## **HINTS & SOLUTIONS**

**EXERCISE - 1 Single Choice** 

**2.**  $Al_2O_3 f Al^{3+} + AlO_3^{3-}$ 

 $Al^{3+} + 3e^{-} \longrightarrow AlO_{3}^{3-} Al \text{ (at cathode)}$ 

 $AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2 + 12e^-$  (at anode)

The overall chemical reaction taking place during electrolysis

$$2\mathrm{Al}_2\mathrm{O}_3 \longrightarrow 4\mathrm{Al} + 3\mathrm{O}_2$$

- 4.  $H_3BO_3 \xrightarrow{\text{Heated}} B_2O_3$  $H_3BO_3 \xrightarrow{100^{\circ}C} BO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7$ Meta boric acid tetra boric acid
- 9.  $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + Heat$  $B_2H_6 + 6H_2O \longrightarrow H_3BO_3 + 6H_2$  $2NaH + B_2H_6 \xrightarrow{ether} NaBH_4$
- 10.  $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$
- 12. (SiH<sub>3</sub>)<sub>3</sub> N(trisilyl amine)



**14.**  $CO_2 + H_2O_f$ H<sub>2</sub>CO<sub>3</sub>

Acidic oxide  $H_2CO_3 f H^+ + HCO_3^$ weak acid

$$HCO_3^-$$
 f H<sup>+</sup> +  $CO_3^{2-}$ 

16. 
$$P_2O_5 + 3H_2O \longrightarrow 2H_2PO_4$$

$$\begin{array}{c} P_2O_5 + H_2O \rightarrow 2HPO_3 \xrightarrow{H_2O} H_4P_2O_7 \xrightarrow{H_2O} 2H_3PO_3 \\ Meta \ phosphoric \\ acid \\ acid \\ \end{array}$$

22. 
$$2HNO_2 \longrightarrow N_2O_3 + H_2O$$
  
Anhydride  
Remayel of H. O from HNO, is call

Removal of  $H_2O$  from  $HNO_2$  is called anhydride.

**26.** HNO<sub>3</sub> oxidation number of N is =+5Highest O.N., only reduces, acid only oxidising agent.  $HNO_2$  oxidation number = +3It reduces as well as oxidise, act both oxidising and reducing agent.

 $H_2SO_4$  oxidation number = +6

Highest O.N., only reduces, act only oxidising agent.

27. 
$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

**28.** 
$$2NO + O_2 \longrightarrow 2NO_2$$
  
Brown fumes

**31.** HCOOH 
$$\xrightarrow{\text{H}_2\text{SO}_4}$$
 CO + H<sub>2</sub>O

- **34.**  $I_2 + 2Na_2S_2O_3 \longrightarrow 2I_2 + Na_2S_4O_6 + 2NaI_6$
- 37. Higher the I.E, higher the acidic strength of hypohalus acid (hydroxides)
- **41.**  $4B + 3O_2 \longrightarrow B_2O_3 \quad 2B + N_2 \longrightarrow 2BN$ Mixture of oxide and nitride
- 42. Due to higher EN of B it attract lone pair of electron with faster rate.
- **43.**  $H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$

44. 
$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl_3$$

- 46. Due to back bonding BF<sub>3</sub>, BCl<sub>3</sub> and BBr<sub>3</sub> are exist in free form. But BH<sub>3</sub> is not.
- **48.**  $\operatorname{Na}_{2}B_{4}O_{7} + 7H_{2}O \longrightarrow 2\operatorname{Na}[B(OH)_{4}] + 2H_{3}BO_{3}$ Aqueous solution of borax acts as a buffer because it contains weak acid and its salt with strong base.
- 49. (NH<sub>2</sub>)<sub>2</sub>CO Urea

Molecular mass 
$$= 60$$
  
mass of nitrogen  $= 28$ 

% of N = 
$$\frac{28}{60} \times 100 = 47\%$$

60

54. 2HNO<sub>3</sub> 
$$\xrightarrow{-H_0}$$
 N<sub>2</sub>O<sub>5</sub>  
Anhydrid





- 57.  $2NaNO_3 \xrightarrow{A} 2NaNO_2 + O_2$   $2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$   $2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$  $NH_4NO_3 \longrightarrow N_2O + 2H_2O$
- 58.  $2KMnO_4 + 5H_2S \xrightarrow{H^+} K_2SO_4 + 2MnSO_4 + 8H_2O + 5S + 3H_2SO_4$
- 62.  $PbS + 4O_3 \longrightarrow PbSO_4 + 4O_2$ (Black)
- 63.  $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$   $AgCl + 2Na_2S_2O_3 \longrightarrow NaCl + Na_3[Ag(S_2O_3)_2]$  $AgCl + NH_3 \longrightarrow [Ag(NH_3)_2]Cl$
- 67.  $PI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HI$  $H_2 + I_2 \xrightarrow{Pt} 2HI$  $I_2 + H_2S \longrightarrow 2HI + S$
- **68.** I<sub>2</sub> can not dissplace Br<sub>2</sub>, Cl<sub>2</sub>, F<sub>2</sub> from KBr, KCl, KF, because it weakest oxidising agent.
- 71.  $\operatorname{CuSO}_4 + 2\operatorname{KI} \longrightarrow \operatorname{CuI}_2 + \operatorname{K}_2\operatorname{SO}_4$  $2\operatorname{CuI}_2 \longrightarrow \operatorname{Cu}_2\operatorname{I}_2 + \operatorname{I}_2$
- 76.  $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$
- 77.  $Ca + C_2 \longrightarrow CaC_2 \xrightarrow{N_2} Ca(CN)_2$
- 81. White or yellow  $P \xrightarrow{470K} Black-P$ (A) (B)

570K CO<sub>2</sub>-atom

85.  $P_4O_{10} + 4HNO_3 \rightarrow 4HPO_3 + 2N_2O_5$ 92.  $CH_2 \qquad COOH \qquad P_4O_{10} \qquad C_3O_2 + 2H_2O_5$ (carbon suboxide)



#### EXERCISE - 2 Part # I : Multiple Choice

I

3. (A) It is a acidic oxide and is anhydride of boric acid and it reacts with alkalies or bases to form borates.

 $3Na_2O + B_2O_3 \rightarrow 2Na_3BO_3$  (sodium orthoborate) It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH<sup>-</sup> from water molecules:

 $B(OH)_3(aq) + 2H_2O(\bullet) = B(OH)_4^{-}(aq) + H_3O^{+}(aq).$ pK = 9.25.

- (B) BX<sub>3</sub> (except BF<sub>3</sub>) get hydrolysed due to presence of vacant p-orbital and SiX<sub>4</sub> get hydrolysed due to presence of vacant d-orbital.
- (C) Controlled pyrolysis of diborane leads to most of the higher boranes.

It catches fire spontaneously in air and explodes with O<sub>2</sub>. Reaction with oxygen is extremely exothermic.

$$B_{2}H_{6} + 3O_{2} \longrightarrow B_{2}O_{3} + 3H_{2}O \qquad \Delta H = -2160 \text{ kJ mol}^{-1}$$
  

$$Si_{2}H_{6} + (4+n)H_{2}O \xrightarrow{\text{trace of alkali}} 2SiO_{2} + nH_{2}O + 7H_{2}O$$

- (D) Aluminium hydride is a polymer due to formation of electron defecient bond (Al —— H – – – Al).
- 10. (A)  $HCO_3^-$  does not give pink colour with phenolphthalein.
  - **(B)** Because phenol is weakly acidic.

(C)  $2\text{HCO}_3^- + \text{Mg}^{2+} \longrightarrow \text{Mg}(\text{HCO}_3)_2$ 

 $Mg(HCO_3)_2$  is water soluble.

**12.** As chain can grow in three places as



**13.** S1 : 
$$B_4O_7^{2-} \xrightarrow{H^+/H_2O}{hydrolysis} > B(OH)_3$$
;

**S2**: SiO<sub>4</sub><sup>4-</sup> 
$$\xrightarrow{\text{H}/\text{H}_2\text{O}}_{\text{hydrolysis}}$$
 Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>



Complex cross-linked polymer of silicones

S4 : As the metallic character decreases, the basic character decreases and acidic character increases. In other words if electronegativities difference between elements and oxygen decreases the acidic character increases. CaO is most basic, CuO is weakly basic, H<sub>2</sub>O is neutral and CO<sub>2</sub> is acidic.

14. (A) 
$$[BeF_4]^{2-}$$
  
 $4-sp^3$  hybrid orbitals

pairs - two form covalent and two form coordinate bonds.

Two  $F^-$  ions each donate an electron pair in to an empty sp<sup>3</sup> hybrid orbital forming two coordinate bonds.

**(B)** 
$$[B_4O_5(OH)_4]^{2-} + 5H_2O \implies 2B(OH)_3 + 2[B(OH)_4]^{-}$$

$$2[B(OH)_{4}] + 2H_{3}O^{+} \longrightarrow 2B(OH)_{3} + 4H_{2}O$$

Only  $[B(OH)_4]^-$  formed in water reacts with HCl.

(C) HCOONa + 
$$H_2SO_4 \longrightarrow CO \uparrow + Na^+ + HSO_4^- +$$

H<sub>2</sub>O.

$$K_{3}[Fe(CN)_{6}] + 6H_{2}SO_{4} + 6H_{2}O \longrightarrow 6CO + Fe^{3+}$$
$$+ 3 K^{+} + 6NH_{4} + 6SO_{4}^{2-}$$

Solid potassium ferrocyanide also liberates CO (g) on heating with concentrated  $H_2SO_4$ .

(**D**) 
$$2I_2O_5 + 5CO \longrightarrow 5CO_2 + 2I_2$$

- 15. (A) The double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles.
  - (B) 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.
  - (C) Orthosilicates contain discrete  $[SiO_4]^4$  units i.e., there is no sharing of corners with one another.
  - (D) The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula  $(Si_4O_{11})_n^{6n-}$ .

16. (B) 
$$2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$$
  
(C)  $2BCl_3 \xrightarrow{1173K} B + 3Cl_2$   
(D)  $K^+ [BF_4]^- \xrightarrow{1073 K} K^+ + [BF_4]^-$   
 $[BF_4]^- + e^- \longrightarrow B + 2F_2$  (At anode)  
 $K^+ + e^- \longrightarrow K$  (At cathode)

7. 
$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2B_4O_7 + NaBO_3$$

**18.** Ammonia, primary amine and secondary amine give unsymmetrical cleavage of diborane according to the following reaction.

 $B_2H_6 + 2NH_3 \longrightarrow [BH_2(NH_3)_2]^+ [BH_4]^-$ 

**19.** Both are good conductor of electricity due to the presence of free electrons.

20. (C) 
$$3CH_2(COOH)_2(malonic acid) + P_4O_{10} \longrightarrow 3C_3O_2 + 4H_3PO_4$$

**(D)**  $-\frac{1}{10}$  O - (Me)<sub>2</sub> Si - O $-\frac{1}{10}$  linear silicates.

**21.** All statements are factual.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$
  
 $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$ 

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

**22.**  $2NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH (fast).$ 

$$2NH_3 + NH_2C1 \longrightarrow NH_2NH_2 + NH_4Cl (slow)$$

All acts as reducing agent and the increasing order of reducing character is NH<sub>3</sub> < PH<sub>3</sub> < AsH<sub>3</sub> < BiH<sub>3</sub> on account of decreasing M–H bond dissociation energies with increasing size of central atoms.

 $NH_3$  is only a mild reducing agent.



- 25. (A) In alkaline solution, its reducing character is more than in acidic medium.
  - $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$
  - $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$
  - (B) Correct statements.
  - (C) Due to H- bonding it forms a hydrate H<sub>2</sub>O<sub>2</sub>.H<sub>2</sub>O (melting point 221 K).
  - **(D)**  $K_2MnO_4 + O_3 + H_2O \longrightarrow KMnO_4 + 2KOH + O_2$
- 27. (A) It removes the chlorine from the surface of fibres (while dyeing) according to following reaction.

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

- Therefore, it is known as antichlor.
- (B) I<sub>3</sub><sup>-+</sup>+S<sub>2</sub>O<sub>3</sub><sup>2−</sup> → 3I<sup>-</sup>+S<sub>4</sub>O<sub>6</sub><sup>2−</sup> This reaction finds application in the iodometric and iodimetric methods of titrimetric analysis.
- (C)  $S_2O_3^{2-} + H^+ \longrightarrow S \downarrow \text{ (white)} + SO_2 + SO_2 + H_2O$ (disproportionation reaction).
- (D)  $2S_2O_3^{2-} + Ag^+ \longrightarrow [Ag(S_2O_3)_2]^{3-}$ (soluble complex) or  $[Ag(S_2O_3)_3]^{5-}$

This reaction is utilized in photography where hypo is used as fixer.

