np^1$

ATOMIC AND PHYSICAL PROPERTIES.

(1) Atomic and Ionic radii

Atomic radii : B < Ga < Al < In < Tℓ

(2) Ionization Enthalpies.

B > Tℓ > Ga > Al > In (First IE values)

(3) Melting and Boiling points

M.P. B > Al > Tl > In > Ga

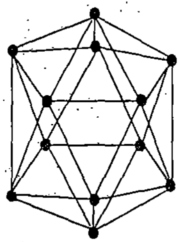
B.P. B > Al > Ga > In > Tl

(4) **Electropositive Character**

Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [∴ B is nonmetals and other elements are metals.]

$$\underset{\text{Non metal}}{\underline{B <}}\ \underset{\text{Metals}}{\underline{Al < Ga < In < Tl}}$$

Note : Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners.For example one is the simplest form : α - rhombohedral boron.



But Al , In & Tℓ all have close packed metal structure.

BORON (B)

Properties

It exists in five forms four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. Melting points are around 2300°C. But amorphous form is brown and chemically active.

(i) $4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$

(ii) $2B + N_2 \xrightarrow{300C} 2BN, \quad BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$

(iii) $Mg_3B_2 + 6HCl \xrightarrow{\text{Hydrolysis}} 3MgCl_2 + B_2H_6\ ; \quad B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

(iv) $SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$

COMPOUNDS OF BORON

BORON SESQUIOXIDE (B_2O_3)

Preparation

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow[100°]{} \underset{\text{Meta boric acid}}{HBO_2} \xrightarrow{\text{red heat}} B_2O_3$$

Properties

It is a weakly acidic oxide and reacts with alkalies or bases to form borates $3Na_2O + B_2O_3 \rightarrow 2Na_3BO_3$ (Sodium orthoborate), It reacts with water slowly to form orthoboric acid. When heated with transition metal salts it forms coloured compounds.

$$H_2O + B_2O_3 \longrightarrow 2HBO_2; \qquad HBO_2 + H_2O \longrightarrow H_3BO_3$$

- The oxyacids of boron are

(a) Orthoboric acid (H_3BO_3)	(b) Metaboric acid (HBO_2)
(c) Tetraboric acid ($H_2B_4O_7$)	(d) Pyroboric acid ($H_4B_4O_8$)

ORTHOBORIC ACID

Orthoboric acid H_3BO_3 behaves as a weak monobasic acid it does not donate protons but rather accepts OH^-. It is therefore a Lewis acid $B(OH)_3$. Due to sp^2 hybridisation of boron, boric acid is a planar molecule and due to H-bonding between different molecules boric acid has layer structure.

Preparation

(i) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$

H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH^-. It is therefore a Lewis acid $(B(OH)_3)$

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

Properties

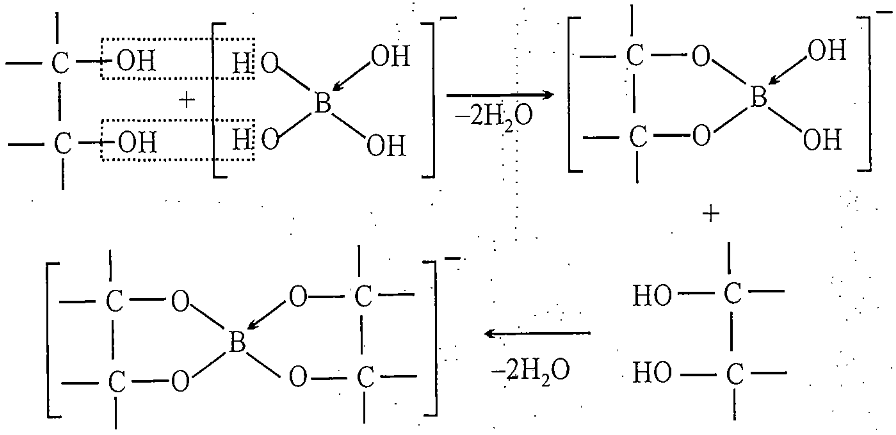
- It is a weak monobasic lewis acid and in aqueous solution the boron atom completes its octet by removing. OH^- from water molecules.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $B(OH)_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is detected using phenolphthalein as indicator.

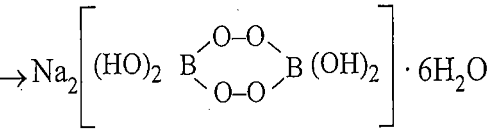
$$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$$
$$NaBO_2 + 2H_2O$$

The added compound must be a cis diol to enhance the acidic properties in this way the cis-diol forms very stable complexes with $[B(OH)_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



- **Heating of boric acid :**

$$H_3BO_3 \xrightarrow{100°C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{140°C} \underset{\text{tetraboric acid}}{H_2B_4O_7} \xrightarrow[\text{red hot}]{\Delta} \underset{\text{Glassy mass}}{B_2O_3}$$

- $H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2B-O-O-H \xrightarrow{NaOH}$ 

Sodium peroxy borate used in washing powder as brightener

- When boric acid is heated with ethyl alcohol, the evolved gas vapours of ethylborate is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \rightarrow \underset{\text{Ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

BORAX ($Na_2B_4O_7$, $10H_2O$)

Preparation of Borax :

$$\underset{\text{Colemanite}}{2CaO \cdot 3B_2O_3} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

↓ Filtered – $CaCO_3$(as residue)

$$\underset{\text{in Filtrate}}{NaBO_2} + \underset{\text{as residue}}{\left[Na_2B_4O_7 \cdot 10H_2O\right]} \xleftarrow[\text{and allowed to crystallise out and filtered}]{\text{Concentrated}} \underbrace{Na_2B_4O_7 + NaBO_2}_{\text{in solution}}$$

↓ CO_2 passed and crystallise out again $[4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3]$

$Na_2B_4O_7 \cdot 10H_2O \downarrow$
as 2nd Crop of the
reaction.

Properties

✶ **Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH**

$$\mathbf{Na_2B_4O_7 + 7H_2O \rightarrow 4H_3BO_3 + 2NaOH}$$

(i) When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7 \bullet 10H_2O + \xrightarrow{\Delta} Na_2B_4O_7 + 10\,H_2O \uparrow$$

$$Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2\,(\text{borax bead}) + B_2O_3$$

(ii) $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$ (boric acid)

(v) $Na_2B_4O_7 \xrightarrow[\Delta]{NaOH} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}}$; $CuO + B_2O_3 \longrightarrow Cu(BO_2)_2$ (blue bead)

BORON HYDRIDES

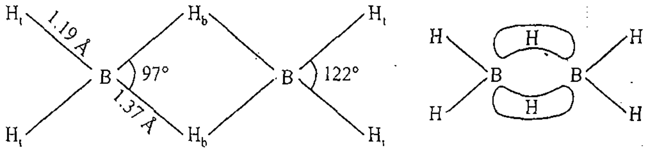
Binary compounds of B with H are called boron hydrides of boranes. These compounds form following two types of seires :

(Nido) $B_nH_{n+4} \rightarrow B_2H_6, B_5H_9, B_6H_{10}, B_{10}H_{14}$

(Arachno) $B_nH_{n+6} \rightarrow B_4H_{10}, B_5H_{11}, B_6H_{12}, B_9H_{15}$

DIBORANE (B_2H_6)

Structure of Diborane



Preparation

(i) $4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$

Properties:

1. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 2H_2O;\ \Delta H = -2137.7\ kJ\ mol^{-1}$
2. Pyrolysis of B_2H_6 in sealed vessels at temperatures above 375 K is an excedingly complex process producing a mixture of various boranes e.g. B_4H_{10}, B_6H_{12} and $B_{10}H_{14}$
3. $B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 6H_2$
4. $B_2H_6 + 2Me_3N \longrightarrow 2Me_3N - BH_3$
5. $B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$
6. $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\ atm} 2BH_3CO$ (boron carbonyl)
7. $B_2H_6 + 2NH_3 \xrightarrow{low\ temperature} B_2H_6 2NH_3 \xrightarrow{200°C} B_3N_3H_6$ (borazine)
8. $B_2H_6 + 2LiH \longrightarrow 2LiBH_4$

- Carbaboranes are compounds of carbon, boron and hydrogen in which carbon and boron atoms occupy the vertices of a triangulated polyhedron. These compounds may be considered to have been derived from boranes by the replacement of BH^- units by CH units. The carbaboranes and the boranes having the same number of electrons in their bonding, frame work have similar skeletal structures. Three structurally different types of carboranes, namely, closo, nido and arachno are known at present.

BORAZINE OR BORAZOLE, $(BH)_3\ (NH)_3$ or $B_3N_3H_6$

This compound is isoelectronic with benzene and hence has been called Inorganic Benzene.

Preparation: Borazine can be prepared by the following methods.

(i) **By Stock and Pohland's method (1926):** By the action of NH_3 on diborane (B_2H_6). The adduct, $B_2H_6.2NH_3$ is first formed, which then gets decomposed by heating in a closed tube at 200°C.

$$\underset{(Ratio = 1:2)}{3B_2H_6 + 6NH_3} \longrightarrow \underset{Adduct}{3[B_2H_6 \cdot 2NH_3]} \xrightarrow{200°C} 2B_3N_3H_6 + 12H_2$$

(ii) **By heating BCl_3 with NH_4Cl:**

$$3NH_4Cl + 3BCl_3 \xrightarrow[C_6H_5Cl \text{ and Fe})]{140°C \text{ (In presence of}} \underset{\text{B. B. B−trichloroborazine}}{Cl_3B_3N_3H_3} + 9HCl$$

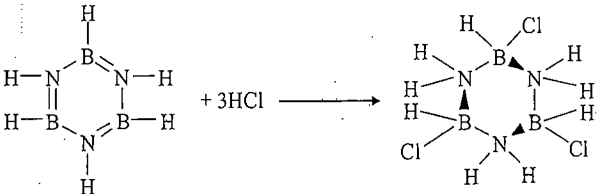
$$3Cl_3B_3N_3H_3 + 6LiBH_4 \xrightarrow{\text{Reduction}} 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

(iii) **By heating a mixture of $LiBH_4$ and NH_4Cl (Laboratory method):**

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230°C} B_3N_3H_6 + 3LiCl + 9H_2$$

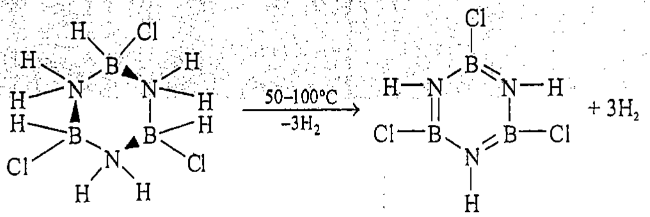
Chemical Properties

(i) **Addition reactions:** (a) One molecule of $B_3N_3H_6$ adds three molecule of HCl or HBr in the cold, without a catalyst. These molecules get attached with all the three B-atoms of $B_3N_3H_6$ molecule, since N-atom is more electronegative than B-atom in B–N or B = N bond and hydrogen chloride derivative ($B_3N_3H_9Cl_3$) is obtained. This addition reaction is not shown by benzene.



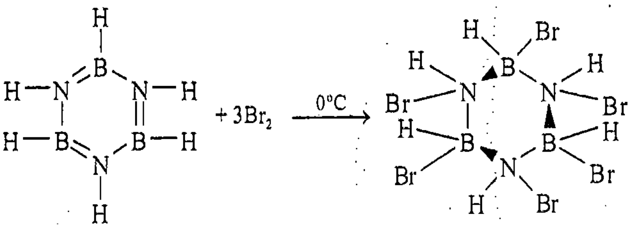
Hydrogen chloride derivative

When this derivative is heated to 50-100°C, it looses three H_2 molecules, to give B, B, B-trichloroborazine, $B_3N_3H_3Cl_3$.

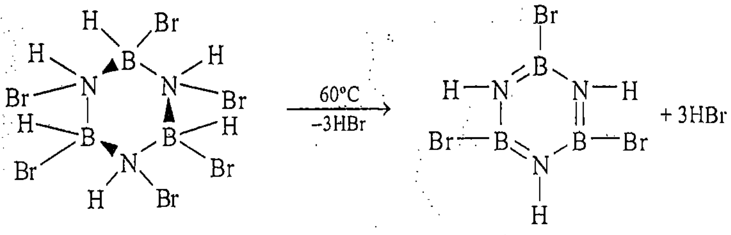


B.B.B-trichlorobe

(b)

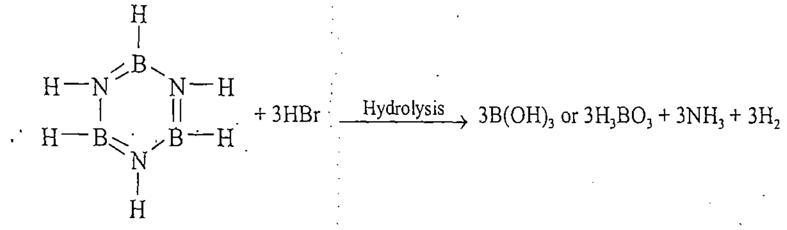


B-tribromo-N-tribromoborazinc

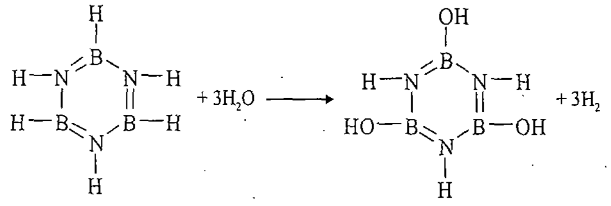


B-tribromoborazine

(ii) **Hydrolysis:** (a) Borazine gets slowly hydrolysed by water to produce boric acid [$B(OH)_3$ or H_3BO_3], NH_3 and H_2. Hydrolysis is favoured by the increase in temperature.

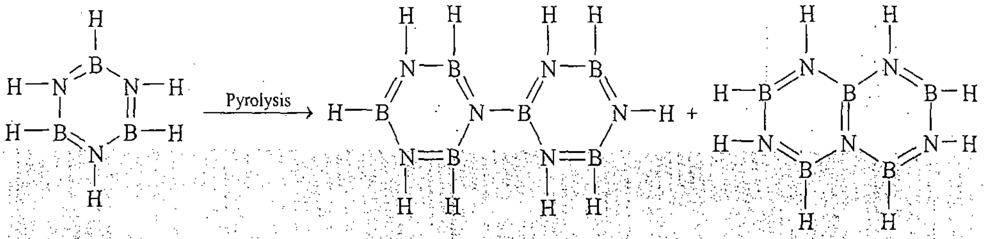


(b) It is reported that under proper conditions, borazine reacts with three molecule of water and gives B-trihydroxyl borazine, $B_3N_3H_3(OH)_3$ (substitution reaction).



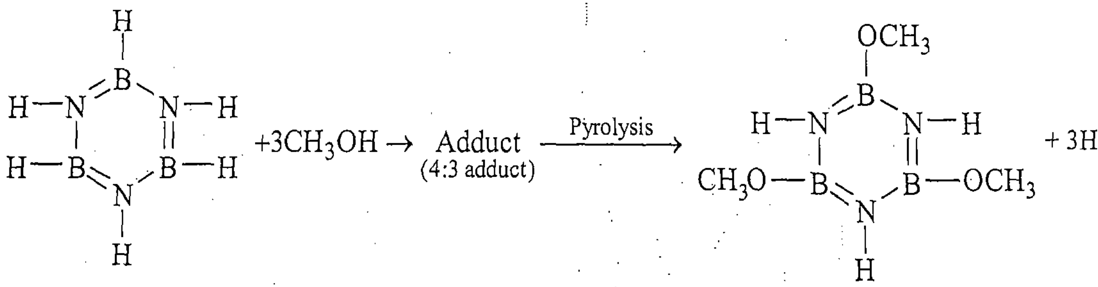
B-tribromoborazine

(iii) **Pyrolysis:** When borazine is pyrolysed above 340°C, $B_6N_6H_{10}$ and $B_5N_5H_8$ are produced. These products are boron-nitrogen analogues of diphenyl and naphthalene respectively



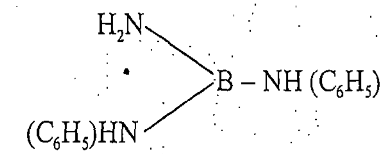
(iv) **Hydrogenation:** Hydrogenation of borazine produces polymeric materials of indefinite composition.

(v) **Formation of adduct:** Borazine forms an adduct with CH_3OH. This adduct undergoes pyrolysis with the elimination of H_2 and gives B-trimethoxy-borazine.



B-trimethoxy-borazine

(vi) **Reaction with aniline:** Borazine undergoes a strongly exothermic reaction with aniline produce tri-aminoborine.



Structure of borazine molecule: In the structure of borazine, both B and N atoms are sp^2 hybridised. Each N-atom has one lone pair of electrons, while each B-atom has an empty p-orbital. (B–N) π-bond in borazine is a dative bond, which arises from the sidewise overlap, between the filled p-orbitals of N-atom and empty p-orbitals of B-atom.

Since borazine is isoelectronic with benzene, both the compounds have aromatic π-electron cloud (electrons in π-orbitals). Due to greater difference in the electronegativity values of B and N-atoms, the π-electron cloud in B_3N_3 ring of borazine molecule is partially delocalised, while in case of benzene ring, the π-electron cloud is completely delocalised. In fact, complete delocalisation of π-electron cloud in B_3N_3 ring in borazine molecule, cannot be expected, since N-π orbitals are of lower energy than the B-π orbitals. Molecular orbital calculations have indicated that π-electron drift from N to B is less than the σ-electron drift from B to N, due to greater electronegativity of N-atom. In C_6H_6 molecule, C = C bonds are nonpolar while in case of $B_3N_3H_6$ molecule due to the difference in electronegativities between B and N atoms, B–N bond is polar.

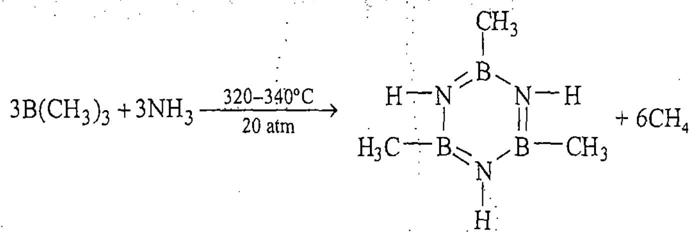
The ring structure of borazine molecule is the same as the layer lattice structure of boron nitride, $(BN)_n$.

It is due to the partial delocalisation of the π-electron cloud that π-bonding in B_3N_3 ring weakened. In addition, N-atom retains some of its basicity and boron atom retains some of its acidity. Polar species like HCl, therefore, attack the double bond between N and B. Thus, borazine in contrast to C_6H_6, readily undergoes addition reactions.

In these reactions, more electronegative atom (e.g., Cl in HCl molecule) is generally attached with B-atom, which is less electronegative than N in B–N bond.

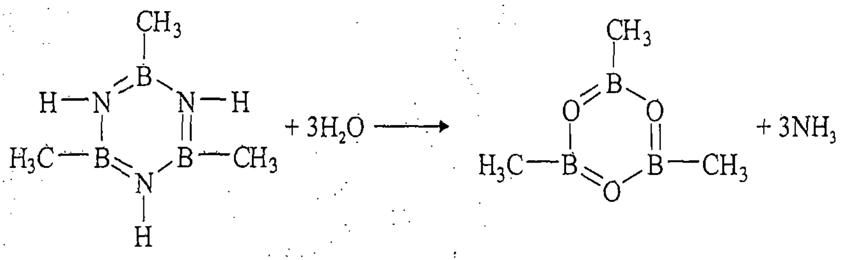
In borazine, B–N bond length is equal to 1.44Å, which is between the calculated single B–N bond (= 1.54 Å) and double bond, B = N (= 1.36 Å) distances. The angles are equal to 120°. In benzene C–C bond length is equal to 1.42Å.

1. **B-trimethyl borazine, $[B(CH_3)]_3(NH)_3$:** It is prepared by heating $B(CH_3)_3$ with NH_3, at 320–340° at 20 atm for 2 hours.



B-trimethyl borazine, $[B(CH_3)]_3\ (NH)_3$

At 100°C, water replaces the NH groups by O-atoms and gives B-trimethyl boroxine, $[B(CH_3)]_3O_3$.

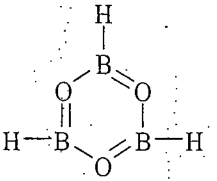


B-trimethyl borazine, $[B(CH_3)]_3(NH)_3$ B-trimethyl boroxine, $[B(CH_3)]_3O_3$

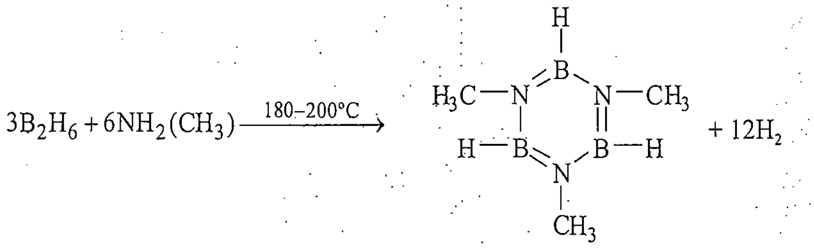
2. **Boroxine, $(BH)_3O_3$:** This compound is isoelectronic with borazine, $B_3N_3H_6$ $(B_3O_3H_3)$ = 3 × 3 + 3 × 6 + 3 × 1 = 30, $B_3N_3H_6$ = 3 × 3 + 5 × 3 + 6 × 1 = 30. It is produced by the explosive oxidation of B_2H_6 or B_5H_9. This compound decomposes at room temperature to diborane (B_2H_6) and boron trioxide (B_2O_3).

$$2B_3O_3H_3 \rightarrow 2B_2O_3 + B_2H_6$$

Boroxine exhibits aromatic properties of benzene. Boroxine is even less stable and presumably has less π-delocalisation than borazine. In this molecule, B–O bond distance is equal to 1.38 Å. The characteristic Roman frequency of the ring is at 807 cm^{-1}. B = O, double bond present in the structure is due to the donation of a lone pair of electrons from O-atom to boron atom. This results in the development of a formal negative charge on B-atom and equal formal positive charge on O-atom.



3. **N-trimethyl borazine, $(BH)_3[N(CH_3)]_3$:** It is obtained in 90% yield by heating a mixture of B_2H_6 and $NH_2.(CH_3)$ in the correct proportions at 180–200°C for 2 hours.



N-trimethyl borazine, $(BH)_3[N(CH_3)_3]$

This compound can also be prepared by reducing monomethyl ammonium chloride, $(CH_3)NH_3Cl$ with lithium borohydridea $LiBH_4$.

$$3(CH_3)NH_3Cl + 3LiBH_4 \rightarrow (BH)_3[N(CH_3)]_3 + 3LiCl + 9H_2$$

Halides:

- The relative strength of lewis acids of boron trihalides increases in the order $BF_3 < BCl_3 < BBr_3$. This order of Lewis acid strength is just reversed of that expected on the basis of the electronegativity of the halogen. This is explained on the basis of overlapping of halogens sidewise with empty 2p-orbital of B forming **pπ-pπ back bonding.** The tendency of back bonding decreases as $BF_3 > BCl_3 > BBr_3 > BI_3$ due to the difference in the energy states of the orbitals involved.
- Both boron and aluminium halides are Lewis acid but only aluminium halides exists as dimers whereas boron halides exists only as monomers. This is due to the reason that boron atom is so small that it cannot accommodate four large sized halide ions around it.
- BF_3 and $AlCl_3$ are widely used as Lewis acid catalyst in Friedel-Crafts reactions and many industrial processes.
- Solution of $AlEt_3$ and $TiCl_4$ in hydrocarbon solvent react endothermically to form a brown solid. This is the important **Ziegler Natta catalyst** for polymerizing ethene to form polythene.

1. **Hydrolysis**

The boron halides are all hydrolysed by water. BF_3 hydrolysis incompletely and forms fluoborates. This is because the HF first formed reacts with the H_3BO_3.

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$

$$\underline{12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O}$$

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

The other halides hydrolysis completely, giving boric acid.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

2. **Electron Deficiency**

The fluorides of Al, Ga, In and Tl are ionic and have high melting points. The other halides are lagely covalent when anhydrous. $AlCl_3$, $AlBr_3$ and $GaCl_3$ exist as dimer, thus attaining an octet of electrons. The dimeric formula is retained when the halides dissolve in non-polar solvents such as benzene. However, when the halides dissolve in water, the high enthalpy of hydration is sufficient to break the covalent dimer into $[M.6H_2O]^{3+}$ and $3X^-$ ions. At low temperature $AlCl_3$ exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes. On heating Al_2Cl_6 species are formed and the volume of the solid greatly increases. This illustrates how close the bonding in this compound is to the ionic/covalent border.

Group 13 elements have only three valency electrons. When these are used to form three covalent bonds, the atom has a share in only six electrons. The compounds are therefore electron deficient. The BX_3 halides attain an octet by π bonding. The other elements in the group have larger atoms and cannot get effective π overlap, so they polymerize to remedy the electron deficiency.

ALUMINIUM (Al)

Properties

(i) **Action of air :** Dry air has no action on Al. But moist air forms a thin layer of Al_2O_3 on its surface and it loses its luster. At very high temperatures it burns to form Al_2O_3 and AlN.

(1) $Al + Air \xrightarrow{\Delta} Al_2O_3 + AlN$

(2) $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

- AlN reacts with hot water to form $Al(OH)_3$ and NH_3.

COMPOUNDS OF ALUMINIUM

(i) **Aluminium Oxide (Al_2O_3) Alumina**

Preparation

1. $2Al(OH)_3 \xrightarrow{+\Delta} Al_2O_3 + 3H_2O\uparrow$

Properties :

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., $AlCl_3$) as well as alkalies (forming $NaAlO_2$). Thus amphoteric in nature. It is a polar covalent compound.

(ii) **Aluminium Chloride ($AlCl_3 \cdot 6H_2O$)**

It is a colourless crystalline solid, soluble in water. It is anhydrous $AlCl_3$ is a deliquescent white solid.

