

# SMART ACHIEVERS Nurturing Success...

CHEMISTRY - XII

**Reasoning Ncert** 

Date: 22/10/2021

- Q1.  $PCI_5$  is well known while  $PI_5$  is unknown. Why?
- Q2.  $[PBr_6]^{\odot}$  anion is not formed but  $[PCl_6]^{\odot}$  anion exist. Why?
- Q3. PF<sub>5</sub> is known but NF<sub>5</sub> not. Explain.
- Q4. The compound  $(CF_3)_3$  N is very weak base  $(CH_3)_3$  N is a strong base. Explain.
- Q5. NH<sub>3</sub> is a strong base but NF<sub>3</sub> does not show any basic property. Explain.
- Q6. NF<sub>3</sub> is not hydrolysed but NCl<sub>3</sub> is readily hydrolysed to show explosion. Explain.
- Q7. Ammonia is a good complexing agent. Why?
- Q8. What is inert pair effect?
- Q9. Of Bi(V) and Sb(V) which may be a stronger oxidizing agent and why?
- Q10. Phosphine has lower boiling point than ammonia. Give reason,
- Q11. Unlike phosphorus, nitrogen shows little tendency for catenation, explain.
- Q12. Why is N<sub>2</sub> less reactive at room temperature?
- Q13. Nitrogen exists as diatomic molecule and phosphorus as P<sub>4</sub>. Why?
- Q14. Why is BiH<sub>3</sub> the strongest reducing agent amongst all the hydrides of Group 15 elements?
- Q15. NF<sub>3</sub> is an exothermic compound ( $\Delta H_f = -109 \text{ kJ} / \text{mol}$ ) whereas NCl<sub>3</sub> is an endothermic compound. ( $\Delta H_f = +230 \text{ kJ} / \text{mol}$ ). Explain.
- Q16. H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> both are acid. Classify then on account of acid-base theories.
- Q17. Nitric oxide is paramagnetic. Explain.
- Q18. All the bond in PCI<sub>5</sub> are not equal explain.
- Q19. Explain, why NH<sub>3</sub> is basic while BiH<sub>3</sub> is only feebly basic.
- Q20. Why are group 15 pentalides more covalent than trihalides?
- Q21. Which of the two NH<sub>3</sub> or PH<sub>3</sub> is soluble in water?
- Q22. What kind of orbital overlap is responsible for the formation of multiple bonds by nitrogen with itself as well as with carbon and oxygen?
- Q23. How do you account for the reducing behaviour of H<sub>3</sub>PO<sub>2</sub> on the basis of its structure?
- Q24. H<sub>3</sub>PO<sub>3</sub> is diprotic, explain.
- Q25. NO<sub>2</sub> readily forms a dimer, explain.

- Q26. How NO<sub>2</sub> and NO<sub>3</sub> ions present in separate solutions can be identified?
- Q27. Pure PH<sub>3</sub> does not burn in air, but impure sample of PH<sub>3</sub> burns in air. Explain.
- Q28. In the ring test for identification of nitrate ion, write the formula of the compound responsible for the brown ring formed at the interface of two liquids?
- Q29. Aqua-regia dissolves noble metals in it. Explain.
- Q30. Name three allotropes of phosphorus, which of these is most reactive?
- Q31. HNO<sub>3</sub> is an oxidizing agent but H<sub>3</sub>PO<sub>4</sub> is not. Explain.
- Q32. PCI<sub>5</sub> is ionic in solid state. Explain.
- Q33. Red phosphorus is denser less volatile and chemically less reactive than yellow phosphorus. Explain.
- Q34. What is difference between the nature of pi-bonds present in H<sub>3</sub>PO<sub>3</sub> and HNO<sub>3</sub> molecules.
- Q35. Which of the two its more covalent SbCl<sub>3</sub> or SbCl<sub>5</sub>?
- Q36. Why does nitrogen show anomalous behaviour?
- Q37. Noble gas have low boiling points. Explain.
- Q38. Phosphorus does not form multiple bonds, explain.
- Q39. What is Holme's signal?
- Q40. Determine the oxidation number of nitrogen in (i)  $N_2O$  (ii)  $NO_2$  (iii)  $HNO_3$  (iv)  $NH_3$ .
- Q41. Why HPO<sub>2</sub> is not formed like HNO<sub>2</sub>?
- Q42. With what neutral molecule is CIO<sup>©</sup> isoelectronic? Is that molecule a Lewis base?
- Q43. In what way it can be proved that PH<sub>3</sub> is basic in nature?
- Q44. Give name and formula of compound formed during ring test of nitrate redical.
- Q45. Oxygen molecule has formula O<sub>2</sub> while sulphur is S<sub>8</sub>. Explain why?
- Q46. Name two compounds in which oxygen has oxidation state different from 2. Given oxidation state also.
- Q47. Why sulphur in vapour state exhibits paramagnetism?
- Q48. Why is  $H_2O$  a liquid  $H_2S$  a gas?
- Q49. Why F show anomalous behaviour give two example to show F anomolous behaviour?
- Q50. Account the SF<sub>6</sub> is known but SH<sub>6</sub> is not known.
- Q51. Comment on the nature of two S O bonds formed in SO<sub>2</sub> molecule. Are the two S O bonds in this molecule equal?
- Q52. Why does  $O_3$  act as a powerful oxidising agent?
- Q53. Name a compound in which oxygen exhibits an oxidation state of +2.

- Q54. Which has the large bond angle H<sub>2</sub>S or H<sub>2</sub>O and why?
- Q55. Give reason SF<sub>6</sub> is not easily hydrolysed though thermodynamically it should be, why?
- Q56. How is nature of  $\pi$  bonding in  $H_2SO_4$  different from that of water?
- **Q57.** Which of the three is the strongest oxidizing agent :  $CIO_4^-$ ,  $BrO_4^-$ ,  $IO_4^-$ ?
- Q58. Which neutral molecule would be isoelectronic with ClO<sup>⊕</sup>?
- Q59. The bond energy of  $F_2$  is less than  $Cl_2$ , explain.
- Q60. Why are halogens strong oxidising agents?
- Q61. HClO<sub>4</sub> is stronger acid than H<sub>2</sub>SO<sub>4</sub> explain?
- Q62. Acidic character of Halogen hydrides increase up to down explain.
- Q63. Explain why flourine forms only one oxoacid, HOF.
- Q64. Why is IC/more reactive than  $I_2$ ?
- Q65. Name the oxides of chlorine that are used as bleaching agent for paper pulp.
- Q66. What are halogens and why are they called so?
- Q67. What is freon?
- Q68. Give an example of a compound in which oxidation state of chlorine is +7?
- Q69. Why is HF the weakest acid among hydrohalo-acids in spite of the fact that fluorine is most electronegative?
- Q70. Write two uses of CIO<sub>2</sub>.
- Q71. Among halogen hydrides which has maximum ionic character?
- Q72. Explain why flourine always exhibits and oxidation state of -1 only?
- Q73. Noble gases have largest radii. Explain.
- Q74. Xe readily form compounds but krypton does not form compounds easily. Why?
- Q75. Does the hydrolysis of XeF<sub>6</sub> lead to a redox reaction?
- Q76. Compare and contrast the maximum covalency of oxygen and sulphur.
- Q77. How are XeF<sub>2</sub> and XeF<sub>4</sub> prepared?
- Q78. Account the Xenon show Fluorides but Xenon chloride not known, explain.
- Q79. Why do Xe form compounds with flourine and oxygen only?
- Q80. The HNH angle value is higher than HPH, HAsH and HSbH angles in hydrides of is 15 group. Why?
- Q81. Give reason
  - (a) NF<sub>3</sub> is an exothermic compound whereas NCl<sub>3</sub> is not.
  - (b) All the bonds in SF<sub>4</sub> are not equivalent.

- Q82. (a) H<sub>3</sub>PO<sub>2</sub> and H<sub>3</sub>PO<sub>3</sub> act as good reducing agents but H<sub>3</sub>PO<sub>4</sub> does not. Why?
  - (b) SOCI<sub>2</sub> can act as a weak Lewis acid as well as a weak Lewis base. Explain.
- Q83. Why is dioxygen a gas but sulphur a solid?
- Q84. Account the following
  - (a) OF<sub>2</sub> should be called oxygen difluoride and not fluorine oxide. Why?
  - (b) lodine is more soluble in KI than in water.
- Q85. Give reason
  - (a) Why interhalogen are more reactive than halogen?
  - (b) Why Cl<sub>2</sub> bleaches a substance permanently but SO<sub>2</sub> does it termporarily?





## SMART ACHIEVERS

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**Reasoning Ncert-Solution** 

Date: 22/10/2021

- **S1.** Due to larger size of I, overlapping between 5-I and P not possible i.e. steric repulsion of 5-lodine PI<sub>5</sub> cannot form while CI is comparable size with P and 5-CI can accommodate around phosphorus.
- **S2.** Because Br is bigger in size and 6-Bromine has steric repulsion around the phosphorous, hence  $[PBr_6]^{\odot}$  cannot exist while CI is comparable size with phosphorus and can accommodate around phosphorus hence  $[PCI_6]^{\odot}$  exist.
- **S3.** N atom cannot expand its covalence beyond 3 as it does not have vacant *d*-orbitals in its valence shell, whereas P has empty 3d orbital and can expand its covalency.

$$_{7}N : 1s^{2}, 2s^{2}2p_{x}^{1}2p_{y}^{1}2p_{z}^{1}$$

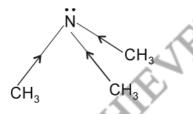
Maximum three unpaired electron

Ground state : 
$$_{15}P$$
 :  $1s^2$ ,  $2s^22p^6 3s^2 3p_x^{-1} 3p_y^{-1} 3p_z^{-1}$ 

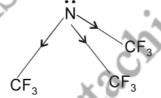
Excited state : 
$$1s^2$$
,  $2s^2 2p^6$ ,  $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1$ 

Maximum five unpaired electron

**S4.** Because of different electronegativity of —CH<sub>3</sub> and —CF<sub>3</sub>. —CH<sub>3</sub> is Electropositive increase electrondensity on N is N(CH<sub>3</sub>)<sub>3</sub>. and increase lone pair donation power act as Lewis base while —CF<sub>3</sub> is electronegative decrease electrondensity on N in N(CF<sub>3</sub>)<sub>3</sub> and decrease lone pair donation tendency act as very-very weak Lewis base.

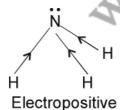


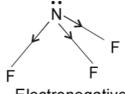
Electropositive



Electronegative

NH<sub>3</sub> is a very strong base. This is because of the lone pair of electrons on N atom which it can donate. In NH<sub>3</sub> H is electropositive which increase electrodensity on N while in NF<sub>3</sub> F is electronegative which decrease electrondensity on nitrogen. On increasing electrondensity electron donating power increase.