**28.** Correct order is :  $H_3PO_2 > H_3PO_3 > H_3PO_4$ 

as number of reducing hydrogen decreases. Reducing nature decreases.



**Note :** Hydrogen atom directly attached to phosphorus is called reducing hydrogen.

29. (A) Sb + 5HNO<sub>3</sub>  $\longrightarrow$  H<sub>3</sub>SbO<sub>4</sub> + 5NO<sub>2</sub> + H<sub>2</sub>O (B) Mn + 2HNO<sub>3</sub>  $\longrightarrow$  Mn(NO<sub>3</sub>)<sub>2</sub> + H<sub>2</sub> (C) 3HNO<sub>2</sub>  $\longrightarrow$  HNO<sub>3</sub> + 2NO + H<sub>2</sub>O (D) 4HNO<sub>3</sub> + P<sub>4</sub>O<sub>10</sub>  $\xrightarrow{250K}$  2N<sub>2</sub>O<sub>5</sub> + 4HPO<sub>3</sub>

- **30.** (A)  $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$ 
  - (B) He is insoluble in blood at higher pressure.
  - (C)  $O_2$  has two unpaired electrons in antibonding  $\pi$  molecular orbitals.
  - (D)  $2BaO + O_2(air) \xrightarrow{500^{\circ}C} 2BaO_2;$ BaO<sub>2</sub>  $\xrightarrow{800^{\circ}C} 2BaO + O_2$





- 32. (A)  $NaNO_2 + NH_4CI \longrightarrow NaCl + NH_4NO_2;$  $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ 
  - **(B)**  $H_2O_2 \longrightarrow H_2O + [O]$ ;  $NaNO_2 + [O] \longrightarrow NaNO_3$

(C) 
$$2NH_3 + 3CuO \longrightarrow 3Cu + N_2 + 3H_2O$$

- (D)  $2KMn^{+7}O_4^{-} + 2NH_3 \longrightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$
- 33.  $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$ ;  $NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$

34. (A) 
$$H_2O_2 + 2CIO_2 + 2OH^- \longrightarrow 2CIO_2^- + 2H_2O + O_2$$
  
(B)  $2NH_3 + 3I_2 \longrightarrow NI_3.NH_3 + 3HI$ ;  
 $8NI_3.NH_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$   
(C)  $4 NH_3 (g) + 5 O_2 (g) (from air) \xrightarrow{Pt/Rh gauge catalyst}{500 K, 9 bar}$   
 $4 NO (g) + 6 H_2O (g)$   
(D)  $N_2O_2 + 2HCIO_4 \longrightarrow 2NO[CIO_4] + H_2O$ 



- **35.** (A) In PH<sub>3</sub> the lone pair of electrons is present in spherical non directional more concentrated s-orbital where as lone pair of electrons is present in directional sp<sup>3</sup> hybrid orbital. As a result, the ease of donation of lone pair of electron is more in NH<sub>3</sub> as compare to PH<sub>3</sub>.
  - (B) It is incorrect statement.
  - (C) The solution of  $PH_3$  in water decomposes in presence of light giving red phosphorus and  $H_3$ .
  - (D)  $PH_3 + 2O_2 \longrightarrow H_3PO_4$  is correct statement ( $PH_3 < NH_3$ )  $NH_3$  is more basic then  $PH_3$ .
- **36.** (A) PH<sub>3</sub> is a lewis base but is neutral towards red litmus.
  - (B) It does not react with HCl(aq) or HI(aq). This is because water decomposes  $PH_4X$  formed to give back  $PH_3$ .
  - (C) It reacts only with anhydrous HCl or HBr.
  - (D)  $2Na_3P + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2PH_3\uparrow$ ;  $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$

Part # II : Assertion & Reason

1. Boron does not have vacant d-orbital.

$$BF_3 + H_2O \longrightarrow H_3BO_3 + 3HF$$
$$BF_3 + HF \longrightarrow HBF_2 \text{ is.}$$

3. Statement-1 : In gaseous phase and in non-polar solvent like benzene AlCl<sub>3</sub> exist as dimer, Al<sub>2</sub>Cl<sub>6</sub>. High enthalpy of hydration in water breaks the covalent dimer forming [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> and 3Cl<sup>-</sup>.

Statement-2 :  $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$ 

4. Both are correct statements but reason is not the correct explanation of assertion.

 $Al(OH)_3$  forms soluble complex with NaOH and not with  $NH_4OH$ .

 $Al(OH)_3 + OH^- \longrightarrow [Al(OH)_4]^-$ 

7. Statement-1 : bond bond energy Si—Si 297 kJ/mole Si—O 464 kJ/mole

Statement-2 : Silicon does not form Si=Si because of larger atomic size.

8. Statement-1 : Due to inert pair effect.

Statement-2 : Diamagnetic as all electrons are paired.

Statement-1 : Al  $(OH)_3$  is amphoteric in nature.

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

 $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$ 

Statement-2 : Al–O and O–H bonds can be broken with equal ease in  $Al(OH)_3$  due to nearly same electronegativity difference between Al–O bond and O–H bond.

- [SiCl<sub>6</sub>]<sup>2-</sup> does not exist as smaller Si cannot accomodate six larger Cl<sup>-</sup> because of steric hindrance. Reason is correct statement.
- Statement-1 : have smooth structure without having 'dangling' bonds.
   Statement-2 : Δ<sub>t</sub>H<sup>o</sup> = zero
- **13.**  $\operatorname{SiO}_{2}(s) + 2C(s) \longrightarrow \operatorname{Si}(s) + 2CO(g)$

(excess)

Statement-1 and Statement-2 are correct statements and Reason is the correct explanation of Assertion.

- 14. Si O bond energy 502 kJ mol<sup>-1</sup>
- 15. Statement-1 : Na<sub>2</sub>[B<sub>4</sub>O<sub>5</sub> (OH)<sub>4</sub>]. 8H<sub>2</sub>O + 2HCl  $\longrightarrow$ 2NaCl+4H<sub>3</sub>BO<sub>3</sub>+5H<sub>2</sub>O

Indicator methyl orange pH range 3.1 - 4.4In water, borax gives both B(OH)<sub>3</sub> and [B(OH)<sub>4</sub>]<sup>-</sup> and only the [B(OH)<sub>4</sub>]<sup>-</sup> reacts with HCl

Statement-2 :  $[B_4O_5 (OH)_4]^{2-} + 5H_2O \implies 3B(OH)_3 + 2[B(OH)_4]$ 

thus acts as a buffer. weak acid its salt



- 17. Ionisation energy required to convert Al to Al<sup>3+</sup> is 5137 kJ mol<sup>-1</sup>.  $\Delta H_{hydration}$  for Al<sup>3+</sup> is 4665 kJ mol<sup>-1</sup> and  $\Delta H_{hydration}$  for Cl<sup>-</sup> is –381 kJ mol<sup>-1</sup>. So total hydration energy 4665 + (3 × 381) = 5808 kJ mol<sup>-1</sup> is greater than ionisation energy.
- 18. T●<sup>3+</sup> acts as an oxidising agent because it has tendency to reduce to T●<sup>+</sup> as +1 oxidation state of T● is more stable on account inert pair effect.



19. Statement-1 :  $Pb^{+4} \xrightarrow{+2e^{-}} Pb^{2+}$  (due to inert pair effect)  $2I^{-} \xrightarrow{-2e^{-}} I_{2}$ , (I<sup>-</sup> acts as a reducing agent) so  $PbI_{4}$  is not a stable compound.

Statement-2: 
$$Pb^{2+} + 4I^{-} \longrightarrow [PbI_{a}]^{-}$$

As nitrogen is more electronegative than iodine. Bond dipoles of all N-I bonds and dipole of lone pair of electrons are acting in the same direction. Hence its dipole moment will be higher.

24. HO 
$$HO$$
  $HO$   $H$  has two ionisable protons.

**30.** Statement-1 :  $H_2SO_4$  is more viscous due to greater extent of intermolecular H-bonding than water.

Statement-2 : Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_{3}SO_{4}} 12C + 11H_{2}O;$$

$$H_{2}C_{2}O_{4} \xrightarrow{H_{2}SO_{4}} CO + CO_{2}$$

$$O$$

$$\|$$

$$CS^{+6}$$

34. Statement-1 : 
$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow (white) + H_2O_2$$

Insoluble  $BaSO_4$  forms a thin layer around  $BaO_2$  and therefore reaction occurs slowly and finally stops. So anhydrous  $BaO_2$ , is not used.







It is cheaper method as only  $O_2$  from air and  $H_2$  are consumed.

9. 
$$CI - N^{\delta^{-}} - CI^{\delta^{+}} + H^{\delta^{+}} - OH^{\delta^{-}}$$
 violently  
CI  
Through H-bonding  
 $CI - N - H + HOCI$   
 $\downarrow L$   
 $CI$   
 $VH_{4}OH \leftarrow H_{2}O$   
 $NH_{4}OH \leftarrow H_{2}O$   
 $NH_{3} + 2HOCI$   
 $CI - P^{\delta^{-}} - CI^{\delta^{+}} + H^{\delta^{+}} - OH^{\delta^{-}}$  slowly  
 $CI$   
 $CI - P - OH + HCI$   
 $\downarrow L$   
 $CI$   
 $CI - P - OH + HCI$   
 $\downarrow H$   
 $HO - P - OH + 2HCI$   
 $\downarrow H$ 

Through coordinate bond formation.

**40.** Na<sub>2</sub>HPO<sub>3</sub> is the salt of H<sub>3</sub>PO<sub>3</sub> which is dibasic in nature (as it contains two OH<sup>-</sup> groups)

$$8Na_{2}HPO_{3} \xrightarrow{\Lambda} 2PH_{3} + 4Na_{3}PO_{4} + Na_{4}P_{2}O_{7} + H_{2}O_{7}$$

**41.**  $ClO_2$  does not dimerise because odd electron is present in 'd' orbital and is declocalised. But in NO<sub>2</sub> it is present in sp<sup>2</sup> hybrid orbital and thus can dimerise to form N<sub>2</sub>O<sub>4</sub>.



31.

- **42.** S-1 : H<sub>3</sub>PO<sub>2</sub> has one ionisable proton and therefore, it is monobasic.
  - S-2: It has two reducing hydrogen atoms.
- 43. S-1 : Higher SRP value of ozone than oxygen.
  - **S-2 :** In ozone all electrons are paired. But  $O_3^-$  is an odd electron species.

#### EXERCISE - 3 Part # I : Matrix Match Type

1. (A)  $3H_2 + 2BBr_3 \xrightarrow{heated} 2B + 6HBr$ 

**(B)** 
$$Na_2B_4O_7$$
.  $10H_2O \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ 

- $2CuSO_4 \rightarrow 2CuO + 2SO_2 + O_3$
- $CuO + B_2O_3 \rightarrow Cu(BO_2)_2$  (blue bead)
- (C)  $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl (white fumes)$
- **(D)**  $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
- 3. (A)  $B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$ (B)  $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$ (C)  $B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 2H_2$ (D)  $BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl.$
- (A) Two oxygen atoms per tetrahedron are shared forming rings. (SiO<sub>3</sub>)<sub>n</sub><sup>2n-</sup>. Hybridisation of each Si is sp<sup>3</sup>.
  - (B) Two oxygen atoms per tetrahedron are shared forming a chain of tetrahedron,  $(SiO_3)_n^{2n-}$ . Hybridisation of each Si atom is sp<sup>3</sup>.
  - (C) One oxygen atom per tetrahedron is shared.  $Si_2O_7^2$ . Hybridisation of each Si atom is sp<sup>3</sup>.
  - (D) Three oxygen atoms per tetrahedron are shared. (Si<sub>2</sub>O<sub>5</sub>)<sup>2-</sup>, sp<sup>3</sup> hybridisation.
  - Note: EN difference between Si O is 1.7.
  - $\therefore$  50% ionic and 50% covalent.
- 5. (A) 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.  $(SiO_3)_n^{2n-}$

Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula  $(Si_4O_{11})_n^{6n-}$ .