Preparation

(1) $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$

(2) $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2$

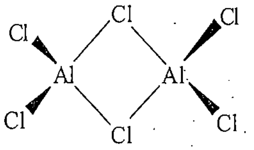
Properties

(1) $2AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 9H_2O$

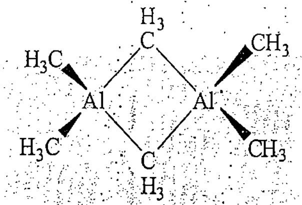
(2) $AlCl_3 + 3H_2O \Leftrightarrow Al(OH)_3 + 3HCl \uparrow$ White fumes

Al_2Cl_6, Al_2Me_6

Aluminium halides are dimers in the gas phase : aluminium chloride, has molecular formula Al_2Cl_6 in the vapour. Each Al atom acts as an acid towards a Cl atom initially belonging to the other Al atom. Aluminium chloride is widely used as a Lewis acid catalyst for organic reactions.



Alkylaluminium dimers are simlar in structure to the analogous dimeric halides but the bonding is differnet. In the halides, the bridging Al – Cl – Al bonds are **3c–4e** bonds; that is each Al – Cl bond involves an electron pair. In the alkylaluminium dimers the Al – C – Al bonds are longer than the terminal Al – Cl bonds, which sugests that they are **3c–2e** bonds, with one bonding pair shared across the Al – C – Al unit, somewhat analogous to the bonding in diborane, B_2H_6.



ALUMNS

M_2SO_4, $M'_2(SO_4)_3 \cdot 24H_2O$ ***Props:*** Swelling characteristics

where $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum

Preparation: $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

$Al_2(SO_4)_3 + K_2SO_4 + \text{aq. sol}^n \longrightarrow$ crystallise

GROUP 14TH ELEMENT (CARBON FAMILY)

Physical Properties

(a) **Covalent Radii :** The covalent radii increase down the group. The difference in size between Si and Ge is less than might be otherwise expected because Ge has a full 3d subshell which shields the nuclear charge rather ineffectively. In a simlar way the small difference in size between Sn and Pb is because of the filling of the 4f subshell.

TABLE : Radii, melting points and electronegativity values

	Covalent Radius (Å)	Ionization energies (kJ mol^{-1}) 1st	2nd	3rd	4th	Melting point (°C)	Boiling point (°C)	Pauling's electro-negativity values
C	0.77	1086	2354	4622	6223	4100		2.5
Si	1.17	786	1573	3232	4351	1420	3280	1.8
Ge	1.22	760	1534	3300	4409	945	2850	1.8
Sn	1.40	707	1409	2943	3821	232	2623	1.8
Pb	1.46	715	1447	3087	4081	327	1751	1.8

(b) **Ionization Energy:** The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling the d and f subshells. The amount of energy required to form M^{4+} ions is extremely large and hence simple ionic compounds are rare. The only elements which will give a large enough electronegativity difference to give ionic character are F and O. The compounds SnF_2, PbF_2, SnF_4, PbF_4, SnO_2, and PbO_2 are significantly ionic, but the only significant metal ion is Pb^{2+}.

(c) **Melting Points:** C has an extremely high melting point. Si melts appreciably lower than C, but the values for Si and gE are still high. They all have the very stable diamond type of lattice. Melting involves breaking the strong covalent bonds in this lattice, and so requires a lot of energy. The melting points decrease on descending the group because the M—M bonds become weaker as the atoms increase in size. Sn and Pb are metalic, and have much lower melting points. They do not use all four outer electrons for metallic bonding.

(d) **Metallic and Non-metallic Character :** The change from non-metal to metal with increasing atomic number is well illustrated in Group 14, where C and Si are non-metals, Ge has some metallic properties, and Sn and Pb are metals. The increase in metallic character shows itself in the structures and apperance of the elements, in physical properties such as malleability and electrical conductivity, and in chemical properties such as the increased tendency to form M^{2+} ions and the acidic or basic properties of the oxides and hydroxides.

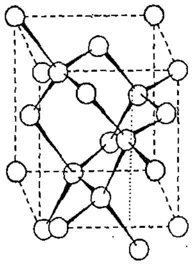
ALLOTROPES OF CARBON

Graphite & Diamond

Carbon exists in a large number of allotropic forms. These include diamond, α- and β-graphite, a rare hexagonal form of diamond and a variety of discrete molecules such as C_{60}, which are rarely clusters of carbon atoms and are called collectively fullerenes.

Diamond is extremely unreactive and in contrast graphite is quite reactive.

Diamond is typically colourless, though industrial diamonds are often black. Most naturaly occuring diamond contain a trace of nitrogen, but blue diamonds contain a trace of Al instead. In diamond each C atom is tetrahedrally surrounded by four other C atoms, each at a distance of 1.54 Å. The tetrahedra are linked together into a three-dimensional giant molecule. The unit cell is cubic. Strong covalent bonds extend in all directions. Thus the melting point is abnormally high (about 3930°C) and the structure is very hard (Figure). (In a rare modification of diamond, the tetraheda are arranged differently to give a wurtzite like structure and a hexagonal unit cell).



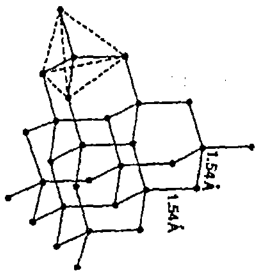
Graphite is composed of flat two-dimensional sheet of carbon atoms. Each sheet is a hexagonal net of C atoms and may be regarded as a fused system of benzene rings. The layers are held together by relatively weak van der Waals forces.

In graphite only three of the valency electrons of each carbon atom are involved in forming σ bonds (using sp^2 hybrid orbitals). The fourth electron forms a π bond. The π electrons are delocalized over the whole sheet and as they are mobile, graphite conducts electricity. Conduction can occur in a sheet, but not from one sheet to another.

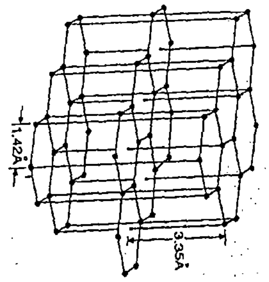
✶ **Graphite is thermodynamically most stable form of carbon.**

Diamond

Diamond occurs naturally in igneous rocks, formed by crystalization of molten form deep within the earth. This igneous rock may contain 0.1 g of diamond per ton. Diamond has a density of 3.5g/cc and is the hardest naturally occuring substance-a property which explains its use in oilwell drills, as an abrasive for sharpenig very hard tools and in dyes for the manufacture of tungsten filaments for electric light bulbs. Both these properties of diamond are readily understood in terms of its structure -a three dimensional array of carbon atoms, each atom being surrounded tetrahedraly by four other carbon. Each diamond crystal is a giant molecule containing very strong bonds.



DIAMOND



GRAPHITE

CARBON DIOXIDE (CO_2)

Preparation

1. $CaCO_3 + 2HCl \rightarrow CO_2 + CaCl_2 + H_2O$

Properties

1. Carbon dioxide is the acid anhydride of carbonic acid, and a solution of it in water will slowly turn blue litmus red. An equilibrium is set up and when the solution is boiled all the CO_2 is evolved.

$$CO_2(g) + H_2O(liq) \Leftrightarrow H_2CO_3(aq) \Leftrightarrow H^+(aq) + CO_3^{2}(aq)$$

2. Carbon dioxide readily reacts with alkalies forming the carbonate and if CO_2 is in excess, then hydrogen carbonate.

This is the basis of the lime-water test for CO_2 gas

$Ca(OH)_2\,(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O\,(liq)$:

$CaCO_3(s) + H_2O(liq) + CO_2(g) \rightarrow Ca(HCO_3)_2\,(aq)$

The above reaction accounts for the formation of temporarily hard water.

CARBON MONOOXIDE (CO)

Preparation

1. $C(s) + CO_2\,(g) \rightarrow 2CO(g)$
2. $HCOOH\,(liq) \rightarrow CO(g) + H_2O$

Properties

1. Carbon monoxide is a powerful reducing agent being employed industrially in the extraction of iron and nickel.

$Fe_2O_3(s) + 2CO(g) \rightarrow 2Fe(s) + 2CO_2(g)$;

$NiO(s) + CO(g) \rightarrow Ni(s) + CO_2(g)$

2. It reacts with many transition metals, forming volatile carbonyls; the formation of nickel carbonyl followed by its decomposition is the basis of the Mond's process for obtaining very pure nickel.

$Ni(s) + 4CO(g) \xrightarrow{90^\circ} Ni(CO)_4(liq) \xrightarrow{180^\circ C} Ni(s) + 4CO(g)$

CARBON SUBOXIDE (C_3O_2)

This is an evil-smelling gas and can be made by dehydrating propanedioic acid (malonic acid) of which it is the anhydride with phosphorus pentoxide.

$3CH_2(COOH)_2 + P_4O_{10} \rightarrow 3C_3O_2 + 4H_3PO_4$

Structure $O = C = C = C = O$ (linear)

CARBIDES

The binary compounds of Carbon with other elements are called carbides. They are classified into following 3 category

(i) Ionic (ii) Covalent (iii) Interstitial (or metallic)

(i) **Ionic Carbides (or salt like carbides):** Generally formed by elements of I, II & III group (B exception)

(1) **Methanides**

These give CH_4 on reaction with H_2O

(i) $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 2CH_4$ (ii) $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$

★ **These carbides contain C^{4-} ions in their constitution.**

(2) **Acetylides**

These give C_2H_2 on reaction with H_2O

(i) $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

✶ Such compounds contain C_2^{2-} ions [$:C \equiv C:$]$^{2-}$.

(3) Allylides

These give 1-propyne on reaction with H_2O

$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + CH_3 - C \equiv CH$

✶ Such compounds contain C_3^{4-} ions [$:C = C = C$]$^{4-}$

(ii) Covalent Carbides (SiC)

(iii) Interstital or metallic carbides

Such carbides are formed by transition metals in which carbon atoms occupy interstitials in the crystal structure of metals.

SILICON

Silicon is the second most abundant element occurring in the earth's crust (about 28 per cent by weight).

Preparation

1. $SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$

Properties

Silicon is a very high melting-point solid with the same structure as diamond. The non-existence of an allotrope with the graphite structure clearly shows the inability of silicon atoms to form multiple bonds with themselves.

1. Si(powdered) + $2Cl_2(g) \rightarrow SiCl_4$(liq)
2. It is not attacked by acids except hydrofluoric acid with which it forms hexaflourosilic acid.

   $Si(s) + 6HF(g) \rightarrow H_2SiF_6(aq) + 2H_2(g)$

Bonding in Silicon

Carbon differs from the other elements in its unique ability to form pπ – pπ multiple bonds, such as C = C, C ≡ C, C = O, C = S and C ≡ N. The later elements do not form pπ - pπ bonds, principally because the atomic orbitals are too large and diffuse to obtain effective overlap, but they can use d orbtials in multiple bonding, particularly between Si and N or O. Thus $N(SiH_3)_3$ is planar and has **pπ - dπ back bonding** but $N(CH_3)_3$ is pyramidal and has no π bonding.

Non metallic element in Period 3 and below can use available d orbitals to expand their valence shells by delocalization of the O or N lone pair, so the silyl ether and silyl amine are the weaker Lewis bases in each pair.

CARBORUNDUM (SiC)

1. It is very hard substance (hardness = 9.5 Mho).
2. Not attacked by acids. However, it gives the following two reactions at high temperature.

   (i) $SiC + 2NaOH + 2O_2 \xrightarrow{\Delta} Na_2SiO_3 + CO_2 + H_2O$;

   (ii) $SiC + 4Cl_2 \xrightarrow{\Delta} SiCl_4 + CCl_4$

✶ It has diamond like structure in which each atom is sp^3 hybridized. Therefore each atom is tetrahedrally surrounded by 4 atoms of other type.

COMPOUNDS OF SILICON

Silicates

Binary Compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.

(i) Since the electronegativity difference between O & Si is about 1.7 so Si-O bond can be considered 50% ionic & 50% covalent.

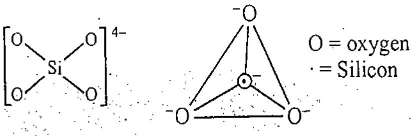
(ii) Radius Ratio $\frac{R_{Si^{+}}}{R_{O^{2-}}} = 0.29$

Silicate structures are based upon SiO_4^{-4} tetrahedral units.

(iii) SiO_4^{-4} tetrahedral units may exists as discrete units or may polymerise into larger units by sharing corners.

Classification of Silicates

(A) **Orthosilicate:** These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown in figure.



e.g., Zircon Zr (SiO_4) Forsterite of Olivine (Mg_2SiO_4)

(B) **Pyrosilicate :** In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units, (–) charges will be present on the oxygen atoms which is bonded with one Si atom.

e.g. Thorteveitite $(Sc_2Si_2O_7)$. Hemimorphite $[Zn_3(Si_2O_7)\ Zn(OH)_2\ H_2O]$

(C) **Cyclic silicates :** If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2})_n^{-}$ or $(SiO_3)_n^{2n-}$ is obtained the silicates containing these anions are called cyclic silicates $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.

(D) **Chain silicates :** Chain silicates may be further classified into simple chain & double chain compounds. In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(SiO_3)_n^{2n-}$.

e.g. $MgSiO_3$ (enstatite), diopside, $CaMg(SiO_3)_2$

(E) **Double Chain Silicate (Amphiboles):** Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compunds are also known as amphiboles. The Asbestos mineral is a well known example of double chain silicates.

e.g. Crocidolite $Na_2Fe_5(OH)_2\ [Si_4O_{11}]_2$ [Blue Asbestos], $(Mg, Fe)_7(OH)_2[Si_4O_{11}]_2$ Amosite

(F) **2D Sheet Silicate**

When SiO_4 units share three corners the structure formed is an infinite two-dimensional sheet of empirical formula $(Si_2O_5)_n^{2n-}$. There are strong bonds within the Si–O sheet, but much weaker forces hold each sheet to the next one. Thus these minerals tend to cleave into thin sheets.

e.g. Pyrophyllite $Al_2(OH)_2Si_4O_{10}$; Serpentine $Mg_3(OH)_4Si_2O_5$

(G) **Three dimensional sheet silicates :** These silicates involve all four oxygen atom in sharing with adjacent tetrahedral units e.g. Quartz, Feldspar, Zeolite etc.

SILICONES STRUCTURES

It is organo silicon polymer

$$CCl_4 + H_2O \longrightarrow \text{no hydrolysis}$$

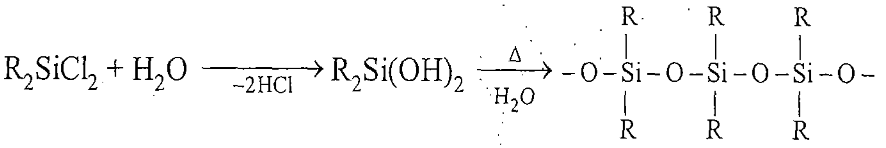
but $CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$

super heated

steam

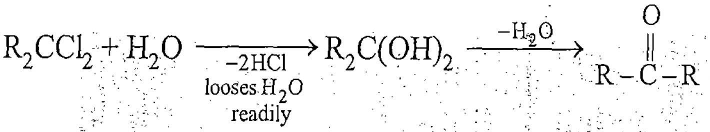
$$SiCl_4 + H_2O \longrightarrow Si(OH)_4 + 4HCl$$

$$\xrightarrow[-2H_2O]{\Delta} SiO_2\text{(3-D silicate)}$$



$$R_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} R_2Si(OH)_2 \xrightarrow[H_2O]{\Delta} -O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-$$

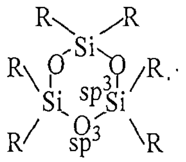
Linear silicone



$$R_2CCl_2 + H_2O \xrightarrow[\substack{-2HCl\\ \text{looses } H_2O\\ \text{readily}}]{} R_2C(OH)_2 \xrightarrow{-H_2O} R-\overset{\overset{O}{\|}}{C}-R$$

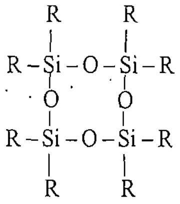
Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring.

Alcohol analogue of silicon is known as silanol



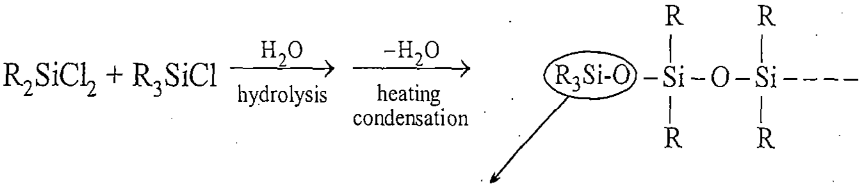
cyclic silicone

not planar



$$R_3SiCl \xrightarrow{H_2O} R_3SiOH \xrightarrow[\Delta]{-H_2O} R_3Si\text{-}O\text{-}SiR_3$$

Silanol

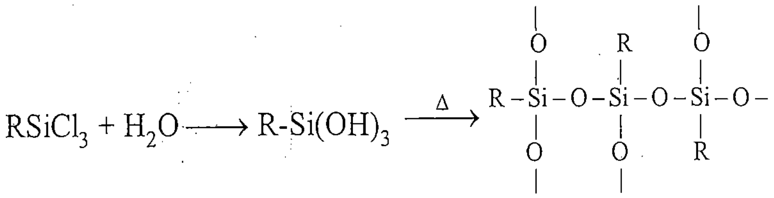


$$R_2SiCl_2 + R_3SiCl \xrightarrow[\text{hydrolysis}]{H_2O} \xrightarrow[\substack{\text{heating}\\ \text{condensation}}]{-H_2O} \boxed{R_3Si\text{-}O}-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}----$$

This end of the chain can't be extended hence

R_3SiCl is called as chain stopping unit

- Using R_3SiCl in a certain proportion we can control the chain length of the polymer



$$RSiCl_3 + H_2O \longrightarrow R\text{-}Si(OH)_3 \xrightarrow{\Delta} \begin{array}{ccccc} | & & & & | \\ O & & R & & O \\ | & & | & & | \\ R-Si & -O- & Si & -O- & Si-O- \\ | & & | & & | \\ O & & O & & R \\ | & & | & & \end{array}$$

cross linked silicone

3 dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controling the proportion of $RSiCl_3$ we can control the hardness of polymer.

Uses

(1) It can be used as electrical insulator (due to inertness of Si–O–Si bonds)

(2) It is used as water repellant (∵ surface is covered) eg. car polish, shoe polish, massonary works in buildings

(3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.

(4) As a lubricant in the gear boxes.

SILICA (SiO_2)

Occurrence:

Silica or silicon dioxide occurs in nature in free state as sand, quartz and flint and in the combined state as silicates like, Feldspar : $K_2O.Al_2O_3.6SiO_2$, Kaolinite : $Al_2O_3.\ 2SiO_2.\ 2H_2O$ etc.

Properties:

(i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

(ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(l) + 2H_2O(l)$$

(iii) It also combines with metallic oxides at high temperature giving silicates e.g.

$$SiO_2(s) + CaO(s) \xrightarrow{\Delta} CaSiO_3(s)$$

(iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$SiO_2(s) + Na_2CO_3(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + CO_2(g)$$

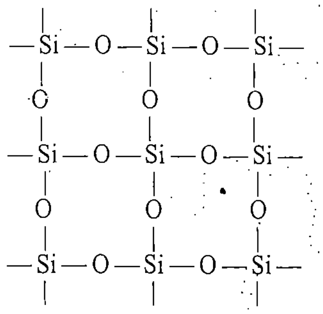
$$SiO_2(s) + Na_2SO_4(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + SO_3(g)$$

$$3SiO_2(s) + Ca_3(PO_4)_2(s) \xrightarrow{\text{high temp.}} 3CaSiO_3(s) + P_2O_5(g)$$

The first two examples quoted here are important in glass making.

Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is sp^3-hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



Uses:

(i) Sand is used in large quantities to make mortar and cement.

(ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.

(iii) Powdered quartz is used for making silica bricks.

(iv) Silica gel ($SiO_2.xH_2O$) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

HYDROLYSIS

The carbon halides are not hydrolysed under normal conditions because they have no vacant d-orbitals and cannot form a five coordinate hydrolysis intermediate. In contrast the silicon halides hydrolyse readily. Silicon has 3d orbitals available and these may be used to coordinate OH ions or water as a first step in hydrolysis. **In any atom there are always empty orbitals, but these are usually too high in energy to be used.** If sufficient energy is provided by using superheated steam then CCl_4 will hydrolyse

$$CCl_4 + H_2O \xrightarrow[\text{stean}]{\text{superheated}} \underset{\text{carbonyl chloride(phosgene)}}{COCl_2 + 2HCl}$$

The silicon halides are rapidly hydrolysed by water to give silicic acid.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

$GeCl_4$ and $GeBr_4$ are hydrolysed less readily, $SnCl_4$ and $PbCl_4$ hydrolyse in dilute solutions, but hydrolysis is often incomplete and can be repressed by the addition of the appropriate halogen acid.

$$Sn(OH)_4 \underset{H_2O}{\overset{HCl}{\rightleftharpoons}} SnCl_4 \underset{H_2O}{\overset{HCl}{\rightleftharpoons}} [SnCl_6]^{2-}$$

TIN (Sn)

Stannous Oxide (SnO):

(a) $Sn(OH)_2 \xrightarrow{\Delta} SnO + H_2O \uparrow$

Properties

SnO is an amphoteric white solid oxide. It dissolves in acids to form stannous salts

$$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$$

SnO dissolves in hot NaOH solution to form (soluble) sodium stannite and water.

$$SnO + 2NaOH \longrightarrow Na_2\,SnO_2 + H_2O$$

Stannous Chloride ($SnCl_2 . 2H_2O$)

It is a colourless solid soluble in water. Its solution becomes milky on standing due to its hydrolysis to $Sn(OH)_2$ and HCl. It aqueous solution is acidic to litmus. It is a strong reducing agent. It is soluble in alcohol and ether also.

Preparation

(a) $Sn + 2HCl\,(concentrated) \longrightarrow SnCl_2\,(aq) + H_2\uparrow$

The solution on crystalization gives colourless crystals of $SnCl_2 . 2H_2O$

Properties

1. When $SnCl_2$ solution is added to an aqueous solution of mercuric chloride, a silky white percipitate of mercurous chloride, Hg_2Cl_2 is formed which turns black due to further reduction of Hg_2Cl_2 to black mercury

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow(white) + SnCl_4\ ;\ Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow(black) + SnCl_4$$

2. It reduces ferric chloride. $FeCl_3$ to ferrous chloride, $FeCl_2$

$2FeCl_3$ (brown solution) + $SnCl_2 \rightarrow 2\ FeCl_2$ (colourless solution) + $SnCl_4$

3. It is hydrolysed with water to produce white percipitate of $Sn(OH)_2$

$SnCl_2 + 2H_2O \Leftrightarrow Sn(OH)_2\,(white)\downarrow + 2HCl$

✶ **As it produces a weak base and strong acid its aqueous solution is acidic.**

Stannic Oxide (SnO_2)

Preparation

1. $Sn + O_2 \rightarrow SnO_2$

Properties

1. It dissolves in conc. H_2SO_4 to form stannic sulphate

$SnO_2 + 2H_2SO_4 \rightarrow Sn(SO_4)_2 + 2H_2O$

2. It also dissolves in conc. Alkalies to form alkali metal stannate solution.

$SnO_2 + 2NaOH \rightarrow Na_2SnO_3(Sodium\ stannate) + H_2O$

LEAD (Pb)

Lithrage (PbO)

1. $2Pb + O_2 \xrightarrow[180°]{\Delta} 2PbO$ It is an amphoteric oxide and dissolves in acids as well as in alkalies

2. $PbO + 2HNO_3 \xrightarrow{\Delta} Pb(NO_3)_2 + H_2O;$

3. $PbO + 2NaOH \xrightarrow{\Delta} Na_2PbO_2(Sodium\ plumbate) + H_2O$

Lead Dioxide (PbO_2)

Properties

(i) On heating at 440°C it gives monoxide :

$2PbO_2 \xrightarrow{440°C} 2PbO + O_2$

(ii) It is not lead peroxide.

(iii) It is strong oxidising agent.

INTERCALATION CHEMISTRY

Intercalation compounds consist of layers ("sandwiches") of different chemical species. The name comes from that describing the insertion of extra days (such as Fabruary 29th) into the calendar to make it match the solar year. Most work on intercalation compounds has been on synthetic systems in which atoms, ions, or molecules have been inserted between layers of the host material. However, some aluminosilicates that we have encountered above provide useful examples. Thus talc and micas form layered structures with ions between the silicate sheets. Some minerals, including all clays, have water molecules intercalcated between the framework sheets. In some, such as vermiculite, the water may rapidly and dramatically be evacuated by heating. The water molecules leave faster than they can diffuse along the layers–exfoliation occurs. The result is the familiar expanded vermiculite used as a packing material and as a potting soil conditioner.

Another example of this type of intercalation compound is sodium beta alumina where the sodium ions are free to move between the spinel layers. The sodium ions can be replaced by almost any +1 cation such as: Li^+, K^+, Rb^+, Cs^+, NH_4^+, H_3O^+, Tl^+, Ga^+, NO^+ etc. The conductivity of these materials varies with the size of the ions moving between the fixed-distance (Al–O–Al) layers.

Graphite is perhaps the simplest layered structure. The intralayer C–C distance (142 pm) is twice the covalent radius of aromatic carbon (cf. 139 pm in benzene) and the interlayer C–C distance is 335 pm, twice the van der Waals radius of carbon. The sheets are held together by weak van der Waals forces. Many substances can be intercalated between the layers of graphite, but one of the longest known and best studied is potassium, which can be intercalated until a limiting formula of C_8K is reached. This is known as the first-stage compound. The earlier, lower stages have the general formula of $C_{12n}K$. The stages form

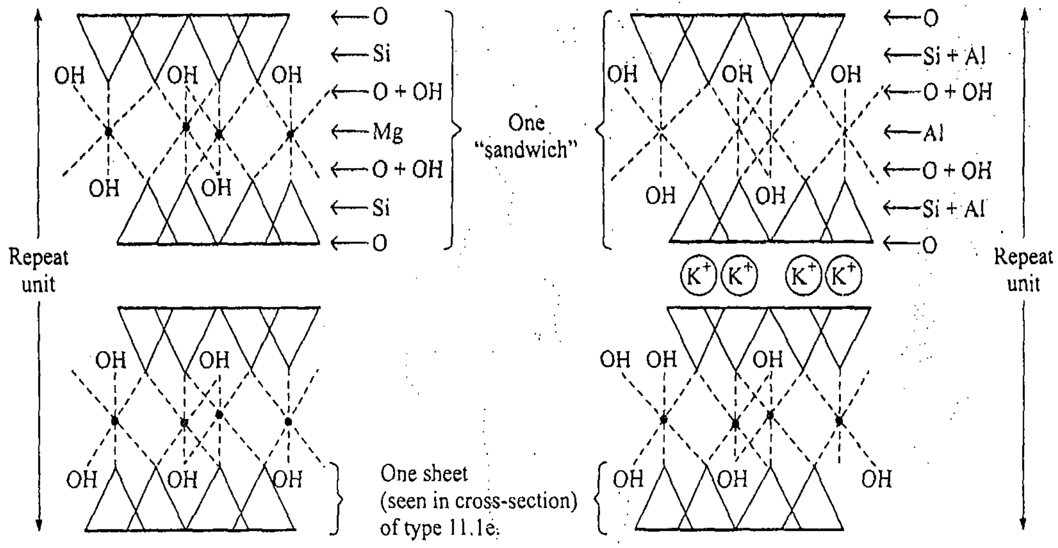


Figure: Layered silicate structures: (a) talc, $Mg_3(OH)_2(Si_4O_{10})$; (b) muscovite (a mica) $Kal_2(OH)_2(Si_3AlO_{10})$. [Note: (1) Electroneutrality is maintained by balance of K(I), Mg(II), Al(III), and Si(IV). (2) The repeating layers in muscovite are bound together by the K^+ cations.]