Electronegative

**S6.** Nitrogen tri flouride is not hydrolysed because neither nitrogen not flourine possess vacant *d*-orbitals to form extra bond with lone pair of electron on oxygen of water molecule. However, NCI<sub>3</sub> has vacant *d*-orbitals on CI atom and hydrolyses violently to show explosion.

$$NCI_3 + 3H_2O \longrightarrow NH_3 + 3HOCI$$

**S7.** Ammonia is a good complexing agent because of the presence of lone pair of electrons on nitrogen. This lone pair can easily be donated to electron deficient compounds forming complexes. For example, it reacts with Cu<sup>2⊕</sup> ion to form a deep blue complex.

$$\operatorname{Cu}^{2\oplus}(aq) + 4\operatorname{NH}_3(aq) \longrightarrow \left[\operatorname{Cu}(\operatorname{NH}_3)_4\right]^{2\oplus}$$
Complex (deep blue

- **S8.** The pair of electrons in valence *s*-orbital is reluctant to take part in bond formation due to poor shielding effect of *d* & *f*-electrons in heavier elements. It is called inert pair effect due to which lower oxidation state becomes more stable than higher oxidation state in case of *p*-block elements.
- **S9.** On moving down the group, the stability of +5 oxidation state decreases while the stability of +3 oxidation state increases due to inert pair effect. Therefore, +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. Thus, Bi(V) is a stronger oxidising agent than Sb(V).
- **\$10.** Ammonia exists as associated molecule due to its tendency to form hydrogen bonding. Therefore, it has high boiling point. Unlike NH<sub>3</sub>, phosphine (PH<sub>3</sub>) molecules are not associated through hydrogen bonding in liquid state. This is because of low electronegativity of P than N. As a result, the boiling point of PH<sub>3</sub> is lower than that of NH<sub>3</sub>.
- **S11.** Nitrogen has little tendency for catenation because <u>N N single bond is weak</u>. This is because nitrogen has small size and the <u>lone pairs on two nitrogen atoms repel each other</u>. On the other hand, phosphorus is comparatively large in size so that lone pairs on P atoms do not repel to the same extent. As a result P P bond is stronger than N N bond. Therefore, P has a tendency for catenation because of high bond enthalpy of P P bond.
- S12. In molecular nitrogen, there is a triple bond between two nitrogen atoms (N ≡ N) and it is non-polar in character. Due to the presence of a triple bond, it has very <u>high bond dissociation</u> <u>energy</u> and therefore, it does not react with other elements under normal conditions and is very unreactive. However, it may react at higher temperatures.
- **S13.** Because of its small size and high electronegativity <u>nitrogen forms  $p\pi-p\pi$  multiple bonds</u>. Therefore, <u>it exists as a diatomic molecule</u> having <u>a triple bond</u> between the two N-atoms. <u>Phosphorus</u>, on the other hand, has larger size and lower electronegativity and usually <u>does not form  $p\pi-p\pi$  multiple bonds</u> with itself. Instead it prefers to <u>form P P single bonds</u> and hence it exists as tetrahderal,  $P_A$  molecules.
- S14. As we move down the Group 15, the size of the element increases and, therefore, the length of the bond with hydrogen increases and its strength decreases. In other words, as we move down the Group, the bond with hydrogen can break more easily to evolve H<sub>2</sub> gas which acts as the reducing agent. Thus, Bi H bond is the weakest amongst the hydrides of elements of Group 15, and hence, BiH<sub>3</sub> is the strongest reducing agent.

- **S15.** NF<sub>3</sub> is an exothermic compound whereas NCl<sub>3</sub> is an endothermic compound because in case of NF<sub>3</sub>, N F bond strength is greater than the F F bond strength while in case of NCl<sub>3</sub>, N CI bond strength is lower than the CI CI bond strength. Thus the formation of NF<sub>3</sub> is spontaneous while energy has to be supplied during the formation of NCl<sub>3</sub>.
- S16.  $H_3PO_3 \text{ an oxoacid of P} \begin{pmatrix} O \\ || \\ HO-P-OH \\ || \\ H \end{pmatrix} \text{ and is Bronsted dibasic acid as it acts as protons}$

donor.

$$H_3PO_3 + H_2O \longrightarrow H_2PO_3^{\odot} + H_3O^{\oplus}$$

$${\rm H_3BO_3}\begin{pmatrix} {\rm OH} \\ {\rm HO-B-OH} \end{pmatrix} {\rm and\ Lewis\ mono\ basic\ acid\ as\ it\ acts\ electron\ pair\ acceptor\ because}$$

Boron have only six electrons (incomplete octet)

$$B(OH)_3 + H_2O \longrightarrow B(OH)_4^{\odot} + H^{\oplus}$$

**\$17.** Nitric oxide in in all has 15 electrons in its molecule i.e. it possesses at least one odd electron which is responsible for paramagnetic nature of NO.

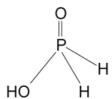
unpaired electron 
$$\longrightarrow \cdot \ddot{N} = O$$

**S18.** PCI<sub>5</sub> has triangular bipyrimidal structure two bonds are in axial position and three bonds are in equatorial position. Axial bonds are longer than equatorial due to greater bond pair electrons repulsion.

- S19. Both N in NH<sub>3</sub> and Bi in BiH<sub>3</sub> have a lone pair of electrons on the central atom and hence should behave as Lewis bases. But NH<sub>3</sub> is much more basic than BiH<sub>3</sub>. This can be explained on the basis of electron density on the central atom. Atomic size of N (70 pm) is much smaller than that of Bi (148 pm), therefore, electron density on the N-atom is much higher than that on Bi-atom. Consequently, the tendency of N in NH<sub>3</sub> to denote its pair of electrons is much higher than that of Bi in BH<sub>3</sub>. Thus, NH<sub>3</sub> is much more basic than BiH<sub>3</sub>.
- **S20.** The elements of group 15 have five electrons in their respective valence shells. It is difficult to lose three electrons to form  $E^{3\oplus}$ . It is even more difficult to lose all the five valence electrons (two s- and three p-) to form  $E^{5\oplus}$  ions. Therefore, higher elements have no tendency to form ionic compounds. They prefer to form covalent compounds by sharing of electrons.

Thus, elements in the +5 oxidation state are more covalent than in the +3 oxidation state.

- **S21.** NH<sub>3</sub> is highly polar compound due to higher electronegative difference between N and H and can break H-bonding of water and can make H-bonding with water while PH<sub>3</sub> is very weak polar and cannot break and make H-bonding with water.
- **S22.**  $p\pi$ - $p\pi$  overlap
- **S23.**  $H_3PO_2$  has one P = O, one P OH and two P H bonds as. Phosphorous has +1 oxidation state.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

**S24.** H<sub>3</sub>PO<sub>3</sub> has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.

$$H_3PO_3 \iff HPO_3^{2@} + 2H^{6}$$

S25. N = 0 has one unpaired electron, therefore, it is unstable and forms dimer, i.e.,  $N_2O_4$  whose

structure is 
$$0 N - N O$$

**S26.**  $NO_2^{\odot}$  on reaction with KI liberates  $I_2$  which turns starch paper blue.

$$NO_2^{\odot}(aq) + KI \longrightarrow I_2$$

 $NO_3^{\circ}$  can be identified by ring test.

- **S27.** The impurity of P<sub>2</sub>H<sub>4</sub>, the liquid hydride present in phosphine catches fire as soon as it comes in contact with air and forms vortex rings of smoke.
- **S28.** [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2</sup>
- **\$29.** Aqua-regia is mixture of 1 part conc. HNO<sub>3</sub> and 3 part conc. HCl. The mixture liberate nascent chlorine which dissolves noble metals.

- **\$30.** Phosphorus allotropes Red, Black and White. White phosphorus is most reactive.
- **S31.** The inability of nitrogen atom to unpair and promote its 2*s* electron results in the pentapositive state of nitrogen being less stable than tripositive. Thus HNO<sub>3</sub> where nitrogen is in +5 oxidation state is an oxidizing agent. On the other hand P has *d*-orbitals to expand its octet and also shows no inert pair effect, is quite stable in V state. Thus H<sub>3</sub>PO<sub>4</sub> in which P is in +5 oxidation state is not oxidizing.
- **S32.** X-ray studies have shown that solid  $PCI_5$  is an ionic compound composed of  $[PCI_4]^{\oplus}$   $[PCI_6]^{\odot}$ ; the cation being tetrahedral and anion being octahedral.
- **S33.** Red phosphorus exists as chains of P<sub>4</sub> tetrahedron linked together, whereas in yellow phosphorus individual P<sub>4</sub> molecules are held together by weak van der Waals forces.
- **S34.** In H<sub>3</sub>PO<sub>3</sub>, there is  $p\pi d\pi$  bond whereas in HNO<sub>3</sub> there is  $p\pi p\pi$  bond.
- **S35.** SbCl<sub>5</sub> is more covalent than SbCl<sub>3</sub>. on increasing oxidation state covalent character increases.
- **\$36.** Within its group, nitrogen shows anomalous behaviour due to:
  - (a) Smallest size
- (b) Highest electronegativity
- (c) Non-availability of d-orbitals
- **S37.** Noble gases are monoatomic gases and are held together by weak van der Waal's forces (dispersion forces). Therefore, they are liquefied at very low temperatures. Hence they have low boiling points.
- **S38.** Due to larger size and presence *d*-orbital of phosphorus,  $p\pi p\pi$  bonds cannot formed.
- **S39.** A mixture of  $CaC_2$  and  $Ca_3P_2$  filled in a container having small holes in it is thrown in sea or river. The water coming through holes gives.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
  
 $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$  (A little  $P_2H_4$ )

 $P_2H_4$  catches fire and  $C_2H_2$  burns with luminous flame which serves as signal to approaching boot or ship.

**S40.** (i) N<sub>2</sub> O

(ii) NO<sub>2</sub>

- (I) N<sub>2</sub> O . T
- (iii) HNO<sub>3</sub> : + 5
- (iv)  $NH_3$  : -3
- **S41.** P-atom can not form  $p\pi p\pi$  bond due to large size and presence of orbital with oxygen while N can form  $p\pi p\pi$  bonding with oxygen due to smaller size and absence of *d*-orbital.
- **S42.**  $CIO^{\odot}$  has 17 + 8 + 1 = 26 electrons. A neutral molecule with 26 electrons is  $OF_2$  (8 + 2 × 9 = 26 electrons).  $OF_2$  is a Lewis base due to the presence of two lone pairs of electrons.

**S43.** PH<sub>3</sub> reacts with acids like HI to form phosphonium iodide, PH<sub>4</sub>I.

This shows that PH<sub>3</sub> is basic in nature. This basic nature of PH<sub>3</sub> is due to presence of lone pair on phosphorus atom and therefore, it acts as a Lewis base.

**\$44.** [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub>

Pentaaquanitrosyli iron (II) sulphate.

**S45.** Oxygen is smaller in size and has ability to form  $P\pi - P\pi$  multiple bond, and satisfy its octate forming (O = O) O<sub>2</sub> molecule.

While S is bigger in size and has not ability to form  $P\pi - P\pi$  multiple bond, satisfy its octate by forming (Puckered shape) S<sub>8</sub> molecule.

- **S46.** Oxygen Floride OF<sub>2</sub> oxygen has +2 oxidation state. Hydrogen peroxide H<sub>2</sub>O<sub>2</sub> oxygen has –1 oxidation state.
- **S47.** In the vapour state sulphur exists as  $S_2$  and not as  $S_8$  the electronic configuration of  $S_2$  has two unpaired electron in antibonding  $\pi^*$  orbitals, due to which it paramagnetic.
- **S48.** Due to greater electronegativity of O than S, H<sub>2</sub>O undergoes intermolecular H–bonding. As a result, H<sub>2</sub>O exists as an associated molecule. And, larger amount of energy is required to break these H-bonds. Therefore, H<sub>2</sub>O is a liquid at room temperature.

While,  $H_2S$  does not undergo H-bonding as the electronegativity difference between H and S is not appreciable. It exists as discrete molecules which are held together by weak van der Waals' forces of attraction. To break these forces of attraction, on a small amount of energy is required. Therefore,  $H_2S$  is a gas at room temperature.

**S49.** Due to smaller size, absence of empty *d*-orbital and high electronegativity F show the anomalous behaviour.

### **Examples:**

- (1) Florine only show 1 oxidation state while other halogen show –1 to +7 oxidation states.
- (2) Due to smaller size higher electron density F F has higher repulsion and its bond dissociation energy is less than CI CI and Br Br.
- **\$50.** F is highly electronegative hence F unpair the paired electron of sulphate to form SF<sub>6</sub> while H is electropositive in respect to sulphur and it cannot unpair to paired electron of sulphur to expained S oxidation state.

- **S51.** In the structure of  $SO_2$ , S is  $sp^2$ -hydridised. Two of the three  $sp^2$ -orbitals form two  $\sigma$ -bonds while the third contains the lone pair of electrons. S is now left with one half-filled p-orbital and one half-filled d-orbitals. They form one  $p\pi p\pi$  and one  $p\pi d\pi$  double bond with oxygen atom. Thus,  $SO_2$  has bent structure with OSO bond angle of 119.5°. Due to resonance, the two  $\pi$ -bonds are equal.
- **S52.** O<sub>3</sub> is an endothermic compound, i.e., it possesses greater internal energy than oxygen. On heating, it readily decomposes to give dioxygen and nascent oxygen.

$$O_3 \xrightarrow{Heat} O_2 + O$$
 (nascent oxygen)

Since nascent oxygen is very reactive, therefore, O<sub>3</sub> acts as a powerful oxidising agent.