- **Ex.**, Synthetic silicates  $(Li_2SiO_3, Na_2SiO_3)$ , Spondumene  $(LiAl(SiO_3)_2)$ ,
- (B) In pyrosilicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving [Si<sub>2</sub>O<sub>7</sub>]<sup>6-</sup> units. Ex. Thorteveitite (Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>), Hemimorphite (Zn<sub>3</sub>(Si<sub>2</sub>O<sub>7</sub>) Zn(OH)<sub>2</sub>H<sub>2</sub>O)
- (C) In two dimensional sheet silicates, three oxygen atoms of each tetrahedral are shared with adjacent  ${\rm SiO_4}^{4-}$  tetrahedrals. Such sharing forms two dimension sheet structure with general formula  $({\rm Si_2O_5})_n^{2n-}$ 
  - Ex. Talc  $(Mg(Si_2O_5)_2 Mg(OH)_2$ , Kaolin  $Al_2(OH)_4$  $(Si_2O_5)$ .
- (D) Three dimensional silicates involve all four oxygen atom in sharing with adjacent SiO<sub>4</sub><sup>4-</sup> tetrahedral units.
   Ex. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

**(A)** 
$$PCl_5 + H_2O \xrightarrow{Hydrolysis} POCl_3 + 2 HCl_{sp^3}$$

$$POCl_3 + 3 H_2O \longrightarrow H_3PO_4 + 3 HCl = sp^3$$

(B) 
$$P_4 + 3 \text{ NaOH} + 3 \text{ H}_2\text{O} \xrightarrow{\Delta} 3 \text{ PH}_3 + 3 \text{ NaH}_2\text{PO}_2$$
  
 $sp^3 sp^3$ 

or 
$$H_2 PO_2^-$$

$$\begin{array}{c}
O \\
\parallel p\pi - d\pi \\
H - P - O^{-}; \text{ Disproportionation reaction} \\
\downarrow \\
H
\end{array}$$

(C) Disproportionation reaction.

 $4 H_3 PO_3 \xrightarrow{\Delta} 3 H_3 PO_4 + PH_3$  (Alkaline hydrolysis)

(D) 
$$P_4O_6 + 6 H_2O (Hot) \xrightarrow{\Delta} 3 H_3PO_4 + PH_3$$
  
 $P_4O_6 + 6 H_2O \longrightarrow 4 H_3PO_3$   
 $4 H_3PO_3 \xrightarrow{\Delta} 3 H_3PO_4 + PH_3$ 



7. (A) 
$$(NH_4)_2S_2O_8 + H_2O \xrightarrow{\text{Distillation}}{\text{Hydrolysis}} 2 NH_4HSO_4 + H_2O_2$$
  
sp<sup>3</sup>

- (B)  $2 \operatorname{NaBO}_2 + 2 \operatorname{H}_2\operatorname{O}_2 + 6 \operatorname{H}_2\operatorname{O} \longrightarrow$ Na<sub>2</sub>[(OH)<sub>2</sub>B<sub>2</sub>[O-O]<sub>2</sub>(OH)<sub>2</sub>]. 6 H<sub>2</sub>O sp<sup>3</sup>
- (C)  $4Na_2SO_3 \longrightarrow Na_2S + 3Na_2SO_4$ sp<sup>3</sup> (disproportionation)
- (**D**) 2-Ethyl anthraquinol + Air ( $O_2$ )  $\xrightarrow{\text{Air}}$ 2-ethylanthraquinone + H<sub>2</sub>O<sub>2</sub>

8. (A) 
$$H_4P_2O_7$$
  $HO = \begin{bmatrix} O & O \\ || \\ P & O \\ || \\ OH & OH \end{bmatrix}$ 

One P—O—P bond and four P—OH bonds

(B) 
$$H_4P_2O_5$$
  
HO  $H_4P_2O_5$   
HO  $H_4P_2O_5$ 

Two P—H bond and one P—O—P bond

(C) 
$$H_4P_2O_6$$
  $HO = OH OH OH OH OH$ 

Four P—OH bonds and one P—P bond



- 9. (A)  $PbO_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + \frac{1}{2}O_2 + H_2O$ (B)  $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$ (C)  $H_2O_2 + 2ClO_2 + 2OH^- \rightarrow 2ClO_2^- + 2H_2O + O_2$ (D)  $XeF_2 + 2NaOH \rightarrow Xe + \frac{1}{2}O_2 + 2NaF + H_2O$
- 10. (A)  $2NO_2 \xrightarrow{\text{Cool}} N_2O_4$  colourless solid / liquid, acidic, mixed anhydride of  $HNO_2$  and  $HNO_3$ 
  - (B)  $2ClO_2 + 2O_3 \xrightarrow{H^+} Cl_2O_6$  (yellow solid)  $+ 2O_2$ ; acidic, mixed anhydride of HClO<sub>3</sub> and HClO<sub>4</sub>.

(C) 
$$K_4 [Fe(CN)_6] + 6H_2O + 6H_2SO_4 \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO^{\uparrow}$$
  
(D)  $2KOH + 5O_3 \longrightarrow 2KO_3$  (orange solid)  $+ 5O_2 + H_2O$ 

#### Part # II : Comprehension

#### Comprehension #1:

I.

 Orthoboric acid acts as lewis-acid in water not as proton donor (as it does not liberater H<sup>+</sup> ion) because it completes its octet by accepting the OH<sup>-</sup> from water. B(OH)<sub>2</sub>+H<sub>2</sub>O → [B(OH)<sub>4</sub>]<sup>-</sup>+H<sup>+</sup>.

In the solid state, the B(OH)<sub>3</sub> units are hydrogen bonded together in to two dimensional sheets with almost hexagonal symmetry. The layered are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.



If certain organic polyhydroxy compounds such as glycerol, manitol or sugars are added to the titration mixture, then  $B(OH)_3$  behaves as a strong monobasic acid and it can be now titrated with NaOH and the end point is detected using phenolphthalein as indicator (pH=8.3 - 10.0).

The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the  $[B(OH)_4]^-$ , thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the  $B(OH)_3$  reacts with NaOH; in effect it acts as a strong acid in the presence of the cis-diol.

 $B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + 2H_2O.$ 

$$HB(OH)_{4} + 2 |$$

$$CH - OH$$

$$CH - OH$$

$$CH - OH$$



2./

$$\begin{bmatrix} I & I & I \\ CH - O & O - CH \\ I & I \\ CH - O & B & O - CH \\ I & I \end{bmatrix}^{-} + H^{+} + 4H_{2}O$$

3. (A)  $B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2$ (B)  $B_2H_6 + NH_3 \xrightarrow{excess NH_3} B_2H_6.2NH_3$ D H 2011 is invit a series account of a commission of the series o

 $\begin{array}{l} B_2H_6.2NH_3 \text{ is ionic compound and comprises } [H_3N \rightarrow BH_2 \leftarrow NH_3]^+ \text{ and } [BH_4]^- \text{ ions.} \\ \textbf{(C)} B_2H_6 + 2(Me)_3N \rightarrow 2[Me_3N.BH_3] \\ \textbf{(D)} B_2H_6 + 6H_2O \rightarrow 2B(OMe)_3 + 6H_2 \end{array}$ 

Reactions involved

(A) 
$$2Na[BH_4]$$
 (A) +  $I_2 \xrightarrow{\text{in diglyme}} B_2H_6$  (B) +  $H_2$  + 2NaI

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3(C) + 3H_2$$

 $B(OH)_3 + 2H_2O = H_3O^+ + [B(OH)_4]^-; pK = 9.25$ 

$$HB(OH)_{4}+2 | \xrightarrow{CH-OH}_{CH-OH} \longrightarrow \begin{bmatrix} I & I \\ CH-O & I \\ I \\ CH-O & B \\ I \\ CH-O & I \end{bmatrix}^{-1}$$

 $+ H^{+} + 4H_{2}O.$ 

$$B_2H_6(\mathbf{B}) + 3O_2 \longrightarrow B_2O_3 + 3H_2O_3$$

 $CoO + B_2O_3 \longrightarrow Co(BO_2)_2$  (cobalt metaborate - blue colour bead).

#### Comprehension #3:

- 1. Due to effective  $p_{\pi}-p_{\pi}$  delocalised bonding between 'B' and 'F', BF<sub>3</sub> is weakest lewis acid in the series.
- 2. Due to effective  $p_{\pi}-p_{\pi}$  delocalised bonding between 'B' and 'F' there is partial double bond character between B and F. As a result there is decrease in bond length as compared to single B-F bond length.

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

- 3. Some of the total  $BF_3$  combine with HF formed during hydrolysis to form  $HBF_4$ .
- 4. Since BCl<sub>3</sub> can accept only one lone pair hence Cl<sub>3</sub> B (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> is not possible.

#### **Comprehension #4 :**

- 1. The more stable oxidation state of thallium is +1 on account of inert pair effect.
- 2. The stable oxidation state of germanium is +3; so it has tendency to oxidise to +3 from +2.

 The stable oxidation state of lead is +2 on account of inert pair effect; so it has tendency to reduce to +2 from +4.

#### Comprehension # 5 :

- (A) due to high heat of hydration in water it converts in to [Al(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>
  - **(B)** due to formation of complexes of type  $R_3NAlCl_3$
- (A) BF<sub>3</sub> forms HBF<sub>4</sub>
   (B) Anhydrous AlCl, is covalent

- 3. (A) It is a covalent compound.
  - (B) Being covalent easily hydrolysed
  - (C) It has lower melting point because it is a covalent compound.
  - **(D)** It is a lewis acid.
- 4. Only one electron pair of pyridine can be accommodated not two electron pairs.

#### **Comprehension #6:**

- 3. (A) is  $PH_{A}I$ . The given changes are :
  - (i)  $PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$ (A) (B) (ii)  $4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O$ (B) (C) (iii)  $4Cu^+ + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu \downarrow + 8H^+$   $3AgNO_3 + PH_3 \longrightarrow Ag_3P \downarrow + 3HNO_3$   $Ag_3P + 3AgNO_3 + 3H_2O \longrightarrow 6Ag \downarrow (black) + 3HNO_3 + H_3PO_3$ or  $6Ag^+ + PH_3 + 3H_2O \longrightarrow 3H_3PO_3 + 6Ag \downarrow$ (black) + 6H<sup>+</sup>

In  $P_4O_{10}$  there are 16  $\sigma$ -bonds and all central atoms have sp<sup>3</sup> hybridisation.





#### Comprehension #9:

1. (A) It is true because of effective  $p\pi$ -d $\pi$  overlaping owing to small size of sulphur as compared to phosphorus and silicon.

(B) 
$$HO - S - S - OH$$
. They have +V and +III oxidation

state.

- (C)  $\text{HNO}_3$  oxidises sulphur to  $\text{H}_2\text{SO}_4$  (+VI) but only oxidises selenium to  $\text{H}_2\text{SeO}_3$  (+IV). The higher oxidation states become less stable on descending the group.
- (D) In M–O electronegativity difference is large while in X–O, it is comparatively smaller (< 1.4). M = metal and X = non-metal
- (A) As bond (H–E) dissociation enthalpy decreases down the group, the acidic character increases from H<sub>2</sub>O to H<sub>2</sub>Te.
  - (B) Order of thermal stability is H<sub>2</sub>O > H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te
  - (C)  $H_2O$  does not have reducing property and this character increases from  $H_2S$  to  $H_2Te$ .
  - (D) Water has highest boiling point because of Hbonding and thus the correct order is H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te < H<sub>2</sub>O.

#### **Comprehension # 10 :**

1. 
$$A = (NH_4)_2 Cr_2 O_7$$
  $O$   $Cr$   $Cr$   $O$ , all electrons

en

are paired. So diamagnetic (3d<sup>0</sup> 4s<sup>0</sup>)

 $Cr_2O_7^{2-}$  acts as strong oxidising agent in acidic medium.

2. (E) = NH<sub>3</sub> (A) Cu<sup>2+</sup> + 4NH<sub>3</sub>  $\longrightarrow$  [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> (deep blue colouration).

3. 
$$B = Cr_2O_3$$
.  
 $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$   
(A) (C) (B)  
 $3 Mg + N_2 \longrightarrow Mg_3N_2$   
(D)

$$Mg_{3}N_{2} + 6H_{2}O \longrightarrow 3Mg(OH)_{2} + 2NH_{3}(E)$$

$$Hg_{2}(NO_{3})_{2} + NH_{3} \longrightarrow Hg \bigvee NO_{3} + Hg + NH_{4}NO_{3}$$
  
Black

#### Comprehension # 11 :

I.

- In successive hydrides starting from N to Sb, the lone pair causes distortion of M–H bonds. The bond angle decreases from 107° to 90°. This suggests that orbitals used in M–H bonding are almost pure p-orbitals.
- 2. A–H bond energy decreases with increase in size of A. Hence Bi–H bond readily breaks to make it the best reducer and the reducing power decreases with decrease of size of A.
- 3. Due to increase in size from PH<sub>3</sub> to SbH<sub>3</sub>, the van der Waal's forces increase. So their boiling points increase from PH<sub>3</sub> to SbH<sub>3</sub>. But due to intermolecular hydrogen bonding, NH<sub>3</sub> has very high boiling point, but less than that of SbH<sub>3</sub>.