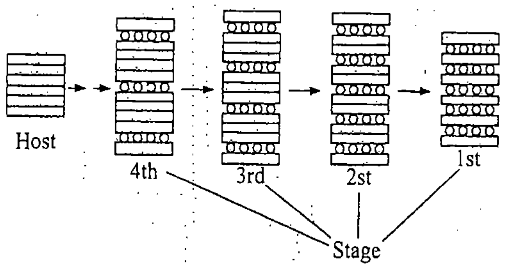


Figure: Staging in graphite intercalation compounds, $C_{12n}K$. Addition of potassium proceeds through n = 4, 3, 2, ... to the limit in stage 1 : $C_{12n}K \rightarrow C_8K$.

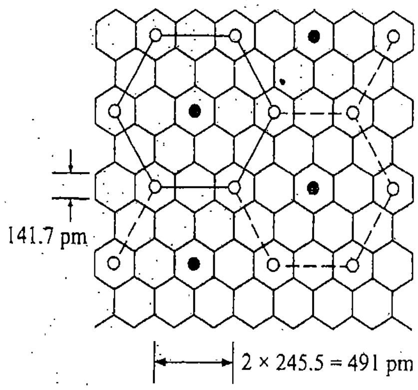


Figure: Filling of available hexagonal sites in each layer of graphite; For the limit of C_8K, K = ● + O; for $C_{12n}K$, K = O only.

stepwise as new layers of potassium are added, giving well-characterized compounds with n = 4, 3, 2. The final step (yielding stage 1) includes filling in all the remaining available sites in addition to forming the maximum number of layers. Presumably, further intercalation cannot take place because of electrostatic repulsion.

Upon intercalation, the graphite layers move apart somewhat (205 pm), through less than expected as estimated from the diameter of the potassium ion (304 pm or greater). This indicates that the K^+ ion "nests" within the hexagonal carbon net, and one can even speculate about weak complexing to the carbon π-electron cloud.

The mention of the K^+ ion presupposes knowledge of the nature of the potassium species present. Because of the similarity in energies of the valence and conduction bands, graphite can be either an electron donor or acceptor. Intercalation of potassium atoms into graphite results in the formation of K^+ ions and free electrons in the conduction band. Graphite will react with an electron acceptor such as bromine to form C_8Br in which electrons have transferred from the valence band of the graphite to the bromine.

Both of the potassium and polybromide intercalation compounds are good conductors of electricity. In the potassium intercalant, the electrons in the conduction band can carry the current directly, as in a metal. In the compounds of graphite with polybromide, holes in the valence band conduct by the mechanism discussed previously for semiconductors.

Recently, it has proved possible to intercalate a variety of organic molecules into transition metal dichalcogenides. Unlike the above examples these do not usually involve electron transfer. When single molecular layers of MoS_2, suspended in water, are shaken with water-immiscible organic molecules such as ferrocene, the latter is adsorbed on to the former. A highly-oriented, conducting ferrocene-MoS_2 film results when exposed to a glass substrate. The interlayer spacing of MoS_2 increases by 560 pm upon ferrocene inclusion. It has been suggested that the best chance for producting a useful high-temperature superconductor may lie with incorporating an organic superconductor into a layered inorganic compound.

GROUP 15th ELEMENTS (NITROGEN FAMILY)

Element		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass		14.91	30.97	74.92	121.76	208.92
Electronic configuration		[He] $2s^2\ 2p^3$	[Ne] $3s^2\ 3p^3$	[Ar] $3d^{10}\ 4s^2\ 4p^3$	[Kr] $4d^{10}\ 5s^2\ 5p^3$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$
Covalent Radius./pm		70	110	120	140	150
Ionization enthalpy / (Kl mol^{-1})	I	1402	1012	947	834	703
Electronegativity		3	2.1	2	1.9	1.9

NITROGEN

Preparation

1. $NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$

2. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$

3. $8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$

Properties

(1) N_2 is a colourless odourless gas insoluble in water.

(2) It is absorbed by heating with Mg and Al. The nitrides formed thus react with water to form NH_3.

$$3Mg + N_2 \rightarrow Mg_3N_2(+6\,H_2O) \rightarrow 3Mg(OH)_3 + 2NH_3\uparrow$$

$$2Al + N_2 \rightarrow 2AlN\ (+6H_2O) \rightarrow 2Al(OH)_3 + 2NH_3\uparrow$$

(3) Reaction with H_2 at 200 atm and 500°C and in the presence of iron catalyst and molybdenum promotes N_2 combination with H_2 reversibly to form ammonia. The process in called Haber's Process and is the industrial method of manufacturing ammonia. The reaction is exothermic.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(4) Reaction with oxygen : When air free from CO_2 and moisture is passed over an electric arc at 2000-3000°C nitric oxide is formed. This reaction its endothermic.

$$N_2 + O_2 \rightarrow 2NO$$

AMMONIA (NH_3)

Preparation:

1. $NH_4Cl + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaCl + H_2O$

2. $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} 2NH_3\uparrow + Na_2SO_4 + 2H_2O$

3. $NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3\uparrow + NaNO_3 + H_2O$

Haber's process : $N_2 + 3H_2 \xrightarrow[Fe+Mo]{500°C-200atm} 2NH_3$

Cyanamide Process

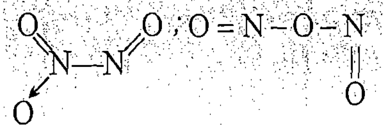
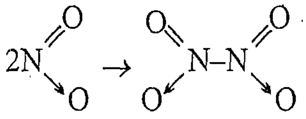
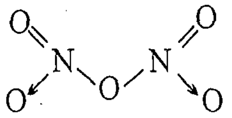
(i) $CaO + 2C + N_2 \xrightarrow{2000°} CaCN_2 + CO\uparrow$

(ii) $CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3\uparrow$

Properties

1. $Na + NH_3 \xrightarrow{\Delta} NaNH_2 + 1/2H_2$
2. $4NH_3 + 5O_2 \xrightarrow{Pt\ 550°C} 4NO + 6H_2O$
3. $CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2\downarrow(\text{blue}) + (NH_4)_2SO_4$
4. $Cu(OH)_2 + (NH_4)_2SO_4 + 3NH_4OH(\text{excess}) \rightarrow [Cu(NH_3)_4]SO_4\ (\text{deep blue solution}) + 4H_2O$

OXIDES OF NITROGEN

Oxides of nitrogen	*Structure*	*Physical state*	*Colour of gas*
N_2O	$\overset{-}{N}=\overset{+}{N}=O$	*Gas*	*Colourless*
NO	$:\ddot{N}=\ddot{O}:$ or $:N\overset{\cdots}{=}O:$	*Gas*	*Colourless*
N_2O_3			*Blue liquid (–30°C)*
NO_2		*Gas*	*Brown*
N_2O_5		*Colourless solid*	*– (no existance in gas phase)*

Preparation:

1. $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$
2. $3Cu + 8HNO_3(\text{dil.}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
3. $Cu + 4HNO_3\ (\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Properties

1. Oxides of nitrogen are all oxidizing agents.
2. (a) N_2O is isoelectronic with CO_2 and also has a linear structure. However, unlike CO_2, N_2O has a small dipole moment.

   (b) NO has a total of 15 electrons. This is an odd electron molecule. In the gaseous state, it is paramagnetic. However the liquid and the solid states are diamagnetic because loose dimmers are formed canceling out the magnetic effects of unpaired electrons.

The bonding in NO is best described by the molecular orbital theory. Its electronic configuration is $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^1$

This gives a bond order of 2.5. If the unpaired electron occupying the antibonding $\pi^* 2p_y$ orbital is removed, nitrosonium ion NO^+ is formed and the bond order becomes 3. This is reflected in the shortening of the bond length from 115 pm in NO to 106 pm in NO^+. Nitrosonium ion is stable and forms salts like NO^+Cl^-. It is isoelectronic with CO and forms complexes with transition elements. The brown ring formed in the test for nitrates is due to the formation of a complex of iron $[Fe(H_2O)_5NO]^{2+}$

(c) NO_2 with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation. NO_2 molecule is angular with ONO angle of 134°. The O–N bond length is 120 pm, intermediate between a single and a double bond. The odd electron is on nitrogen. The dimer has been shown to have a linear structure. The N-N bond length is very large 174 cm making this a very week bond Liquid N_2O_4 undergoes self-ionization to form NO^+ and NO_3^- ions and (therefore it has been extensively studied as a non-aqueous solvent

(d) Solid N_2O_5 exists in the ionic form $NO_2^+ NO_3^-$ in the gaseous form, the discreate N_2O_5 molecules have a N-O-N bond angle close to 112°

Properties:

N_2O : (a) Reduction: $Cu\ (hot) + N_2O \rightarrow CuO + N_2$.

(b) Oxidation : $2KMnO_4 + 2H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 10NO$

NO : (a) Oxidising properties (Reduction of NO)

$$5H_2 + 2NO \xrightarrow{\text{Pt-Black}} 2NH_3 + 2H_2O$$

(b) Reducing properties (oxidation of NO) :

$$2NO + X_2 \rightarrow 2NOX$$

$$6KMnO_4 + 9H_2SO_4 + 10NO \rightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$$

NO_2 : It behaves both like HNO_2 as a reducing agent and like HNO_3 as an oxidising agent according to following reactions respectively.

$$2KMnO_4 + 3H_2SO_4 + 10NO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$$

$$SO_2 + H_2O + NO_2 \rightarrow H_2SO_4 + NO$$

OXYACIDS OF NITROGEN

Nitrous Acid (HNO_2)

Preparation

1. $Ba(NO_3)_2 + H_2SO_4 \rightarrow 2HNO_2 + BaSO_4 \downarrow$

Properties

(i) Nitrous acid and nitrites are good oxidizing agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates eg.

$$2KI + 2HNO_2 + 2HCl \rightarrow 2H_2O + 2NO + 2KCl + I_2$$

(ii) With strong oxidizing agents like $KMnO_4$, nitrous acid and nitrites function as reducing agents and get oxidized to NO_3^- ions

$$2KMnO_4 + 5KNO_2 + 6HCl \rightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$$

NITRIC ACID (HNO_3)

Preparation

HNO_3 is exclusively manufactured by the Ostwald process. In this process NH_3 is catalytically oxidized to NO over a Pt–Rh catalyst at 1200K

(i) $4NH_3 + 5O_2 \xrightarrow[1200K]{Pt-Rh} +4NO + 6H_2O; \quad \Delta H = -904kJ$

The mixture is then diluted with air NO combines with O_2 to give NO_2 which is absorbed in water to give HNO_3 and NO which is then recycled.

(ii) $2NO + O_2 \rightarrow 2NO_2$

(iii) $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Properties

(i) Thermal stability

$$4HNO_3 \xrightarrow{\Delta} 2H_2O + 4NO_2 + O_2$$

(ii) Oxidising Properties:

(a) $H_2S + 2HNO_3(conc.) \rightarrow 2H_2O + 2NO_2 + S\downarrow$

(b) $3H_2S + 2HNO_3(dilute) \rightarrow 4H_2O + 2NO + 3S$

(c) $SO_2 + 2HNO_3(conc.) \rightarrow H_2SO_4 + 2NO_2\uparrow$

(d) $3SO_2 + 2H_2O + 2HNO_3(dilute) \rightarrow 3H_2SO_4 + 2NO$

(e) $\mathbf{Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2}$

(f) $\mathbf{4Zn + 10HNO_3(dil.) \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O}$

(g) $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(h) $3Cu + 8HNO_3\ (v.dil) \rightarrow 3Cu(NO_3)_2 + NO + 4H_2O$

PHOSPHOROUS (P)

It is a very reactive non-metal. It catches fire in air. It occurs in nature in the form of stable phosphates. The important minerals are :

(i) Phosphorite, $Ca_3(PO_4)_2$

(ii) Vivianite, $Fe_3(PO_4)_2\ 8H_2O$

EXTRACTION

$$Ca_3(PO_4)_2 + 2SiO_2 \xrightarrow{\Delta} 3CaSiO_3 + P_2O_5$$

$$P_2O_5 + 5C \xrightarrow{\Delta} 2P\uparrow + 5CO\uparrow$$

ALLOTROPIC FORMS OF PHOSPHOROUS

(i) WHITE OR YELLOW PHOSPHORUS (P_4)

Properties

(1) It is white-too-transparent and soft waxy solid.

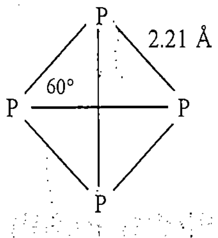
(2) It is soluble in CS_2 but insolube in water.

(3) It glows in dark due to slow oxidation producing yellowish-green light. This phenomenon is called phosphorescence.

(4) White phosphrous is poisonous.

(5) It turns yellow after some time, it is called yellow phosphorus.

(6) It undergoes oxidation in the presence of air which slowly raises its temperature and due to its low ignition temperature (30°C) after a few moments it catches fire spontaneously. Due to this reason it is stored under water.



(ii) RED PHOSPHOROUS

Preparation

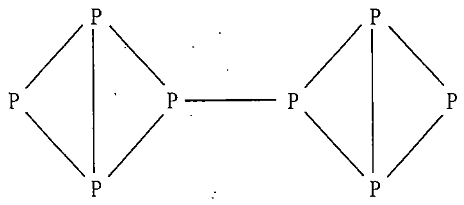
When white phosphorus is heated in the atomosphere of CO_2 or coal gas at 250°C red phosphrous is produced. This red phosphorous may still contain some white phosphorus which is removed by boiling the mixture with NaOH where white phosphorus is converted into PH_3 gas but red phosphorus remains inert

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

It is also prepared by heating white phosphorus with a few crystals of iodine catalyst at 250°C under high pressure.

Properties

It is a red crystalline solid having a density of 2.2 g/cc. It is less reactive than white phosphorous and does not dissolve in liquid CS_2. It does not catch fire at room temperature because its ignition temperature is 260°C. It is a polymeric substance forming linear chains like this.



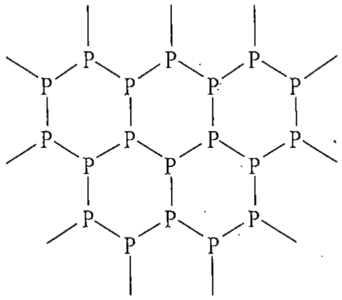
(iii) BLACK PHOSPHOROUS

Preparation

When white phosphorus is heated at about 200°C under very high pressure then black phosphorus is produced.

Properties

It is an electrical conductor resembling graphite in this respect and also in its flakiness and luster. It is often called metallic phosphorous. Its density (2.69 g/cc) is higher than of red phosphorous. It is insoluble in CS_2. It has layered structure like graphite.



(iv) **BROWN PHOSPHORUS**

Above 1600°C P_4 molecules break into P_2 molecules. Rapid cooling of this vapour gives brown phosphorus which probably contains P_2 molecules.

(v) **SCARLET PHOSPHORUS**

This allotrope is obtained in the form of an amorphous scarlet powder by boiling a 10 per cent solution of phosphorus in phosphorus tribromide for about 10 hours. Pure scarlet phosphorus may be prepared by heating phosphorus tribromide with mercury at 240°C.

$$2PBr_3 + 3Hg \rightarrow 3HgBr_2 + \underset{\text{Scarlet phosphorus}}{2p}$$

Scarlet phosphorus resembles the red variety in its physical properties and the white phosphorus in its chemical properties. It is, however, only slowly oxidised in air.

(vi) **VIOLET PHOSPHORUS**

This variety is obtained by heating white phosphorus with a trace of sodium at 230°C under high pressure. It is crystalline in structure.

CHEMICAL PROPERTIES OF PHOSPHORUS

Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order.

Brown > white > red > black, **the last one being almost inert & thermodynamically most stable form of phosphorus.**

(i) **Action of air :** White phosphorous burns in air to form phosphorous trioxide and pentoxide.

$P_4 + 5O_2 \rightarrow 2P_2O_5$; $P_4 + 3O_2 \rightarrow 2P_2O_3$

Red and other forms of phosphorus also burn in air or oxygen but on heating.

(ii) **Halide:** Nitrogen is unable to form pentahalides because the second shell contains a maximum of eight electrons, i.e. four bonds. The subsequent elements have suitable d orbitals and form the following pentahalides PX_5.

$$PCl_5 + 4H_2O \rightarrow \underset{\text{phosphoric acid}}{H_3PO_4} + 5HCl$$

Despite the existence of pentahalides no hydrides MH_5 are known. To attain the five valent state, d orbitals must be used. Hydrogen is not sufficiently electronegative to make the d orbitals contract sufficiently, though PHF_4 and PH_2F_3 have been isolated.

(iii) **Action with Non metals :** When heated with non-metals phosphorous forms compounds PX_3, PX_5, P_2S_3 and P_2S_5

$2P + 3X_2 \rightarrow 2PX_3$, $2P + 5X_2 \rightarrow 2PX_5$. (where X = Cl, Br, and I)

(iv) **Action with metals :** Alkali metals when heated with white phosphorus in vacuum produce alkali metal phosphide, which react with water to form phosphine gas.

$$3M + P \xrightarrow{\Delta} M_3P$$

$$M_3P + 3H_2O \xrightarrow{\Delta} 3MOH + PH_3\uparrow \text{ (where M = Na, K etc.)}$$

(v) **Action of NaOH :** When white phosphorous is heated with NaOH solution, phosphine gas is evolved.

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3\uparrow$$

(vi) **Action of conc. HNO_3/H_2SO_4 :** When heated with conc. HNO_3 phosphorous is oxidized to H_3PO_4.

$$P + 5HNO_3 \rightarrow H_3PO_4 + 5NO_2\uparrow + H_2O$$

PHOSPHORUS TRIOXIDE (P_2O_3)

It is preapred by burning phosphorus in a limited supply of oxygen when gaseous P_4O_{10} and P_4O_6 are formed.

Properties

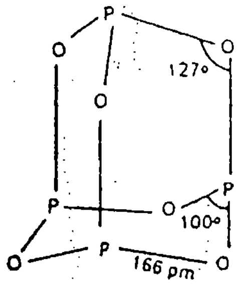
(i) It is colourless crystalline solid having mp 23.8°C and bp 178°C.

(ii) It dissolves in cold water to form phosphorus acid, it is thus the anhydride of phosphorus acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

(iii) It burns in Cl_2 gas forming phosphorous oxytrichloride ($POCl_3$) and phosphoryl chloride (PO_2Cl)

$$P_2O_3 + 2Cl_2 \rightarrow POCl_3 + PO_2Cl$$



P_4O_6

PHOSPHOROUS PENTOXIDE (P_2O_5)

Preparation

It is obtained by burning phosphorus in air.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

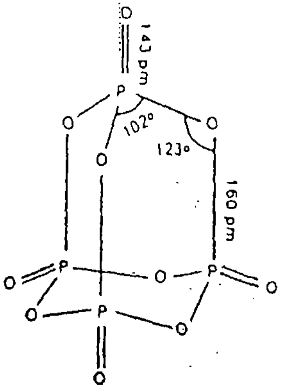
Properties

(i) It is a white powder acidic in nature and is the anhydride of orthophosphoric acid. Its empirical formula is P_2O_5 and its molecular formula is P_4O_{10}.

(ii) **Action of water :** It dehydrates in water with hissing sound forming metaphospharic acid and finally orthophosphoric acid.

$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$; $HPO_3 + H_2O \rightarrow H_3PO_4$

(iii) **Dehydrating power :** It dehydrates conc. H_2SO_4 and conc. HNO_3 to SO_3 and N_2O_5 respectively.



P_4O_{10}

OXY-ACIDS OF PHOSPHOROUS

Phosphorous Acid (H_3PO_3)

Preparation

(i) By dissolving P_2O_3 in water

$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$

(ii) By hydrolysis of PCl_3 with water.

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

Properties

(i) It is a white crystalline solid soluble in water and having melting point of 74°C.

(ii) It is a weak acid and a reducing agent.

(iii) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$ (Disproportionation)

(iv) $H_3PO_3 + 3PCl_3 \rightarrow PCl_3 + 3POCl_3 + 3HCl$

(v) It is a strong reducing agent

$2AgNO_3 + H_3PO_3 + H_2O \rightarrow 2Ag + 2HNO_3 + H_3PO_4$

Orthophosphoric Acid (H_3PO_4)

Preparation

(i) $Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$

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

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

Properties

Reaction of H_3PO_4 : The simplest phosphorous acid is H_3PO_4 (orthophosphoric acid). The acid contains three replaceable H atoms and is tribasic.

(i) Pure orthophosphoric acid is a white crystalline solid highly soluble in water having melting point of 42°C. It is a weak acid. It forms two acid salts and one normal salt. NaH_2PO_4 is sodium dihydrogen phosphate, Na_2HPO_4 is disodium hydrogen phosphate & Na_3PO_4 is sodium orthophosphate.

(ii) Action of Heat :

$$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \text{(pyrophosphoric acid)};$$

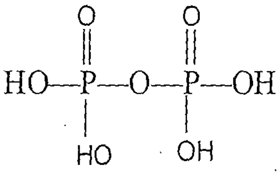
$$H_4P_2O_7 \xrightarrow{316°C} HPO_3 \text{(metaphosphoric acid)}$$

(iii) Neutralization with alkalis or bases :

$$H_3PO_4 \xrightarrow[-H_2O]{220°C} NaH_2PO_4 \text{(pri. phosphate)} \xrightarrow[-H_2O]{NaOH} Na_2HPO_4 \text{(sec phosphate)}$$

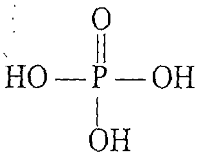
$$\xrightarrow[-H_2O]{NaOH} Na_3PO_4 \text{(tert. phosphate)}$$

$H_4P_2O_7$:



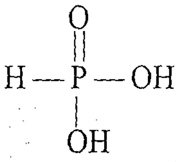
$$HO-\overset{\displaystyle O}{\underset{\displaystyle HO}{\overset{\|}{\underset{|}{P}}}}-O-\overset{\displaystyle O}{\underset{\displaystyle OH}{\overset{\|}{\underset{|}{P}}}}-OH$$

H_3PO_4:



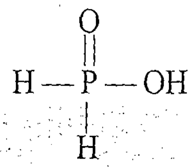
$$HO-\overset{\displaystyle O}{\underset{\displaystyle OH}{\overset{\|}{\underset{|}{P}}}}-OH$$

H_3PO_3:



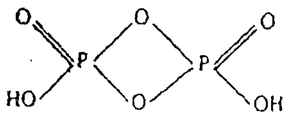
$$H-\overset{\displaystyle O}{\underset{\displaystyle OH}{\overset{\|}{\underset{|}{P}}}}-OH$$

H_3PO_2:

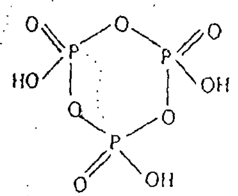


$$H-\overset{\displaystyle O}{\underset{\displaystyle H}{\overset{\|}{\underset{|}{P}}}}-OH$$

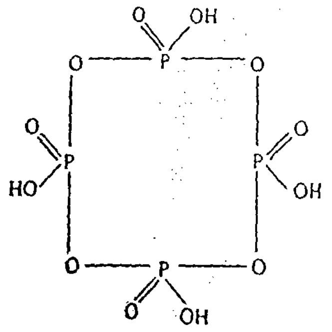
Structure of Polymetaphosphates



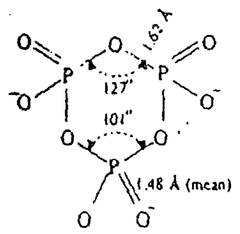
Structure of $(HPO_3)_2$ (dimer)



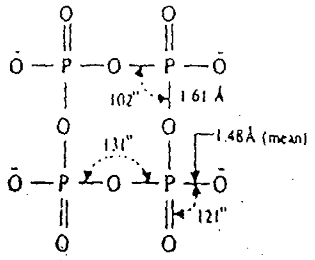
Structure of $(HPO_3)_3$ (trimer)



Structure of $(HPO_3)_4$ (tetramer)

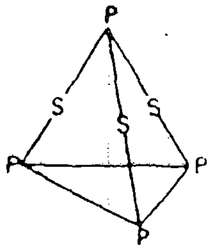


Structure of trimetaphosphate ion $[(PO_3)_3]^{3-}$ or $P_3O_9^{\ 3-}$

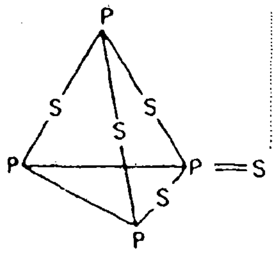


Structure of tetrametaphosphate ion, $[(PO_3)_4]^{4-}$ or $P_4O_{12}^{\ 4-}$

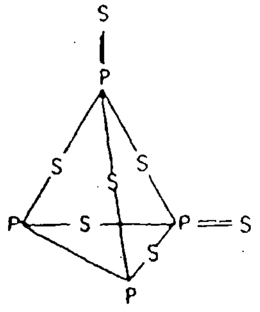
Structure of Sulphides of Phosphorus



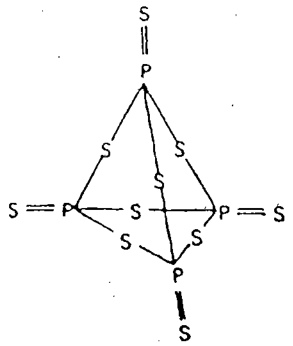
Tetra phosphorus trisulphide P_4S_3



Tetra phosphorus pentasulphide P_4S_5



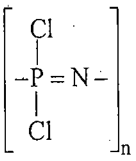
Tetra phosphorus heptasulphide P_4S_7



Tetra phosphorus decasulphide P_4S_{10}

Polyphsphonitrilic chlorides $(PNCl_2)$ (n = 3 to 7)