- **S53.** Oxygen difluoride OF<sub>2</sub>
- **S54.** H<sub>2</sub>O, because Oxygen being electronegative than sulphur, higher polarity is developed on O and H atoms leading to a higher H—O—H bond angle.
- **S55.** Due to sterically protection of six F atom, which do not allow to water molecules to attack on sulphure and due to steric repulsion of F at SF<sub>6</sub> thermodynamically unstable.
- **S56.** In water, there is lone pair of electron on oxygen whereas in  $H_2SO_4$  there is one  $p\pi p\pi$  bond and another  $p\pi d\pi$  bond.
- **S57.** IO<sub>4</sub> is the strongest oxidising agent.
- **S58.**  $OF_2$  and CIF are isoelectronic with  $CIO^{\ominus}$ .
- **S59.** Due to higher electron-density on F, the bond length of F–F increase due to electron-electron repulsion and B.d.E. decrease while CI is bigger in size and has less electron-density and has not electron-electron repulsion in CI<sub>2</sub> and bond length is comparatively shorter than F<sub>2</sub>.
- **S60.** Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and reduce.

$$X + M \longrightarrow M^{\oplus}X^{\odot}$$

Hence, halogens act as strong oxidising agents.

- **S61.** In HCIO<sub>4</sub> due to 'greater electronegativity of CI and higher oxidation state +7 make it more acidic than H<sub>2</sub>SO<sub>4</sub>,' respectively S is less electronegativity and less oxidation state +6.
- **S62.** Because up to down atomic size of halogen increase and overlapping between H and X decrease i.e., bond length of H X increase and Bond-dissociation energy decrease which increase the degree of dissociation of HX up to down

**S63.** This is due to limitation of having only one oxidation state that it forms only one oxo acid. Chlorine, bromine and iodine form four series of oxoacids of the general formula HOX, HOXO, HOXO<sub>2</sub> and HOXO<sub>3</sub> in which the oxidation states of halogen (X = Cl, Br or I) is +1, +3, +5 and +7, respectively. However, due to high electronegativity and small size, flourine forms only HOF with oxidation state +1.

- **S64.** IC/is more reactive than I<sub>2</sub> because <u>I C/bond is weaker than I I bond</u>. Abond between two different atoms is always weaker than that between identical atoms. Consequently, IC/breaks easily to form halogen atoms which readily bring about the reactions.
- **S65.** CIO<sub>2</sub> and Cl<sub>2</sub>O are used for bleaching paper pulp.
- **\$66.** Halogens are F, CI, Br and I. They are called halogens because halogens means salt producers, i.e., they form salts.
- **\$67.** CF<sub>2</sub>Cl<sub>2</sub>, dichlorodifluoromethane is called freon.
- **S68.** HClO<sub>4</sub> is a compound in which Cl is in +7 oxidation state.
- **S69.** HF is weakest acid among hydrohalo-acid because of high bond dissociation energy due to small bond length.
- **\$70.** (i) As a bleaching agent for paper pulp and textiles.
  - (ii) Used in water treatment.
- **S71.** HF has maximum ionic character because of greater difference in electronegativity.
- **S72.** Fluorine shows only –1 oxidation state because of it is the most electronegative element.
- **\$73.** In noble gases, we can measure only van der Waals radii which are larger than covalent radii.
- **\$74.** Xe has lower ionization energy than Kr, therefore, Xe outermost electron excited with F and O and form compound.
- **S75.** No the products of hydrolysis are XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub> where oxidation state of Xe in reactants and product remain same (+6).
- **\$76.** Oxygen shows maximum covalency equal to 2 due to presence of 2 unpaired electrons where as 'S' exhibits maximum covalancy upto 6 due to presence of empty *d*-orbital.
- **S77.**  $XeF_2$  is prepared in Lab in Nickel tube at 673 and 1 bar pressure

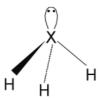
$$Xe + F_2 \xrightarrow{\text{Nickel tube}} XeF_2$$

 $\mathrm{XeF_4}$  is prepared in Lab in nickel tube at 673 K and 7 bar pressure.

$$Xe + 2F_2 \xrightarrow{\text{Nickel tube}} XeF_4$$

- **S78.** Xe is noble gas, its ionization energy is much higher. F is highly electronegativity element it can unpair the paired electron of Xe to form covalence bond.
- **S79.** Because Xe is a noble gas which is stable, and high ionization energy. F and O are most electronegative element which can unpair Xe paired electrons to form covalent bond.

**S80.** In all the hydrides of Group 15 elements, the central atom is  $sp^3$ -hybridised. Three of the four  $sp^3$ -orbitals form three X — H (X stands for element of Group 15),  $\sigma$ -bonds while the fourth contains the lone pair of electrons as shown in below :



Since the lone pair-bond pair repulsions are stronger than the bond pair-bond pair repulsions, therefore, the bond angle decreases from 109°28′ to 107.8° in NH<sub>3</sub>. As we move from N to P to As to Sb, the atomic size goes on increasing. As a result, bond pairs of electrons, lie away and away from the central atom. In other words, force of repulsion between the adjacent bond pairs goes on decreasing and, consequently, the bond angles keep on decreasing from NH<sub>3</sub> to SbH<sub>3</sub>.

- **S81.** (a) F is highly electronegativity element and it is strong oxidising agent than CI due to which N F bond become stronger by releasing high amount of energy and NF<sub>3</sub> is exothermic.
  - (b) SF₄ has see-saw structure and two S F bonds are in different plane with two other S F bonds are in different plane with two other S F bonds, and have different electronic repulsion depend on bond angles, *i.e.*, bond length of two bonds are not same with two other bonds in other plane.
- **S82.** (a) The structures of  $H_3PO_2$ ,  $H_3PO_3$  and  $H_3PO_4$  are:

$$\begin{array}{c|ccccc} O & O & O & O \\ \parallel & \parallel & \parallel & \parallel \\ P & P & P & P \\ H & OH & HO & HO & HO \\ \\ Hypophosphorous & Phosphorous & Phosphoric \\ acid(H_3PO_2) & acid(H_3PO_3) & acid(H_3PO_4) \\ \end{array}$$

Due to the presence of P — H bonds, both  $H_3PO_2$  and  $H_3PO_3$  act as reducing agents. On the other hand,  $H_3PO_4$  does not have any P — H bond and hence it does not act as a reducing agent.

(b) The basic character of  $SOCl_2$  is due to the presence of lone pair of electrons on S atom, like ammonia. It has a pyramidal structure involving  $sp^3$  hybridisation with a lone pair of electrons as:



So, Lewis basic character is due to the presence of a lone pair. In addition, SOCI<sub>2</sub> has also empty d-orbitals which can be used to accept electron pairs and hence it behaves as a Lewis acid.

**S83.** Due to small size and high electronegativity, oxygen atom forms  $p\pi-p\pi$  multiple bonds with another oxygen atom. As a result, oxygen exists as diatomic (O<sub>2</sub>) molecules. These molecules are held together by weak van der Waals' forces of attraction. Therefore, O<sub>2</sub> is a gas at room temperature.

Sulphur, on the other hand, because of its bigger size and lower electronegativity, does not form  $p\pi-p\pi$  multiple bonds. Instead, it forms S — S single bonds. Further because of stronger S — S than O — O single bonds, sulphur has a much greater tendency for catenation than oxygen.

Consequently, sulphur forms octaatomic  $(S_8)$  molecules having eight-membered puckered ring structure. Because of bigger size, the forces of attraction holding the  $S_8$  molecules together are much stronger. Consequently., sulphur is a solid at room temperature.

- **S84.** (a) In OF<sub>2</sub> oxygen is electropositive and Flourine is electronegative. According to IUPAC system electronegative written in right in formate of 'id'.
  - (b) Because  $I_2$  is nonpolar and insolute in water and lodine react with KI to form soluble complex.  $KI_3$ .

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

- **S85.** (a) Because interhalogens compounds (ICl, IBr, BrF<sub>3</sub>) bonds are weaker due to different atomic size of halogens while halogens (Cl<sub>2</sub>, Br<sub>2</sub>, F<sub>2</sub>) having same atomic size of halogen bonds are respectively stronger.
  - (b) Cl<sub>2</sub> bleaches by oxidation while SO<sub>2</sub> does it by reduction the reduced product gets oxidized again and the colour returns.

**CHEMISTRY - XII** 

Shapes, Hybridization and Bono Angle NCERT

Date: 22/10/2021

- Q1. Give shape and hybridization of SF<sub>4</sub>.
- Q2. Give shape and hybridization of SCI<sub>2</sub>.
- Q3. Give hybridization oxidation shape and basically of Pyrophosphoric acid (H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>)
- Q4. Give hybridization oxidation shape and basically of orthophosphric acid.
- Q5. Give hybridization oxidation shape and basicity of orthophroprous acid.
- Q6. Give hybridization, shape and basically of hypophosphrous acid.
- Q7. Give hybridization and shape of phosphine
- Q8. Give shape of PCI, and hybridization.
- Q9. Give hybridization oxidation shape and basicity of Dithionic acid H<sub>2</sub>S<sub>2</sub>O<sub>6</sub>
- Q10. Give hybridization oxidation shape and basicity of Peroxomonosulphuric acid (or Caro's acids) H<sub>2</sub>SO<sub>5</sub>.
- Q11. Give hybridization oxidation shape and basicity of Thiosulphuric acid H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.
- Q12. Give hybridization oxidation shape and basicity of Sulphuric acid H<sub>2</sub>SO<sub>4</sub>.
- Q13. Give hybridization oxidation shape and basicity of Sulphurous acid H2SO3
- Q14. Give shape of Rhombic Sulphur (S<sub>o</sub>).
- Q15. Give shape and hybridization of SF<sub>6</sub>,
- Q16. Give hybridization and shape of ICI.
- Q17. Give hybridization and shape of  $ICl_2^{\ominus}$ .
- Q18. Give hybridization and shape of IF,
- Q19. Give hybridization and shape of IF5.
- Q20. Give hybridization and shape of CIF<sub>3</sub>.
- Q21. Give hybridization oxidation shape and basicity of Pyrosulphuric acid (Oleum) H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>(+6).
- Q22. Give hybridization oxidation shape and basicity of Peroxodisulphuric acid (or Marshall's acid)  $H_2S_2O_8$ .
- Q23. Give hybridization and shape of XeO<sub>4</sub>.
- Q24. Give hybridization and shape of XeO<sub>3</sub>.

Q25.	Give	nyb	ridiza	ation	and	snape	ot	Xe	J٢
						_	_		_

Q26. Give hybridization and shape of XeF<sub>1</sub>.

Q27. Give hybridization and shape of XeF<sub>3</sub>.

Q28. Give hybridization and shape of XeF<sub>6</sub>.

Q29. Give hybridization and shape of XeOF<sub>4</sub>.

Q30. Name of the state of hybridization of orbitals in XeF<sub>2</sub> molecule.

Q31. Give hybridization and shape of XeO<sub>2</sub>F<sub>2</sub>.

Q32. Name the geometry of XeOF<sub>4</sub> and XeO<sub>3</sub>.

Q33. Which compound of xenon has distorted octahedral shape?

AMING Pyt. I tid. Q34. Explain hybridization of P in  $PX_5$  in box notation and draw shape.

Q35. All the five bonds in  $PCI_5$  are not equavalent. Justify.

Q36. Write the structural formula for PCI<sub>5</sub> (Solid).

Q37. Write the structure of following phosphorus <sup>3</sup> Ring acid

Q38. Compare the structure of SO<sub>3</sub> and SeO<sub>3</sub>.

Q39. Give the reasoning structures of NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>.