#### Comprehension # 12 :

- 1. All reactions are responsible for the depletion of ozone layer.
- 2. (D) Its (i.e.,ozone) advantage over chlorine is that it avoids the unpleasant smell and taste of chlorine.

(C) True, 
$$O_2 \xrightarrow{2500^{\circ}C} 2O; O+O_2 \xrightarrow{quenching} O_3$$

- 3. (A) The dark blue colour of ozone is due to intense absorption of red light.
  - (B) Oxides of nitrogen and the halogen can damage the  $O_3$  layer.

(C) 
$$2 I_2 + 9[O_3] \longrightarrow I_4O_9 + 9O_2$$

(D) 
$$2 \operatorname{KOH} + 5 \operatorname{O}_3 \longrightarrow 2 \operatorname{KO}_3 + 5 \operatorname{O}_2 + \operatorname{H}_2 \operatorname{O}_3$$

#### EXERCISE - 4 Subjective Type

1. (A)  $\operatorname{Na}_{2}B_{4}O_{7} \xrightarrow{\Delta} 2\operatorname{NaBO}_{2} + 2\operatorname{H}_{2}O_{2} + 6\operatorname{H}_{2}O \longrightarrow$   $\operatorname{Na}_{2}[(OH)_{2}B(O - O)_{2}B(OH)_{2}].6\operatorname{H}_{2}O$ (B)  $3\operatorname{NaBH}_{4} + 4BF_{3} \xrightarrow{\text{ether}} 3\operatorname{NaBF}_{4} + 2B_{2}\operatorname{H}_{6}$   $B_{2}\operatorname{H}_{6} + 2\operatorname{NH}_{3} \xrightarrow{100^{\circ}\mathrm{C}} B_{2}\operatorname{H}_{6}.2\operatorname{NH}_{3}$   $B_{2}\operatorname{H}_{6}.2\operatorname{NH}_{3} \xrightarrow{200^{\circ}\mathrm{C}} B_{3}\operatorname{N}_{3}\operatorname{H}_{6} + \operatorname{H}_{2}$ (C)  $2B + 6\operatorname{HNO}_{3}$  (or  $\operatorname{H}_{2}\operatorname{SO}_{4}$ )  $\longrightarrow 2\operatorname{H}_{3}\operatorname{BO}_{3} + 6\operatorname{NO}_{2}$  $4\operatorname{H}_{3}\operatorname{BO}_{3} + \operatorname{Na}_{2}\operatorname{CO}_{3} \longrightarrow \operatorname{Na}_{2}\operatorname{B}_{4}\operatorname{O}_{7} + 6\operatorname{H}_{2}\operatorname{O} + \operatorname{CO}_{2}$ 



2. 
$$X = Na_2B_4O_7 Y = \underbrace{2NaBO_2 + B_2O_3}_{Glassy material} Z = H_3BO_3$$
  
(i)  $Na_2B_4O_7 + 2H_2O \longrightarrow 4H_3BO_3 + 2NaOH$   
(due to NaOH)

(ii) 
$$\operatorname{Na}_{2}B_{4}O_{7} \xrightarrow{/40^{\circ}C} \xrightarrow{\operatorname{2NaBO}_{2} + B_{2}O_{3}}$$
  
(iii)  $\operatorname{Na}_{2}B_{4}O_{7} + 5H_{2}O + H_{2}SO_{4} \longrightarrow \operatorname{Na}_{2}SO_{4} + 4H_{3}BO_{3}$ 

3. (i) 
$$\operatorname{Na}_{2}B_{4}O_{7} \cdot 10H_{2}O \xrightarrow{\Delta} \operatorname{Na}_{2}B_{4}O_{7} \xrightarrow{\Delta} \underbrace{2\operatorname{NaBO}_{2} + B_{2}O_{3}}_{\text{Glassy material}}$$

(ii) 
$$2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3H_2$$
  
(iii)  $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_2$ 

 $B_2O_3 + CoO \longrightarrow Co(BO_2)_2$ (iv) AIN + 3H<sub>2</sub>O  $\longrightarrow$  AI(OH)<sub>3</sub> + NH<sub>3</sub>

- (v) Nitric acid whether dilute or concentrated hardly affects aluminium at all. Aluminium is rendered passive. A thin film of  $Al_2O_3$  is formed on the surface of the metal.
- 4. Protective layer of  $Al_2O_3$  is formed over Al metal.
- 5.  $A = Na_2CO_3$ ;  $B = H_2SO_4$  or HCl  $Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$  $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$
- (A) Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>.5H<sub>2</sub>O; (B) CaCO<sub>3</sub>; (C) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; (D) NaBO<sub>2</sub>;
   (E) B<sub>2</sub>O<sub>3</sub>; (F) Co(BO<sub>2</sub>)<sub>2</sub> The reactions are :

 $\begin{array}{c} Ca_2B_6O_{11} + 2Na_2CO_{3(aq)} \longrightarrow 2CaCO_3 \downarrow + \\ (A) & (B) \end{array}$ 

 $\begin{array}{c} Na_2B_4O_7 + 2NaBO_2\\ (C) & (D) \end{array}$ 

$$4\text{NaBO}_{2} + \text{CO}_{2} \longrightarrow \text{Na}_{2}\text{BO}_{4} + \text{Na}_{2}\text{CO}_{3}$$
(D) (C)  

$$\text{Na}_{2}\text{B}_{4}\text{O}_{7} \xrightarrow{\Delta} 2\text{NaBO}_{2} + \text{B}_{2}\text{O}_{3}$$
(C) (D) (E)  

$$\text{B}_{2}\text{O}_{3} + \text{CoO} \longrightarrow \text{Co}(\text{BO})_{2}(\text{F})$$
(E) (Blue)  
(i) Cr\_{2}\text{O}\_{2} + 3\text{Al} \longrightarrow 3\text{Cr} + \text{Al}\_{2}\text{O}\_{3}

(ii) Due to small size of boron, the sum of its first three ionisation enthalpies is very high. This prevents it to form +3 ions.

- 8. Due to bigger atomic size of silicon, its reluctance for  $p\pi$ -  $p\pi$  bond does not allow to form graphite like structure.
- CaSO<sub>4</sub> formed with H<sub>2</sub>SO<sub>4</sub> forms a protective layer over lime stone and then reaction slowly ceases and stop. But CaCl<sub>2</sub> is soluble.
- 10. Carbonates evolve  $CO_2$  with phenol but bicarbonate do not. Soluble carbonates give pink colour with phenolphthalein but soluble bicarbonates do not.

11. 
$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O_3$$

L

- Low electronegativity and bigger size, Si does not have tendency to form pπ-pπ bonds like carbon.
- 13. Ultra pure elemental silicon is used for making semiconductors.

 $\begin{aligned} \operatorname{SiCl}_{4}(\operatorname{pure}) + 2\operatorname{H}_{2}(g) & \xrightarrow{\Delta} \operatorname{Si}(s) + 4\operatorname{HCl}(g) \\ \operatorname{SiHCl}_{3}(s) + \operatorname{H}_{2}(g) & \xrightarrow{\Delta} \operatorname{Si}(s) + 3\operatorname{HCl}(g) \\ \operatorname{SiH}_{4}(g) & \xrightarrow{675 \text{ K}} \operatorname{Pyrolysis} \bullet \operatorname{Si}(s) + 2\operatorname{H}_{2}(g) \end{aligned}$ 

4. 
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$
  
 $SnO_2 + 2H_2SO_4 (conc.) \longrightarrow Sn(SO_4)_2 + 2H_2O$   
 $SnO_2 + 2KOH \longrightarrow K_2SnO_3 + H_2O$ 

- 15. (i) covalent (ii), (iii) interstitial (iv) salt like (i.e. ionic)
  - (i) Covalent carbides : Compounds like  $CH_4$ ,  $CO_2$ ,  $CS_2$  can be considered to be covalent carbides. Besides these, some giant molecules like SiC and  $B_4C$  are also examples of covalent carbides.
  - (ii & iii) Interstitial or metallic carbides : Such carbides are formed by transition metals and some of the lanthanides and actinides. Interstitial carbides retain many of the properties of metals. They conduct electricity by metallic conduction and have properties of metals (a lusture like a metal). In these compounds carbon atoms occupy octahedral holes in the closed packed metal lattice. These are generally very hard and have very high melting point (e.g. WC).
  - (iv) Ionic carbides (or salt like carbides) : Generally formed by the most electropositive elements such as alkali and alkaline earth metals and aluminium (Boron is exception).

 $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$ 



7.

- **16.** Binary compounds of silicon with oxygen are called silicates but they contain other metals also in their structures.
  - (i) **Orthosilicates :** These contain discrete  $[SiO_4]^4$  units i.e., there is no sharing of corners with one another.
  - (ii) Pyrosilicate : In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving [Si<sub>2</sub>O<sub>7</sub>]<sup>6-</sup> units.
  - (iii) 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<sub>3</sub>O<sub>9</sub><sup>6-</sup> and Si<sub>6</sub>O<sub>18</sub><sup>12-</sup> anions are the typical examples of cyclic silicates.
  - (iv) 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.  $(SiO_3)_n^{2n-}$ 

- (v) Two dimensional sheet silicates : In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent  $SiO_4^{-4}$  tetrahedrals. Such sharing forms two dimension sheet structure with general formula  $(Si_2O_5)_n^{2n-4}$
- (vi) Three dimensional sheet silicates : These silicates involve all four oxygen atom in sharing with adjacent  $SiO_4^{4-}$  tetrahedral units.
- 17. Silicones are synthetic organosilicon compounds having repeated  $R_2SiO$  units held by Si O Si linkages. These compounds have the general formula  $(R_2SiO)_n$  where R = alkyl or aryl group.

The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.

- (A)  $\text{RCl} + \text{Si} \xrightarrow{\text{Cu}} \text{R}_3 \text{SiCl} + \text{R}_2 \text{SiCl}_2 + \text{RSiCl}_3$
- (B)  $\operatorname{RMgCl} + \operatorname{SiCl}_4 \longrightarrow \operatorname{RSiCl}_3 + \operatorname{MgCl}_2$   $2\operatorname{RMgCl} + \operatorname{SiCl}_4 \longrightarrow \operatorname{R}_2\operatorname{SiCl}_2 + 2\operatorname{MgCl}_2$  $3\operatorname{RMgCl} + \operatorname{SiCl}_4 \longrightarrow \operatorname{R}_3\operatorname{SiCl} + 3\operatorname{MgCl}_2$



In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups.

The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

- **18.**  $PbO + 2HC1 \longrightarrow PbCl_2 \downarrow H_2O$   $PbO + H_2SO_4 \longrightarrow PbSO_4 \downarrow + H_2O$  $PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 (soluble) + H_2O$
- 19. (A)  $\operatorname{SnO} + 2\operatorname{HNO}_3 \longrightarrow \operatorname{Sn(NO}_3)_2 + \operatorname{H}_2 O$ (B)  $\operatorname{Sn} + 2\operatorname{Cl}_2 \xrightarrow{\Lambda} \operatorname{SnCl}_4$ (C)  $2\operatorname{PbS} + 3\operatorname{O}_2 \xrightarrow{\Lambda} 2\operatorname{PbO} + 2\operatorname{SO}_2$ ;  $\operatorname{PbS} + 2\operatorname{O}_2 \longrightarrow \operatorname{PbSO}_4$  $\operatorname{PbS} + 2\operatorname{PbO} \longrightarrow 3\operatorname{Pb} + \operatorname{SO}_2$

20. (i) 
$$\text{RSiCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{RSi(OH)}_3 \xrightarrow{\text{Polymerisation of}} 8 \text{ moles} - 3\text{H}_2\text{O}$$





Cross linked silicon

(ii) 
$$R_3SiCl \xrightarrow{H_2O} R_3SiOH \underline{Dimension} R_3Si-O-SiR_3$$



Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 21. (A) Silicones are formed from the hydrolysis of a mixture of (CH<sub>3</sub>)<sub>3</sub> SiCl & (CH<sub>3</sub>)<sub>2</sub> SiCl<sub>2</sub>

The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



- (B)  $CH_2 \xrightarrow{P_4O_{10}} C_3O_2$  (Carbon suboxide) + 2H<sub>2</sub>O COOH
- (C) It absorbs moisture and becomes converted into hydrated stannic chlorides, SnCl<sub>4</sub>·3H<sub>2</sub>O, SnCl<sub>4</sub>·5H<sub>2</sub>O, SnCl<sub>4</sub>·6H<sub>2</sub>O and SnCl<sub>4</sub>·8H<sub>2</sub>O.
- 22.  $Na_2B_4O_7 + 3H_2O \longrightarrow NaBO_2 + 3H_3BO_3$ ; NaBO\_2 + 2H\_2O \longrightarrow NaOH(strong alkali) + H\_3BO\_3
- 23. In borazine B = N bonds are polar while in benzene C=C and C-C bonds are non-polar and, therefore, reactivity of borazine is more than benzene.
- 24. Two electron three centre bond (banana bond) and covalent bond.
- 25. Because its melting point is very high and liquid obtained is corrosive.
- 26.  $GaCl_3 + 3NaOH \longrightarrow Ga(OH)_3 \downarrow + 3NaCl$  $Ga(OH)_3 + NaOH \longrightarrow NaGaO_2 + 2H_2O$
- **27.**  $X = Na_2B_4O_7$ 
  - (i) Aqueous solution of (X) is alkaline, so (X) may be an alkali metal salt.
  - (ii) On strong heating, (X) swells up to give a glassy mass, it may be borax.
  - (iii) This is further supported by the fact that its concentrated solution on treatment with concentrated solution of  $H_2SO_4$  yields crystals of boric acid (a weak monobasic acid).
  - (iv) Hence, (X) is borax ( $Na_2B_4O_7.10H_2O$ ).