These polymers are also called inorganic rubbers. These compounds can be represented by the general structure,



$$\left[\begin{array}{c} Cl \\ | \\ -P=N- \\ | \\ Cl \end{array}\right]_n .$$

Preparation:

(i) $(NPCl)_3$ and $(NPCl_2)_4$ can be prepared by the ammonolysis of PCl_5.

$$3PCl_5 + 3NH_3 \rightarrow (NPCl_2)_3 + 9HCl$$

$$4PCl_5 + 4NH_3 \rightarrow (NPCl_2)_4 + 12HCl$$

(ii) These compounds can be prepared by the reaction between PCl_5 and NH_4Cl in presence of $C_2H_4Cl_2$ or C_6H_5Cl or by heating PCl_5 with solid NH_4Cl at 145–160°C.

$$nPCl_5 + nNH_4Cl \xrightarrow[\text{or } C_6H_5Cl]{C_2H_4Cl_2} (NPCl_2)_n + 4nHCl$$

$$nPCl_5 + nNH_4Cl(s) \xrightarrow{145-160^\circ} (NPCl_2)_n + 4nHCl$$

Properties:

Reactions involving replacement of Cl-atom of P–Cl bond:

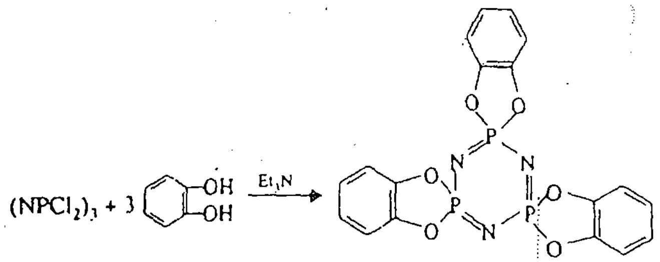
(i) $$(NPCl_2)_3 + 6NaF \xrightarrow{\text{Acetonitrile}} (NPF_2)_3 + 6NaCl$$

(ii) $$[NPCl_2]_3 + 2NaOCH_3 \longrightarrow \underset{\text{Tri(dimethoxy) phosphazine}}{[NP(OCH_3)_2]} + 2NaCl$$

(iii) $$[NPCl_2]_3 + \underset{\text{Grignard reagent}}{6C_6H_5MgBr} \xrightarrow[\text{toluene}]{\text{Boilingo}} [NP(C_6H_5)_2]_3 + 3MgCl_2 + 3MgBr_2$$

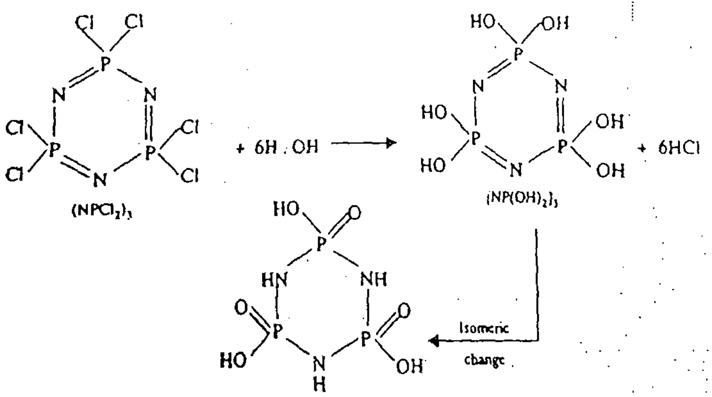
(iv) $$[NPCl_2]_3 + \underset{\text{1, 2-phenol}}{3C_6H_4(OH)_2} \xrightarrow{Et_3N} [NP(C_6H_4O_2)]_3 + 6HCl$$

or

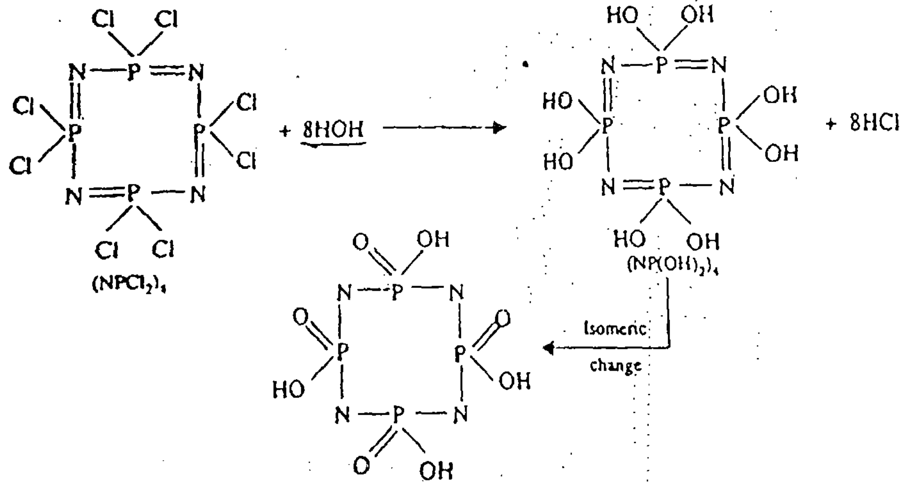


Hydrolysis:

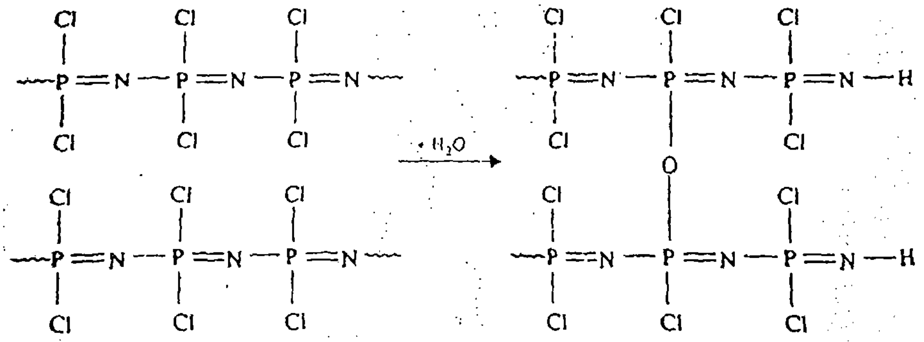
(a)



(b)

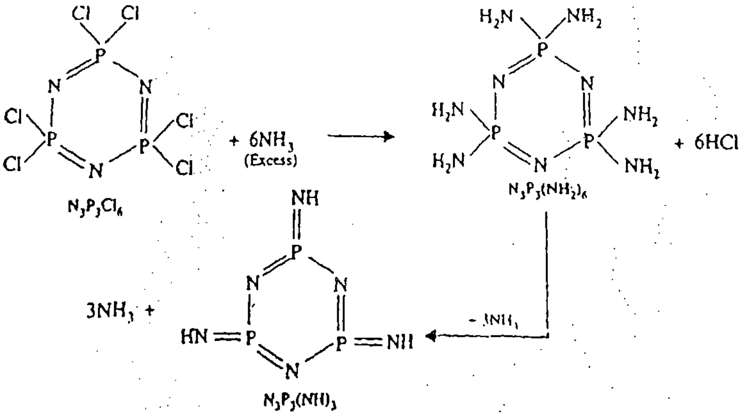


(c) When $[NPCl_2]_n$ polymers are stored in air they become cross linked due to the action H_2O which forms O-bridges between P-atoms

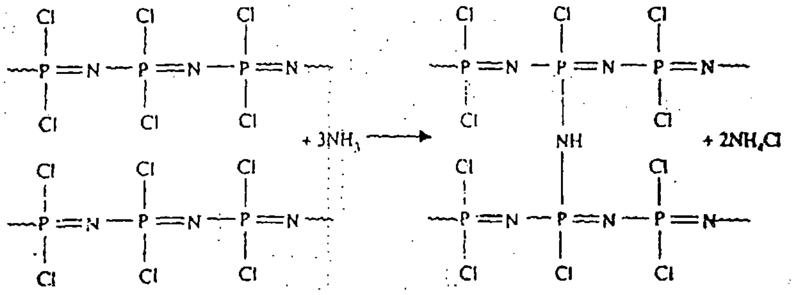


Reaction with NH_3:

(a)



(b) When $(PNCl_2)_n$ reacts with NH_3 (not excess) and amines, cross-linked polymers aye produced.



Cross-linked polymer

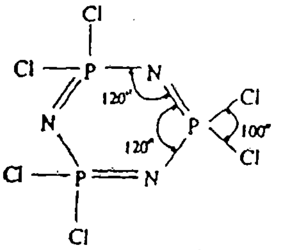
Reaction with benzene, C_6H_6 (Friedel-Crafts reaction):

$$N_3P_3Cl_6 + 2C_6H_6 \xrightarrow{AlCl_3} N_3P_3Cl_4(C_6H_5)_2 + 2HCl$$

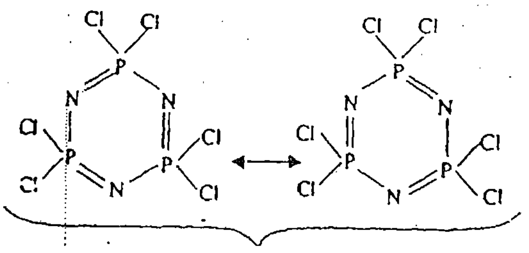
PbF_2 fluorinates $N_3P_3Cl_6$ (trimer) giving ultimately $N_3P_3F_6$.

$$N_3P_3Cl_6 + 3PbF_2 \longrightarrow N_3P_3F_6 + 3PbCl_2$$

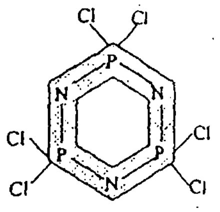
Structure of $(NPCl_2)_3$ molecule: X-ray analysis has shown that $(NPCl_2)_3$ molecule has a planar six-membered ring structure (Structurel) in which each N-atom is sp^2 hybridised and each P-atom is sp^3 hybridised. The lone pair of electrons on each N-atom resides in one of the three sp^2 hybrid orbitals. It is this lone pair of electrons which makes $(NPCl_2)_3$ molecule to show basic properties. The bond angles are as shown in the structure. Resonance structures can also be drawn as in case of C_6H_6 molecule, indicating aromaticity in the ring.



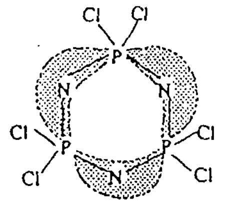
Planar ring structures of $(NPCl_2)_3$ molecule (I)



Two resonating structures of $(NPCl_2)_3$ molecule



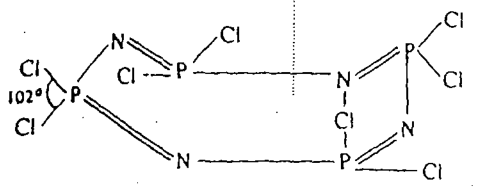
(a)



(b)

Unlike benzene which involves extensive (pπ-pπ) bonding. ($N_3P_3Cl_6$) molecule involves (dπ-pπ) bonding. The extent of (dπ-pπ) bonding appears to be quite appreciable as the N–P distance (1.6 Å) is considerably shorter than the N–P single bond distance (1.75 – 1.80Å). Whether there is complete delocalisation of π-electron charge cloud on all the ring atoms as in C_6H_6 molecule or there are intensely-localised islands of the electron cloud within the PNP segments cannot be answered with certainity.

Structure of $(NPCl_2)_4$ molecule: This molecule has a tube-like puckered structure.



Borophosphate glasses

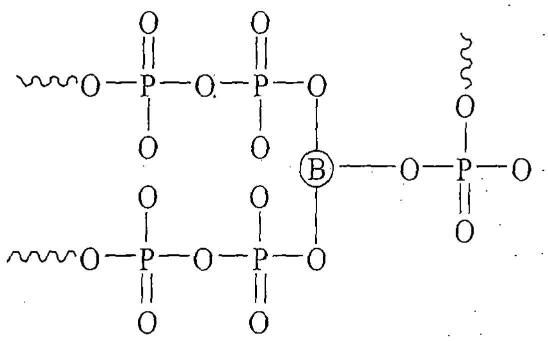
These are formed by heating H_3PO_4, B_2O_3 and alkali metal carbonates or oxides at 700°C. Borophosphate glasses are of the following three types.

(i) Those which contain excess of alkali over P_2O_5 in this variety all the B atoms are present as trignal BO_3 groups.

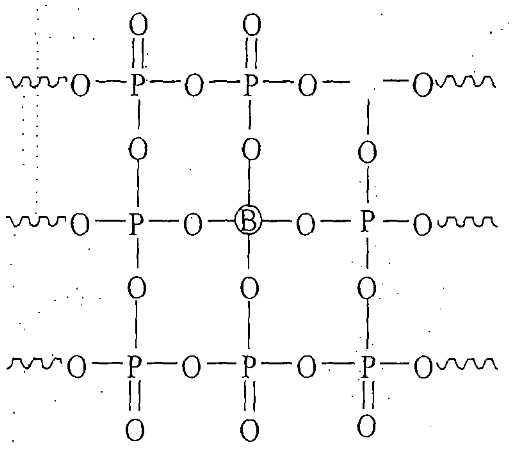
(ii) Those which contain excess of P_2O_5 over alkali. These borophosphate glasses are called acidic borophosphate glasses. If there is less than 10 mole percent of B_2O_3 all B-atoms are four coordinated.

(iii) Those which contain P_2O_5 and alkali in equivalent proportions. The number of coordinated B-atoms decreases steadily with the increase in the content of B_2O_3 and becomes almost zero at about 47 mole per cent of B_2O_3.

Structure of borophosphate glass having three and four coordinated B atoms are shown below in following figure.



(a) Borophosphate glass having 3-coordinated B-atom



(b) Borophosphate glass having 4-coordinated B-atom

PHOSPHAZENES

Early workers noted the extreme reactivity of phosphorus pentachloride toward basic reagents such as water or ammonia. With the former the reaction is reasonably straightforward, at least for certain stoichiometries:

$$PCl_5 + H_2O \longrightarrow OPCl_3 + 2HCl$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

For reactions with ammonia analogous products such as $HN = PCl_3$ and $HN = P(NH_2)_3$ were proposed, but characterization was hampered by incomplete reactions, separation-resistant mixtures, and sensitivity to moisture. Furthermore, gradual polymerization occurred with loss of ammonia to yield "phospham", a poorly characterized solid of approximate formula $(PN_2H)_x$ as the ultimate product. If instead of free ammonia its less reactive conjugate acid is used, reaction with PCl_5 proceeds at a moderate rate and the results are more definitive

$$NH_4Cl + PCl_5 \xrightarrow[\text{Refluxing } CHCl_2CHCl_2]{146°C} "PNCl_2"$$

If the product was a monomer, its structure could be draw as $Cl_2P \equiv N$, which is analogous to organic nitriles, $R-C\equiv N$. For this reason the original names used for these compounds were phosphonitriles, phosphonitrilic chloride, etc. However, the products are actually either cyclic or linear polymers of general formula $[NPCl_2]_n$. Thus, by analogy with benzene, borazine, etc., these compounds have become known as phosphazenes. The major product of the reaction in Eq. and the easiest to separate is the trimer, n = 3. Smaller amounts of the tetramer and other oligomers up to n = 8 have been characterized and higher polymers exist as well. Analogous bromo compounds may be prepared in the same manner, except that bromine must be added to suppress the decomposition of the phosphorus pentabromide:

$$PBr_5 \rightleftharpoons PBr_3 + Br_2$$

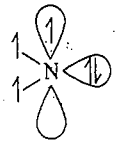
$$PBr_5 \xrightarrow[\text{excess } Br_2]{NH_4Br} [NPBr_2]_3$$

The fluoride must be prepared indirectly by fluorination of the chloride:

$$[NPCl_2]_3 + 6NaF \longrightarrow [NPF_2]_3 + 6NaCl$$

The corresponding iodide is unknown, but a phosphazene with a single phosphorus-iodine bond, $N_3(PCl_2)_2P(R)I$, has been reported.

The halide trimers consists of planar six-membered rings. The bond angles are consistent with sp^2 hybridization of the nitrogen and approximately sp^3 hybridization of the phosphorus. Two of the sp^2 orbitals of nitrogen, containing one electron each, are used for σ bonding and the third contains a lone pair of electrons. This leaves one electron left for the unhybridized p_z orbital.



The four sp^3 hybrid orbitals (housing four electrons) for phosphorus are used for σ bonding leaving a fifth electron to occupy a d orbital. As shown in Figure resonance structures can be drawn analogous to those for benzene indicating aromaticity in the ring. However, the situation is more complex than these simple resonance structures indicate. The planarity of the ring, the equal P–N bond distances, the shortness of the P–N bonds, and the stability of the compounds suggest delocalization. However, not all phosphazenes are planar, and the absence of planarity does not appear to make them any less stable. Furthermore, the phosphazenes yield UV spectra unlike those of aromatic organic compounds and they are much more difficult to reduce. Thus the extent of delocalization and the nature of the aromaticity have been debated for years. Unlike in benzene, π bonding in cyclophosphazenes involves d and p orbitals. There have been several descriptions offered for such $d_\pi - p_\pi$ bonding. Craig and Paddock suggested the following model. The d_{xz} orbital of the phosphorus atom overlaps with the pz orbitals of the nitrogen atoms adjacent to it. As a result of the gerade symmetry of the d orbitals, an inevitable mismatch in the signs of the wave functions occur in the trimer resulting in a node which reduces the stability of the delocalized molecular orbital. The d_{yz} orbital, which is perpendicular to the d_{xz}, can also overlap with the p_z orbitals of nitrogen, but in this case nodal surface results. There may also be in-plane π bonding the sp^2 non bonding orbital of nitrogen and the d_{xy} and/or $d_{x^2-y^2}$ orbitals of phosphorus.

Dewar and coworkers offered an alternative view. In their model the d_{xz} and d_{yz} orbitals are hybridized to give two orbitals which are directed toward the adjacent nitrogen atoms. This allows for formation of three center bonds about each nitrogen. This scheme, sometimes called the "island" model, results in de-localization over selected three-atom segments of the ring, but nodes are present at each

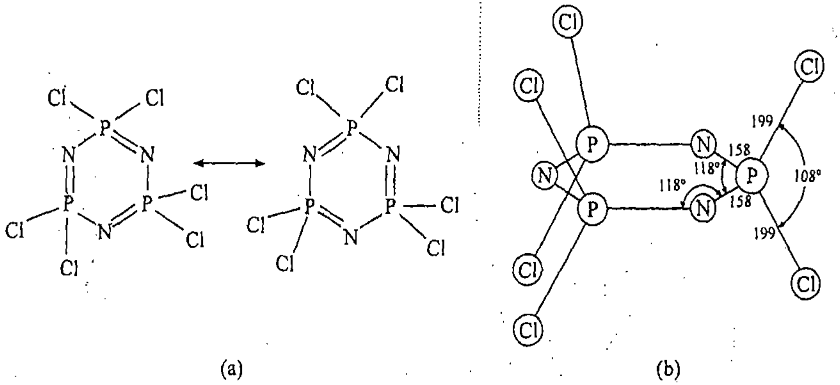
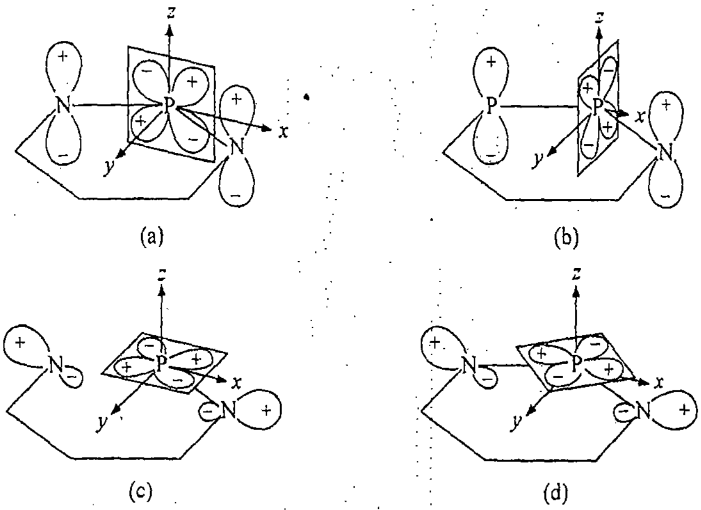


Figure: Structure of trimeric phosphazene, $P_3N_3Cl_6$; (a) contributing resonance structures: (b) molecular structure as determined by X-ray diffraction.



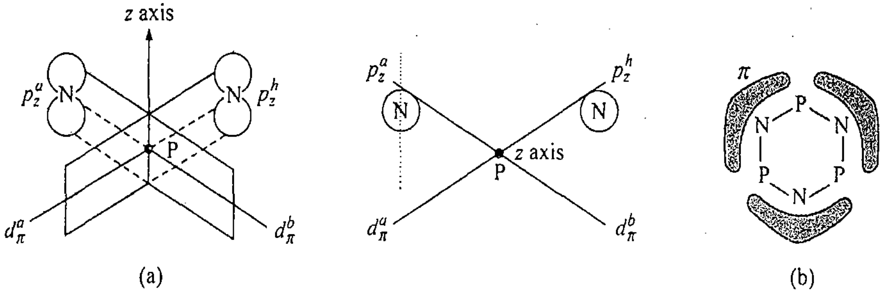


Figure: Theory of Craig and Paddock for π bonding in phosphazenes: (a) interaction of P_z(N) and d_{xz} (P); (b) interaction of P_z(N) and d_{yz}(P); (c) interaction of sp^2(N) and d_{xy}(P); (d) interaction of sp^2(N) and $d_{x^2-y^2}$ (P).

phosphorus atom since the two hybrid orbitals of phosphorus are orthogonal to each other. Evidence has been offered in support of both models, but neither theory has been confirmed to the exclusion of the outer. A third viewpoint holds that d orbital participation is relatively unimportant in the bonding in these molecules.

The structures of tetrameric phosphazenes are more flexible than those of the trimers. The structure of $(NPF_2)_4$ is planar, but others are found in a variety of conformations (tub, boat, chair, crown, saddle and structures in between). The particular structure adopted is not very predictable and suggests that inter-molecular forces play a major role. The tetrameric chlorophosphazene has been isolated in two forms the most stable of which assumes a chair arrangement (sometimes called the T form). The other form (metastable K) has a tub conformation. An interesting feature of these compounds is that the nonplanar structures do not militate against extensive delocalization in the rings. The corresponding organic compound, cyclooctatetraene, C_8H_8, is nonaromatic for two reasons: (1) Its nonplanar, chair structure

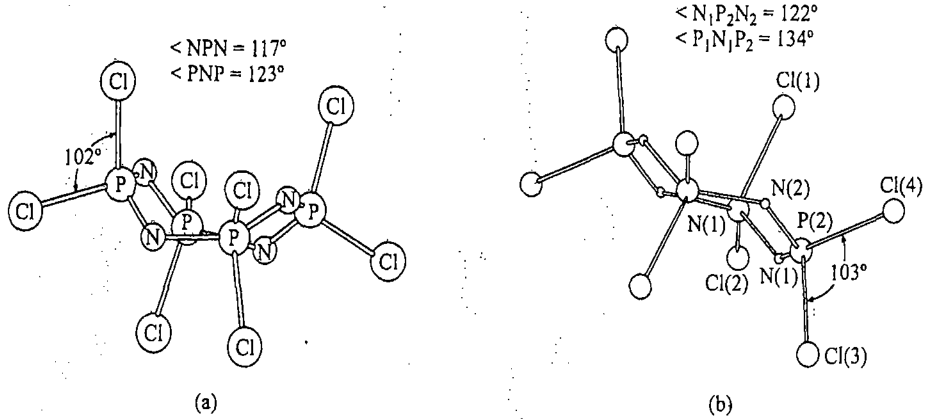
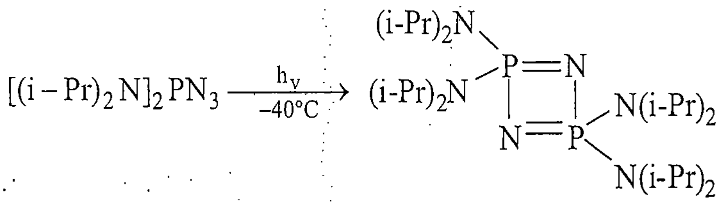


Figure: Structure of tetrameric phosphazene, $P_4N_4Cl_8$: (a) tub conformation; (b) chair conformation.

precludes efficient $p_\pi - p_\pi$ overlap: and (2) it does not obey the Huckel rule of $(4n + 2)\pi$ electrons. The huckel rule was formulated on the basis of p_π–p_π bonding and holds for cyclic organic compounds from n = 1 (benzene) to n = 4 ([18]annulene). The use of d orbitals removes the restrictions of the Huckel rule and also allows greater flexibility of the ring since the diffuse d orbitals are more amenable to bonding in nonplanar systems. Both the Craig/Paddock and Dewar models predict that the tetramer is stabilized by delocalization (unlike cyclooctatetraene) and the stabilization is either equal to (Dewar) or more than (Craig/Paddock) that of the trimer.

Our discussion has dealt with trimeric and tetrameric (phosphazenes, but many other ring sizes have been synthesized. For example, all of the compounds, $(NPMe_2)_n$ {n = 3 – 12), have been studied crystallographically. Furthermore, the first cyclo-diphosphazene has been prepared:



Diphosphazenes were long thought to be too unstable for isolation because of ring strain.