Q40. Bond angle in  $PH_4^{\oplus}$  is higher than that in  $PH_3$ . Why?

Q41. Give the hybridization and structures of the following species:

(a) NO₃<sup>⊙</sup>

(b) CIO₄<sup>⊙</sup>

Q42. (a) Give Hybridization of P and shape of Red Phosphorous.

(b) Give Hybridization of P in P<sub>4</sub> and give shape of P<sub>4</sub> (White phosphorous)

Q43. Give the formula of the noble gas species which is isostructural with

- (a) IBr<sub>2</sub>
- (b) **ICI**<sup>©</sup>
- (c) BrO<sub>2</sub>

Q44. Write the structure of

- P<sup>2</sup> P<sup>2</sup> acid



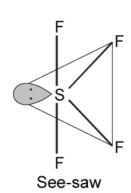
### **SMART ACHIEV**

**CHEMISTRY - XII** 

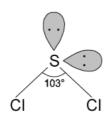
Shapes, Hybridization and Bono Angle NCERT-Solution

Date: 22/10/2021

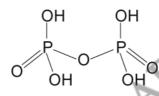
S1. Hybridization - sp3d Shape - See-saw



S2. Hybridization - sp3 Shape - Bent

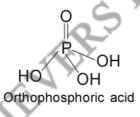


S3. Hybridization - sp3 Shape - Bitetrahedral Basicity - 4



chievers Pyrophosphoric acid (H<sub>2</sub>P<sub>2</sub>O<sub>2</sub>)

S4. Hybridization - sp3 Shape - Tetrahedral Basicity - 3



S5.

Hybridization - sp3 Shape - Tetrahedral Basicity - 2

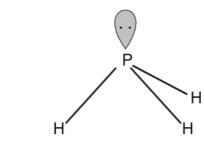
Phosphonic acid or Orthophosphorous acid

S6.

Hybridization - sp3 Shape - Tetrahedral Basicity-1

Phosphinic acid or Hypophosphorous acid

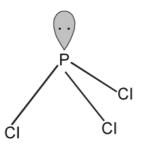
Hybridization –  $sp^3$ Shape – bent pyramidal



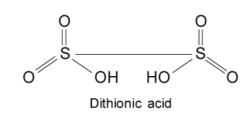
Phosphine

S8.

Hybridization –  $sp^3$ Shape – bent pyramidal



Oxidation no - + 5Hybridization  $- sp^3$ Basicity - 2



**S10.** Oxidation no -+6Hybridization  $-sp^3$ Basicity -3

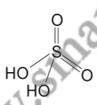
Peroxomonosulphuric acid OR Caro's acids

S11. Oxidation no -+2Hybridization  $-sp^3$  - Central Sulphur Basicity -2

Thiosulphuric acid

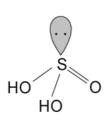
Oxidation no – 6

Hybridization –  $sp^3$ Basicity – 2



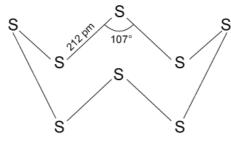
Sulphuric acid

Shape – bent



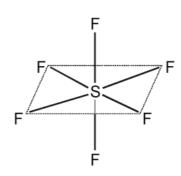
Sulphurous acid

**S14.** Shape – Puckered ring

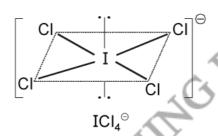


Rhombic Sulphur

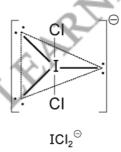
S15. Hybridization  $-sp^3d^2$ Shape – Octahedral



S16. Hybridization  $-sp^3d^2$ Shape – Square planar



S17. Hybridization –  $sp^3d$ Shape – linear

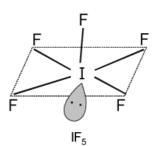


S18. Hybridization 
$$-sp^3d^3$$
  
Shape – Pentagonal bipyramidal



 $IF_7$ 





Hybridization –  $sp^3d^2$ Shape – Square pyramidal S20.

Hybridization  $-sp^3d$ Shaped - T-shaped

S21. Oxidation no -+6Hybridization  $-sp^3$ Basicity -2

Oxidation no – +6

Hybridization –  $sp^3$ Basicity – 2

**S23.** Hybridization  $-sp^3$ Shape - Tetrahedral

S24.

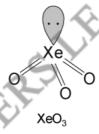
Hybridization –  $sp^3$ Shape – Pyramidal

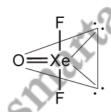
**S25.** Hybridization  $-sp^3d$ Shape - T-shaped

S26. Hybridization  $-sp^3d^2$ Shape – Square Planner

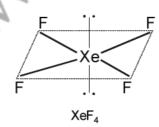
Pyrosulphuric acid (Oleum)

Peroxodisulphuric acid OR Marshall's acid

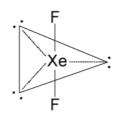




XeOF,



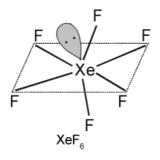
**S27.** Hybridization  $-sp^3d$ Shape – Linear



XeF<sub>2</sub>

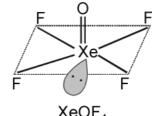
S28.

 $\label{eq:continuous} \begin{aligned} & \text{Hybridization} - sp^3d^3 \\ & \text{Shape} - \text{Distorted octahedral} \end{aligned}$ 



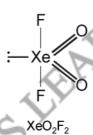
S29.

Hybridization  $-sp^3d^2$ Shape – Square pyramidal



**S30.** In  $XeF_2$ , Xe is  $sp^3d$  hybridized.

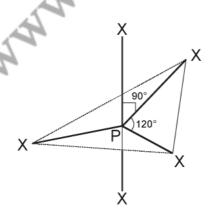
Hybridization  $- sp^3d$ Shape - See-saw



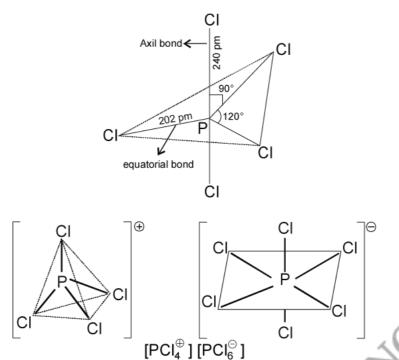
- **S32.** XeOF<sub>4</sub> is square pyramidal, XeO<sub>3</sub> is pyramidal.
- **S33.** XeF<sub>6</sub> has distorted octahedral shape.
- S34.

 $P - \underbrace{\uparrow \downarrow}_{3s} \underbrace{\uparrow \uparrow \uparrow}_{3p} - \text{outer most electronic configuration}$   $P - (excited) \underbrace{\uparrow \uparrow}_{hybridization - sp^3d} \underbrace{\uparrow}_{3s} \underbrace{\uparrow}_{3p} \underbrace{\uparrow}_{3d}$ 

hybridization –  $sp^3d$ Trigonal bipyramidal



**S35.** PCI<sub>5</sub> has trigonal bipyramidal structure in which there are three P — CI equatorial bonds and two P — Cl axial bonds. The two axial bonds are being repelled by three bond pair at 90° while the three equatorial bonds are bing repelled by two bond pairs at 90°. Therefore, axial bonds are repelled more by bond pairs than equatorial bonds and hence are larger (219 pm) than equatorial bonds (204 pm).



PCl<sub>5</sub> in solid found in PCl<sub>4</sub><sup>⊕</sup> of PCl<sub>6</sub><sup>□</sup> ions having strong lattice energy.

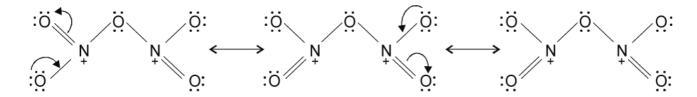
S36.

jevers. **S37.** <sup>3</sup><sub>6</sub> P ring acid is (PHO<sub>2</sub>)<sub>6</sub> with each P total 3 atoms 2 oxygen and 1-hydrogen.

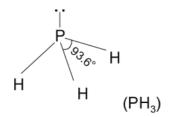
**S38.** SO<sub>3</sub> in gas phase, exits as planar triangular structure whereas SeO<sub>3</sub> exists as cyclic tetramer. (because Se has less tendency to form  $\pi$  bonding than S)

### **S39.** Resonating structures of $NO_2$ are:

Resonating structures of N2O5 are:



**S40.** P in PH $_3$  is  $sp^3$  -hybridised. It has three bond pairs and one lone pair around P. Due to stronger lone pair-bond pair repulsions than bond pair-bond pair repulsions, the tetrahedral angle decreases from 109°28′ to 93.6°. As a result, PH $_3$  is pyramidal. However, when it reacts with a proton, it forms PH $_4^\oplus$  ion which has four bond pairs and there are no lone pair-bond pair repulsions. PH $_4^\oplus$ , therefore assumes tetrahedral geometry with a bond angle of 109°28′. Hence bond angle of PH $_4^\oplus$  is higher than in PH $_3$ .

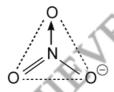


PH<sub>3</sub> molecule (Pyramide)



PH₄<sup>⊕</sup> ion (Tetrahedral)

**S41.** (a)  $NO_3^{\odot}$  Hybridization =  $sp^2$ 



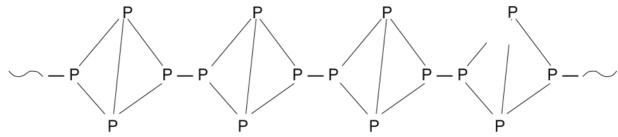
Triangular planner

(b)  $CIO_4^{\circ}$  Hybridization =  $sp^3$ 



Tetrahedral

**S42.** (a)

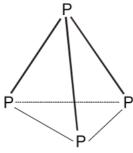


Red Phosphorous

Structure - Tetrahedral Polymeric

Hybridization - sp3

(b)



White phosphorous

Shape  $-P_4$  of tetrahedron Hybridazation –  $sp^3$ 

S43. Isostructural noble gas molecules:

(a) IBr<sub>2</sub><sup>⊖</sup>

XeF<sub>2</sub>

(b)  $ICI_4^{\odot}$ 

XeF₄

(c) BrO<sub>3</sub> :

XeF<sub>3</sub>

**S44**. (a)

(b)



## SMART ACHIEVERS

**CHEMISTRY - XII** 

**Reaction NCERT-Solution** 

Date: 22/10/2021

**S1.** 
$$P_4 + 10SO_2CI_2 \longrightarrow 4PCI_5 + 10SO_2$$

**S2.** 
$$PCI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCI$$

**S3.** 
$$PCI_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCI$$

**S4.** Sn + 
$$2PCI_5 \longrightarrow SnCI_4 + 2PCI_3$$

**S5.** 
$$PH_3 + HBr \longrightarrow PH_4Br$$

**S6.** 
$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

**S7.** 
$$P_4 + 20HNO_2(conc.) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

**S8.** 
$$P_4 + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

**S9.** (a) 
$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3$$
 (Cold)

(b) 
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$
(Hot)

**S10.** (a) 
$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$
 (Cold)

(b) 
$$P_4O_6 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$
(Hot)

**S11.** 
$$8NH_3 + 3CI_2 \longrightarrow 6NH_4CI + N_2$$
(excess)

**S12.** C + 
$$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + CO_2$$

**S13.** 
$$3NO_2(g) + H_2O \longrightarrow 2HNO_3(aq) + NO(g)$$

**S14.** 
$$2HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2HPO_3$$

**S15.** 2NO + 
$$N_2O_4 \longrightarrow 2N_2O_3$$

**S16.** 
$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

**S17.** 
$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

**S18.** 
$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$

**S19.** 
$$2\text{FeCl}_3(aq) + 6\text{NH}_4\text{OH}(aq) \longrightarrow \text{Fe}_2\text{O}_3.\text{xH}_2\text{O}(s) + 6\text{NH}_4\text{CI}(aq)$$