Reactions :

(i)  $\operatorname{Na}_{2}B_{4}O_{7}(X) + 7H_{2}O \longrightarrow 2\operatorname{NaOH}(\operatorname{Alkali}) + 4H_{3}BO_{3}$ (ii)  $\operatorname{Na}_{2}B_{4}O_{7} \cdot 10H_{2}O \xrightarrow{\operatorname{Heat}} \operatorname{Na}_{2}B_{4}O_{7} + 10H_{2}O$   $\operatorname{Na}_{2}B_{4}O_{7} \xrightarrow{\operatorname{Heat}} 2\operatorname{NaBO}_{2} + B_{2}O_{3}$ Glassy mass (iii)  $\operatorname{Na}_{2}B_{4}O_{7} + H_{2}SO_{4} + 5H_{2}O \longrightarrow \operatorname{Na}_{2}SO_{4} + 4H_{3}BO_{3}$ 

(Weak acid)

**28.**  $X = AlCl_3$ 

X is anhydrous AlCl<sub>3</sub>, a Lewis acid

(i) 
$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl - (Fumes)$$
  
(ii)  $HCl + NH_4OH \longrightarrow NH_4Cl - H_2O$   
(iii)  $AlCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Al(OH)_3^{-}$  (White)

Al(OH)<sub>3</sub> + NaOH  $\longrightarrow$  NaAlO<sub>2</sub> (soluble) + 2H<sub>2</sub>O (iv) AlCl<sub>3</sub> + H<sub>2</sub>S  $\longrightarrow$  No precipitate in acidic medium

- 29. (i)  $2BF_3 + 6LiH \xrightarrow{450 \text{ K}} B_2H_6 + 6LiF$  glassy mass (ii)  $B_2H_6 + 6H_2O \rightarrow 2B(OH)_3(aq) + 6H_2(g)$ (iii)  $2NaH + B_2H_6 \rightarrow 2NaBH_4$ (iv)  $2AI + 2NaOH + 2H_2O \rightarrow 2NaAIO_2 + 3H_2(g)$ (v)  $2AI + 2NaOH + 2H_2O \rightarrow 2NaAIO_2 + 3H_2(g)$
- 30. (i)  $K_4 [Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$ (ii)  $2CS_2 + 10 NO \longrightarrow 2CO + 4SO_2 + 5N_2$ (iii)  $Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2 + 2Pb (NO_3)_2 + 2H_2O$ (iv)  $2CaF_2 + SiO_2 + 2H_2SO_4 \longrightarrow 2CaSO_4 + SiF_4 + 2H_2O$ (v)  $2Pb^{2+} + H_2S + 2Cl^- \longrightarrow Pb_2SCl_2 \downarrow (red) + 2H^+$
- **31.** PbCl<sub>4</sub> is less stable than SnCl<sub>4</sub> due to more effective inert pair effect in lead. Pb–Cl bond length is more than that of Sn–Cl.
- 32. (A)  $\operatorname{CaC}_2$  (B) CO (C)  $\operatorname{CaCN}_2$  (D)  $\operatorname{CaCO}_3$ .  $\operatorname{CaO} + 3C \xrightarrow{\Delta} \operatorname{CaC}_2(A) + \operatorname{CO}(B)$   $\operatorname{CaC}_2(A) + \operatorname{N}_2 \xrightarrow{\Delta} \operatorname{CaCN}_2(C) + \operatorname{carbon}$  $\operatorname{CaCN}_2(C) + 3\operatorname{H}_2O \longrightarrow \operatorname{CaCO}_3(D) + 2\operatorname{NH}_3$
- **33.** Silicon and Germanium.
- 34. (i) water proofing textiles (ii) as lubricants (iii) as anti-foaming agents.
- **35.** If  $SiO_2$  not taken in excess, SiC will be formed.



- 36. (i)  $PbCl_2 + Cl_2 \longrightarrow PbCl_4 (Pb^{+2} to being oxidised by oxidising agent Cl_2)$ 
  - (ii)  $PbCl_4(s) \xrightarrow{\Lambda} PbCl_2(s) + Cl_2(g)$  (inert pair effect)
  - (iii) I strong reducing agent. reduces Pb<sup>+4</sup> (strong oxidising agent) to PbI, and I, is liberated.
- **37.** Forms carboxy haemoglobin which reduces the ability of haemoglobin to absorb the oxygen.
- 38. (i)  $2NH_3 + 2KMnO_4 \longrightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$ ; (ii)  $Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$ .
- **39.**  $4\text{Zn} + 7\text{NaOH} + \text{NaNO}_3 \longrightarrow \text{NH}_3 + 4\text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O};$  $3\text{CaO} + 8\text{P} + 9\text{H}_2\text{O} \longrightarrow 3\text{Ca}(\text{H}_2\text{PO}_2)_2 + 2\text{PH}_3$
- 40.  $N_2O_4(\bullet) \longrightarrow NO^+(acid) + NO_3^-(base)$  $ZnCl_2 + 2N_2O_4(\bullet) \longrightarrow Zn(NO_3)_2 + 2NOCl.$

41. (a) 
$$\operatorname{NH}_4\operatorname{Cl} + \operatorname{NaNO}_3 \longrightarrow \operatorname{NH}_4\operatorname{NO}_3 + \operatorname{NaCl};$$
  
 $\operatorname{NH}_4\operatorname{NO}_3 \longrightarrow \operatorname{N}_2\operatorname{O} + 2\operatorname{H}_2\operatorname{O}$   
(b)  $\operatorname{OH}_4 \supset \operatorname{CO}_2 \longrightarrow \operatorname{OH}_2 \supset \operatorname{CO}_2 \rightarrow \operatorname{H}_2\operatorname{O}_2$ 

- **(b)**  $(NH_4)_2CO_3 \xrightarrow{\Lambda} 2NH_3 + CO_2 + H_2O$
- (c)  $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$
- (d)  $Mg_3N_2 + 6H_2O \xrightarrow{\Lambda} 3 Mg(OH)_2 + 2NH_3$
- (e)  $2Mg + O_2 \xrightarrow{\Delta} 2MgO$ ;  $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$ ;  $Mg_3N_2 + 6H_2O \xrightarrow{\Delta} 3Mg(OH)_2 + 2NH_3$
- **42.** (A) CaO + 3C  $\xrightarrow{800-1000^{\circ}C}$  CaC<sub>2</sub> + CO  $\uparrow$

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$
  
(calcium cyanamide)

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

- (B)  $2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$  $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
- **43.** (A)  $(NH_4)_2 Cr_2 O_7$ ; (B)  $Cr_2 O_3$ ; (C)  $N_2$ ; (D)  $Mg_3 N_2$ ; (E)  $NH_3$ Assume compound (A);  $(NH_4)_2 Cr_2 O_7$ Reaction:

$$(NH_4)_2 Cr_2 O_7 \xrightarrow{\Delta} N_2 + Cr_2 O_3 + 4H_2 O;$$
(A)
(C) Green (B)
$$N_2 + 3Mg \xrightarrow{\Delta} Mg_3 N_2$$
(D)

$$Mg_{3}N_{2} + 6H_{2}O \longrightarrow 3Mg(OH)_{2} + 2NH_{3};$$
(D)
(E)
$$NH_{3} + HCl \longrightarrow NH_{4}Cl$$
(E)
(White fumes)

44. (A) 
$$CaO + 3C \xrightarrow{2800-2900^{\circ}C} CaC_2 + CO;$$

$$\operatorname{CaC}_2 + \operatorname{N}_2 \xrightarrow{500-600^{\circ}\mathrm{C}}{6-8 \operatorname{atm}} \xrightarrow{\operatorname{CaCN}_2 + \mathrm{C}}_{\operatorname{Nitrolim}}$$

- (B)  $P_4 + 2I_2 + 8H_2O \longrightarrow 2PH_4I + 2HI + 2H_3PO_4$  $PH_4I + NaOH \longrightarrow PH_3 + NaI + H_2O$
- **45.** (A) P<sub>4</sub>O<sub>6</sub>; (B) PH<sub>3</sub>; (C) H<sub>3</sub>PO<sub>4</sub>; (D) Ag The given changes are :

$$P_4 + 3O_{2(s)}(air) \longrightarrow P_4O_6(Garlic odour) ;$$
(A)

$$P_4O_6 + 6H_2O \text{ (hot)} \longrightarrow 3H_3PO_4 + PH_3$$
(C) (B)

(B) is PH<sub>3</sub> having rotten fish smell and neutral towards litmus

$$6Ag^{+} + PH_{3} + 3H_{2}O \longrightarrow H_{3}PO_{3} + 6Ag \downarrow + 6H^{+}$$
(D)

**46.** (A)  $PH_4I$ ; (B)  $PH_3$ ; (C) KI; (D)  $P_4O_{10}$ ; (E)  $Cu_2I_2$ (A) is  $PH_4I$ . The given changes are :

(i) 
$$PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$$
  
(A) (C) (B)  
(ii)  $4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O$   
(B) (D)

- (iii)  $4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu \downarrow + 8H^+$ (iv)  $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 \downarrow + 2K_2SO_4 + I_2$ (E)
- 47. Mercury is a mobile liquid but in presence of ozone it loses its mobility due to the formation of mercury suboxide and starts sticking to the glass. This is called as tailing of mercury.  $2Hg + O_3 \rightarrow Hg_2O + O_2$ .



## **CHEMISTRY FOR JEE MAIN & ADVANCED**

- 49. (i)  $I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$ (ii)  $CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$
- 50. (i)  $P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$ (ii)  $NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH (fast)$  $NH_3 + NH_2Cl \longrightarrow NH_2NH_2 + NH_4Cl (slow)$
- 51.  $HNO_2 + 2H_2SO_3 + H_2O \longrightarrow NH_2OH + 2H_2SO_4$ (A) (B) (C) (D)

52. (a) 
$$4K_2Cr_2O_7 \xrightarrow{\Lambda} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

**(b)** 
$$3O_2 \xrightarrow{\text{shehr}} 2O_3$$

(c) 
$$2I_2 + 9O_3 \rightarrow I_4O_9 + 9O_2$$

(d) 
$$C_2H_5$$
 air  $C_2H_5$  +H<sub>2</sub>O<sub>2</sub>

(e) 
$$2H_2S + SO_2 \xrightarrow{Moisture} 2H_2O + 3S.$$
  
(f)  $3Mg + SO_2 \rightarrow 2MgO + MgS$   
(g)  $2KIO_3 + 5SO_2 + 4H_2O \rightarrow K_2SO_4 + 4H_2SO_4 + I_2$   
(h)  $H_2SO_4 + P_2O_5 \rightarrow 2HPO_3 + SO_3$ 

53. (i) SO<sub>2</sub> (moist) + 2H<sub>2</sub>S  $\longrightarrow$  2H<sub>2</sub>O + 3S  $\downarrow$ 

(ii) 
$$2\text{FeCl}_3 + \text{H}_2\text{S} \longrightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$$

54. (a) 
$$HO = S = OH; (b) H=O = S = O-H;$$
  
 $HO = S = OH; (b) H=O = S = S = O-H;$   
 $HO = S = OH; (b) H=O = S = S = O-H;$ 

(c) 
$$H-O-O-S-O-H$$
; (d)  $H-O-S-O-H$ 

55. (a)  $N_2 + 3H_2 \xrightarrow{500^\circ, 200 \text{ atm}}{\text{Ironoxide} + K_2O \& Al_2O_3} > 2NH_3$ 

(4 mole gases ( $N_2$  and  $H_2$ ) forms two mole  $NH_3$ )

- **(b)**  $2NO + O_2 \longrightarrow 2NO_2$  (Brown)
- (c) Copper is placed below hydrogen in electrochemical series and does not liberate H<sub>2</sub> from acid. However, HNO<sub>3</sub> oxidises copper due to its strong oxidising nature.

$$3Cu + 8HNO_3 (dil.) \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$
  
(d)  $Pb(NO_3)_2 \xrightarrow{\Delta} N_2O_4 \xrightarrow{\Delta} NO_2^{\uparrow} (Brown)$ 

- 56. (i)  $2P + 3I_2 + 6H_2O \longrightarrow 2H_3PO_3 + 6HI$ ; (ii)  $7Cu + 20HNO_3 \longrightarrow 7Cu(NO_3)_2 + 4NO + 2NO_2 + 10H_2O$
- **57.** Four

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- 58. Critical tempt of nitrogen is very low where as the critical tempt. of ammonia is higher than the ordinary tempt. So NH, is easily liquefied.
- **59.**  $NO_2$  being odd molecule, on dimerisation is converted to stable  $N_2O_4$  molecule with even number of electrons.