GROUP 16 (OXYGEN FAMILY)

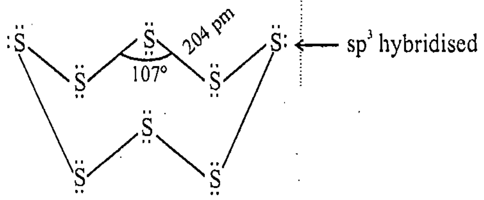
(1) ATOMIC & PHYSICAL PROPERTIES

Element	O	S	Se	Te
Atomic Number	8	16	34	52
Atomic Mass	16	32.06	78.96	127.6
Electronic configuration	(He) $2s^2\ 3p^4$	(Ne) $3s^2\ 3p^4$	[Ar] $3d^{10}\ 4s^2\ 4p^4$	[kr] $4d^{10}\ 5s^2\ 5p^4$
Covalent Radius/pm	74	103	119	142
Ionization enthalpy/(kJ mol^{-1})	1314	133	941	869
Electronegativity	3.5	2.44	2.48	2.01
Boiling Point / K	90	718	958	1260

(2) ABUNDANCE IN THE EARTH CRUST: O > S > Se > Te

(3) PHYSICAL STATE

Oxygen is gas while other are solids at room temperature. Oxygen exists as diatomic molecule where as other elements e.g. sulphur exists as shown into the following crown shape (puckered ring structure S_8)



(4) METALLIC AND NON-METALLIC CHARACTER

Metallic character increases with increase in atomic number.

$$\underbrace{\text{Oxygen, Sulphur}}_{\text{Non-metallic}}\ \underbrace{\text{Selenium Tellurium}}_{\text{Show both metallic and non-metallic behaviour}}\ \underbrace{\text{Polonium}}_{\text{metal}}$$

(5) ALLOTROPIC FORMS

S.No.	Oxygen	Sulphur	Selenium	Tellurium
1.	Ordinary oxygen	Rhombic	Red form (non-metallic)	Crystalline
2.	Ozone Monoclinic	Grey form (Metallic)	Amorphous	
3.	Plastic Amorphous			

(6) OXIDATION STATES

- Oxygen shows–2 oxidation state in most of its compounds (being highly electronegative). Exception, in OF_2 & O_2F_2 oxidation state of oxygen is + 2 & + 1.
- Sulphur shows –2, + 2, + 4 and + 6 oxidation states. Availability of +4 and +6 oxidation states are due to the presence of empty d-orbitals.
- Sulphur shows higher oxidation states with compounds of oxygen and fluorine (highly electronegative elements) (SO_2, SO_3, SF_4, SF_6)
- The tendency to show - 2 oxidation state decreases down the group since the electronegativity decreases.

(A) Oxygen (O)

It differs from the remaining element of the VIth group because of the following properties -

(A) Small Size (B) High electronegativity (C) non-availability of d-orbitals

(i) Preparation

1. $2HgO \xrightarrow{450°C} 2Hg + O_2$; $2Ag_2O \xrightarrow{350°C} 4Ag + O_2$
2. $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$; $2KClO_3 \longrightarrow 2KCl + 3O_2$(laboratory method)
3. $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$; $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

(ii) Physical Properties

Colourless, odourless and tasteless gas. It is paramagnetic and exhibits allotropy. Three isotopes of oxygen are ${}^{16}_{8}O$, ${}^{17}_{8}O$ and ${}^{18}_{8}O$. Oxygen does not burn but is a strong supporter of combustion.

(iii) Chemical Properties

(a) Oxides

(a-i) Acidic oxides

Oxides of Non-metals and metals in highest oxidation state.

They dissolve in water forming oxyacids. e.g. CO_2, SO_2, SO_3, N_2O_3, P_4O_6, P_4O_{10}, Cl_2O_7, CrO_3, Mn_2O_7 etc.

Ex. : $Cl_2O_7 + H_2O \rightarrow 2HClO_4$; $SO_3 + H_2O \rightarrow H_2SO_4$

(a-ii) Basic oxides (Oxides of metals)

They either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts.

Li_2O, Na_2O, BeO, MgO, CaO, SrO, BaO, CuO, FeO etc.

$Na_2O + H_2O \rightarrow 2NaOH$

(a-iii) Neutral Oxides (Oxides of Non metals)

They neither combine with acids nor with the bases to form salts e.g. CO, N_2O, NO, H_2O etc.

(a-iv) Amphoteric oxides (Metal oxides)

These can combine with acids as well as bases e.g., ZnO, Al_2O_3, BeO, Sb_2O_3, Cr_2O_3, PbO, PbO_2, etc.

$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$; $PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$

(a-v) Peroxides (Metal oxides)

They react with dil. acids and form H_2O_2 e.g. Na_2O_2, K_2O_2, BaO_2 etc.

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

(a-vi) Dioxides (metal oxides)

Like peroxide they contain excess of oxygen but do not yield H_2O_2 with dil. acids e.g. PbO, MnO_2 etc. They evolve Cl_2 with conc. HCl and O_2 with conc. H_2SO_4.

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

(a-vii) Super Oxides (metal oxides)

They contaon O_2^- ion, e.g. KO_2, RbO_2 and CsO_2. These oxides react with water forming H_2O_2 and O_2

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

(a-viii) Sub Oxides

They contain less oxygen than expected from the normal valency of the elements e.g. C_3O_2, N_2O, Pb_2O, Hg_2O etc.

$$C_3O_2 \rightarrow O = C = C = C = O$$

(b) Ozone (O_3)

(i) Preparation

It is prepared by passing silent electric discharge through pure and dry oxygen

$$O_2 \xrightarrow[\text{Silent electric discharge}]{\text{Energy}} O + O$$

$$O_2 + O \longrightarrow O_3;\ \Delta H = 245\,kJ\ mol^{-1} \qquad 3O_2 \rightleftharpoons 2O_3$$

(ii) Properties

(a) Oxidising agent : Ozone is a strong oxidising agent in acidic medium

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O;\ SRP = +2.07\,V\,(\text{acidic medium})$$

$$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-,\ SRP = +1.24\ V_1\ (\text{alkaline medium})$$

$$O_3 \rightarrow O_2 + [O]$$

E.g.

1. $2KI + H_2O + [O] \rightarrow 2KOH + O_2 + I_2$
2. $KI + 3O_3 \rightarrow KIO_3 + 3O_2;$
3. $S + 3O_3 + H_2O \rightarrow H_2SO_4 + 3O_2$
4. $2I_2 + 9[O_3] \rightarrow I_4O_9 + 9O_2$

- I_4O_9 yellow solid has the compostion $I^{+3}\ (IO^-{}_3)_3$. Formation of this compound is a direct evidence in favour of basic nature of I_2 (i.e. its tendency of form cations)

5. $\underset{\substack{\text{Oxidising}\\ \text{agent}}}{O_3} + \underset{\substack{\text{Reducing}\\ \text{agent}}}{H_2O_2} \rightarrow 2O_2 + H_2O$

TAILING OF MERCURY

Pure mercury is mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O (mercury suboxide) in Hg.

$2Hg + O_3 \rightarrow Hg_2O + O_2$

- O_3 is used as a germicide and disinfectant for sterilizing water and improving the atomsphere of crowded places.

HYDROGEN PEROXIDE (H_2O_2)

(i) **Preparation**

(1) $BaO_2 . 8H_2O + H_2SO_4(\text{cold}) \rightarrow BaSO_4 \downarrow (\text{white}) + H_2O_2 + 8H_2O$

(2) $H_2S_2O_8 + H_2O \xrightarrow[\text{distillation}]{80-90°C} H_2SO_4 + H_2SO_5 \xrightarrow{BaCl_2} BaSO_4 \downarrow (\text{white}) + H_2O_2(aq)$

Comparison (H_2O & H_2O_2)

(i) Its boiling point 144°C more than water but freezing point (–4) less than water. Density and dielectric constant are higher than H_2O.

(ii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2.

$2H_2O_2 \rightarrow 2H_2O + O_2$

H_2O_2 is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H_2O_2. Therefore, aqueous solution is stored in plastic containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2.

(iii) **Acidic nature**

Behaves as a weak acid according to the following equation

$H_2O_2(aq) \rightleftharpoons H^+ + HO_2^-, K_a = 1.5 \times 10^{-12}$ at 25°C

Aqueous solution of H_2O_2 turns blue litmus red which is then bleached by the oxidising property of H_2O_2.

$Na_2CO_3 + H_2O_2 \rightarrow Na_2O_2 + H_2O + CO_2$

$Ba(OH)_2 + H_2O_2 + 6H_2O \rightarrow BaO_2 8H_2O \downarrow$

A 30% H_2O_2 solution has pH = 4.0

(iv) **Oxidising Agent**

$2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$; SRP = 1.77v (in acidic medium)

$2e^- + H_2O_2 \rightarrow 2OH^-$; SRP = 0.87 v (In alkaline medium)

On the basis of the above potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

$Cr_2O_7^{-2} + 2H^+ + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$

CrO_5 bright blue coloured compound is soluble in ether.

Uses

(i) In bleaching of delicate materials such as silk, wool, cotton, ivory etc.

Properties of Hydrides

Table : Some Properties of H_2O, H_2S, H_2Se and H_2Te

	Enthalpies of formation (kJ mol^{-1})	Bond angle	Boiling Point (°C)
H_2O	– 242	H – O – H = 104°28'	100
H_2S	– 20	H – S – H = 92°	– 60
H_2Se	+ 81	H – Se – H = 91°	– 42
H_2Te	+ 154	H–Te–H=90°	– 2.3

The hydrides decreases in stability from H_2O to H_2Te. They become less stable because the bonding orbitals become larger and more diffuse hence overlap with the hydrogen '1s orbital' is less effective.

The H–O–H bond angle in water is 104°28', in accordance with the VSEPR prediction of slightly less than tetrahedral due to the presence of lone pairs of electrons. Thus the orbitals used for bonding by O are close to sp^3 hybrids. In H_2S to H_2Te the bond angles become close to 90°. This suggests that almost pure p orbitals on Se and Te are used for bonding to hydrogen.

In a series of similar compounds, the boiling points usually increase as the atoms become larger and heavier. If the boiling points increase, then the volatility decreaes. This trend is shown by the boiling points of H_2S. H_2Se & H_2Te, but the boiling point of water is anomalous.

Water has an abnormally low volatility because its molecules are associated with each other by means of hydrogen bonds in both the solid and liquid states.

SULPHUR (S)

Sodium Thiosulphate ($Na_2S_2O_3.10H_2O$) : (Hypo)

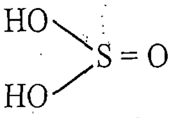
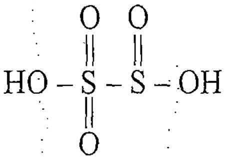
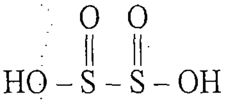
Preparation

(i) $Na_2SO_3 + S \xrightarrow[\text{in absence of air}]{\text{boiled}} Na_2S_2O_3$

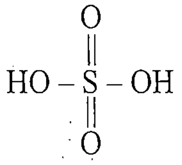
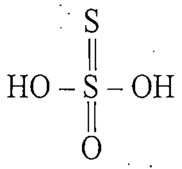
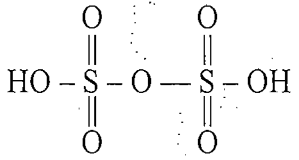
(ii) $Na_2CO_3 + 2SO_2(\text{excess}) + H_2O \rightarrow 2NaHSO_3 + CO_2;$
$2NaHSO_3 + Na_2CO_3 \rightarrow 2Na_2S_2O_3 + H_2O + CO_2$

Structure of Oxoacids of S

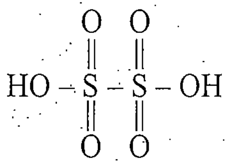
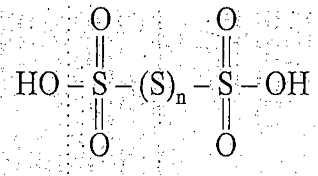
1. **Sulphurous acid series**

H_2SO_3 Sulphurous acid		S(+IV)
$H_2S_2O_5$ pyrosulphurous acid	 $HO-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-\overset{O}{\overset{\parallel}{S}}-OH$	S(+V), S(+III)
$H_2S_2O_4$, dithionous acid	 $HO-\overset{O}{\overset{\parallel}{S}}-\overset{O}{\overset{\parallel}{S}}-OH$	S(+III)

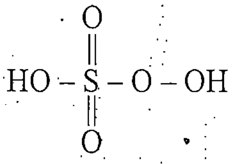
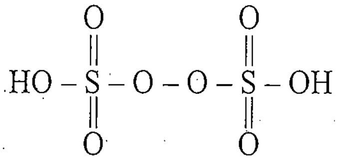
2. **Sulphuric acid series**

H_2SO_4 sulphuric acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	S(+VI)
$H_2S_2O_3$ thiosulphuric acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}-OH$	S(+VI), S(–II)
$H_2S_2O_7$ di or pyrosulphuric acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	S(+VI)

3. **Thionic acid series**

$H_2S_2O_6$ dithionic acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	S(+V)
$H_2S_2S_nO_6$ polythionic acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-(S)_n-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	S(+V)
	(n = 1 – 12)	S(0)

4. **Peroxoacid series**

H_2SO_5 peroxomonosulphuric acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-OH$	S(+VI)
$H_2S_2O_8$ peroxodisulphuric acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	S(+VI)

SULPHAZENE

Compounds which contain sulfur-nitrogen rings were known in the last century, but many new ones have been prepared in the last decade. It is currently an area of considerable interest. The ammonolysis of sulfur monochloride, S_2Cl_2, either in solution in an inert solvent or heated over solid ammonium chloride, yields tetrasulfur tetranitride:

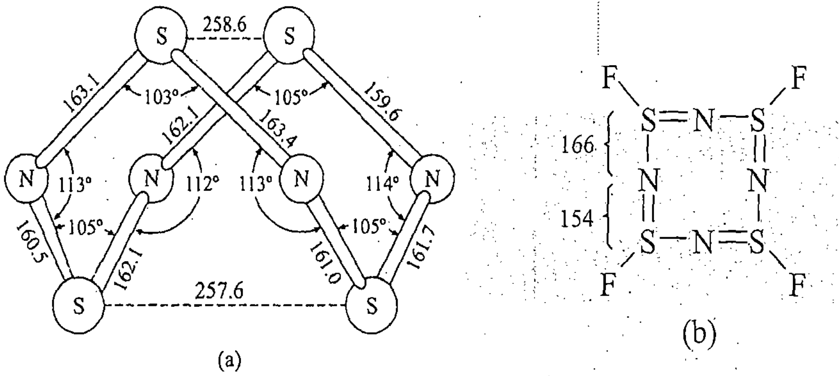
$$S_2Cl_2 \xrightarrow{NH_3} S_4N_4 + S_8 + NH_4Cl$$

The product is a bright orange solid insoluble in water but soluble in some organic solvents. Although the crystals are resonably stable to attack by air, they are explosively sensitive to shock or friction.

A few moments reflection will show that it is impossible to write a simple Lewis structure for S_4N_4. Furthermore, the cage structure has been found to have two pairs of nonbonding sulfur atoms at a distance is longer than the normal S–S bond length (206 pm), some interaction must occur between the transannular sulfur atoms. All of the S–N bond distances within the ring are approximately equal ($\approx$ 162 pm), indicating extensive delocalization (12π electrons) rather than alternating discrete single and double bonds. The situation is similar to but more complicated than that of the cyclophosphazenes.

We have seen that S_2N_2 and $(SN)_x$ can be prepared from S_4N_4. Other neutral binary sulfides may be obtained from it as well. When S_4N_4 is heated under pressure in a solution of CS_2 containing sulfur, S_4N_4 is formed. This molecule has a "half-chair" conformation. Others such as S_5N_6 and $S_{11}N_2$ have also been reported.

An even larger number of binary sulfur-nitrogen cations and anions are known. Reduction of S_4N_4 (with metallic potassium or sodium azide) yields the planar six-membered ring, $S_3N_3^-$. At first glance one might think that this is another benzene analogue. An electron count dispels that notion as their are ten π-electrons instead of six. Still, the Huckel 4n + 2 rule is obeyed and the system satisfies the requirement for aromaticity. However, four of the π-electrons occupy antibonding orbitals, which has the effect of weakening the S–N bond.



(a)

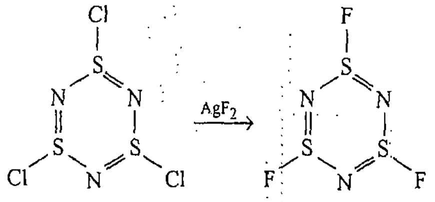
(b)

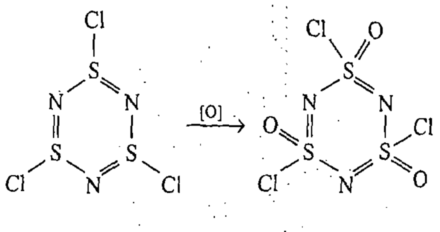
Figure: Eight-membered sulfur-nitrogen rings: (a) molecular structure of S_4N_4; (b) diagrammatic structure of $N_4S_4F_4$ illustrating alternating bond lengths.

S_4N_4 can also be oxidised when it is subjected to chlorine, trithiazyl trichloride is produced:

$$3S_4N_4 + 6Cl_2 \rightarrow 4N_3S_3Cl_3$$

This compound may be converted into the corresponding fluoride or oxidized to sulfanuryl chloride:





GROUP 17 (VIIA-THE HALOGEN FAMILY)

Physical Properties of the Halogens

S.No.	Properties	F	Cl	Br	I
1.	Atomic Number	9	17	35	53
2.	Electronic configuration	(He) $2s^2\ 2p^5$	(Ne) $3s^2\ 3p^5$	[Ar] $3d^{10}4s^2\ 4p^5$	[Kr] $4d^{10}\ 5s^2\ 5p^5$
3.	Atomic radius/pm	72	99	114	133
4.	(IE)I/kJ mol^{-1}	1681	1256	1143	1009
5.	Electronegativity (Pauling)	4.0	3.0	2.8	2.5
6.	Bond energy (X-X)/kJ mol^{-1}	126	210	158	118
7.	Oxidising power (X_2)	Most	–	–	least
8.	Common oxidation state	– 1	–1, +1, +3, +5, +7	–1, +1, +3, +5, +1	–1, +5, +1, +3, +7
9.	Physical form (X_2) at room temp.	pale yellow gas	yellow-green gas	dark red liquid	violet-black solid
10.	Melting point (X_2)/°C	– 219	–101	– 7	114

- HF has a high b.p. (19.5°C) as a result of strong intermolecular hydrogen bonding, whereas all other hydrogen halide have much lower b.p.
- HF is a weak acid, whereas all other hydrohalic acids (HCl, HBr and HI) are strong acids.
- F_2 reacts with cold NaOH solution to produce OF_2 (oxygen difluoride) gas

  $$2F_2 + 2NaOH \longrightarrow 2NaF + H_2O + OF_2$$

  The same reaction with chlorine or bromine produces a halides (X^-) and hypohalite (XO)

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

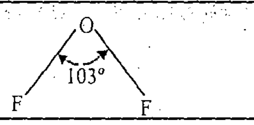
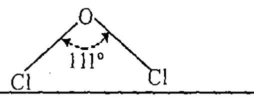
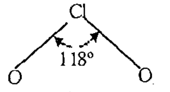
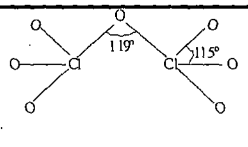
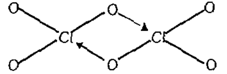
  X stands for Cl or Br, Iodine (I_2) does not react under the same condition
- $Ca(OH)_2 + Cl_2 \longrightarrow CaCl(OCl) + H_2O$
- Hot NaOH $6NaOH + 3X_2 \longrightarrow 5NaX + NaXO_3 + 3H_2O$ (X = Cl, Br, I)

Reactions of Halogen

Compound	Reaction	Comment
H_2O	$2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$	Vigorous reaction with F_2
	$2X_2 + 2H_2O \longrightarrow 4H^+ + 4X^- + O_2$	Atmospheric O_2 can oxidise I^- to I_2 hence, reverse reaction
	$X_2 + H_2O \xrightarrow{\text{disproportionate}} X^- + HOX + H^+$	$Cl_2 > Br_2 > I_2$ (F_2 does not disproportionate)

H_2	$H_2 + X_2 \longrightarrow 2HX$	All the halogens with Br_2 photo chemical reaction, with I_2 very slow even at high temperature.
Metals	$2M + nX_2 \longrightarrow 2MX_n$	Most metals form halides.
CO	$CO + X_2 \longrightarrow COX_2$	Only Cl_2, Br_2 form carbonyl halide
P	$2P + 3X_2 \longrightarrow 2PX_3$	For F, Cl, Br, I
	$2P + 5X_2 \longrightarrow 2PX_5$	For F, Cl, Br
S	$2S + X_2 \longrightarrow S_2X_2$	
	$S + 2Cl_2 \longrightarrow SCl_4$	Cl, Br
	$S + 3F_2 \longrightarrow SF_6$	
H_2S	$H_2S + X_2 \longrightarrow 2HX + S$	All the halogens oxidise $H_2S(S^{2-})$ to S
SO_2	$SO_2 + X_2 \longrightarrow SO_2X_2$	F and Cl
NH_3	$8NH_3 + 3X_2 \longrightarrow N_2 + 6NH_4X$	F, Cl, Br
X_2	$X_2 + X'_2 \longrightarrow 2XX'$	Interhalogen compounds

Compounds of Halogen With Oxygen

Compound	Preparation	Structure	Properties
1. Oxides of fluorine			
(a) OF_2	$2F_2 + 2NaOH \rightarrow 2NaF + H_2O + OF_2$		Strong fluorinating agent
(b) O_2F_2	$F_2 + O_2 \xrightarrow[\text{Liq. air temp. low pressure}]{\text{Electric discharge}} O_2F_2$	Similar to H_2O_2	Strong fluorinating agent
2. Oxides of chlorine			
(a) Cl_2O	$2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow Cl_2O + 2NaHCO_3 + 2NaCl$		Explosive in nature
(b) ClO_2	$2AgClO_3 + Cl_2 \rightarrow 2AgCl + 2ClO_2 + O_2$ $2KClO_3 + 2(COOH)_2 \rightarrow 2ClO_2 + 2CO_2 + (COOK)_2 + 2H_2O$		Odd electron molecule but do not dimerise because odd electron is delocalize
(c) Cl_2O_7	$2HClO_4 \xrightleftharpoons{P_4O_{10}} Cl_2O_7 + H_2O$		It is less reactive than other chlorine oxides
(d) Cl_2O_6	$2ClO_2 + 2O_3 \rightarrow 2ClO_3 + 2O_2 \rightarrow Cl_2O_6 + 2O_2$		Diamagnetic in nature

Structure of Oxoacids of halogens

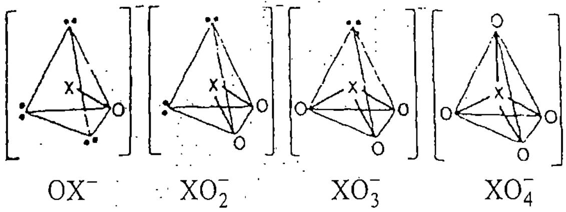


Figure: Structures of the oxoacids.

Pseudohalogens and Pseudohalides

A few ions are known consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions. Pseudohalide ions are univalent and these form salts resembling the halide salts. For example, the sodium salts are soluble in water, but the silver salts are insuluble. The hydrogen compounds are acids like the halogen acids HX.

Table: The important pseudohalogens

Anion	Acid	Dimer
CN^- cyanide ion	HCN hydrogen cyanide	$(CN)_2$ cyanogen
SCN^- thiocyanate ion	HSCN thiocyanic acid	$(SCN)_2$ thiocyanogen
$SeCN^-$ selenocyanate ion		$(SeCN)_2$ selenocyanogen
OCN^- cyanate ion	HOCN cyanic acid	
NCN^{2-} cyanamide ion	H_2NCN cyanamide	
ONC^- fulminate ion	HONC fulminic acid	
N_3^- azide ion	HN_3 hydrogen azide	

Some of the pseudohalide ions combine to form dimers comparable with the halogen molecules X_2. These include cyanogen $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$.

The best known pseudohalide is CN^-. This resembles Cl^-, Br^- and I^- in the following respects.

1. It forms an acid HCN.
2. It can be oxidized to form a molecule cyanogen $(CN)_2$.
3. It forms insoluble salts with Ag^+, Pb^{2+} and Hg^+.
4. Interpseudohalogen compounds ClCN, BrCN and ICN can be formed.
5. AgCN is insoluble in water but solube in ammonia, as is AgCl.
6. It forms a large number of complexes similar to halide complexes.
   e.g. $[Cu(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$ and $[Co(CN)_6]^{3-}$ and $[CoCl_6]^{3-}$.

GROUP 18TH ELEMENTS (ZERO GROUP FAMILY)

ATOMIC & PHYSICAL PROPERTIES

S.No.	Element	He	Ne	Ar	Kr	Xe
1.	atomic Number	2	10	18	36	54
2.	Atomic Mass	4	20.18	39.1	83.8	131.1
3.	Electronic configuration	$1s^2$	$[He]\ 2s^2\ 2p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$
4.	Atomic Radius (pm)	120	160	190	200	220
5.	Ionization enthalpy/(kJ mol^{-1})	2372	2080	1520	1351	1170
6.	Boiling point / K	4.2	27.1	87.2	119.7	165
7.	Electronegativity					

Initially their electronegativities were taken to be zero. But it is not zero (ref. NCERT)

(1) All are gases at room temperature. The only radioactive element in them is Radon (Rn)

(2) Order of abundance in the air Ar > Ne > Kr > He > Xe.

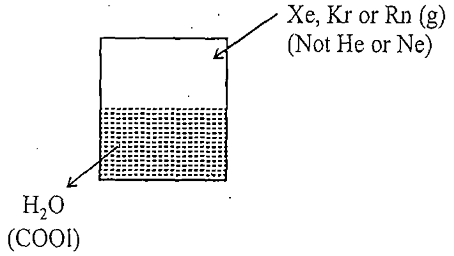
(3) If Helium is compressed and liquified it forms He (I) liquid at 4.2K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He (II) is obtained at 2.2 K. Which is known as super fluid because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

Compounds of inert gases are of following two types:

(i) **Clatherate Compounds**

Intert gas molecules get trapped in the cages formed by the crystal structure water.

During the formation of ice, Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal strucutre of ice. Compound thus obtained are called clatherate compounds. There are no chemical bonds in clatherate compound.