**S20.** 
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCI$$

**S21.** 
$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

**S22.** 
$$Ca_3P_2 + 6HCI \longrightarrow 3CaCl_2 + 2PH_3$$

**S23.** 
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

**S24.** 
$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

**S25.** 
$$2NH_3 + NaOCI \longrightarrow N_2H_4 + NaCI + H_2O$$

**S26.** 
$$NH_3 + 3CI_2 \longrightarrow NCI_3 + 3HCI$$
 (excess)

**S27.** Na<sub>3</sub>P + 
$$3H_2O \longrightarrow 3NaOH + PH_3$$

**S28.** Thermal decomposition of sodium azide gives dinitrogen gas.  $2NaN_3 \longrightarrow 2Na + 3N_2$ 

**S29.** 
$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

**S30.** 
$$4Zn + 10HNO_3 \xrightarrow{\text{(dil)}} 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O_3$$

**S31.** 
$$P_4 + 10HNO_3 + H_2O \longrightarrow 4H_3PO_4 + 5NO + 5NO_2$$

**S32.** 
$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 10CO + 6CaSiO_3$$

s33. 
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

**S34.** 
$$4NH_3 + 5O_2 + \frac{Pt}{750-900^{\circ}C} \rightarrow 4NO + 6H_2O$$

**S35.** 
$$(NH_4)_2SO_4 + NO + NO_2 \longrightarrow 2N_2 + H_2SO_4 + 3H_2O_4$$

**S36.** 
$$Cu^{2+}[aq] + 4NH_3[aq] \longrightarrow [Cu(NH_3)_4]$$
 (deep blue)

**S37.** 
$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

**S38.** 
$$(NH_4)_2Cr_2O_7(s) \xrightarrow{\Delta} Cr_2O_3(s) + 4H_2O(l) + N_2(g)$$

**S39.** On heating,  $H_3PO_3$  disproportionates to give orthophosphoric acid and phosphine.

$$+3 +5 -3$$
 $4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$ 
ortho phosphoric phosphine acid

**S40.** It is prepared by the action of heavy water on magnesium nitride.

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$
Deuterated ammonia

**S41.** 
$$As_4O_{10} + 6H_2O \longrightarrow 4H_3AsO_4$$
 (Arsenic acid)

(Slow reaction)

**S42.** 
$$4As_4O_6 + 6H_2O \longrightarrow 4H_3AsO_3$$
 (Arsenous acid)

(As₄O₄ is only sparingly soluble in water)

**S43.** 
$$S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

**S44.** 
$$SO_2 + 2H_2O + CI_2 \longrightarrow H_2SO_4 + 2HCI$$

**S45.** 
$$3S + 2H_2SO_4(conc.) \longrightarrow 3SO_2 + 2H_2O$$

**S46.** 
$$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(I)$$

**S47.** ICI + 
$$H_2O \longrightarrow HCI + HOI$$

**S48.** S + 6HNO<sub>3</sub> 
$$\longrightarrow$$
 H<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O + 6NO<sub>2</sub>

**S49.** 
$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$

**S50.** 
$$Cl_2 + F_2 \xrightarrow{437K} 2CIF$$
 (equal volume)

**S51.** 
$$I_2 + CI_2 \xrightarrow{437K} 2ICI$$
 (equimolar)

**S52.** 
$$Cl_2(g) + H_2O(1) \longrightarrow HCl(aq) + HOCl(aq)$$

**S53.** 
$$I_2 + 8H_2O + 7CI_2 \longrightarrow 2HIO_4 + 14HCI_4$$

**S47.** ICI + H<sub>2</sub>O 
$$\longrightarrow$$
 HCI + HOI  
**S48.** S + 6HNO<sub>3</sub>  $\longrightarrow$  H<sub>2</sub>SO<sub>4</sub> + 2H<sub>2</sub>O + 6NO<sub>2</sub>  
**S49.** H<sub>2</sub>S + 2HNO<sub>3</sub>  $\longrightarrow$  2H<sub>2</sub>O + 2NO<sub>2</sub> + S  
**S50.** Cl<sub>2</sub> + F<sub>2</sub>  $\xrightarrow{437K}$  2CIF  
(equal volume)  
**S51.** I<sub>2</sub> + Cl<sub>2</sub>  $\xrightarrow{437K}$  2ICI  
(equimolar)  
**S52.** Cl<sub>2</sub>(g) + H<sub>2</sub>O(I)  $\longrightarrow$  HCI(aq) + HOCI(aq)  
**S53.** I<sub>2</sub> + 8H<sub>2</sub>O + 7Cl<sub>2</sub>  $\longrightarrow$  2HIO<sub>4</sub> + 14HCI  
**S54.** 2F<sub>2</sub>(g) + 2H<sub>2</sub>O(I)  $\longrightarrow$  4H  $\stackrel{\oplus}{}$  (aq) + 4F  $\stackrel{\ominus}{}$  (aq) + O<sub>2</sub>

**S55.** 
$$I_2 + 10HNO_3(conc.) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

**S56.** 
$$4I^{\ominus}(aq) + 4H^{\oplus}(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(1)$$

**S57.** 
$$IO_3^{\ominus} + 5I^{\ominus} + 6H^{\oplus} \longrightarrow 3I_2 + 3H_2O$$

**\$58.** 
$$2XeF_2(s) + 2H_2O(1) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

**S59.** 
$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

**S60.** 
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

\$52. 
$$\text{Cl}_2(g) + \text{H}_2\text{O}(\hbar) \longrightarrow \text{HCl}(aq) + \text{HOCl}(aq)$$
\$53.  $I_2 + 8\text{H}_2\text{O} + 7\text{Cl}_2 \longrightarrow 2\text{HIO}_4 + 14\text{HCl}$ 
\$54.  $2\text{F}_2(g) + 2\text{H}_2\text{O}(\hbar) \longrightarrow 4\text{H}^\oplus(aq) + 4\text{F}^\ominus(aq) + \text{O}_2$ 
\$55.  $I_2 + 10\text{HNO}_3(\text{conc.}) \longrightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$ 
\$56.  $4\text{I}^\ominus(aq) + 4\text{H}^\oplus(aq) + \text{O}_2(g) \longrightarrow 2\text{I}_2(s) + 2\text{H}_2\text{O}(\hbar)$ 
\$57.  $I\text{O}_3^\ominus + 5\text{I}^\ominus + 6\text{H}^\oplus \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ 
\$58.  $2\text{XeF}_2(s) + 2\text{H}_2\text{O}(\hbar) \longrightarrow 2\text{Xe}(g) + 4\text{HF}(aq) + \text{O}_2(g)$ 
\$59.  $\text{XeF}_4 + \text{O}_2\text{F}_2 \longrightarrow \text{XeF}_6 + \text{O}_2$ 
\$60.  $\text{XeF}_6 + 3\text{H}_2\text{O} \longrightarrow \text{XeO}_3 + 6\text{HF}$ 
\$61.  $\text{Ag}^\oplus(aq) + \text{Cl}^\ominus(aq) \longrightarrow \text{AgCl}(s)$ 
 $\text{Colourless} \qquad \text{white ppt}$ 
 $\text{AgCl}(s) + 2\text{NH}_3[aq] \longrightarrow [\text{Ag}(\text{NH}_3)_2] \text{Cl}(aq)$ 

$$AgCI(s) + 2NH3[aq] \longrightarrow [Ag(NH3)2] CI(aq)$$

white ppt colourless

**S62.** 
$$P_4 + 3 \text{ NaOH} + 3H_2O \longrightarrow 3 \text{ NaH}_2PO_2$$

Sodiumhydrophosphite

Phosphine

S63. 
$$2KCIO_3 \xrightarrow{MnO_2} 2KCI + 3O_2$$

MnO<sub>2</sub> lower the B.P. of KClO<sub>3</sub>

**S64.** 
$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

**S65.** 
$$XeF_6 + NaF \longrightarrow Na [XeF_7]$$

**S66.** 
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^{\oplus} [SbF_6]^{\ominus}$$

**S67.** 
$$XeF_2 + PF_5 \longrightarrow [XeF]^{\oplus} [PF_6]^{\ominus}$$

**S68.** (a) 
$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_3$$

(b) 
$$XeF_4 + H_2O \xrightarrow{195 \text{ K}} XeOF_2 + 2HF$$

**S69.** (a) 
$$3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(b) 
$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

**S70.** (a) 
$$2NH_3 + NaOCI \longrightarrow N_2H_4 + NaCI + H_2O$$

(b) 
$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}$$
(excess) (deep blue colour)

**S71.** Hydrolysis of XeF<sub>4</sub> and XeF<sub>6</sub> with water produces XeO<sub>3</sub>.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$
  
 $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ 

Partial hydrolysis of XeF<sub>6</sub> gives XeOF<sub>4</sub>

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

**S72.** HCl can be oxidised to  $Cl_2$  by a number of oxidising agents such as  $MnO_2$ ,  $KMnO_4$ ,  $K_2Cr_2O_7$ , etc.

Reaction with MnO<sub>2</sub> is given below

$$MnO_2 + 4HCI \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

 $\mathrm{Cl_2}$  can be reduced to HCl by reaction of  $\mathrm{H_2}$  in presence of diffused sunlight.

$$H_2 + CI_2 \xrightarrow{\text{Diffused sunlight}} 2HCI$$

**S73.** Fluorine reacts vigorously with water giving oxygen and ozone.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$
  
 $3F_2 + 3H_2O \longrightarrow 6HF + O_3$ 

Chlorine reacts slowly with water giving oxygen.

$$2CI_2 + 2H_2O \longrightarrow 4HCI + O_2$$

**S74.** SOCl<sub>2</sub> is preferred because in this case both the other products formed are gases (SO<sub>2</sub> and HCl) and escape readily leaving behind pure chloroethane.

$$C_2H_5OH + SOCI_2 \xrightarrow{Pyridine} C_2H_5CI + SO_2 + HCI$$
 $C_2H_5OH + HCI \xrightarrow{Anh. ZnCI_2} C_2H_5CI + H_2O$ 

The second reaction is generally carried out in the presence of dehydrating agent such as anhydrous ZnCl<sub>2</sub>.

(b) Cl<sub>2</sub> being an oxidising agent oxidises NaI to I<sub>2</sub>.

$$Cl_2(g) + 2NaI(aq) \longrightarrow 2NaCl(aq) + I_2(s)$$

**\$76.** Zn with dil HNO<sub>3</sub> gives N<sub>2</sub>O (Nitrous oxide)

$$4 \text{ Zn} + 10 \text{HNO}_3 \text{ (dil)} \longrightarrow 4 \text{Zn} \text{ (NO}_3)_2 + 5 \text{H}_2 \text{O} + \text{N}_2 \text{O}$$

Zn with conc. HNO<sub>3</sub> gives NO<sub>2</sub> (nitrogen dioxide)

$$Zn + 4HNO_3(conc.) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

**S77.**  $F_2$  being a strong oxidising agent oxidises  $H_2O$  to  $O_2$  or  $O_3$ . The reactions are given as under:

$$2\mathsf{F}_{2}\left(g\right)+2\mathsf{H}_{2}\mathsf{O}\left(\mathit{I}\right)\longrightarrow 4\mathsf{H}^{\oplus}\left(aq\right)+4\mathsf{F}^{\ominus}\left(aq\right)+\mathsf{O}_{2}\left(g\right)$$

$$2\mathsf{F}_{2}\left(g\right)+3\mathsf{H}_{2}\mathsf{O}\left(\mathit{1}\right)\longrightarrow 6\mathsf{H}^{\oplus}\left(aq\right)+6\mathsf{F}^{\odot}\left(aq\right)+\mathsf{O}_{3}\left(g\right)$$

 ${\rm Cl}_2$ , on the other hand, reacts with  ${\rm H}_2{\rm O}$  to form hydrochloric acid and hypochlorous acid as per the following equation :

$$\text{Cl}_2\left(g\right) + \text{H}_2\text{O}\left(I\right) \longrightarrow \qquad \text{HCI}\left(aq\right) + \qquad \text{HOCI}\left(aq\right)$$
Hydrochloric acid  $\qquad \text{Hypochlorous acid}$ 

**S78.** (a) 
$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

(b) 
$$I_2 + 10HNO_3$$
 (conc.)  $\longrightarrow$   $2HIO_3 + 10NO_2 + 4H_2O_3$  lodic acid Nitrogen dioxide

(c) 
$$Cu + 4HNO_3$$
 (conc.)  $\longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$   
Copper nitrate

**\$79.** (a) 
$$2NaI(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + I_2(g)$$

(b) 
$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

(c) 
$$I_2 + 10HNO_3$$
 (conc.)  $\longrightarrow 2HIO_3 + 10 NO_2 + 4H_2O$ 

MG Pyt. Lid.