60. (a) 
$$HSO_3N H_2(sulphamic acid) + HNO_3 (conc.) \xrightarrow{\Delta} N_2O + H_2SO_4 + H_2O$$
  
(b)  $Ag_2N_2O_2 + 2HCl \longrightarrow 2AgCl \downarrow + H_2N_2O_2$   
(c)  $2HNO_3 (50\%) + As_2O_3 + 2H_2O \longrightarrow NO + NO_2 + H_2O_2$ 

$$2H_{3}AsO_{4}$$
(d)  $4AgNO_{3} + 2Cl_{2} \xrightarrow{60-90^{\circ}C} 4AgCl \downarrow + 2N_{2}O_{5} + O_{2}$ 
(e)  $HPO_{3} + H_{3}PO_{4} \xrightarrow{100^{\circ}C} H_{4}P_{2}O_{7}$ 
(f)  $2Ca_{3} (PO_{4})_{2} + 6SiO_{2} \longrightarrow 6CaSiO_{3} + P_{4}O_{10}; P_{4}O_{10} + 10C \longrightarrow P_{4} + 10CO$ 

- **61.**  $F_2$ , Atomic oxygen,  $OF_2$ .
- 62. Due to presence of empty d-orbitals.
- 63. Dioxygen exists as diatomic molecules (weak van der Waal's force) where as sulphur as polyatomic molecules (strong van der Waal's forces.).

64. 
$$X = SO_2$$
  
(i)  $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$   
(ii)  $H_2O_2 \longrightarrow H_2O + O$   
 $SO_2 + H_2O + [O] \longrightarrow H_2SO_4$   
 $H_2SO_4 + Ba^{2+} \longrightarrow BaSO_4 \downarrow \text{ (white)} + 2H^+$   
(iii)  $H_2S + SO_2 \xrightarrow{H_2O} 2H_2O + 2S \downarrow \text{ (white turbidity)}$ 



- 65. On heating,  $S_8$  rings are broken and long chain polymers are formed up to 200°C. Thus due to polymerisation, liquid becomes viscous but beyond 200°C long chains are broken into short chains and ultimately  $S_2$  molecules are formed in the vapour phase, so viscosity of liquid decreases.
- 66.  $Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow (white) + H_2O$   $CaSO_3 + H_2O + SO_2 (excess) \longrightarrow Ca(HSO_3)_2$  milkiness disappears.
- 67. Freons.
- **68.** Oxygen has no d-orbitals while other have d-orbitals. Therefore, the paired electrons can be made unpaired by exciting electrons to d-orbitals.



## Group 13th and 14th

- 1. White metallic tin i.e.  $\beta$ -Sn changes to another allotrope, the grey tin the  $\alpha$ -Sn at low temperature.
- 2. AlCl<sub>3</sub> + 6H<sub>2</sub>O  $\implies$  [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> + 3Cl<sup>-</sup>
- **3.** Silicon dioxide exhibits polymorphism. It is a network solid in which each Si atom is surrounded tetrahedrally by four oxygen atoms.

- 4.  $2\text{AICI}_3 + 6\text{H}_2\text{O} \xrightarrow{\Delta} \text{AI}_2\text{O}_3 + 6\text{HCl} + 3\text{H}_2\text{O}$
- Due to the inert pair effect (the reluctance of ns<sup>2</sup> electrons of outermost shell to participate in bonding), the stability of M<sup>2+</sup> ions (of group IV elements) increases as we go down the group.
- 6.  $CO+H_2O(g) \xrightarrow{673 \text{ K}} CO_2+H_2; CO_2+2KOH \longrightarrow K_2CO_3+H_2O$
- 7. When a compound like CH<sub>3</sub>SiCl<sub>3</sub> undergoes hydrolysis, a complex cross-linked polymer is obtained as chain can grow in three places.





- 9. Sulphur exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.
- **10.** Due to non-availability of d-orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

11. (1) ONCl = 
$$8 + 7 + 17 = 32e^{-1}$$
  
ONO<sup>-</sup> =  $8 + 7 + 8 + 1 = 24e^{-1}$  (correct)

(2) Central atom O is 
$$sp^2$$
 hybridised with

1 lone pair, so bent shape (correct) (3) Ozone is violet-black in solid state. (Ref. NCERT & shriver atkins)

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

**12.** BCl<sub>3</sub> & AlCl<sub>3</sub> both have vacant p-orbital & incomplete octet. So they act as Lewis acid.

## Group 15th and 16th

Hypophosphorus acid



Number of hydrogen atom(s) attached to phosphorus atom is 2 which are called as reducing hydrogen.

2. 
$$2HI + H_2SO_4 \qquad I_2 + SO_2 + 2H_2O$$

3.  $(NH_4)_2SO_4 + 2H_2O \rightarrow (2H^+ + SO_4^{-2-}) + 2NH_4OH$ Strong acid Weakbase

 $(NH_4)_2 SO_4$  on hydrolysis produces strong acid  $H_2SO_4$ , which increases the acidity of the soil.

• The stability of hydrides decreases from  $NH_3$  to  $BiH_3$ which can be observed from their bond dissociation enthalpy. The correct order is  $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ .



#### **Alternate Solution**

 $\rm N_2O_4$  may has four resonating structure but in NCERT only two resonating structure .

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Resonating structures of  $N_2O_4$  are





- 5. Sulphur exhibit +2, +4, +6 oxidation states but +4 and +6 are more common.
- 6. (1)  $ONCl = 8 + 7 + 17 = 32e^{-1}$  $ONO^{-1} = 8 + 7 + 8 + 1 = 24e^{-1}$  (correct)

(2) Central atom O is 
$$sp^2$$
 hybridised with

1 lone pair, so bent shape (correct)

- (3) Ozone is violet-black in solid state. (Ref. NCERT & shriver atkins)
- (4) O<sub>3</sub> has no unpaired electrons, so diamagnetic (correct)
- 7.  $H_3PO_3 \& H_4P_2O_5$
- **8.** 4

9. 1. 
$$(NH_4)_2 Cr_2 O_7 \xrightarrow{\Delta} Cr_2 O_3 + N_2 + 4H_2 O$$

2.  $NH_4NO_2 \xrightarrow{\Lambda} N_2 + 2H_2O$ 

3. 
$$(NH_4)_2SO_4 \xrightarrow{A} 2NH_3 + H_2SO_4$$

$$4. \operatorname{Ba}(N_3)_2 \xrightarrow{\Lambda} \operatorname{Ba} + 3N_2$$

In reaction (3)  $NH_3$  is evolved where as in reaction 1, 2 and 4  $N_2$  is evolved.

### Halogen Group and Noble Gas

**1.** 3 **2.** 4 **3.** 2 **4.** 4 **5.** 4 **6.** 2

- 7. 4
- 8.  $Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$ [cold & dilute]

#### Part # II : IIT-JEE ADVANCED

## Group 13th and 14th

1. If certain organic polyhydroxy compounds such as glycerol, manitol or sugars are added to the titration mixture, then  $B(OH)_3$  behaves as a strong monobasic acid and it can be now titrated with NaOH and the end point is detected using phenolphthalein as indicator (pH=8.3-10.0).

The added compound must be a cis-diol, to enhance the acid properties. The cis-diol forms very stable complex with the  $[B(OH)_4]^-$ , thus removing it from solution. The reaction is reversible and thus removal of one of the products shifts the equilibrium in the forward direction and thus all the  $B(OH)_3$  reacts with NaOH; in effect it acts as a strong acid in the presence of the cis-diol.

$$B(OH)_3 + NaOH \longrightarrow Na[B(OH)_4] + NaBO_2 + 2H_2O.$$

$$\begin{bmatrix} I & I \\ CH - O \\ I \\ CH - O \end{bmatrix} B \begin{bmatrix} O - CH \\ I \\ O - CH \\ I \end{bmatrix}^{-} + H^{+} + 4H_{2}O.$$

- A:  $\operatorname{Bi}^{3+} + \operatorname{H}_2 O \rightarrow \operatorname{Bi}O^+ + 2\operatorname{H}^+ \operatorname{thus}(q) \text{ and } (s)$
- **B**:  $\operatorname{Al} O_2^- + \operatorname{H}_3 O^+ \to \operatorname{Al}(OH)_3 \downarrow \operatorname{thus}(r)$
- C:  $2 \operatorname{Si} O_4^{4-} + 2 \operatorname{H}^+ / \operatorname{H}_2 O \xrightarrow{\text{Hydrolysis}} \operatorname{Si}_2 O_7^{6-}$ thus (q) (r), (s)

**D**: 
$$B_4 O_7^{2-} \xrightarrow{H^+} B(OH)_3$$
;

$$B_4 O_7^{2-} \xrightarrow{H_2O} B(OH)_3$$
 thus (q) and (r).

 Orthoboric acid acts as lewis-acid in water not as proton donor (as it does not liberate H<sup>+</sup> ion) because it completes its octet by accepting the OH<sup>-</sup> from water.

$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

- 4. In crystalline state AlCl<sub>3</sub> exists as AlCl<sub>3</sub>. 6H<sub>2</sub>O or [Al(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub>.
- 5. (i)  $3SiCl_4(vapour) + 4Al(molten) \longrightarrow 4AlCl_3 + 3Si$ (ii) (a)  $3SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$

**(b)** Si + 2CH<sub>3</sub>Cl 
$$\xrightarrow{\text{Cu powder}}$$
 (CH<sub>3</sub>)<sub>2</sub> SiCl



2.

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8.

(d) nHO - Si - OH  

$$|$$
  
CH<sub>3</sub>  
 $\stackrel{\Delta}{\longrightarrow}$ 



- (iii) (a) SiCl<sub>4</sub> + 4H<sub>2</sub>O  $\longrightarrow$  H<sub>4</sub>SiO<sub>4</sub> or Si(OH)<sub>4</sub> (ortho silicic acid) + 4HCl
  - (b)  $H_4SiO_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$
  - (c)  $\operatorname{SiO}_2 + \operatorname{Na}_2\operatorname{CO}_3 \xrightarrow{2\operatorname{H}_2\operatorname{O}} \operatorname{Na}_2\operatorname{SiO}_3 + \operatorname{CO}_2$







In this manner several molecules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.



- (A) In two dimensional sheet silicates, three oxygen atoms of [SiO<sub>4</sub>]<sup>4-</sup> are shared with adjacent tetrahedral [SiO<sub>4</sub>]<sup>4-</sup> units,
  - (B) One oxygen atom is shared between two adjacent tetrahedra,  $[SiO_4]^{4-}$ .
  - (C) All four oxygen atoms are shared between adjacent tetrahedra,  $[SiO_4]^4$ .

(D) Two oxygen atoms are shared between adjacent tetrahedra,  $[SiO_4]^4$  forming a linear chain.

In p-block elements (i.e. 14<sup>th</sup> group here), the lower oxidation state becomes more stable on going down the group due to inert pair effect. Thus Pb<sup>+4</sup> is less stable then Sn<sup>+4</sup>. This makes the Pb<sup>+4</sup> a stronger oxidising agent. Therefore, the statement-2 is incorrect.

9. Small amines such as  $NH_3$ ,  $CH_3NH_2$  and  $(CH_3)_2NH$  give unsymmetrical cleavage of diborane according to following reaction.