(ii) **Interstitial compounds:**

These compounds are formed when small atoms occupy positions in the interstices of the metal lattice. Only He forms such compounds since the atomic size of He is the smallest amongst the noble gases and matches the size of the interstices available in the lattice of most of the heavy metals.

Uses of Noble Gases

1. **Uses of Helium**

(i) The chief use of helium is in filling of balloons which are employed for meterological observations. Although lifting power of helium is 8% less than that of hydrogen, yet it is preferred because it is non-inflammable.

(ii) Liquid helium (b.p. 4.2 K) is used as a cryogenic agent for carrying out various experiments at low temperatures.

(iii) An oxygen-helium mixture is used for artificial respiration in deep sea diving.

(iv) Helium is less soluble in blood than nitrogen. Therefore, an oxygen helium mixture is also used in the treatment of asthma.

(v) helium is also used for creating inert atmosphere during welding of Mg and Al which are easily oxidizable.

(vi) Helium is chemically inactive and does not become radioactive. Hence it is used in gas cooled atomic reactors as a heat transfer agent.

2. **Uses of Neon**

(i) Neon is mainly used in discharge tubes and fluorescent lamps for advertising purpose.

(ii) Neon has a remarkable property of carrying extremely high currents even under high voltage. Therefore, neon is used in safety devices for protecting electrical instruments such as voltmeters, relays and rectifiers from high voltage.

(iii) It is used in beacon light as saftey signal for air nevigators since its light has fog penetration power.

(iv) It is used for filling sodium vapour lamps.

3. **Uses of Argon**

(i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes such as arc welding of metals and alloys.

(ii) It is used in filling incandescent and flouorescent lamps where its presence retards the sublimation of the filament and thus increases the life of the lamp.

(iii) It is also used in 'neon signs' for obtaining lights of different colours.

4. **Uses of Krypton**

(i) Krypton and xenon are more efficient than argon in gas filled lamps because of their lower thermal conductivities but due to their scarcity and high cost they are used to a much smaller extent.

(ii) A mixture of krypton and xenon has also been used in some tubes for high speed photography.

5. **Uses of Radon**

(i) Being radioactive, radon is used in radioactive research.

(ii) It is used for normal treatment of cancer and other malignant growths.

(iii) It is used in X-ray photography for the detection of flaws in metals and other solids.

COMPOUNDS OF XENON

(a) Xenon difluoride (XeF_2)

1. $Xe + F_2 \xrightarrow[\text{Ni Tube or monel metal (alloy of Ni)}]{\text{400°C high pressure}} XeF_2$

(2 : 1)

2. $Xe + O_2F_2 \xrightarrow{118°C} XeF_2 + O_2$

Reactions

(1) $XeF_2 + H_2 \rightarrow Xe + 2HF$

(2) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$ (Slow)

(3) $XeF_2 + 2NaOH \rightarrow Xe + \frac{1}{2}O_2 + 2NaF + H_2O$ (fast)

Oxidising properties

The standard reduction potential for XeF_2 is measured to be + 2.64V. Therefore it acts as a strong oxidising agent.

(1) $2e + 2H^+ + XeF_2 \rightarrow Xe + 2HF$ (SRP = + 2.64 V)

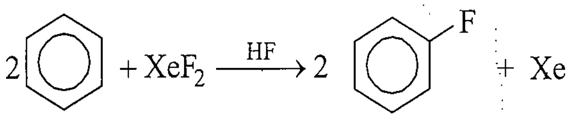
(2) $XeF_2 + 2NaX \rightarrow Xe + X_2 + 2NaF$

In this manner XeF_2 will oxidise halide ions (except F^- into free halogens).

(3) $S_8 + 24XeF_2 \rightarrow 8SF_6 + 24Xe$

(4) $2CrF_2 + XeF_2 \rightarrow 2CrF_3 + Xe$

(5)



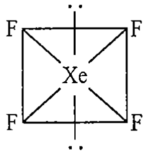
(6) $8NH_3 + 3XeF_2 \rightarrow N_2 + 6\,NH_4F + 3Xe$

(7) $2NO_2\,XeF_2 \rightarrow 2NO_2F$ (Nitronium fluoride) + Xe

(8) IF_5 (lewis acid) + $XeF_2 \rightarrow [XeF]^+ [IF_6]^-$; $2SbF_5$ (lewis acid) + $XeF_2 \rightarrow [XeF]^+ [SbF_6]^-$

(b) Xenon Tetrafluoride (XeF_4)

Sturcutre : Shape square planar & Geometry octahedral



hybridisation = sp^3d^2

Properties

1. $6\,XeF_4 + 12H_2O \rightarrow 4XeO_3 + 24\,HF + 3O_2 + 4Xe$

It disproportionates into perxenate ion in basic medium.

(i) $\underset{\text{Perxenate ion}}{[XeO_6]^{4-}} \xrightarrow[\text{Water}]{H^+} XeO_3 + O_2$

(ii) $[XeO]_6^{4-} + Mn^{+2} \rightarrow MnO_4^- + XeO_3$ (slow decomposition)

2. $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$

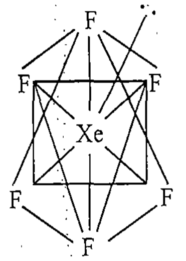
3. Fluorinating agent

$XeF_4 + Pt \rightarrow PtF_4 + Xe$; $XeF_4 + 4NO \rightarrow Xe + 4NOF$ (nitrosyl fluoride)

4. $XeF_4 + 4NO_2 \rightarrow Xe + 4NO_2\,F$ (nitroniumfluoride)

(c) Xenon Hexafluoride (XeF_6)

Structure : Capped octhedral (distorted octahedral) hybridisation sp^3d^3



Solid XeF_6 exists as tetramer in which $2[XeF_5]^+$ ions are brdiged by F^- ions

(i) $Xe + 3F_2 \xrightarrow[\text{50 atm, Ni tube}]{400°C} XeF_6$ (1 : 20)

(ii) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

Properties

(i) HF is a good solvent for all three fluorides.

(ii) Hydrolysis

(a) Complete hydrolysis : $XeF_6 + 3H_2O \rightarrow XeO_3$ (white solid) + 2HF

(b) Partial hydrolysis : $XeF_6 + H_2O \rightarrow XeOF_4$ (colourless solid) + 2HF

$$\begin{tikzcd} XeOF_4 \arrow[d, "2H_2O"] & \\ XeO_2F_2 \arrow[r, "2H_2O"'] & XeO_3 \end{tikzcd}$$

(iii) Reaction with silica (SiO_2): $2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$

(iv) Thermal decomposition (effect of heat): $2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4 + 3F_2$

XeF_2 & XeF_4 do not undergo decomposition

(v) Formation of addition compounds

$XeF_6 + SbF_5 \rightarrow [XeF_5]^+ [SbF_6]^-$;

$XeF_6 + BF_3 \rightarrow [XeF_5]^+ [BF_4]^-$

(vi) Reaction with H_2

$XeF_6 + 3H_2 \rightarrow 6HF + Xe$;

(vii) $XeO_3 + 2XeF_6 \rightarrow 3XeOF_4$

Order of oxidising power

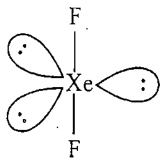
$XeF_2 > XeF_4 > XeF_6$

(viii) F–donating/F – accepting properties

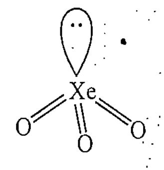
donating $XeF_6 + PtF_5 \rightarrow (XeF_5)^+ (PtF_6^-)$

$$\text{acceptance}\left\{\begin{array}{llll} CsF & + \; XeF_6 & \rightarrow & CsXeF_7 \\ \text{(alkali metal} & & & \text{(caesium heptafluoroxenate)} \\ \text{fluoride)} & & & \\ 2CsXeF_7 & & \rightarrow & XeF_6 \rightarrow Cs_2XeF_8 \\ & & & \text{(caesium octafluoroxenate)} \end{array}\right.$$

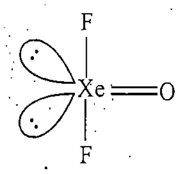
Structure of compounds of Xenon



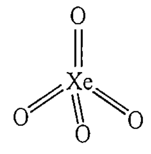
XeF$_2$ linear



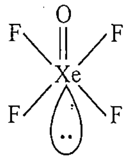
XeO$_3$ Pyramidal



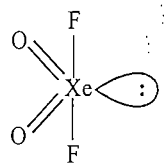
XeOF$_2$ T-shaped



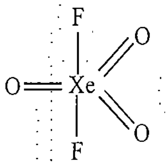
XeO$_4$ Tetrahedral



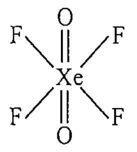
XeOF$_4$
Square pyramidal



XeO$_2$F$_2$
See-Saw



XeO$_3$F$_2$
Trigonal bipyramidal



XeO$_2$F$_4$
Octahedral

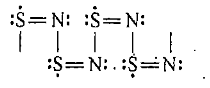
ONE-DIMENSIONAL CONDUCTORS

There is an unusual hetero chain, $(SN)_x$, discovered in 1910, which did not receive detailed attention until the 1970s. Interest centers on the fact that although it is composed of atoms of two nonmetals, polymeric sulfur nitride (also called polythiazyl) has some physical properties of a metal. The preparation is from tetrasulfur tetranitride.

$$S_4N_4 \xrightarrow{Ag} S_2N_2 \longrightarrow (SN)_x$$

The S_4N_4 is pumped in a vacuum line over silver wool at 220°C, where it polymerizes slowly to a lustrous golden material. The resulting product is analytically pure, as is necessary for it to show metallic properties to a significant degree. It has a conductivity near that of mercury at room temperature, and it becomes a superconductor at low temperatures (below 0.26 K).

X-ray diffraction studies show that the SN chains have the structure shown in Figure. This chain can be generated from adjacent square planar S_2N_2 molecules. The S–N bonds in this starting material have a bond order of 1.5 and a bond length of 165.4 pm, intermediate between single (174 pm) and double (154 pm) sulfur-nitrogen bonds. A free radical mechanism has been suggested leading to the linear chains of



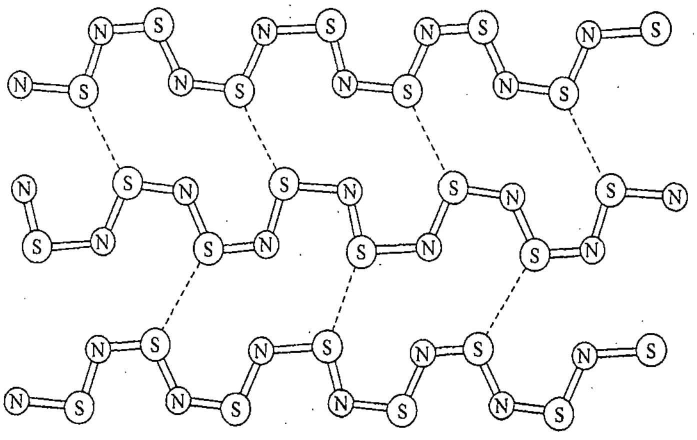


Figure: $(SN)_x$ chains in one layer of polymeric sulfur nitride.

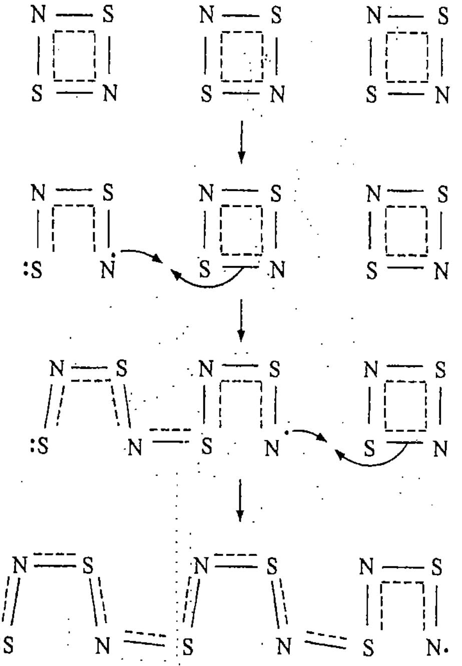


Figure: Polymerization of S_2N_2 to form $(SN)_x$ chains with minimal movement of atoms.

the polymer. Since polymerization can take place with almost no movement of the atoms, the starting material and product are pseudomorphs and the crystallinity of the former is maintained.

If one attempts to draw a unique Lewis structure for the $(SN)_x$ chain, one is immediately frustrated by the odd number of electrons available. Many resonance structures can be drawn and they contribute to the hybrid structure, but the single structure: illustrates many features: a conjugated single-bond-double-bond resonance system with nine electrons on each sulfur atom rather than a Lewis octet; every S–N unit will thus have one antibonding π* electrons. The half-filled, overlapping π* orbital will combine to form a half-filled conduction band in much the same way as we have seen half-filled 2s orbitals on a mole of lithium atoms form a conduction band. Note, however, that this conduction band will lie only along the direction of the $(SN)_x$ fibers; the polymer is thus a "one dimensional metal".

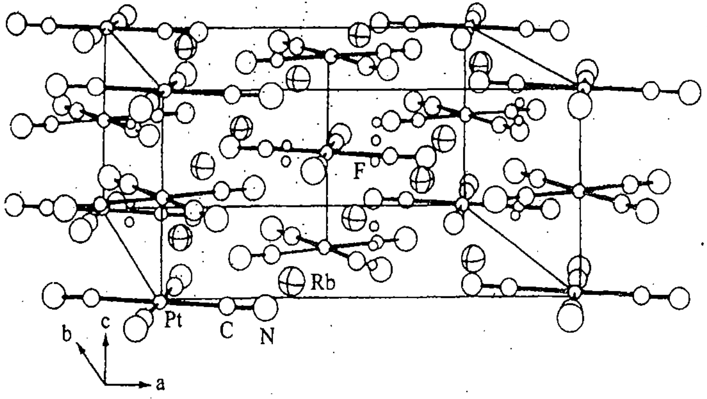


Figure: Perspective view of the unit cell of $Rb_2[Pt(CN)_4](FHF)_{0.40}$. One-dimensional chains of staggered $[Pt(CN)_4]^{2-}$ ions occupy the corners and center of the unit cell. The triad of small circles represents the partially occupied positions of the FHF^- ions. Note the very short Pt–Pt distance (279.8 pm).

Similar to $(SN)_x$ in their one-dimensional conductivity properties are the stacked columnar complexes typified by $[Pt(CN_4)]^{2-}$. These square planar ions adopt a closely spaced parallel arrangement, allowing for considerable interaction among the d_{z^2} orbitals of the platinum atoms. These orbitals are normally filled with electrons, so in order to get a conduction band some oxidation (removal of electrons) must take place. This may be readily accomplished by adding a little elemental chlorine or bromine to the pure tetracyanoplatinate salt to get stoichiometries such as $K_2[Pt(CN)_4]Br_{0.3}$ in which the platinum has an average oxidation state of +2.3. The oxidation may also be accomplished electrolytically, as in the preparation of $Rb_2[Pt(CN)_4](FHF)_{0.4}$, which has a short Pt–Pt separation. The Pt-Pt distance is only 280 pm, almost as short as that found in platinum metal itself (277 pm).

CAGE STRUCTURES

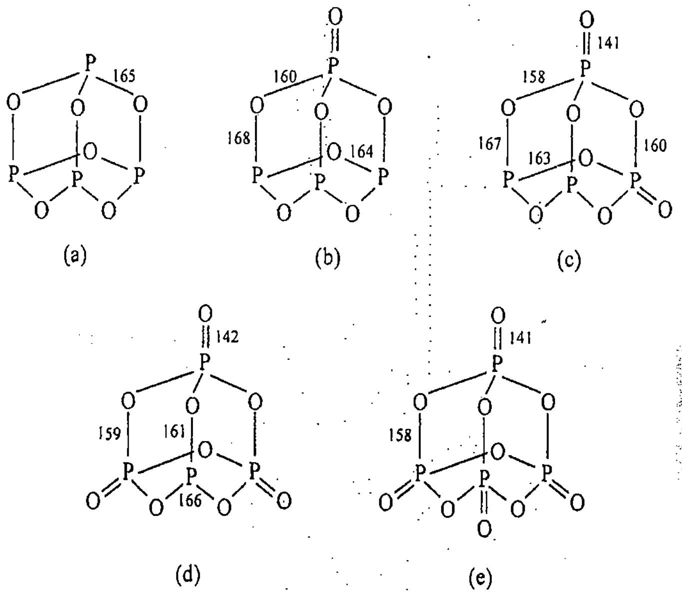
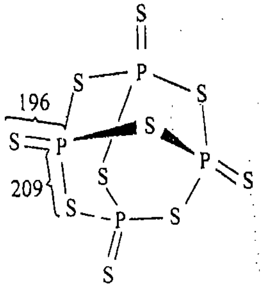
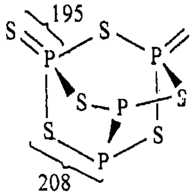
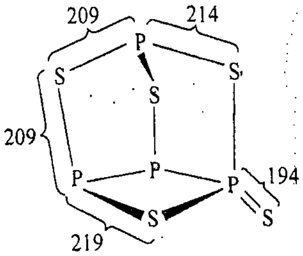
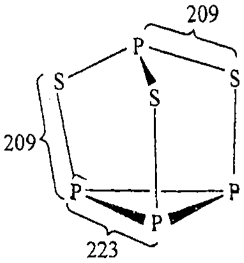


Figure: Phosphorus cage molecules: (a) P_4O_6 (b) P_4O_7 (c) P_4O_8 (d) P_4O_9 (e) P_4O_{10}. [Data distances in pm]









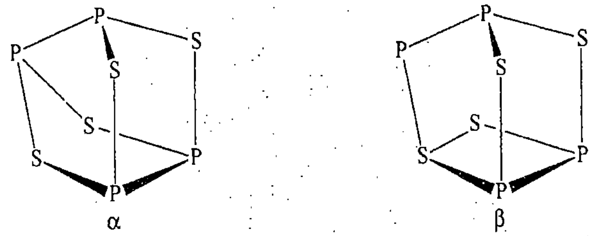


Figure: Molecular structures of some phosphorus sulfides. Distance in picometers. (a) P_4S_{10} (b) P_4S_7 (c) P_4S_5 (d) P_4S_3 (e) P_4S_4 (f) P_4S_4

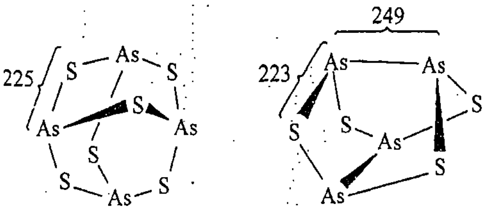


Figure: Molecular structures of two arsenic sulfides. Distances in picometers.

EXERCISE - I

Single Correct Type

Back Bonding

1. The strength of pπ – dπ bonding in ε – O (ε = Si, P, S and C) follows the order
   (a) Si – O > P – O > S – O > Cl – O (b) P – O > Si – O > S – O > Cl – O
   (c) S – O > Cl – O > P – O > Si – O (d) Cl – O > S – O > P – O > Si – O
2. Which of the following is an electron deficient molecule according to the octet rule ?
   (a) CH_4 (b) $H_3N{\cdot}BH_3$ (c) AlH_3 (d) GeH_4
3. The order of acidity in boron trihalides is
   (a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$
   (c) $BF_3 > BBr_3 > BCl_3$ (d) $BBr_3 > BF_3 > BCl_3$
4. The lewis acidity of BF_3 in less than BCl_3 even fluorine is more electronegative than chlorine. It is due to
   (a) Stronger 2p(B) – 2p(F) – σ bonding (b) Stronger 2p(B) – 2p(F) – π bonding
   (c) Stronger 2p(B) – 3p(Cl) – σ bonding (d) Stronger 2p(B) – 3p(Cl) – π bonding
5. The compound $(SiH_3)_3N$ is
   (a) pyramidal and more basic than $(CH_3)_3N$ (b) planar and less basic than $(CH_3)_3N$
   (c) pyramidal and less basic than $(CH_3)_3N$ (d) planar and more basic than $(CH_3)_3N$
6. Hybridisation state of Boron and oxygen in boric acid in gas phase
   (a) sp^3, sp^2 (b) sp^2, sp^3 (c) sp^2, sp^2 (d) sp^3, sp^3
7. Which is correct statement among
   (a) Oxygen is sp^3 hybridised in $O(SiPh_3)_2$
   (b) Bond angle in $N(CH_3)_3$ is greater than that in $N(SiH_3)_3$
   (c) The d_{B-O} in $B(OH)_3 < d_{B-O}$ in $[B(OH)_4]^{\ominus}$
   (d) All are correct
8. Lewis acidity of BCl_3, BPh_3 and BMe_3 with respect to pyridine follows the order
   (a) $BCl_3 > BPh_3 > BMe_3$ (b) $BMe_3 > BPh_3 > BCl_3$
   (c) $BPh_3 > BMe_3 > BCl_3$ (d) $BCl_3 > BMe_3 > BPh_3$
9. The geometry with respect to the central atom of the following molecules are:
   $N(SiH_3)_3$; Me_3N ; $(SiH_3)_3P$
   (a) planar, pyramidal, planar (b) planar, pyramidal, pyramidal
   (c) pyramidal, pyramidal, pyramidal (d) pyramidal, planar, pyramidal
10. Which of the following statement is correct for CCl_3^- and $:CCl_2$
    (a) Back bonding in both cases from Cl to C-atom
    (b) Back bonding in both cases from C to Cl-atom
    (c) Back bonding in CCl_3^- from C to Cl but reverse in $:CCl_2$
    (d) Direction of back bonding is just same in two cases.

Statement-1 & Statement-2 (Q.11)

(a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1

(b) Statement-1 is true, statement-2 is true and statement -2 is NOT the correct explanation for statement-1

(c) Statement-1 is true, statement-2 is false

(d) Statement-1 is false, statement-2 is true.

11. Statement 1 : The B-F bond length in BF_3 is not identical with that in BF_4^-

Statement 2 : Back bonding is involved in BF_4^- but not in BF_3

12. Choose the incorrect statement

(a) CH_3NCS molecule is linear (b) SiH_3NCS molecule is linear

(c) GeH_3NCS molecule is bent (d) $P(SiH_3)_3$ molecule is pyramidal

13. Which of the following is most stable

(a) CF_2 (b) CCl_2 (c) CBr_2 (d) CI_2

14. Arrange the following Boron derivatives in increasing order of their thermal stability:

(a) $B_2Cl_4 < B_2F_4 < B_2(OR)_4 < B_2(NR_2)_4$ (b) $B_2F_4 < B_2Cl_4 < B_2(OR)_4 < B_2(NR_2)_4$

(c) $B_2Cl_4 < B_2(NR_2)_4 < B_2(OR)_4 < B_2F_4$ (d) $B_2(NR_2)_4 < B_2(OR)_4 < B_2F_4 < B_2Cl_4$

15. The actual magnitude of π-bond energy in Boron trihalides follows the order:

(a) $BF_3 < BCl_3 < BBr_3 < BI_3$ (b) $BF_3 < BBr_3 < BI_3 < BCl_3$

(c) $BI_3 < BBr_3 < BCl_3 < BF_3$ (d) $BCl_3 < BBr_3 < BI_3 < BF_3$

16. Arrange the following compounds in order of their decreasing thermal stability:

(a) $B_2(NMe_2)_4 > B_2(OMe)_4 > B_2(OH)_4 > B_2F_4 > B_2Cl_4 > B_2Br_4$

(b) $B_2(OH)_4 > B_2F_4 > B_2Cl_4 > B_2Br_4 > B_2(NMe_2)_4 > B_2(OMe)_4$

(c) $B_2Br_4 > B_2(NMe_2)_4 > B_2(OMe)_4 > B_2(OH)_4 > B_2F_4 > B_2Cl_4$

(d) $B_2(NMe_2)_4 > B_2(OH)_4 > B_2F_4 > B_2Cl_4 > B_2Br_4 > B_2(OMe)_4$

Bridge Bonding

17. Number of three-centre two electron ($3C - 2e^-$) bonds present in diborane is

(a) 2 (b) 4 (c) 6 (d) 8

18. Which one of the following statements is not true regarding diborane

(a) It is an electron deficient compounds

(b) The e^- deficiency of boron is filled up by the formation of bridge bonds by H

(c) On methylation, the product is $Me_4B_2H_2$

(d) The delocalisation of σ bonds takes place through H bridges

19. Which of the following statement is correct regarding the structure of B_2H_6

(a) It has 2 bridging hydrogens in a plane $\perp$ to the rest four hydrogens

(b) Both Borons are sp^2 hybridized

(c) The highest e^- density lies along the $B - H$ bonds of the $B - H - B$ bridges

(d) The $B - H - B$ bridges are shorter and stronger than the terminal bonds

20. What is the hybridisation of Be atom in the following compounds – $BeCl_2$ (vapour), $BeCl_2$ (dimeric form), $BeCl_2$ (solid), BeF_2

(a) sp^3, sp^2, sp, sp^3 (b) No hybridisation, sp^2, sp^3, sp^3

(c) sp, sp^2, sp^3, no hybridisation (d) sp, sp^2, sp^3, sp^3

21. Consider the following statements

(A) In Al_2Cl_6, all bonds are similar

(B) In Al_2Me_6, the bridging Al–C–Al bonds are larger than the terminal bonds

(a) A, B both correct (b) A, B both incorrect

(c) A–correct, B–incorrect (d) A–incorrect, B–correct

22. Which of the following statements is incorrect regarding B_2H_6?

(a) banana bonds are longer but stronger than normal B–H bonds

(b) B_2H_6 is also known as 3c–2e compound

(c) the hybrid state of B in B_2H_6 is sp^3 while that of sp^2 in BH_3

(d) it cannot be prepared by reacting BF_3 with $LiBH_4$ in the presence of dry ether

23. When an inorganic compound (X) having 3c-2e as well as 2c-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a hard substance (Z). Then incorrect statement is

(a) (X) is B_2H_6 (b) (Z) is known as inorganic graphite

(c) (Z) having structure similar to graphite (d) (Z) having structure similar to (X)

24. In the reaction $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$

Which of the following (X) is (are) not possible is

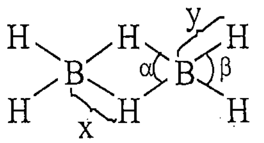
(a) NH_3 (b) CH_3NH_2 (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

25. $2NaBH_4 + I_2 \rightarrow A + 2NaI + H_2$

The number of 3c-2e⁻ bonds in 'A' are:

(a) 0 (b) 2 (c) 4 (d) 6

26. The correct statement regarding the structure of Diborane is



(a) x = y and α = β (b) x > y and α < β (c) x < y and α > β (d) x > y and α > β

27. Which of the following 'Al' compound does not exists as a dimer?

(a) AlH_3 (b) $Al(CH_3)_3$ (d) $Al(CH_2CH_3)_3$ (d) Trimesityl Aluminium

28. Number of 3c-2e⁻ bond in $Al(BH_4)_3$ are:

(a) zero (b) 3 (c) 6 (d) 9

29. Which of the following compound(s) of boron undergoes dimerisation?

(a) BF_3 (b) BH_3 (c) BBr_3 (d) $B(CH_3)_3$

30. Calculate the number of 3c–2e$^-$ bond in B_4H_{10}

(a) 0 (b) 4 (c) 6 (d) 2

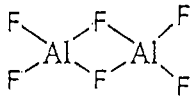
31. Calculate the number of 3c-2e$^-$ bond in $Hg(BH_4)_4$.