**\$80.** These xenon fluorides are obtained by direction reaction between Xe and F<sub>2</sub>, under different conditions as shown below:

$$Xe(g) + F_2 \xrightarrow{673 \text{ K, 1 bar}} (g) XeF_2(s)$$
(Excess)

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

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

**S81.** (a) 
$$NH_4NO_3$$
 (s)  $\xrightarrow{\text{Heat}} N_2O(g) + 2H_2O(l)$ 

(b) 
$$N_2O + 2NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH$$
  
(c)  $3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$   
(a)  $P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2 PO_2$   
Phosphine  
(b)  $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$   
(c)  $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$   
(d)  $POCI_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCI$   
(e)  $3HgCI_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCI$   
(a)  $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$   
(b)  $2XeF_2(s) + 2H_2O(I) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$ 

(c) 
$$3\text{CuO} + 2\text{NH}_3 \longrightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$$

**S82.** (a) 
$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2 PO_2$$
  
Phosphine

(b) 
$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

(c) 
$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

(d) 
$$POCI_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCI$$

(e) 
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCI$$

**S83.** (a) 
$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

(b) 
$$2XeF_2(s) + 2H_2O(1) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$$

(c) 
$$XeF_4 + PF_5 \longrightarrow [XeF_3]^{\oplus} [PF_6]^{\ominus}$$

(d) 
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^{\oplus} [SbF_6]^{\ominus}$$

(e) 
$$XeF_6 + NaF \longrightarrow Na[XeF_7]$$

**S84.** (a) Au + HNO<sub>3</sub> + 4HCI 
$$\longrightarrow$$
 H[AuCl<sub>4</sub>] + NO + 2H<sub>2</sub>O

(b) 
$$Pb(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$
  
(c)  $2Se_2Cl_2 \xrightarrow{\Delta} SeCl_4 + 3Se$ 

(c) 
$$2Se_2Cl_2 \xrightarrow{\Delta} SeCl_4 + 3Sec_4$$

(d) 
$$POCI_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCI$$

(e) 
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$



### SMART ACHIEVERS

**CHEMISTRY - XII** 

**Reasoning Ncert-Solution** 

Date: 22/10/2021

- **S1.** Due to larger size of I, overlapping between 5-I and P not possible i.e. steric repulsion of 5-lodine PI<sub>5</sub> cannot form while CI is comparable size with P and 5-CI can accommodate around phosphorus.
- **S2.** Because Br is bigger in size and 6-Bromine has steric repulsion around the phosphorous, hence  $[PBr_6]^{\odot}$  cannot exist while CI is comparable size with phosphorus and can accommodate around phosphorus hence  $[PCI_6]^{\odot}$  exist.
- **S3.** N atom cannot expand its covalence beyond 3 as it does not have vacant *d*-orbitals in its valence shell, whereas P has empty 3d orbital and can expand its covalency.

$$_{7}N : 1s^{2}, 2s^{2}2p_{x}^{1}2p_{y}^{1}2p_{z}^{1}$$

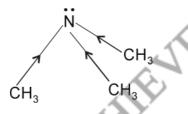
Maximum three unpaired electron

Ground state : 
$$_{15}P$$
 :  $1s^2$ ,  $2s^22p^6 3s^2 3p_x^{-1} 3p_y^{-1} 3p_z^{-1}$ 

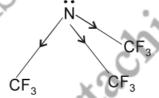
Excited state : 
$$1s^2$$
,  $2s^2 2p^6$ ,  $3s^1 3p_x^1 3p_y^1 3p_z^1 3d_{xy}^1$ 

Maximum five unpaired electron

**S4.** Because of different electronegativity of —CH<sub>3</sub> and —CF<sub>3</sub>. —CH<sub>3</sub> is Electropositive increase electrondensity on N is N(CH<sub>3</sub>)<sub>3</sub>. and increase lone pair donation power act as Lewis base while —CF<sub>3</sub> is electronegative decrease electrondensity on N in N(CF<sub>3</sub>)<sub>3</sub> and decrease lone pair donation tendency act as very-very weak Lewis base.

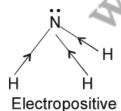


Electropositive



Electronegative

S5. NH<sub>3</sub> is a very strong base. This is because of the lone pair of electrons on N atom which it can donate. In NH<sub>3</sub> <u>H is electropositive</u> which increase electrodensity on N while in NF<sub>3</sub> <u>F is electronegative</u> which decrease electrondensity on nitrogen. On <u>increasing electrondensity</u> electron donating power increase.



F F

Electronegative

**S6.** Nitrogen tri flouride is not hydrolysed because neither nitrogen not flourine possess vacant *d*-orbitals to form extra bond with lone pair of electron on oxygen of water molecule. However, NCI<sub>3</sub> has vacant *d*-orbitals on CI atom and hydrolyses violently to show explosion.

NCI<sub>3</sub> + 3H<sub>2</sub>O 
$$\longrightarrow$$
 NH<sub>3</sub> + 3HOCI

**S7.** Ammonia is a good complexing agent because of the presence of lone pair of electrons on nitrogen. This lone pair can easily be donated to electron deficient compounds forming complexes. For example, it reacts with Cu<sup>2⊕</sup> ion to form a deep blue complex.

$$Cu^{2\oplus}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2\oplus}$$
Complex (deep blue

- **S8.** The pair of electrons in valence *s*-orbital is reluctant to take part in bond formation due to poor shielding effect of *d* & *f*-electrons in heavier elements. It is called inert pair effect due to which lower oxidation state becomes more stable than higher oxidation state in case of *p*-block elements.
- **S9.** On moving down the group, the stability of +5 oxidation state decreases while the stability of +3 oxidation state increases due to inert pair effect. Therefore, +5 oxidation state of Bi is less stable than +5 oxidation state of Sb. Thus, Bi(V) is a stronger oxidising agent than Sb(V).
- **\$10.** Ammonia exists as associated molecule due to its tendency to form hydrogen bonding. Therefore, it has high boiling point. Unlike NH<sub>3</sub>, phosphine (PH<sub>3</sub>) molecules are not associated through hydrogen bonding in liquid state. This is because of low electronegativity of P than N. As a result, the boiling point of PH<sub>3</sub> is lower than that of NH<sub>3</sub>.
- **S11.** Nitrogen has little tendency for catenation because <u>N N single bond is weak</u>. This is because nitrogen has small size and the <u>lone pairs on two nitrogen atoms repel each other</u>. On the other hand, phosphorus is comparatively large in size so that lone pairs on P atoms do not repel to the same extent. As a result P P bond is stronger than N N bond. Therefore, P has a tendency for catenation because of high bond enthalpy of P P bond.
- S12. In molecular nitrogen, there is a triple bond between two nitrogen atoms (N ≡ N) and it is non-polar in character. Due to the presence of a triple bond, it has very <u>high bond dissociation</u> <u>energy</u> and therefore, it does not react with other elements under normal conditions and is very unreactive. However, it may react at higher temperatures.
- **S13.** Because of its small size and high electronegativity <u>nitrogen forms  $p\pi-p\pi$  multiple bonds</u>. Therefore, <u>it exists as a diatomic molecule</u> having <u>a triple bond</u> between the two N-atoms. <u>Phosphorus</u>, on the other hand, has larger size and lower electronegativity and usually <u>does not form  $p\pi-p\pi$  multiple bonds</u> with itself. Instead it prefers to <u>form P P single bonds</u> and hence it exists as tetrahderal,  $P_A$  molecules.
- S14. As we move down the Group 15, the size of the element increases and, therefore, the length of the bond with hydrogen increases and its strength decreases. In other words, as we move down the Group, the bond with hydrogen can break more easily to evolve H<sub>2</sub> gas which acts as the reducing agent. Thus, Bi H bond is the weakest amongst the hydrides of elements of Group 15, and hence, BiH<sub>3</sub> is the strongest reducing agent.

- **S15.** NF<sub>3</sub> is an exothermic compound whereas NCl<sub>3</sub> is an endothermic compound because in case of NF<sub>3</sub>, N F bond strength is greater than the F F bond strength while in case of NCl<sub>3</sub>, N CI bond strength is lower than the CI CI bond strength. Thus the formation of NF<sub>3</sub> is spontaneous while energy has to be supplied during the formation of NCl<sub>3</sub>.
- S16.  $H_3PO_3 \text{ an oxoacid of P} \begin{pmatrix} O \\ || \\ HO P OH \\ || \\ H \end{pmatrix} \text{ and is Bronsted dibasic acid as it acts as protons}$

donor.

$$H_3PO_3 + H_2O \longrightarrow H_2PO_3^{\odot} + H_3O^{\oplus}$$

$${\rm H_3BO_3}\begin{pmatrix} {\rm OH} \\ {\rm HO-B-OH} \end{pmatrix} {\rm and\ Lewis\ mono\ basic\ acid\ as\ it\ acts\ electron\ pair\ acceptor\ because}$$

Boron have only six electrons (incomplete octet)

$$B(OH)_3 + H_2O \longrightarrow B(OH)_4^{\odot} + H^{\oplus}$$

**\$17.** Nitric oxide in in all has 15 electrons in its molecule i.e. it possesses at least one odd electron which is responsible for paramagnetic nature of NO.

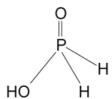
unpaired electron 
$$\longrightarrow \cdot \ddot{N} = O$$

**S18.** PCI<sub>5</sub> has triangular bipyrimidal structure two bonds are in axial position and three bonds are in equatorial position. Axial bonds are longer than equatorial due to greater bond pair electrons repulsion.

- **S19.** Both N in NH<sub>3</sub> and Bi in BiH<sub>3</sub> have a lone pair of electrons on the central atom and hence should behave as Lewis bases. But NH<sub>3</sub> is much more basic than BiH<sub>3</sub>. This can be explained on the basis of electron density on the central atom. Atomic size of N (70 pm) is much smaller than that of Bi (148 pm), therefore, electron density on the N-atom is much higher than that on Bi-atom. Consequently, the tendency of N in NH<sub>3</sub> to denote its pair of electrons is much higher than that of Bi in BH<sub>3</sub>. Thus, NH<sub>3</sub> is much more basic than BiH<sub>3</sub>.
- **S20.** The elements of group 15 have five electrons in their respective valence shells. It is difficult to lose three electrons to form  $E^{3\oplus}$ . It is even more difficult to lose all the five valence electrons (two s- and three p-) to form  $E^{5\oplus}$  ions. Therefore, higher elements have no tendency to form ionic compounds. They prefer to form covalent compounds by sharing of electrons.

Thus, elements in the +5 oxidation state are more covalent than in the +3 oxidation state.

- **S21.** NH<sub>3</sub> is highly polar compound due to higher electronegative difference between N and H and can break H-bonding of water and can make H-bonding with water while PH<sub>3</sub> is very weak polar and cannot break and make H-bonding with water.
- **S22.**  $p\pi$ - $p\pi$  overlap
- **S23.**  $H_3PO_2$  has one P = O, one P OH and two P H bonds as. Phosphorous has +1 oxidation state.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

**S24.** H<sub>3</sub>PO<sub>3</sub> has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.

$$H_3PO_3 \iff HPO_3^{2@} + 2H^{6}$$

S25. N = 0 has one unpaired electron, therefore, it is unstable and forms dimer, i.e.,  $N_2O_4$  whose

structure is 
$$0 N - N O$$

**S26.**  $NO_2^{\odot}$  on reaction with KI liberates  $I_2$  which turns starch paper blue.

$$NO_2^{\odot}(aq) + KI \longrightarrow I_2$$

 $NO_3^{\circ}$  can be identified by ring test.