 $\mathrm{B_2H_6} + 2 \mathrm{NH_3} \longrightarrow [\mathrm{H_2B(\mathrm{NH_3)_2}]^+} [\mathrm{BH_4}]^-$ 

Large ammines, such as  $(CH_3)_3$  N gives symmetrical cleavage of diborane according to following reaction.

 $B_2H_6 + 2N(CH_3)_3 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$ 

10.  $Be_nAl_2Si_6O_{18}$ . The value of n = 3 by charge balancing.

$$(\mathrm{Be}^{2+})_3 (\mathrm{Al}^{3+})_2 (\mathrm{Si}_6 \mathrm{O}_{18})^{12-} [2 \times n + 2(+3) + (-12) = 0 \therefore n = 3].$$

11.  $B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 3H_2$   $1 \mod B_2H_6 \text{ formed } 2 \mod of B(OMe)_3$ Hence,  $3 \mod B_2H_6 \text{ formed } 6 \mod of B(OMe)_3$ 





## Group 15th and 16th

- 1.  $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O.$   $N_2$  gas is also given by  $NH_4NO_2.$   $NH_4NO_2 \longrightarrow N_2 + 2H_2O.$  $NH_4NO_3 \longrightarrow N_2O + 2H_2O.$
- 2. NO + NO<sub>2</sub>  $\xrightarrow{-30^{\circ}\text{C}}$  N<sub>2</sub>O<sub>3</sub>( $\bullet$ ) pale blue
- 3. Black phosphours has layered structure like graphite and has highest ignition temperature (> 673 K).



least stable(max. angle strain)

intermediate stability



4. (a)  $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$   $6\times[40+16] [31\times4+16\times10]$  Calcium phosphate = 336 = 284

284 g of  $P_4O_{10}$  are completely reacted with 336 g of CaO.

$$\therefore 852 \text{ g of P}_4\text{O}_{10} \text{ will react with } \frac{336 \times 852}{284} \text{ g of CaO}$$

Hence, required weight of CaO =  $\frac{336 \times 852}{284}$  = 1008 g.

- 5. Because of following two reasons, the nitrates are less abundant in earth crust.
  - (i) Nitrates have greater solubility in water.
  - (ii) Nitrates are prone to microbial action.
- 6. NH<sub>3</sub> is better electron donor as the lone pair of electrons are present in diffued and more directional sp<sup>3</sup> hybridised orbital. In PH<sub>3</sub> the lone pair of electrons is supposed to be present in more concentrated s-orbital which is closer to the nucleus. As a result the donation of electron pair is some what difficult.
- 7. It is disproportionation reaction,

$${\stackrel{0}{\mathsf{P}}}_4$$
 + 3NaOH + 3H<sub>2</sub>O  $\rightarrow$  3NaH<sub>2</sub>  ${\stackrel{5+}{\mathsf{P}}}_2$  +  ${\stackrel{3-}{\mathsf{P}}}_3$ 

8. 
$$P_4 + 3O_2 \xrightarrow{\text{in presence of } N_2} P_4O_6$$

Here nitrogen acts as diluent.

Note :

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In dry O, following reactions may take place.

$$P_4 + 3O_2 \longrightarrow P_4O_6.$$

$$P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$$

In moist  $O_2$  the  $P_4O_6$  gets hydrolysed forming  $H_3PO_3$ .

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3.$$

In presence of NaOH.

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2$$

- 9. (A)  $3Cu + 8HNO_3$  (dilute)  $\longrightarrow 2NO + Cu(NO_3)_2 + 4H_2O$ (B)  $Cu + 4HNO_3$  (concentrated)  $\longrightarrow 2NO_2 + Cu(NO_3)_2$ 
  - $(b) Cu + 4HiVO_3 (concentrated) \longrightarrow 2HO_2 + Cu(HO_3)_2 + 2H_2O$

(C)  $4Zn + 10HNO_3$  (dilute)  $\longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$ 

**(D)**  $Zn + 4HNO_3$  (concentrated)  $\longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O_3$ 

**10.** Ba 
$$(N_3)_2(s) \triangleq Ba(s) + 3N_2(g)$$

11. PCl<sub>5</sub> produces POCl<sub>3</sub> on reaction with these compounds

$$PCl_{5} + SO_{2} \longrightarrow POCl_{3} + SOCl_{2}$$

$$PCl_{5} + H_{2}O \longrightarrow POCl_{3} + 2HCl$$

$$PCl_{5} + H_{2}SO_{4} \longrightarrow SO_{2}Cl_{2} + 2POCl_{3} + 2HCl$$

$$6PCl_{5} + P_{4}O_{10} \longrightarrow 10POCl_{3}$$



12.	Compound	<b>Oxidation state of Nitrogen</b>
	HNO <sub>3</sub>	=+5
	NO	=+2
	NH <sub>4</sub> Cl	=-3
	N <sub>2</sub>	=0

I.

24.

So, correct order will be HNO3, NO, N2, NH4Cl

13. It is peroxodisulphuric acid, the Marshall's acid and contains one -O-O- linkage as given in structure

$$\begin{array}{cccc} 0 & 0 \\ \parallel & \parallel \\ HO - S - O - O - S - OH \\ \parallel & \parallel \\ 0 & O \\ (H_2S_2O_2) \end{array}$$

- 14. Mn in  $KMnO_4$  is in highest oxidation state can not be oxidised. I<sup>-</sup>,  $MnO_4^{2-}$  and  $Fe^{2+}$  can be oxidised to  $I_2$ ,  $MnO_4^{-}$  and  $Fe^{3+}$  respectively by  $O_3$ .
- 15.  $PbO_2 + 4HNO_3 \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O + O_2$ .
- 16.  $Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8 HCl$ It destroys the chlorine present in fibres during dyeing. That is why the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is called as antichlor.
- 17.  $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
- **20.**  $H_3 P O_4^{+5} > H_4 P_2 O_6 > H_3 P O_3^{-3} > H_3 P O_2^{+1}$

$$KClO_{3} \xrightarrow{MnO_{2}} KCl + O_{2}$$

$$\downarrow P_{4}$$

$$\xrightarrow{2HPO_{3}} Z + \xrightarrow{N_{3}O_{3}} Y \xleftarrow{HNO_{3}} P_{4}O_{10}$$

$$(X)$$

21. [N<sub>2</sub>O<sub>5</sub>, HPO<sub>3</sub>]

22.  $[O_{2}, P_{4}O_{10}]$ 

23.

- $\Rightarrow$  Bi<sub>2</sub>O<sub>5</sub> is more basic than N<sub>2</sub>O<sub>5</sub>
- $\Rightarrow$  NF<sub>3</sub> is more covalent than BiF<sub>3</sub>
- $\Rightarrow$  NH<sub>3</sub> boiling point is higher than PH<sub>3</sub>
- $\Rightarrow$  P–P single bond is stronger than N–N single bond.



ClO<sub>4</sub> weak base (Resonance stable) More stable

+ H<sub>3</sub>O

strong acid

(C)  $\frac{\text{HClO}_4}{\text{strong acid}} + \frac{\text{H}_2\text{O}}{\text{weak acid}}$ 

(**D**)

#### **MOCK TEST**

- It forms a stable cyclc complex with polyhydroxy compounds like cis-glycerol, cathechol, etc. This helps in therelease of H<sup>+</sup> as H<sub>3</sub>O<sup>+</sup> and, therefore, boric acids acts as a strong acid and hence can be titrated with sodium hydroxide using phenolphathalein.
- 2. (A)  $Mg_3B_2 \xrightarrow{HCl(aq)}{Hydrolysis} MgCl_2 + B_2H_6$  [X], X is not BCl<sub>3</sub>,

It 
$$B_2H_6$$
  
(B)  $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3[Y] + 6H_2$ ,  
(C) Both [X] and [Y] gives  $B_2O_3$ ;  $B_2H_6 + 3O_2 \longrightarrow B_2O_3$   
 $+ 3H_2O$ ;  $H_3BO_3 \xrightarrow{\text{Red } \Delta} B_2O_3$   
(D)  $B(OH)_3(aq) + 2H_2O \longrightarrow B(OH)_4^- + H_3O^+(aq)$   
So B, C & D are correct options.

3.

$$B(s) \leftarrow Mg \text{ of } Fe \xrightarrow{Mg \text{ of } Fe} B(OH)_{3} \leftarrow H_{2}O(OH)_{4}B(OH)_{4}B(OH)_{3} \leftarrow H_{2}O(OH)_{3} \leftarrow H_{2$$

- 4. (A) This is due to the inert pair effect in the heavier p-block elements.
  - **(B)**  $3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$
  - (C) This is due to the presence of completely filled d and or f orbitals in heavier elements.

Covalent radius / pm; N = 70, P = 100, As = 120, Sb = 140, Bi = 150.



Oxidation state P is +3 can be decrease to -e and increase to +5. Hence it can act as both reducing as well as oxidising agent.

6.  $4 \text{ NH}_3(g) + 5 \text{ O}_2(g) \xrightarrow{\text{Platinum/Rhodium catalyst}}{850^{\circ}\text{C}, 5 \text{ atmosphere}} 4 \text{ NO}(g)$ 

$$4 \operatorname{NO}(g) + \operatorname{O2}(\operatorname{from air}) \xrightarrow{\operatorname{cool to}} 2 \operatorname{NO}_2(g)$$

 $H_2O + NO_2 + O_2 \longrightarrow HNO_3 + NO_3$ 

7. Mn in  $\text{KMnO}_4$  is already in its highest oxidation state (i.e. + 7). So  $\text{KMnO}_4$  can not be oxidised by O<sub>3</sub>.

8. 
$$3S + H_2SO_4 \longrightarrow 3SO_4 + 2H_2O$$

L

(A) inert pair effect (B) SO<sub>2</sub> is acidic, TeO<sub>2</sub> is amphoteric and dissolves in alkali to form tellurites and also dissolves in acids to form basic salts. Basic character of oxides increase down the group as metallic character i.e. electropositive character increases down the group with increasing atomic number.

$$10. 2Cu + 6HNO_3 \longrightarrow 2Cu(NO_3)_2 + NO + NO_2 + 3H_2O$$

$$NO + NO_2 \xrightarrow{-20^\circC} N_2O_3 (blue); (A) 2HNO_2 \longrightarrow$$

$$N_2O_3 + H_2O$$

$$(B) N_2O_3 + 2KOH \longrightarrow 2KNO_2 + H_2O$$

$$(C) 2HNO_3 + As_2O_3 + 2H_2O \longrightarrow$$

$$NO + NO_2 + 2H_2AsO_4$$

$$\underbrace{\frac{\text{NO} + \text{NO}_2}{\bigvee_{\text{N},\text{O}_2}} + 2\text{H}_3\text{AsO}_4}_{\text{N},\text{O}_2}$$

All options are correct.

11.  $HCN + 2H_2O \longrightarrow HCOOH(X) + 2NH_3$ ;

HCOOH  $\xrightarrow{\Delta}$  CO [Y] + H<sub>2</sub>O

- (C) Only  $K_4[Fe(CN)_6]$  gives CO with conc.  $H_2SO_4$  according to the following reaction.
- $\begin{array}{l} \mathrm{K_4[Fe(CN)_6]} + 6\mathrm{H_2SO_4\,(conc.)} + 6\mathrm{H_2O} \rightarrow 2\mathrm{K_2SO_4} + \mathrm{FeSO_4} \\ + 3(\mathrm{NH_4)_2SO_4} + 6\mathrm{CO} \end{array}$
- (A) Malonic acid gives C<sub>3</sub>O<sub>2</sub>; (D) action of conc. HNO<sub>3</sub> on charcoal gives CO<sub>2</sub>. (B) C<sub>3</sub>O<sub>2</sub> gives CO<sub>2</sub>.
- 12.  $Cl_2[X] + H_2O \longrightarrow HOCl + HCl$   $AgNO_3 + HCl \longrightarrow AgCl \downarrow (white) + HNO_3$  $Mg + 2HCl \longrightarrow MgCl_2 + H_2(Y)$
- F<sup>-</sup> is smaller and thus valence shell electrons are strongely bound with the nucleus and so it can not lose electron easily. Hence HF does not act as reducing agent.
- 14. It is used because it has very low solubility in blood.
- 15.  $2\operatorname{Na}_2S(\operatorname{aq}) + 3\operatorname{SO}_2(\operatorname{g}) \longrightarrow S \downarrow + \operatorname{Na}_2S_2O_3(\operatorname{aq})$



- **16.** Compound [X] is  $Na_2B_4O_7$ .
  - (A) two boron atoms are sp<sup>2</sup> while other two boron atoms are sp<sup>3</sup> hybridised.
  - (B) product is sodium peroxoborate which is used as brightner in soaps.
  - (C)  $H_3BO_3$  is formed which with HF gives  $HBF_4$ .
  - (D) Green bead in oxidising as well as in reducing flame in cold.
- 17. (A) SbH<sub>3</sub> has higher boiling point than NH<sub>3</sub> due to greater vander Wall's force of attraction.