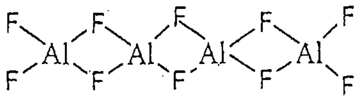
(a) 0 (b) 3 (c) 6 (d) 12

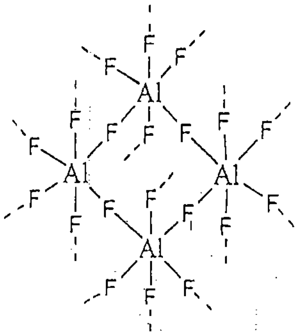
32. The C.No. of Al in $[Al(BH_4)_2Me]$ is:

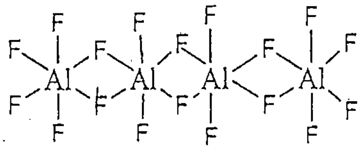
(a) 3 (b) 4 (c) 5 (d) 6

33. The solid state structure of aluminium fluoride is

(a)


(b)


(c)


(d)


34. A borane (X) is reacted with ammonia to give a salt of borohydride (Y). The ^{11}B NMR spectrum of Y consists of a triplet and a quintet. The borane X is

(a) B_2H_6 (b) B_3H_9 (c) B_4H_8 (d) B_5H_9

35. When an inorganic compound (X) having 3C – 2e$^-$ as well as 2C – 2e$^-$ bonds reacts with ammoia gas as

$$X + NH_3 \xrightarrow[\text{high temp}]{\text{excess } NH_3} A$$

$$\xrightarrow[\substack{2NH_3:1X \\ \text{high temp.}}]{} B$$

$$\xrightarrow{\text{1000 temp.}} C$$

Consider the following statements

(a) A is an acid-base adduct

(b) A is a hard substance and its structure is similar to graphite

(c) C is an acid-base adduct

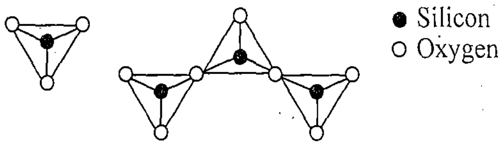
(d) B is a aromatic compound with localised polar coordinate bonds

The correct statement are

(a) a, d (b) b, c, d (c) b, d (d) d, c

Silicates

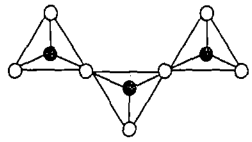
36. The following pictures represent various silicate anions. Their formulae are respectively:

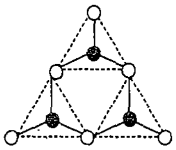


(a) SiO_3^{2-} $Si_3O_7^{2-}$ (b) SiO_4^{4-} $Si_3O_{10}^{8-}$

(c) SiO_4^{2-} $Si_3O_9^{2-}$ (d) SiO_3^{4-} $Si_3O_7^{8-}$

37. $Si_3O_9^{6-}$ (having three tetrahedral) is represented as:

(a)


(b)


(c) both (d) none

38. $BaTi[Si_3O_9]$ is a class of

(a) orthosilicate (b) cyclic silicate (c) chain silicate (d) sheet silicate

39. $Mg_6Si_4O_{10}(OH)_8$ is commercially known as

(a) asbestos (b) water-glass (c) soda-glass (d) zeolite

40. What is the nature of silicon-oxygen bond in slica (SiO_2) ?

(a) Polar covalent (b) Ionic

(c) Non-polar covalent (d) Coordinate covalent

41. Egyption blue $CaCuSi_4O_{10}$ is a example of

(a) Sheet silicate (b) Cyclic silicate (c) Pyrosilicate (d) Chain silicate

42. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is

(a) 2 (b) 3 (c) 4 (d) 5

43. Which is incorrect regarding three dimensional network silicates?

(a) It is pure SiO_2

(b) It has all four oxygen of tetrahedraon shared

(c) Feldspars, zeolites and ultramarines are the common examples

(d) It contains some isomorphously substituted Al^{3+} ion

44. Which of the following silicate is formed when three oxygen atoms of $[SiO_4]^{4-}$ tetrahedral units are shared ?

(a) Sheet silicate (b) Pyrosilicate

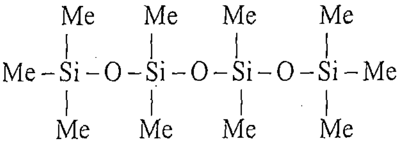
(c) Three dimensional silicate (d) linear chain silicate

45. What is the ring size and no. of tetrahedralunits linked together in the given silicate $(Si_6O_{18})^{-12}$?

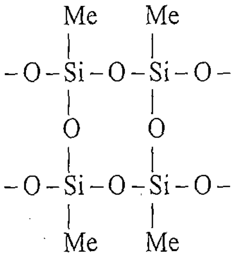
(a) 12, 6 (b) 6, 6 (c) 12, 12 (d) 8, 2

Silicones

46. If we mix Me_3SiCl with Me_2SiCl_2, we get silicones of the type:

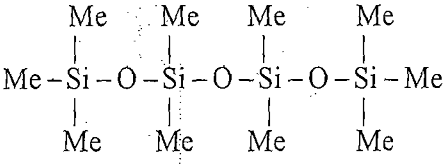
(a) 

$Me-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-Me$

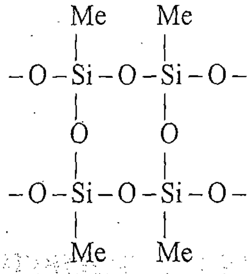
(b) 

(c) both of the above (d) none of the above

47. If we start with $MeSiCl_3$ as the starting material, silicones formed is:

(a) 

$Me-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-O-\overset{Me}{\underset{Me}{Si}}-Me$

(b) 

(c) Both of the above (d) None of the above

48. Which of the following compound will form a silicone having highest molecular weight

(a) $R\ Si(OH)_3$ (b) $R_2\ Si(OH)_2$ (c) $R_3\ Si(OH)$ (d) $R_4\ Si$

49. A complex cross-linked polymer (silicone) is formed by

(a) hydrolysis of $(CH_3)_3\ SiCl$.

(b) hydrolysis of a mixture of $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$

(c) hydrolysis of $CH_3\ SiCl_3$ (d) hydrolysis of $SiCl_4$.

50. Hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiCl_3 leads to

(a) linear chain and cross-linked silicones, respectively

(b) cross-linked and linear chain silicones, respectively

(c) linear chain silicones only (d) cross-linked silicones only

51. $(Me)_2\ SiCl_2$ on hydrolysis will produce :

(a) $(Me)_2\ Si(OH)_2$ (b) $(Me)_2\ Si = O$

(c) $-[—O—(Me)_2\ Si—O—]_n—$ (d) $Me_2SiCl(OH)$

52. $RCl \xrightarrow[Si]{cu-powder} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{condensation} A$

Compound (a) is

(a) a linear silicone (b) a chlorosilane (c) a linear silane (d) a network silane

Inert Pair Effect

53. The correct order of stability of difluorides is
(a) $GeF_2 > SiF_2 > CF_2$ (b) $CF_2 > SiF_2 > GeF_2$ (c) $SiF_2 > GeF_2 > CF_2$ (d) $CF_2 > GeF_2 > SiF_2$

54. Among the following, the element having maximum inert pair effect is
(a) Cu (b) Pb (c) Si (d) Sn

55. The correct order of stability of fluorides is
(a) $BF < GaF < TlF$ (b) $TlF < GaF < BF$ (c) $BF < TlF < GaF$ (d) $GaF < BF < TlF$

56. **Statement-1 :** Pb^{+4} compounds are stronger oxidizing agents than Sn^{4+} compounds

Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

57. In which of the following +1 oxidation state is more stable than +3.
(a) Ga (b) Tl (c) Al (d) B

58. Which of the following compound does contain Tl^+ ion
(a) Both $TlCl_3$ and TlI_3 (b) $TlCl_3$
(c) TlI_3 (d) None

59. Which of the following compound does not exist
(a) PbF_4 (b) $PbCl_4$ (c) $PbBr_4$ & PbI_4 (d) None

60. Arrange the following in decreasing order of their $E^0_{M^{3+}|M}$ value
(a) $Al > In > Tl$ (b) $Al > Tl > In$ (c) $Tl > In > Al$ (d) $Tl > Al > In$

61. The total number of lone pairs of electron in I_3^- is
(a) zero (b) Three (c) Six (d) Nine

Hydrolysis

62. What is the correct trend of extent of hydrolysis
(a) $MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$ (b) $PCl_5 < SiCl_4 < AlCl_3 < MgCl_2$
(c) $PCl_5 < SiCl_4 = AlCl_3 < MgCl_2$ (d) $MgCl_2 < SiCl_4 < AlCl_3 < PCl_5$

63. Which of the following will produce H_2O_2 on hydrolysis ?
(a) $H_4P_2O_7$ (b) $H_2S_2O_8$ (c) $H_4P_2O_6$ (d) $H_2S_2O_7$

64. $BiCl_3$ on hydrolysis produces a white turbidity due to the formation of
(a) $Bi(OH)_3$ (b) $BiOCl$ (c) $BiCl_2(OH)$ (d) $Bi(OH)_2Cl$

65. Among the compounds A – D which hydrolyse easily are
(A) NCl_3 (B) NF_3 (C) $BiCl_3$ (D) PCl_3
(a) A and B only (b) A, C and D only (c) B, C and D only (d) A, B and C only

66. Which is most acidic ?

(a) $[Na(H_2O)_6]^+$ (b) $[Mg(H_2O)_6]^+$ (c) $[K(H_2O)_6]^+$ (d) $[Al(H_2O)_6]^{3+}$

67. Hydrolysis of one mole of peroxidisulphuric acid produces

(a) two moles of sulphuric acid (b) two moles of peroxomono sulphuric aicd

(c) one mole of sulphuric acid and one more of peroxomono sulphuric acid

(d) one moleof sulphuric acid, one mole of peroxomono sulphuric acid and one mole of hydrogen peroxide

68. The pH of an aqueous solution of Al^{3+} is likely to be

(a) neutral (b) acidic (c) slightly basic (d) highly basic

69. Among the following, the number of anhydrides of acids are

CO, No, N_2O, B_2O_3, N_2O_5, SO_3 and P_4O_{10}

(a) 3 (b) 4 (c) 5 (d) 6

70. The correct order of acidity among the following species is

(a) $[Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+}$

(b) $[Sc(H_2O)_6]^{3+} > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Na(H_2O)_6]^+$

(c) $[Mn(H_2O)_6]^{2+} > [Ni(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+$

(d) $[Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+}$

Solvent Theory

71. Arrange the following in decreasing order of their Lewis Acidic strength towards ethyl acetate:

(a) $GaCl_3 > AlCl_3 > BCl_3$ (b) $BCl_3 > AlCl_3 > GaCl_3$

(c) $AlCl_3 > BCl_3 > GaCl_3$ (d) $BCl_3 > GaCl_3 > AlCl_3$

72. Arrange the following in decreasing order of their Lewis Acidic strength towards dimethyl sulfane:

(a) $GaX_3 > AlX_3 > BX_3$ (b) $BX_3 > AlX_3 > GaX_3$

(c) $AlX_3 > GaX_3 > BX_3$ (d) None

73. BH_3 . CO is more stable than BF_3 . CO because

(a) CO is a soft base and BH_3 and BF_3 are soft and hard acids respectively

(b) CO is a hard base and BH_3 and BF_3 are hard and soft acids respectively

(c) CO is a soft base and BH_3 and BF_3 are hared and soft acids respectively

(d) CO is a soft acid and BH_3 and BF_3 are soft and hard bases respectively

74. The species responsible for the super acidity of $SbF_5 - HSO_3F$ system is

(a) HSO_3F (b) SbF_5 (c) HF (d) $H_2SO_3F^+$

75. Which will behave as a strong acid with H_2SO_4 ?

(a) HCl (b) $HClO_4$ (c) $HF + SbF_5$ (d) HNO_3

76. Which of the following will act as a base in H_2SO_4 among $HClO_4$, HNO_3, HCl, NH_3

(a) NH_3 (b) HCl and NH_3

(c) HNO_3, HCl and NH_3 (d) HNO_3 and NH_3

77. In the reactions (A) and B,

$$nH_2O + Cl^- \rightarrow [Cl(H_2O)_n]^- \quad \dots (A)$$

$$6H_2O + Mg^{2+} \rightarrow [Mg(H_2O)_6]^{2+} \quad \dots (B)$$

water behaves as

(a) An acid in both (A) and (B) (b) An acid in (A) and a base in (B)

(c) A base in (A) an acid in (B) (d) A base in both (A) and (B)

78. In the following reations carried out in liquid NH_3.

$$Zn(NH_2)_2 + 2KNH_2 \rightarrow K_2[Zn(NH_2)_4]$$

$$K_2[Zn(NH_2)_4] + 2NH_4NO_3 \rightarrow Zn(NH_2)_2 + 2KNO_3 + 4NH_3$$

KNH_2 and NH_4NO_3 act respectively as

(a) Solvo-acid solvo-base (b) Solvo-base and solvo-acid

(c) Conjugate acid and conjugate base (d) Conjugate base and conjugate acid

79. Match each item from the List-I (compound in solvent) with that from the List-II (Its behaviour) and select the correct combination using the codes given below.

	List I		**List II**
A.	CH_3COOH in pyridine	i.	strong acid
B.	CH_3COOH in H_2SO_4	ii.	weak acid
C.	$HClO_4$ in H_2SO_4	iii.	strong base
D.	SbF_5 in HF	iv.	weak base

(a) A-i, B-ii, C-iii, D-iv (b) A-ii, B-i, C-iii, D-iv

(c) A-iii, B-iv, C-ii, D-i (d) A-iv, B-ii, C-iii, D-i

80. The compound that will behave as an acid in H_2SO_4 is

(a) CH_3COOH (b) HNO_3 (c) $HClO_4$ (d) H_2O

81. Treatment of ClF_3 with SbF_5 leads to the formation of a/an

(a) polymeric material (b) convalent cluster

(c) ionic compound (d) lewis acid-base adduct

82. The reaction between SbF_5 and two equivalents of HF leads to the formation of

(a) $H_2SbF_3 + 2F_2$ (b) $H\,SbF_2 + 3F_2$ (c) $SbF_3 + H_2 + 2F_2$ (d) $[SbF_6]^- [H_2F]^+$

Compound Chemistry

83. Which of the following Borate Anion does not exist?

(a) $BH_4^{\ominus}$ (b) $BF_4^{\ominus}$ (c) $BCl_4^{\ominus}$ (d) $[B(C_6H_5)_4]^{\ominus}$

84. The co-ordination number of Be in BeB_2H_8 is

(a) 2 (b) 4 (c) 6 (d) 8

85. The number of H-atoms attached to Be in discrete unit of polymer of BeB_2H_8 are

(a) zero (b) 4 (c) 6 (d) 8

86. Which of the following species does not exist:

(a) $[BF_6]^{3-}$ (b) $[AlF_6]^{3-}$ (c) $[GaF_6]^{3-}$ (d) $[InF_6]^{3-}$

87. The correct order of acidic strength of oxides of nitrogen is

(a) $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$ (b) $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$

(c) $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$ (d) $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$

88. The correct order of acidic strength of oxy-acids of chlorine is

(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) $HClO_4 < HClO_2 > HClO_3 > HClO$

89. Which of the following is the correct order of acidic strength?

(a) $Cl_2O_7 > SO_3 > P_4O_{10}$ (b) $CO_2 > N_2O_5 > SO_3$

(c) $Na_2O > MgO > Al_2O_3$ (d) $K_2O > CaO > MgO$

90. There is no S–S bond in

(a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$ (c) $S_2O_3^{2-}$ (d) $S_2O_7^{2-}$

91. The number of hydroxyl (OH) groups present in phosphorus acid is

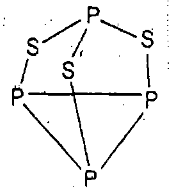
(a) one (b) two (c) three (d) four

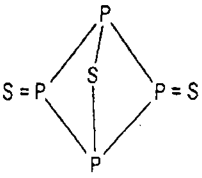
92. The perxenate ion XeO_4^{4-} can be prepared by

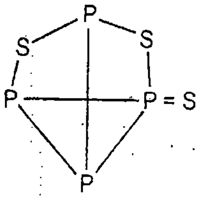
(a) direct reaction of Xe with oxygen (b) reaction of XeF_6 with oxygen

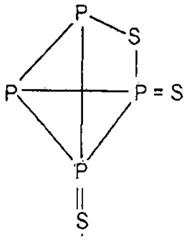
(c) hydrolysis of XeF_6 in acidic medium (d) hydrolysis of XeF_6 in basic medium

93. The correct structure of P_4S_3 is

(a) 

(b) 

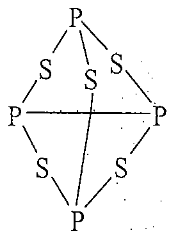
(c) 

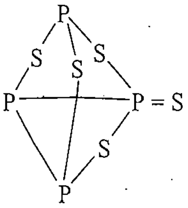
(d) 

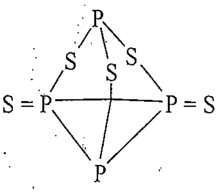
94. The material that exhibits the highest electrical conductivity among the following sulphur-nitrogen compounds is

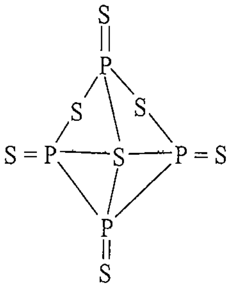
(a) S_4N_4 (b) S_7NH (c) S_2N_2 (d) $(SN)_x$

95. The correct structure of P_4S_5 is

(a) 

(b) 

(c) 

(d) 

96. At room temperature, HCl is a gas while HF is a liquid because

(a) of a strong bond between H and F in HF (b) HF is less acidic as compared to HCl

(c) of strong intermolecular H-bonding in HF

(d) HCl is less acidic as compared to HF

97. The compound having an S–S single bond

(a) $H_2S_2O_3$ (b) $H_2S_2O_4$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

98. The atomicity & and the total no. of bond in the elemental white phosphorus molecuale are, respectively

(a) 4 and 6 (b) 6 and 4 (c) 4 and 4 (d) 6 and 6

99. Identify the correct order of acidic strength of CO_2, CuO, CaO, H_2O

(a) $CaO < CuO < H_2O < CO_2$ (b) $H_2O < CuO < CaO < CO_2$

(c) $CaO < H_2O < CuO < CO_2$ (d) $H_2O < CO_2 < COO < CuO$

100. A compound of boron (A) that contains 8 water of crystallisation give a weak acid (B) and its salt (C) on hydrolysis.

Then select the correct statement

(a) Acid B is a tri basic acid & its yield can be increased by adding cis-diols

(b) Acid B is a monobasic acid and its yield can be increased by adding trans-diols

(c) Compound A is a buffer and its titration can be made using methyl orange as indicator

(d) Compound A is a buffer and its titration can be made using phenol phthalein as an indicator

101. The number of P = O bonds present in the tetrabasic acid $H_4P_2O_7$ is

(a) three (b) two (c) one (d) none

102. What is the correct order of the boiling point of the hydrides ?

(a) $H_2O > H_2S > H_2Se > H_2Te$ (b) $H_2O > H_2Te > H_2Se > H_2S$

(c) $H_2Te > H_2Se > H_2S > H_2O$ (d) $H_2O > H_2Te > H_2S > H_2Se$

103. Three allotropes (a), (b) and (c) of phosphorus in the following change are respectively

$$A \xrightarrow[1200\text{ atm}]{513\text{ K}} B \xrightarrow[\text{In an inert atm, and then rapid cooling at R.T}]{823\text{ K}} C$$

A is the thermodynamically most stable form of phosphorus

(a) black, red, white (b) red, black, white (c) black, white, red (d) red, violet, black

104. When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a voilet colouration is obtained. On passing more of chlorine water, the voilet colour is disappeared and solution becomes colourless. This test confirms the presence of .... in aqueous solution.

(a) chlorine (b) fluorine (c) bromine (d) iodine

105. First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is

(a) $XePtF_6$ (b) XeO_3 (c) XeF_6 (d) $XeOF_4$

106. What is the correct order of acidity

(a) $XeF_6 > XeOF_4 > XeO_4 > XeO_2F_4$ (b) $XeF_6 > XeO_2F_4 > XeO_4 > XeOF_4$

(c) $XeO_2F_4 > XeOF_4 > XeO_4 > XeF_6$ (d) $XeO_2F_4 > XeOF_4 > XeF_6 > XeO_4$

107. Which of the following has a square planar geometry according tot he VSEPR theory ?

(a) XeO_2F_2 (b) SF_4 (c) BF_4^- (d) XeF_4

108. The number P = O bonds present in the tetrabasic acid $H_4P_2O_7$ is

(a) three (b) two (c) one (d) none

109. The most abundant element in earth's crust is

(a) aluminium (b) iron (c) silicon (d) oxygen

110. The fluoride, whose values of dipole moment is NOT equal to zero, is

(a) XeF_4 (b) CF_4 (c) SF_4 (d) PF_5

111. The number of P—O—P bonds in cyclic trimetaphosphoric acid is :

(a) zero (b) two (c) three (d) four

112. For H_3PO_3 and H_3PO_4, the correct choice is :

(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

113. Thermodynamically most stable allotrope of phosphorus is :

(a) Red (b) White (c) Black (d) Yellow

114. Amongest H_2O, H_2S, H_2Se and H_2Te the one with highest boiling point is :

(a) H_2O because of H-bonding. (b) H_2Te because of higher molecular weight.

(c) H_2S because of H-bonding. (d) H_2Se because of lower molecular weight.

115. The number of S–S bonds, in sulphur trioxide trimer (S_3O_9) is :

(a) three (b) two (c) one (d) Zero

116. Which of the following oxoacids of sulphur has –O–O– linkage ?

(a) $H_2S_2O_3$ (b) $H_2S_2O_5$ (c) $H_2S_2O_6$ (d) $H_2S_2O_8$

117. H_3BO_3 is :

(a) monobasic and weak Lewis acid (b) monobasic and weak Bronsted acid

(c) monobasic and strong Lewis acid (d) tribasic and weak Bronsted acid

118. **Statement-1:** In water, orthoboric acid behaves as a weak monobasic acid, because

Statement-2: In water, orthoboric acid acts as a proton donor.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

119. The structure of XeO_3 is :

(a) linear (b) planar (c) pyramidal (d) T-shaped

120. Xenon forms several fluorides and oxofluorides which exihibit acidic behaviour. The correct sequence of descending Lewis acidity among the given species is represented by

(a) $XeF_6 > XeOF_4 > XeF_4 > XeO_2F_2$ (b) $XeOF_4 > XeO_2F_2 > XeOF_4 > XeF_6$

(c) $XeF_4 > XeO_2F_2 > XeOF_4 > XeF_6$ (d) $XeF_4 > XeF_6 > XeOF_4 > XeO_2F_6$

121. The gas commonly used in generating plasma in Inductivtely Coupled Plasma Atomic Emission Spectroscopy (ICPAES) is

(a) Argon (b) Carbon dioxide (c) Nitrous oxide (d) hydrogen

122. Which of the following species is not a pseudohalide?

(a) CNO^- (b) $RCOO^-$ (c) OCN^- (d) N_3^-

123. A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is

(a) oxygen (b) nitrogen (c) carbon mono-oxide (d) hydrogen

124. An inorganic salt (a) is decomposed at about 523 K to give products (b) and (c). Compound (c) is a liquid at room temperature and is neutral to litmus paper while oxide (b) on burning with white phosphorous, gives a dehydrating agent (d). Compounds (a), (b), (c) and (d) will be identified as

(a) NH_4NO_3, N_2O, H_2O, P_2O_5 (b) NH_4NO_2, K_2O, H_2O, P_2O_5

(c) $CaCO_3$, CaO, H_2O, $CaCl_2$ (d) $CaCO_3$, CaO, H_2O, $Ca(OH)_2$

125. The correct statement related to allotropes of carbon is

(a) graphite is the most stable allotropes of carbon and having three dimensional sheet like structure of hexagonal rings of carbon (sp^2)

(b) diamond is the hardest allotrope of carbon and having a three dimensional network structure of C(sp^3)

(c) fullerene (C_{60}) is recently discovered non-crystalline allotrope of carbon having a football-like structure.