- **S27.** The impurity of P<sub>2</sub>H<sub>4</sub>, the liquid hydride present in phosphine catches fire as soon as it comes in contact with air and forms vortex rings of smoke.
- **S28.** [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2</sup>
- **\$29.** Aqua-regia is mixture of 1 part conc. HNO<sub>3</sub> and 3 part conc. HCl. The mixture liberate nascent chlorine which dissolves noble metals.

- **\$30.** Phosphorus allotropes Red, Black and White. White phosphorus is most reactive.
- **S31.** The inability of nitrogen atom to unpair and promote its 2*s* electron results in the pentapositive state of nitrogen being less stable than tripositive. Thus HNO<sub>3</sub> where nitrogen is in +5 oxidation state is an oxidizing agent. On the other hand P has *d*-orbitals to expand its octet and also shows no inert pair effect, is quite stable in V state. Thus H<sub>3</sub>PO<sub>4</sub> in which P is in +5 oxidation state is not oxidizing.
- **S32.** X-ray studies have shown that solid  $PCI_5$  is an ionic compound composed of  $[PCI_4]^{\oplus}$   $[PCI_6]^{\odot}$ ; the cation being tetrahedral and anion being octahedral.
- **S33.** Red phosphorus exists as chains of P<sub>4</sub> tetrahedron linked together, whereas in yellow phosphorus individual P<sub>4</sub> molecules are held together by weak van der Waals forces.
- **S34.** In H<sub>3</sub>PO<sub>3</sub>, there is  $p\pi d\pi$  bond whereas in HNO<sub>3</sub> there is  $p\pi p\pi$  bond.
- **S35.** SbCl<sub>5</sub> is more covalent than SbCl<sub>3</sub>. on increasing oxidation state covalent character increases.
- **\$36.** Within its group, nitrogen shows anomalous behaviour due to:
  - (a) Smallest size
- (b) Highest electronegativity
- (c) Non-availability of d-orbitals
- **S37.** Noble gases are monoatomic gases and are held together by weak van der Waal's forces (dispersion forces). Therefore, they are liquefied at very low temperatures. Hence they have low boiling points.
- **S38.** Due to larger size and presence *d*-orbital of phosphorus,  $p\pi p\pi$  bonds cannot formed.
- **S39.** A mixture of  $CaC_2$  and  $Ca_3P_2$  filled in a container having small holes in it is thrown in sea or river. The water coming through holes gives.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
  
 $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$  (A little  $P_2H_4$ )

 $P_2H_4$  catches fire and  $C_2H_2$  burns with luminous flame which serves as signal to approaching boot or ship.

**S40.** (i) N<sub>2</sub> O

(ii) NO<sub>2</sub>

- (I) N<sub>2</sub> O . T
- (iii) HNO<sub>3</sub> : + 5
- (iv)  $NH_3$  : -3
- **S41.** P-atom can not form  $p\pi p\pi$  bond due to large size and presence of orbital with oxygen while N can form  $p\pi p\pi$  bonding with oxygen due to smaller size and absence of *d*-orbital.
- **S42.**  $CIO^{\odot}$  has 17 + 8 + 1 = 26 electrons. A neutral molecule with 26 electrons is  $OF_2$  (8 + 2 × 9 = 26 electrons).  $OF_2$  is a Lewis base due to the presence of two lone pairs of electrons.

**S43.** PH<sub>3</sub> reacts with acids like HI to form phosphonium iodide, PH<sub>4</sub>I.

This shows that PH<sub>3</sub> is basic in nature. This basic nature of PH<sub>3</sub> is due to presence of lone pair on phosphorus atom and therefore, it acts as a Lewis base.

**\$44.** [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub>

Pentaaquanitrosyli iron (II) sulphate.

**S45.** Oxygen is smaller in size and has ability to form  $P\pi - P\pi$  multiple bond, and satisfy its octate forming (O = O) O<sub>2</sub> molecule.

While S is bigger in size and has not ability to form  $P\pi - P\pi$  multiple bond, satisfy its octate by forming (Puckered shape) S<sub>8</sub> molecule.

- **S46.** Oxygen Floride OF<sub>2</sub> oxygen has +2 oxidation state. Hydrogen peroxide H<sub>2</sub>O<sub>2</sub> oxygen has –1 oxidation state.
- **S47.** In the vapour state sulphur exists as  $S_2$  and not as  $S_8$  the electronic configuration of  $S_2$  has two unpaired electron in antibonding  $\pi^*$  orbitals, due to which it paramagnetic.
- **S48.** Due to greater electronegativity of O than S, H<sub>2</sub>O undergoes intermolecular H–bonding. As a result, H<sub>2</sub>O exists as an associated molecule. And, larger amount of energy is required to break these H-bonds. Therefore, H<sub>2</sub>O is a liquid at room temperature.

While,  $H_2S$  does not undergo H-bonding as the electronegativity difference between H and S is not appreciable. It exists as discrete molecules which are held together by weak van der Waals' forces of attraction. To break these forces of attraction, on a small amount of energy is required. Therefore,  $H_2S$  is a gas at room temperature.

**S49.** Due to smaller size, absence of empty *d*-orbital and high electronegativity F show the anomalous behaviour.

### **Examples:**

- (1) Florine only show 1 oxidation state while other halogen show –1 to +7 oxidation states.
- (2) Due to smaller size higher electron density F F has higher repulsion and its bond dissociation energy is less than CI CI and Br Br.
- **\$50.** F is highly electronegative hence F unpair the paired electron of sulphate to form SF<sub>6</sub> while H is electropositive in respect to sulphur and it cannot unpair to paired electron of sulphur to expained S oxidation state.

- **S51.** In the structure of  $SO_2$ , S is  $sp^2$ -hydridised. Two of the three  $sp^2$ -orbitals form two  $\sigma$ -bonds while the third contains the lone pair of electrons. S is now left with one half-filled p-orbital and one half-filled d-orbitals. They form one  $p\pi p\pi$  and one  $p\pi d\pi$  double bond with oxygen atom. Thus,  $SO_2$  has bent structure with OSO bond angle of 119.5°. Due to resonance, the two  $\pi$ -bonds are equal.
- **S52.** O<sub>3</sub> is an endothermic compound, i.e., it possesses greater internal energy than oxygen. On heating, it readily decomposes to give dioxygen and nascent oxygen.

$$O_3 \xrightarrow{Heat} O_2 + O$$
 (nascent oxygen)

Since nascent oxygen is very reactive, therefore, O<sub>3</sub> acts as a powerful oxidising agent.

- **S53.** Oxygen difluoride OF<sub>2</sub>
- **S54.** H<sub>2</sub>O, because Oxygen being electronegative than sulphur, higher polarity is developed on O and H atoms leading to a higher H—O—H bond angle.
- **S55.** Due to sterically protection of six F atom, which do not allow to water molecules to attack on sulphure and due to steric repulsion of F at SF<sub>6</sub> thermodynamically unstable.
- **S56.** In water, there is lone pair of electron on oxygen whereas in  $H_2SO_4$  there is one  $p\pi p\pi$  bond and another  $p\pi d\pi$  bond.
- **S57.** IO<sub>4</sub> is the strongest oxidising agent.
- **S58.**  $OF_2$  and CIF are isoelectronic with  $CIO^{\ominus}$ .
- **S59.** Due to higher electron-density on F, the bond length of F–F increase due to electron-electron repulsion and B.d.E. decrease while CI is bigger in size and has less electron-density and has not electron-electron repulsion in  $\text{CI}_2$  and bond length is comparatively shorter than  $\text{F}_2$ .
- **S60.** Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and reduce.

$$X + M \longrightarrow M^{\oplus}X^{\odot}$$

Hence, halogens act as strong oxidising agents.

- **S61.** In HCIO<sub>4</sub> due to 'greater electronegativity of CI and higher oxidation state +7 make it more acidic than H<sub>2</sub>SO<sub>4</sub>,' respectively S is less electronegativity and less oxidation state +6.
- **S62.** Because up to down atomic size of halogen increase and overlapping between H and X decrease i.e., bond length of H X increase and Bond-dissociation energy decrease which increase the degree of dissociation of HX up to down

**S63.** This is due to limitation of having only one oxidation state that it forms only one oxo acid. Chlorine, bromine and iodine form four series of oxoacids of the general formula HOX, HOXO, HOXO<sub>2</sub> and HOXO<sub>3</sub> in which the oxidation states of halogen (X = Cl, Br or I) is +1, +3, +5 and +7, respectively. However, due to high electronegativity and small size, flourine forms only HOF with oxidation state +1.

- **S64.** IC/is more reactive than I<sub>2</sub> because <u>I C/bond is weaker than I I bond</u>. Abond between two different atoms is always weaker than that between identical atoms. Consequently, IC/breaks easily to form halogen atoms which readily bring about the reactions.
- **S65.** CIO<sub>2</sub> and Cl<sub>2</sub>O are used for bleaching paper pulp.
- **\$66.** Halogens are F, CI, Br and I. They are called halogens because halogens means salt producers, i.e., they form salts.
- **\$67.** CF<sub>2</sub>Cl<sub>2</sub>, dichlorodifluoromethane is called freon.
- **S68.** HClO<sub>4</sub> is a compound in which Cl is in +7 oxidation state.
- **S69.** HF is weakest acid among hydrohalo-acid because of high bond dissociation energy due to small bond length.
- **\$70.** (i) As a bleaching agent for paper pulp and textiles.
  - (ii) Used in water treatment.
- **S71.** HF has maximum ionic character because of greater difference in electronegativity.
- **S72.** Fluorine shows only –1 oxidation state because of it is the most electronegative element.
- **\$73.** In noble gases, we can measure only van der Waals radii which are larger than covalent radii.
- **\$74.** Xe has lower ionization energy than Kr, therefore, Xe outermost electron excited with F and O and form compound.
- **S75.** No the products of hydrolysis are XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub> where oxidation state of Xe in reactants and product remain same (+6).
- **\$76.** Oxygen shows maximum covalency equal to 2 due to presence of 2 unpaired electrons where as 'S' exhibits maximum covalancy upto 6 due to presence of empty *d*-orbital.
- **S77.**  $XeF_2$  is prepared in Lab in Nickel tube at 673 and 1 bar pressure

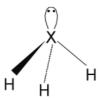
$$Xe + F_2 \xrightarrow{\text{Nickel tube}} XeF_2$$

 $\mathrm{XeF_4}$  is prepared in Lab in nickel tube at 673 K and 7 bar pressure.

$$Xe + 2F_2 \xrightarrow{\text{Nickel tube}} XeF_4$$

- **S78.** Xe is noble gas, its ionization energy is much higher. F is highly electronegativity element it can unpair the paired electron of Xe to form covalence bond.
- **S79.** Because Xe is a noble gas which is stable, and high ionization energy. F and O are most electronegative element which can unpair Xe paired electrons to form covalent bond.

**S80.** In all the hydrides of Group 15 elements, the central atom is  $sp^3$ -hybridised. Three of the four  $sp^3$ -orbitals form three X — H (X stands for element of Group 15),  $\sigma$ -bonds while the fourth contains the lone pair of electrons as shown in below :



Since the lone pair-bond pair repulsions are stronger than the bond pair-bond pair repulsions, therefore, the bond angle decreases from 109°28′ to 107.8° in NH<sub>3</sub>. As we move from N to P to As to Sb, the atomic size goes on increasing. As a result, bond pairs of electrons, lie away and away from the central atom. In other words, force of repulsion between the adjacent bond pairs goes on decreasing and, consequently, the bond angles keep on decreasing from NH<sub>3</sub> to SbH<sub>3</sub>.