**(B)** 
$$\operatorname{CaC}_2 + \operatorname{N}_2 \xrightarrow{1100^{\circ} \mathrm{C}} \underbrace{\operatorname{CaCN}_2 + \mathrm{C}}_{\operatorname{nitrolim}}$$

- (C) is correct statement
- (D) Availability of electrons for metallic bonding decreases on account of inert pair effect.
- **18.** (A) As number of reducing hydrogen increases, the reducing character also increases. In  $H_3PO_4$  there is no reducing hydrogen so it should be least reducing.
  - **(B)** +1 < +2 < +3 < +5
  - (C) Down the group the avgailability of lone pair of electrons decreases as they are presentin more concentrated s-orbital.
  - (D) As down the group bond energy decreases, the removal of H becomes easier.
- 19. (A) Two hydroxl groups lie in different plane (have open book like structure)
  - (B) It turns blue litmus red because of acidic character which is then bleached by bleaching action of H<sub>2</sub>O<sub>2</sub>.

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21. Cl<sub>2</sub> and SO<sub>3</sub> being stronger oxidising agent, oxidies Brto Br<sub>2</sub> gas

$$2Br^{-} + Cl_{2} \longrightarrow Br_{2} + 2Cl^{-}$$
$$SO_{3} \longrightarrow SO_{2} + [O]$$

 $2 \operatorname{Br}^{-} + 2\operatorname{H}^{+} + [O] \longrightarrow \operatorname{Br}_{2} + \operatorname{H}_{2}O$ 

Т

 $2 \operatorname{Br}^- + \operatorname{SO}_3 + 2\operatorname{H}^+ \longrightarrow \operatorname{Br}_2 + \operatorname{H}_2\operatorname{O} + \operatorname{SO}_2$ 

HI being reducing agent and  $I_2$  being weak oxidising agent (comes after bromine) don't liberate bromine from Br<sup>-</sup>.

- 22. (B)  $ClO_4^- < IO_4^- < BrO_4^-$  according to their reduction potential.
  - (D) HClO<sub>4</sub> < HClO<sub>3</sub> < HClO<sub>2</sub> < HClO. As charge dispersionon oxygen atom(s) increase, the stability of their anions increases and thus reducing character increases and oxidising powre decreases.

Given (B) and (D) are correct order.

23. 
$$\operatorname{XeF}_4 + \operatorname{O}_2\operatorname{F}_2 \longrightarrow \operatorname{XeF}_6[X] + \operatorname{O}_2$$

- (A)  $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
- (B)  $XeF_6$  turns to yellowliquid on melting where as  $XeF_2$ &  $XeF_4$  turn white.
- (C)  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$
- (D)  $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$
- **24.**  $2Hg + O_3 \longrightarrow Hg_2O + O_2$

 $Hg_2O$  dissolves in Hg and thus its mobility decreases and starts sticking to the glass surface.

- **25.**  $2 \operatorname{NaOH} + 2 \operatorname{NO}_2 \longrightarrow \operatorname{NaNO}_2 + \operatorname{NaNO}_3 + \operatorname{H}_2 O$
- 26. 1. Ammonium salts form yellow precipitate of  $(NH_4)_2[PtCl_6]$  and  $(NH_4)_3[Co(NO_2)_6]$  with chloroplatinic acid and sodium cobaltinitrite respectively.
  - 2. Only oxidising anions give N<sub>2</sub>O or N<sub>2</sub>. SO<sub>4</sub><sup>2-</sup> is not oxidising so NH<sub>3</sub> should be obtained.
- 27. Inertness of  $SF_6$  is due to the presence of sterically protected sulphur atom which does not allow thermody-namically favourable reactions like hydrolysis to take place.
- **28.**  $\operatorname{XeF}_6 + \operatorname{H}_2 O \longrightarrow \operatorname{XeOF}_4 + 2\operatorname{HF}$

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

**29.** Fe+2HCl  $\longrightarrow$  FeCl<sub>2</sub>+H<sub>2</sub>

Liberation of hydrogen prevents the formation of ferric chloride.

**31.** 
$$Na_2Al_2Si_2O_8 \cdot xH_2O + Ca^{2+} \longrightarrow CaAl_2Si_2O_8 \cdot xH_2O + 2Na^+$$



$$Na_2Al_2Si_2O_8.xH_2O + Mg^{2+} \longrightarrow MgAl_2Si_2O_8.xH_2O + 2Na^+$$

- **32.** Fillingof 10 electons in 3d- subshell enhances the effective nuclear charge on account of the poor shielding and thus the electrons are held more tightly. This is the reason why selenium is reluctant to attain the highest oxidation state of (VI).
- **33.** (B) test of ozone (not given by  $H_2O_2$

(C) 
$$2 \operatorname{BaO} + \operatorname{O}_2(\operatorname{air}) \xrightarrow{500^\circ \text{C}} 2 \operatorname{BaO}_2;$$
  
 $2 \operatorname{BaO}_2 \xrightarrow{800^\circ \text{C}} \operatorname{BaO} + \operatorname{O}_2$ 

(A)  $O_3$  forms  $I_4O_9$  with dry iodine (incorrect statement)

34. (A) F<sub>2</sub> gives O<sub>2</sub> gas (C) H<sub>2</sub>O<sub>2</sub> in acidic medium form CrO<sub>5</sub>, not O<sub>3</sub>

(B) 
$$KI + 3O_3 \longrightarrow KIO_3 + 3O_2$$
  
 $KI + 4O_3 \longrightarrow KIO_4 + 4O_2$   
 $XeF_2 \xrightarrow{H_2} Xe + 2HF$   
(A) (B) (C)  
 $XeF_4 + H_2O \xrightarrow{H_2} Xe + HF$ 

$$XeF_2 + H_2O \xrightarrow{H_2} Xe + HF + O_2$$
(B) (C) (D)

 $3O_2 f = 2O_3; 5O_3 + 2KOH \longrightarrow 2KO_3 (orange solid) + 5O_2 + H_2O$ (D) (E)

$$HF + KF \longrightarrow KHF_2(molten) \xrightarrow{\text{Electrolysis}} F_2$$
(C)
(C)

35.  $F \xrightarrow{2p} B \xrightarrow{F} B \xrightarrow{F} B$ 

There is  $2p\pi - 2p\pi$  bonding.

 $4BF_{2}(X) + 3LiAlH_{4} \xrightarrow{\text{Ether}} 2B_{2}H_{6}(Y) + 3LiAlH_{4};$ 

 $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + Heat.$ 

Molecular weight of compound (Y) = 21.76 + 6 = 27.76.

% of H in compound (Y) i.e.,  $B_2H_6 = \frac{6}{27.76} \times 100 = 21.72$ 

 $B_{2}H_{6} + NH_{3} \xrightarrow{\Lambda} B_{3}N_{3}H_{6} \text{ (inorganic benzene)} + H_{2}.$  1 : 2

**36.** (A) It is true because of effective  $p\pi - d\pi$  overlaping owing to small size of sulphur as compared to phosphorus and silicon.

$$(\mathbf{B}) \operatorname{HO}_{\mathbf{U}}^{(+V)} \stackrel{O}{=} \stackrel{O}{=} \stackrel{O}{=} \stackrel{O}{=} \stackrel{O}{\to} \stackrel$$

They have +V and +III oxidation state.

- (C)  $\text{HNO}_3$  oxidises sulphur to  $\text{H}_2\text{SO}_4$  (+VI) but only oxidises selenium to  $\text{H}_2\text{SeO}_3$  (+IV). They is poor shielding of 3d electrons as a result the electrons are held more tightly with nucleus in case of selenium.
- (D) M O electronegativity difference is large while in X O, its is comparatively smaller (< 1.4).</li>
- 37. (A) As bond (H E) dissociation enthalphy decreases down the group, the acidic character increases from H<sub>2</sub>O to H<sub>2</sub>Te.
  - (B) Order of thermal stability is  $H_2O > H_2S > H_2Se > H_2Te$ .
  - (C)  $H_2O$  does not have reducing property and this character increases from  $H_2S$  to  $H_2Te$ .
  - (D) Water has highest boiling point because of H-bonding and thus the correct order is H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te < H<sub>2</sub>O.

**39.** (A)  $3H_3PO_2 \xrightarrow{415K} 2H_3PO_3 + PH_3 \uparrow$ 

$$4 H_3 PO_3 \xrightarrow{435K} 3H_3 PO_4 + PH_3$$

**(B)**  $PCl_3 + 3H_2O$  Hydrolysis  $H_3PO_3 + 3HCl$ 

$$4H_3PO_3 \xrightarrow{435K} 3H_3PO_4 + PH_3^{\uparrow}$$

(C)  $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$ 

(D) 
$$4\text{HNO}_3 + P_4O_{10} \longrightarrow 4\text{HPO}_3 + 2N_2O_5$$

\* PH<sub>3</sub> and HNO<sub>2</sub> act as reducing agents.



38.

40. (A) 
$$(NH_4)_2 S_2 O_8 + H_2 O \xrightarrow{Hydrolysis} 2NH_4 HSO_4 + H_2 O_2$$
  
(B)  $2NaBO_2 + H_2 O_2 + 6H_2 O \xrightarrow{Alkaline hydrolysis} Na[(OH)_2 B_2(O-O)_2(OH)_2]6H_2 O$   
(C)  $4Na_2 SO_3 \xrightarrow{disproportionation} Na_2 S + Na_2 SO_4$   
(D)  $2$ -Ethylanthraqunol + air  $(O_2) \longrightarrow$   
 $2$ -ethylanthraquinone +  $H_2 O_2$ 

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41. (a) 
$$\operatorname{Cl}_2O_6 + 2OH^- \longrightarrow \operatorname{ClO}_3^-(\operatorname{sp}^3) + \operatorname{ClO}_4^-(\operatorname{sp}^3) + \operatorname{H}_2O^-(\operatorname{sp}^3) + \operatorname{H}_2O^-(\operatorname{sp}^3) + \operatorname{ClO}_4^-(\operatorname{sp}^3) + \operatorname{ClO}_4^-(\operatorname{sp$$

(b) 
$$2\text{KClO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HClO}_4(\text{sp}^3) + 2\text{ClO}_5(\text{sp}^2) + \text{H}_5\text{O}_5(\text{sp}^2) + \text{H}_5\text{O}_5$$

(c)  $H_2O_2 + HSO_3 Cl \longrightarrow HOOSO_2OH(sp^3) + HCl;$ Caro's acid has -O - O - linkage

(d) 
$$4 H_3 PO_3 \longrightarrow 3H_3 PO_4 + PH_3$$

(e)  $N_2O_5 + H_2O_2 \longrightarrow HNO_3 + HNO_4$ ;  $HNO_4$  has -O - O - linkage

42. (A) 3 HNO<sub>2</sub> 
$$\xrightarrow{\text{disproportionation}}$$
 HNO<sub>3</sub> + 2 NO + H<sub>2</sub>O

one of the product is paramagnetic (NO) and colourless gas, one of the products gives "brown ring test'.

(B) 
$$NH_4Cl(aq) + NaNO_2(aq) \xrightarrow{comproportionation} N_2(g)$$
  
+ 2  $H_2O(I) + NaCl(aq).$ 

one of the products is diamagnetic and colourless gas. Laboratory method of preparation.

(C) 
$$6 \text{ HN}_3 + 4 \text{ Li} \longrightarrow 4 \text{ LiN}_3 + 2 \text{ NH}_3 + 2 \text{ N}_2$$

one of the products is diamagnetic and colourless gas.

(D) Mg + 2 HNO<sub>3</sub> (cold dilute)  $\longrightarrow$  Mg<sup>2+</sup> (NO<sub>3</sub>)<sub>2</sub> + H<sub>2</sub> one of the products gives "brown ring test", one of the products is diamagnetic and colourless gas.

43. (A) 
$$XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 3/2O_2 + 12HF$$
  
(B)  $2[HXeO_4]^+ + 2OH^- \longrightarrow [XeO_6]^4 + Xe + O_2 + 2H_2O$   
(C)  $3H_2O + 3F_2 \longrightarrow 6HF^- + O_3$   
 $2H_2O + 2F_2 \longrightarrow 4HF + O_2$   
(D)  $2NOCl + O_3 \longrightarrow 2NO_2 + Cl_3$ 