(d) Vander Waal's force of attraction acts between the layers of graphite 6.14 Å away from each other

126. Using chlorobenzene as solvent, the reagents needed for an efficient synthesis of borazine are

(a) NH_4Cl and BCl_3 (b) NH_4Cl and BCl_3 and $NaBH_4$

(c) NH_4Cl and $NaBH_4$ (d) NH_3 and BCl_3

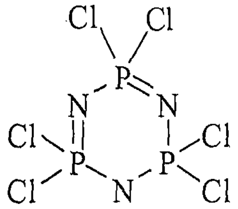
127. The reagents required for the synthesis of cyclic phosphazene $N_4P_4Cl_8$ are

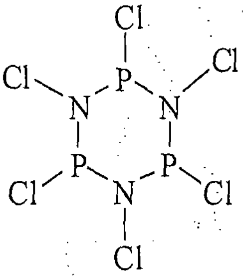
(a) PCl_5 and NH_3 (b) $POCl_3$ and NH_4Cl (c) $POCl_3$ and NH_3 (d) PCl_5 and NH_4Cl

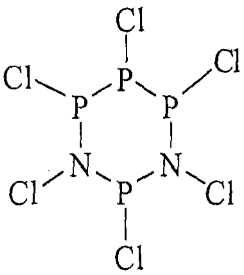
128. The material that exhibits the highest electrical conductivity among the following sulphur-nitrogen compounds is

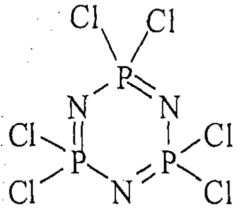
(a) S_4N_4 (b) S_7NH (c) S_2N_2 (d) $(SN)_x$

129. The structure of triphosphazene is

(a)


(b)


(c)


(d)


130. Which is most planar ?

(a) $S_4N_4H_4$ (b) $S_4N_4F_4$ (c) $S_4N_4Ph_4$ (d) $S_4N_4Cl_4$

131. What is the correct order of stabilities of the given phosphazenes ?

(a) $P_4N_4Cl_8 > P_4N_4R_8 > P_3N_3Cl_6 > P_2N_2Cl_4$

(b) $P_4N_4Cl_8 > P_3N_3Cl_6 > P_2N_2Cl_4 > P_4N_4R_8$

(c) $P_2N_2Cl_4 > P_3N_3Cl_6 > P_4N_4R_8 > P_4N_4Cl_8$

(d) $P_4N_4Cl_8 > P_4N_4R_8 > P_3N_3Cl_6 > P_2N_2Cl_4$

132. The compound formed by dissolving elemental gold in aqua regia is

(a) $AuCl$ (b) $AuNO_3$ (c) $H[AuCl_4]$ (d) $H[Au(O_3)_4]$

133. The pair of semimetals in the following is

(a) Al, Si (b) Ge, As (c) Sb, Te (d) Ca, B

Miscellaneous Reactions

134. $LiEH_4 + [(CH_3)_3NH]Cl \rightarrow A + LiCl + H_2$ [E = Al, Ga]

$A + N(CH_3)_3 \rightarrow B$.

The co-ordination number of central atom 'E' in B is:

(a) 3 (b) 4 (c) 5 (d) 6

135. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be

(a) $X = O_2$ and $Y = NCl_3$ (b) $X = NH_3$ and $Y = NCl_3$

(c) $X = O_2$ and $Y = NH_4Cl$ (d) $X = NH_3$ and $Y = NH_4Cl$

CHEM ACADEMY

136. The reation of solid XeF_2 with AsF_5 in 1 : 1 ratio affords

(a) XeF_4 and AsF_3 (b) XeF_6 and AsF_3 (c) $[XeF]^+[AsF_6]^-$ (d) $[Xe_2F_3]^+[AsF_6]^-$

137. Extra pure N_2 can be obtained on heating

(a) NH_3 with CuO (b) NH_4NO_3 (c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

138. Which of the following reactions does not give H_3PO_4 ?

(a) $Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow$ (b) $P_4O_6 + H_2O \longrightarrow$

(c) $PCl_5 + H_2O \longrightarrow$ (d) $P_4S_{10} + H_2O \longrightarrow$

139. $H_3PO_3 \xrightarrow{\Delta} X + PH_3$ is

(a) Dehydration reaction, $X = POCl_3$ (b) Oxidation reaction, $X = H_3PO_4$

(c) Disproportionation reaction, $X = H_3PO_4$ (d) Dephosphorylation reaction, $X = H_2O$

140. What will happen or what will be the product formed when white phosphorus and red Phosphorus reacts with NaOH

(a) PH_3, No reaction (b) No reaction, PH_3

(c) $P(OH)_3$, NO reaction (d) No reaction, $P(OH)_3$

141. Iodine reacts with hot NaOH soluiton. The product are NaI and

(a) $NaIO_3$ (b) $NaOI$ (c) NaO_2 (d) Na_2O_2

142. XeF_4 reacts with SF_4 to give

(a) $XeOF_4$ and SO_2 (b) Xe and SF_6 (c) XeF_2 and SF_6 (d) SF_6 and XeO_3

143. Consider two reactions

I. $Zn + \text{conc. } HNO_3 \text{ (hot)} \rightarrow Zn(NO_3)_2 + X + H_2O$

II. $Zn + \text{dil. } HNO_3 \text{ (cold)} \rightarrow Zn(NO_3)_2 + Y + H_2O$

Compounds X and Y are respectively

(a) N_2O, NO (b) NO_2, N_2O (c) N_2, N_2O (d) NO_2, NO

144. $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).

Then addition of which of the following proceeds the reaction in the forward direction.

(a) cis-1, 2 diol (b) Trans 1, 2 diol (c) Borax (d) Na_2HPO_4

145. The reaction, $3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$ is an example of :

(a) oxidation reaction (b) reduction reaction

(c) disproportionation reaction (d) decomposition reaction

146. H_2O_2 reduces

(A) $[Fe(CN)_6]^{3-}$ (B) KIO_4 (C) $Ce(SO_4)_2$ (D) SO_3^{2-}

(a) A and B only (b) B and C only (c) C and D only (d) B and D only

147. The reaction that yields $Li[AlH_4]$ is:

(a) HCl (excess) + $AlCl_3$ + Li → (b) H_2 + Al + Li →

(c) LiH (excess) + $AlCl_3$ → (d) LiH (excess) + Al →

148. The main products of the reaction of equimolar quantities of XeF_6 with $NaNO_3$ are

(a) $XeOF_4$, NaF and NO_2F (b) XeO_2F_2, NaF, NOF and F_2

(c) $XeOF_4$, $NaNO_2$ and F_2 (d) XeF_4, $NaNO_2$ and F_2O

149. The species that do not undergo(es) disproportionation in an alkaline medium is

(a) Cl_2 (b) MnO_4^{2-} (c) NO_2 (d) ClO_4^-

150. Among the following donors, the one that forms most stable adduct with the Lewis acid $B(CH_3)_3$ is

(a) 4–methyl pyridine (b) 2, 6-dimethyl pyridine

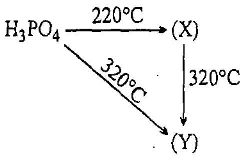
(c) 4-nitro pyridine (d) 2, 6-di-tert-butyl pyridine

151. The BCl_3 & NH_4Cl were heated at 140°C to give a compound X, which when treated with $NaBH_4$ gave another compound Y. Compound X and Y are

(a) $X = B_3N_3H_3Cl_3$, $Y = B_3N_3H_6$ (b) $X = B_3N_3H_9Cl_3$, $Y = B_3N_3H_6$

(c) $X = B_3N_3H_9Cl_3$, $Y = B_3N_3H_{12}$ (d) $X = B_3N_3Cl_6$, $Y = B_3N_3H_6$

152.



(a) (X) = Phosphorous acid , (Y) = Metaphosphoric acid

(b) (X) = Pyrophosphoric acid , (Y) = Metaphosphoric acid

(c) (X) = Metaphosphoric acid , (Y) = Pyrophosphoric acid

(d) (X) = Metaphosphoric acid , (Y) = Phosphene gas

153. $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} B_2O_3$

if $T_1 < T_2$ then X and Y respectively are

(a) X = Metaboric acid and Y = Tetraboric acid

(b) X = Tetraboric acid and Y = Metaboric acid

(c) X = Borax and Y = Metaboric acid

(d) X = Tetraboric acid and Y = Borax

EXERCISE - II

One or More Than One Correct Type

1. Which of the following facts regarding boron and silicon is true ?

(a) Boron is used to make boron steel or boron carbide control rods for nuclear reactor.

(b) Boron and silicon form halides which are not hydrolysed.

(c) Boron and silicon react with magnesium to form magnesium boride and magnesium silicide which are decomposed by acids to give volatile borane and silane, respectively.

(d) Both boron and silicon react with alkali to form borates and silicates containing BO_3^{3-} and SiO_4^{4-} tetrahedral units, respectively.

2. $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).

Then addition of which of the following proceeds the reaction in the forward direction.

(a) Glycerol (b) Mannitol (c) Catachol (d) Ethanol

3. The carbide which does/do not give propyne on hydrolysis is/are :

(a) Al_4C_3 (b) CaC_2 (c) MgC_2 (d) Mg_2C_3

4. Which of the following reactions is/are correct ?

(a) $CF_4 + 2F^- \rightarrow [CF_6]^{2-}$ (b) $SiF_4 + 2F^- \rightarrow [SiF_6]^{2-}$

(c) $GeCl_4 + 2Cl^- \rightarrow [GeCl_6]^{2-}$ (d) $SnCl_4 + 2Cl^- \rightarrow [SnCl_6]^{2-}$

5. Which species exist:

(a) $[BF_6]^{3-}$ (b) $[AlF_6]^{3-}$ (c) $[GaF_6]^{3-}$ (d) $[InF_6]^{3-}$

6. Borax bead test is given by:

(a) An aluminium salt (b) A cobalt salt

(c) A copper salt (d) A nickel salt

7. Which of the following statement(s) is/are correct ?

(a) The oxide, B_2O_3 and $B(OH)_3$ are acidic

(b) The halides of B (except BF_3) and Si are readily hydrolysed.

(c) The hydrides of B and Si are volatile, spontaneously flammable and readily hydrolysed.

(d) Aluminium hydride is a polymer, $(AlH_3)_n$.

8. Which is/are true in case of BF_3 ?

(a) It is volatile liquid even at room temperature

(b) It is Lewis acid

(c) It has planar geometry

(d) It forms adduct with NH_3

9. Which of the following statements about anhydrous aluminium chloride is/are incorrect ?

(a) It exists as $AlCl_3$ molecule in gaseous phase

(b) It is a strong Lewis base

(c) coordination number of aluminium ($AlCl_3$) in solid phase is 6

(d) It is not easily hydrolysed

10. Select the correct statement(s).

(a) The graphite is diamagnetic and diamond is paramagnetic in nature.

(b) Graphite acts as a metallic conductor along the layers of carbon atoms and as semi-conductor perpendicular to the layers of the carbon atoms.

(c) Graphite is less denser than diamond

(d) C_{60} is called as Buckminster fullerene

11. Which of the following give(s) ethyne on reaction with water?

(a) $Al_2(C_2)_3$ (b) Al_4C_3 (c) SrC_2 (d) Mg_2C_3

12. Select the correct statement(s)

(a) Double chain silicates are known as amphiboles.

(b) In cyclic silicates two oxygen atoms per tetrahedron are shared.

(c) Orthosilicates contain discrete $(SiO_4)^{4-}$ units.

(d) Asbestos mineral is a double chain silicate and mica is a sheet silicate.

13. Select correct statement about N_2O_4.

(a) It self ionises as NO^+, NO_3^- (b) N_2O_4 is paramagnetic

(c) Substance containing NO^+ is said to be acid and that containing NO_3^- is said to be base

(d) NO_2 dimerises to N_2O_4 with disappearance in paramagnetism

14. The compound which on strong heating gives oxygen is :

(a) $AgNO_3$ (b) BaO_2 (c) $Pb(NO_3)_2$ (d) $CaCO_3$

15. Which of the following species is basic and reducing ?

(a) SO_3^{2-} (b) SO_4^{2-} (c) $S_2O_4^{2-}$ (d) HSO_4^-

16. Which of the following statements is (are) correct ?

(a) The hydrides of group 15 elements act as oxidising agents

(b) The hydrides of group 15 elements act as reducing agents

(c) The oxidising power increases in going from NH_3 to BiH_3

(d) The reducting power increases in going from NH_3 to BiH_3

17. Which of the following statements is (are) correct ?

(a) Antimony on reaction with conc. HNO_3 gives antimonic acid.

(b) Manganese on reaction with cold and dilute HNO_3 gives NO_2 gas.

(c) HNO_2 disproportionate to give HNO_3 and NO

(d) HNO_3 on reaction with P_4O_{10} gives N_2O_5

18. Which of the following product(s) is/are obtained when a mixture of $NaNH_2$ and N_2O is heated at temperature 175°C ?

(a) NaOH (b) NH_3 (c) Na_2O (d) NaN_3

19. Sulphuric acid acts as

(a) hygroscopic agent (b) sulphonating agent

(c) reducing agent (d) oxidising agent.

20. Which among the following is/are peroxo acid (s) ?

(a) $H_2S_2O_3$ (b) H_2SO_5 (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

21. $NaHSO_3 + I_2 + H_2O \longrightarrow$ products.

Select the correct statement(s) about the product(s).

(a) One of the product is a strongest halogen acid (HX).

(b) One of the products is obtained by the reaction of $Na_2S_2O_3$ and chlorine.

(c) One of the products is SO_2. (d) One of the products is $Na_2S_4O_6$.

22. Which statement is correct about halogen ?

(a) They are all diatomic and form univalent ions

(b) Halogen have the smallest atomic radii in there respective periods

(c) They are all diatomic and form diatomic ions

(d) They are all reducing agents

23. Which of the following will not displace the halogen from the solution of the halide ?

(a) Br_2 added to NaI (b) Br_2 added to NaCl (c) Cl_2 added to KBr (d) Cl_2 added to NaF

24. Which is / are true statement(s) ?

(a) Basic nature of X^- is in order $F^- > Cl^- > Br^- > I^-$

(b) HI is strongest acid of HF, HCl, HBr and HI in aqueous solution

(c) The ionic character of M—X bond decreases in the order M—F > M—Cl > M—Br > M—I

(d) Among F, Cl, Br and I, F has the highest enthalpy of hydration.

25. Which of the following salts will evolve Halogen gas on treatment with conc. H_2SO_4 ?

(a) NaCl (b) KI (c) NaBr (d) none of these

26. Cl_2 reacts with hot aqueous NaOH to give :

(a) NaCl (b) $NaClO_3$ (c) $NaClO_2$ (d) $NaClO_4$

27. Select the correct order of acidity :

(a) HI > HBr > HCl > HF (b) $HClO_4 > HBrO_4 > HIO_4$

(c) HClO < HBrO > HIO (d) $HClO_4 > HClO_3 > HClO_2 > HClO$

28. Which of the following product(s) is/are obtained when Cl_2O_6 reacts with KOH ?
(a) KCl (b) $KClO_2$ (c) $KClO_3$ (d) $KClO_4$

29. Select the incorrect order.
(a) He > Ar > Kr > Ne > Xe – (abundance in air).
~~(b) He < Ne < Ar < Kr < Xe – (boiling point).~~
(c) $XeF_6 > XeF_4 > XeF_2$ – (melting point). (d) $XeF_6 < XeF_4 < XeF_2$ – (Xe – F bond length).

30. Which of the following is/are properties of helium?
(a) It is chemically inert. (b) It has very high thermal conductivity.
(c) It has extremely low boiling point. (d) It has very low viscosity.

31. CCl_4 is inert towards hydrolysis through SN^2 under ordinary conditions.
(a) due to non-avaibility of vacant low lying d-orbitals of carbon
(b) due to steric crowding of four Cl atoms H_2O cannot attack the σ^* orbital of C–Cl atoms
(c) due to absence of vacant d orbitals on Cl atoms
(d) due to the presence of partial negative charge on Cl atom, it repels H_2O

32. White phosphorus P_4 has
(a) Six P – P single bonds (b) Four P – P single bonds
(c) Four lone pairs of electrons (d) PPP angle of 60°

33. Select the correct statement(s) :
(a) Black phosphorus has layered graphite like structure & thermodynamically most stable
(b) White phosphorus is less reactive than red phosphorus
(c) Red phosphorus has a polymeric structure with P–P linkages
(d) Angle strain in red phosphorous is less than white phosphorous

34. Which of the following statements is/are correct regarding inter-halogen compounds of ABx types?
(a) x may be 1,3,5 and 7
(b) A is a more electronegative halogen than B
(c) FBr_3 cannot exit
(d) the structures of ClF_3 and IF_7 show deviation from normal structures and could be explained on the basis of VSEPR theory

35. Which of the following are sp^2 hybridised?
(a) $CF_3^{\oplus}$ (b) $CCl_3^{\oplus}$ (c) $CF_3^{\ominus}$ (d) $CCl_3^{\ominus}$

EXERCISE - III

Previous Year Questions

IIT-JAM Previous Year Questions

1. The most polar compound among the following is
(a) SF_4 (b) BF_3 (c) XeF_4 (d) SO_3

2. Molecular shape of $SOCl_2$ is
(a) square planar (b) trigonal pyramidal (c) triangular planar (d) T-shaped

3. Number of three centre two-electron (3c-2e) bonds present in diborane is
(a) 2 (b) 4 (c) 6 (d) 8

4. The correct order of acidic character is
(a) $Al_2O_3 > MgO > SiO_2 > P_4O_{10}$ (b) $P_4O_{10} > Al_2O_3 > MgO > SiO_2$
(c) $P_4O_{10} > SiO_2 > Al_2O_3 > MgO$ (d) $SiO_2 > P_4O_{10} > Al_2O_3 > MgO$

5. In the structure of $B_4O_5(OH)_4^{2-}$
(a) all four B atoms are trigonal planar
(b) one B atom is tetrahedral and the other three are trigonal planar
(c) three B atoms are tetrahedral and one is trigonal planar
(d) two B atoms are tetrahedral and the other two are trigonal planar

6. The pH of an aqueous solution of Al^{3+} is likely to be
(a) neutral (b) acidic (c) slightly basic (d) highly basic

7. Hydrolysis of $(CH_3)_2SiCl_2$ and CH_3SiCl_3 leads to
(a) linear chain and cross-linked silicones, respectively
(b) cross-linked and linear chain silicones, respectively
(c) linear chain silicones only
(d) cross-linked silicones only

8. Draw the structures of X and Y in the following reactions
(i) Borazine + HCl $\rightarrow$ X
(ii) Borazine + $Br_2 \rightarrow$ Y

9. Which of the following has a square planar geometry according to the VSEPR theory ?
(a) XeO_2F_2 (b) SF_4 (c) BF_4^- (d) XeF_4

10. Which of the following is an electron deficient molecule according to the octet rule ?
(a) CH_4 (b) $H_3N:BH_3$ (c) AlH_3 (d) GeH_4

11. At room temperature, HCl is a gas while HF is a liquid because
(a) of a strong bond between H and F in HF
(b) HF is less acidic as compared to HCl
(c) of strong intermolecular H-bonding in HF
(d) HCl is less acidic as compared to HF

12. Identify X, Y and Z in the following sequence

$$Li + N_2(g) \xrightarrow{\text{heat}} \underset{\text{(red)}}{X} \xrightarrow{H_2O} Y(g) \xrightarrow{\text{alkaline } K_2HgI_4} \underset{\text{(brown)}}{Z}$$

Y turns moist litmus paper blue. Write balanced chemical equation for the conversion of Y to Z.

13. The number P = O bonds present in the tetrabasic acid $H_4P_2O_7$ is
(a) three (b) two (c) one (d) none

14. The element E on burning in the presence of O_2 gives F. Compound F on heating with carbon in an electric furnace gives G. On passing nitrogen over a heated mixture of F and carbon produces H. Stream can decompose H to produe boric acid and a colourless gas tghat gives white fumes with HCl. Identify F, G and H and give balanced equations for their formation.

15. The correct order of the mean bond energies in the binary hydrides is
(a) $CH_4 > NH_3 > H_2O > HF$ (b) $NH_3 > CH_4 > H_2O > HF$
(c) $HF > H_2O > NH_3 > CH_4$ (d) $HF > H_2O > NH_3 > CH_4$

16. The compound having an S–S single bond is
(a) $H_2S_2O_3$ (b) $H_2S_2O_4$ (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

17. The shape of CH_3^- ion is
(a) trigonal planar (b) tetrahedral (c) trigonal pyramidal (d) linear

18. The average value of C–C bond order in graphite is
(a) 1 (b) 3/2 (c) 3/4 (d) 4/3

19. A. Write the steps involved in the production of pure elemental silicon from silica.
B. Both the products A and B, in the following reactions, contain boron and nitrogen. Identify A and B.

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{heat}]{C_6H_5Cl} A \xrightarrow[\text{THF}]{LiAlH_4} B$$

IIT-JEE Previous Year Questions

20. The number of P—O—P bonds in cyclic trimetaphosphoric acid is :
(a) zero (b) two (c) three (d) four

21. For H_3PO_3 and H_3PO_4, the correct choice is :
(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

22. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by :
(a) heating NH_4NO_2 (b) heating NH_4NO_3
(c) treating Mg_3N_2 with H_2O (d) treating Na(compound) with H_2O_2

23. Thermodynamically most stable allotrope of phosphorus is :
(a) Red (b) White (c) Black (d) Yellow

24. Amongest H_2O, H_2S, H_2Se and H_2Te the one with highest boiling point is :
(a) H_2O because of H-bonding. (b) H_2Te because of higher molecular weight.
(c) H_2S because of H-bonding. (d) H_2Se because of lower molecular weight.

25. The number of S–S bonds, in sulphur trioxide trimer (S_3O_9) is :
(a) three (b) two (c) one (d) Zero

26. Which of the following oxoacids of sulphur has –O–O– linkage ?
(a) $H_2S_2O_3$ (b) $H_2S_2O_5$ (c) $H_2S_2O_6$ (d) $H_2S_2O_8$

27. Which of the following is not oxidised by O_3?
(a) KI (b) $KMnO_4$ (c) K_2MnO_4 (d) $FeSO_4$

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

29. H_3BO_3 is :
(a) monobasic and weak Lewis acid (b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid (d) tribasic and weak Bronsted acid

30. $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4]$ (aq).
Then addition of which of the following proceeds the reaction in the forward direction.
(a) cis-1, 2 diol (b) Trans 1, 2 diol (c) Borax (d) Na_2HPO_4

31. Statement-1: In water, orthoboric acid behaves as a weak monobasic acid, because

Statement-2: In water, orthoboric acid acts as a proton donor.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

32. $(Me)_2SiCl_2$ on hydrolysis will produce :

(a) $(Me)_2Si(OH)_2$ (b) $(Me)_2Si = O$

(c) $-[—O—(Me)_2Si—O—]_n—$ (d) $Me_2SiCl(OH)$

33. Which of the following silicate is formed when three oxygen atoms of $[SiO_4]^{4-}$ tetrahedral units are shared ?

(a) Sheet silicate (b) Pyrosilicate

(c) Three dimensional silicate (d) linear chain silicate

34. **Statement-1 :** Pb^{+4} compounds are stronger oxidizing agents than Sn^{4+} compounds

Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

35. In the reaction, $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+ [BH_4]^-$

the amine(s) X is(are) :

(a) NH_3 (b) CH_3NH_2 (c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

36. The reaction, $3ClO^- (aq) \rightarrow ClO_3^- (aq) + 2Cl^- (aq)$ is an example of :

(a) oxidation reaction (b) reduction reaction

(c) disproportionation reaction (d) decomposition reaction

37. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'.

(a) $X = CO_2, Y = Cl_2$ (b) $X = Cl_2, Y = CO_2$ (c) $X = Cl_2, Y = H_2$ (d) $X = H_2, Y = Cl_2$

38. The structure of XeO_3 is :

(a) linear (b) planar (c) pyramidal (d) T-shaped

39. XeF_4 and XeF_6 are expected to be :

(a) oxidizing (b) reducing (c) unreactive (d) strongly basic

ANSWER KEY

EXERCISE-I

1. d 2. c 3. b 4. b 5. b 6. c 7. c
8. b 9. b 10. c 11. c 12. a 13. a 14. a
15. c 16. a 17. a 18. b 19. a 20. c 21. a
22. d 23. d 24. d 25. b 26. b 27. d 28. c
29. b 30. b 31. d 32. c 33. c 34. a 35. b
36. b 37. b 38. b 39. a 40. a 41. a 42. b
43. a 44. a 45. a 46. a 47. b 48. a 49. c
50. a 51. c 52. a 53. b 54. b 55. a 56. c
57. b 58. c 59. c 60. c 61. d 62. a 63. b
64. b 65. b 66. d 67. c 68. b 69. b 70. b
71. b 72. a 73. a 74. d 75. c 76. c 77. b
78. b 79. c 80. c 81. c 82. d 83. c 84. c
85. c 86. a 87. b 88. a 89. a 90. d 91. b
92. d 93. a 94. d 95. b 96. c 97. b 98. a
99. a 100. c 101. b 102. a 103. a 104. d 105. a
106. b 107. d 108. b 109. d 110. c 111. c 112. a
113. c 114. a 115. d 116. d 117. a 118. c 119. c
120. a 121. a 122. b 123. b 124. a 125. b 126. b
127. d 128. d 129. d 130. b 131. b 132. c 133. b
134. c 135. b 136. c 137. d 138. b 139. c 140. a
141. a 142. b 143. b 144. a 145. c 146. b 147. c
148. a 149. d 150. a 151. a 152. b 153. a

EXERCISE - II

1. a,c,d 2. a,b,c 3. a,b,c 4. b,c,d 5. b,c,d 6. b,c,d 7. a,b,c,d
8. b,c,d 9. a,b,d 10. b,c,d 11. a,c 12. a,b,c,d 13. a,c,d 14. a,b,c
15. a,c 16. b,d 17. a,c,d 18. a,b,d 19. a,b,d 20. b,d 21. a
22. a,b 23. b,d 24. a,b,c,d 25. a,b,c 26. a,b 27. a,b,d 28. c,d
29. a,c 30. a,b,c,d 31. a,b,d 32. a,c,d 33. a,c,d 34. a,c 35. a,b,d

EXERCISE - III

1. a 2. b 3. a 4. c 5. d 6. b 7. a
8. X = $B_3N_3H_3Cl_3$; Y = $B_3N_3H_3Br_3$ 9. d 10. c 11. c
12. Z = $HgO.Hg(NH_2)I$; X = Li_3N; Y = NH_3 13. b
14. E = B, F = B_2O_3, G = B_4C_3, H = BN 15. a 16. b 17. c
18. d
19. (a) $SiO_2 + C \rightarrow Si + CO_2$; $SiO_2 + 2C \rightarrow Si + 2CO$; $2SiC + SiC_2 \rightarrow 3Si + 2CO$; $SiCl_4 + 2Zn \rightarrow Si + 2ZnCl_2$
(b) A = $B_3N_3H_3Cl_3$; B = $B_3N_3H_6$
20. c 21. a 22. a 23. c 24. a 25. d 26. d
27. b 28. b 29. a 30. a 31. c 32. c 33. a
34. c 35. a,b,c 36. c 37. c 38. c 39. a