- **S81.** (a) F is highly electronegativity element and it is strong oxidising agent than CI due to which N F bond become stronger by releasing high amount of energy and NF<sub>3</sub> is exothermic.
  - (b) SF₄ has see-saw structure and two S F bonds are in different plane with two other S F bonds are in different plane with two other S F bonds, and have different electronic repulsion depend on bond angles, *i.e.*, bond length of two bonds are not same with two other bonds in other plane.
- **S82.** (a) The structures of  $H_3PO_2$ ,  $H_3PO_3$  and  $H_3PO_4$  are:

$$\begin{array}{c|ccccc} O & O & O & O \\ \parallel & \parallel & \parallel & \parallel \\ P & P & P & P \\ H & OH & HO & HO & HO \\ \\ Hypophosphorous & Phosphorous & Phosphoric \\ acid(H_3PO_2) & acid(H_3PO_3) & acid(H_3PO_4) \\ \end{array}$$

Due to the presence of P — H bonds, both  $H_3PO_2$  and  $H_3PO_3$  act as reducing agents. On the other hand,  $H_3PO_4$  does not have any P — H bond and hence it does not act as a reducing agent.

(b) The basic character of  $SOCl_2$  is due to the presence of lone pair of electrons on S atom, like ammonia. It has a pyramidal structure involving  $sp^3$  hybridisation with a lone pair of electrons as:



So, Lewis basic character is due to the presence of a lone pair. In addition, SOCI<sub>2</sub> has also empty d-orbitals which can be used to accept electron pairs and hence it behaves as a Lewis acid.

**S83.** Due to small size and high electronegativity, oxygen atom forms  $p\pi-p\pi$  multiple bonds with another oxygen atom. As a result, oxygen exists as diatomic (O<sub>2</sub>) molecules. These molecules are held together by weak van der Waals' forces of attraction. Therefore, O<sub>2</sub> is a gas at room temperature.

Sulphur, on the other hand, because of its bigger size and lower electronegativity, does not form  $p\pi-p\pi$  multiple bonds. Instead, it forms S — S single bonds. Further because of stronger S — S than O — O single bonds, sulphur has a much greater tendency for catenation than oxygen.

Consequently, sulphur forms octaatomic  $(S_8)$  molecules having eight-membered puckered ring structure. Because of bigger size, the forces of attraction holding the  $S_8$  molecules together are much stronger. Consequently., sulphur is a solid at room temperature.

- **S84.** (a) In OF<sub>2</sub> oxygen is electropositive and Flourine is electronegative. According to IUPAC system electronegative written in right in formate of 'id'.
  - (b) Because  $I_2$  is nonpolar and insolute in water and lodine react with KI to form soluble complex.  $KI_3$ .

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

- **S85.** (a) Because interhalogens compounds (ICI, IBr, BrF<sub>3</sub>) bonds are weaker due to different atomic size of halogens while halogens (CI<sub>2</sub>, Br<sub>2</sub>, F<sub>2</sub>) having same atomic size of halogen bonds are respectively stronger.
  - (b) Cl<sub>2</sub> bleaches by oxidation while SO<sub>2</sub> does it by reduction the reduced product gets oxidized again and the colour returns.



## SMART ACHIE

**CHEMISTRY - XII** 

Ascending and Descending NCERT

Date: 22/10/2021

Pyt. Lid

- Q1. Arrange the following according to acidic strength of pentoxides: As<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>5</sub>, Sb<sub>2</sub>O<sub>5</sub>
- Q2. Arrange the following according to Acidic strength of trioxides:  $P_2O_3$ ,  $N_2O_3$ ,  $As_2O_3$
- Q3. Arrange the following according to thermal stability: NH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub>
- Q4. Arrange the following according to bond angle: AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub>, NH<sub>3</sub>, PH<sub>3</sub>
- Q5. Arrange the following according to basic nature: AsH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub>, NH<sub>3</sub>, PH<sub>3</sub>
- Q6. Arrange the following according to oxydising ability of pentoxides:  $Sb_2O_5$ ,  $N_2O_5$ ,  $P_2O_5$ ,  $As_2O_5$ ,  $Bi_2O_5$
- Q7. Arrange the following according to acidic strength of oxides of nitrogen:  $N_2O_4$ ,  $N_2O_5$ ,  $N_2O$ , NO,  $N_2O_3$
- Vers.I Q8. Arrange the following according to ease of hydrolysis of trichlorides: PCI<sub>3</sub>, AsCI<sub>3</sub>, SbCI<sub>3</sub>, NCI<sub>3</sub>, BiCI<sub>3</sub>
- Q9. Arrange the following according to Lewis base strength: AsCl<sub>3</sub>, SbCl<sub>3</sub>, NF<sub>3</sub>, PCl<sub>3</sub>
- Q10. Arrange the following according to stability of trihalides of nitrogen: NBr<sub>3</sub>, NF<sub>3</sub>, NCl<sub>3</sub>
- Q11. Arrange the following according to covalent nature of hydrides: AsH<sub>3</sub>, SbH<sub>3</sub>, NH<sub>3</sub>, PH<sub>3</sub>, BiH<sub>3</sub>
- Q12. Arrange the following according to poisonous nature: SbH<sub>3</sub>, NH<sub>3</sub>, AsH<sub>3</sub>, BiH<sub>3</sub>, PH<sub>3</sub>
- Q13. Arrange the following according to reducing power: NH<sub>3</sub>, AsH<sub>3</sub>, BiH<sub>3</sub>, PH<sub>3</sub>, SbH<sub>3</sub>
- Q14. Arrange the following according to Lewis acid strength of trihalides of P, As and Sb: PCl<sub>3</sub>, SbCl<sub>3</sub>, AsCl<sub>3</sub>
- Q15. Arrange the following according to volatility of hydrides: H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>O, H<sub>2</sub>Te
- Q16. Arrange the following according to melting and boiling point of hydrides: H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Te, H<sub>2</sub>Se

- Q17. Arrange the following according to bond angle, among the halides of phosphorus:  $PCI_3$ ,  $PBr_3$ ,  $PF_3$ ,  $PI_3$
- Q18. Arrange the following according to Lewis acid strength among phosphorus trihalides:  $PBr_3$ ,  $PI_3$ ,  $PF_3$ ,  $PCI_3$
- Q19. Arrange the following according to acidic character of oxide of sulphur: SO<sub>2</sub>, SO<sub>3</sub>, SO
- Q20. Arrange the following according to acidic character of oxides: TeO<sub>2</sub>, PoO<sub>2</sub>, SO<sub>2</sub>, SeO<sub>2</sub>
- Q21. Arrange the following according to ease of hydrolysis of hexahalides:  ${\sf TeF}_6,\,{\sf SF}_6,\,{\sf SeF}_6$
- Q22. Arrange the following according to bond angle and dipole moment of hydrides:  $H_2Se$ ,  $H_2Te$ ,  $H_2O$ ,  $H_2S$
- Q23. Arrange the following according to covalent character of hydrides: H<sub>2</sub>Se, H<sub>2</sub>Te, H<sub>2</sub>O, H<sub>2</sub>S
- Q24. Arrange the following according to reduding nature of hydrides: H<sub>2</sub>Se, H<sub>2</sub>Te, H<sub>2</sub>S
- Q25. Arrange the following according to thermal stability of hydrides: H<sub>2</sub>Se, H<sub>2</sub>Te, H<sub>2</sub>O, H<sub>2</sub>S
- Q26. Arrange the following according to enthalpy of hydration of  $X^{\odot}$  ion: Br $^{\odot}$ , I $^{\odot}$ , F $^{\odot}$ , CI $^{\odot}$
- Q27. Arrange the following according to oxidising power:  $\mathrm{Br_2},\ \mathrm{I_2},\ \mathrm{F_2},\ \mathrm{CI_2}$
- Q28. Arrange the following according to solubility of halogen in water:  $CI_2$ ,  $Br_2$ ,  $F_2$ ,  $I_2$
- Q29. Arrange the following according to bond length in  $X_2$  molecule:  $Br_2$ ,  $I_2$ ,  $F_2$ ,  $CI_2$
- Q30. Arrange the following according to bond energy of halogens:  $Br_2$ ,  $F_2$ ,  $I_2$ ,  $CI_2$
- Q31. Arrange the following according to stability of dioxides: SeO<sub>2</sub>, PoO<sub>2</sub>, SO<sub>2</sub>, TeO<sub>2</sub>
- Q32. Arrange the following according to reducing character of X  $^{\odot}$  ion: CI  $^{\odot},$  F  $^{\odot}$  I  $^{\odot},$  Br  $^{\odot}$
- Q33. Arrange the following according to ionic character of M X bond in halides: M Br, M I, M F, M CI

- Q34. Arrange the following according to reactivity of halogens: CI, F, Br, I
- Q35. Arrange the following according to boiling point or volatility of hydrides: HI, HF, HCI, HBr
- Q36. Arrange the following according to reducing property of hydrogen halides: HF, HBr, HI, HCI
- Q37. Arrange the following according to conjugate base strength of halogen acids:  $F^{\ominus}$ ,  $I^{\ominus}$ ,  $Br^{\ominus}$ ,  $CI^{\ominus}$
- Q38. Arrange the following according to acidic strength of halogen acids: HCI, HF, HI, HBr
- Q39. Arrange the following according to thermal stability of hydrides: HCI, HBr, HI, HF
- Q40. Arrange the following according to dipole moment of hydrogen halides: HBr, HI, HF, HCI
- Q41. Arrange the following according to oxidising power of oxides of chlorine:  $Cl_2O_7$ ,  $Cl_2O_6$ ,  $Cl_2O$ ,  $ClO_2$
- Q42. Arrange the following according to thermal stability of oxyacids of chlorine: HCIO<sub>4</sub>, HCIO<sub>2</sub>, HCIO, HCIO<sub>3</sub>
- Q43. Arrange the following according to oxidising power of oxyacids of chlorine: HCIO<sub>2</sub>, HCIO<sub>4</sub>, HCIO<sub>3</sub>, HCIO
- Q44. Arrange the following according to strength of conjugate bases of oxyacids of chlorine:  $CIO^{\odot},\ CIO^{\odot}_4,\ CIO^{\odot}_2,\ CIO^{\odot}_3$
- Q45. Arrange the following according to acidic character of oxyacids of chlorine:  ${\rm HCIO,\ HCIO_3,\ HCIO_4,\ HCIO}$
- Q46. Arrange the following according to stability of anions of oxyacids of chlorine:  $CIO_4^{\odot},\ CIO_2^{\odot}\ CIO_3^{\odot},\ CIO^{\odot}$
- Q47. Arrange the following according to given trend:
  - (a) HCIO<sub>2</sub>, HCIO<sub>3</sub>, HCIO<sub>4</sub>, HCIO acidic character
  - (b) HCIO<sub>2</sub>, HCIO<sub>4</sub>, HCIO<sub>3</sub>, HCIO oxidising power
- Q48. Arrange the following according to given trend:
  - (a) TeO,, PoO,, SO,, SeO, acidic character
  - (b) Br<sub>2</sub>, F<sub>2</sub>, I<sub>2</sub>, Cl<sub>2</sub> bond energy
- Q49. Arrange the following according to given trend:
  - (a) HCIO<sub>4</sub>, HCIO<sub>2</sub>, HCIO, HCIO<sub>3</sub> thermal stability
  - (b) CIO<sup>⋄</sup><sub>4</sub>, CIO<sup>⋄</sup><sub>2</sub> CIO<sup>⋄</sup><sub>3</sub>, CIO<sup>⋄</sup> stability of anions

- Q50. Arrange the following according to given trend
  - (a) H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>5</sub>, H<sub>2</sub>SO<sub>5</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>3</sub> decreasing acidic character.
  - (b) HCIO, HCIO<sub>2</sub>, HCIO<sub>3</sub>, HCIO<sub>4</sub> decreasing acidic character
  - (c) NH<sub>3</sub>, PH<sub>3</sub>, ASH<sub>3</sub>, SbH<sub>3</sub>, BiH<sub>3</sub> decreasing basic character.
- Q51. Arrange the following according to given trend
  - (a) H<sub>2</sub>Se, H<sub>2</sub>Te, H<sub>2</sub>O, H<sub>2</sub>S thermal stability of hydrides
  - (b) H,Se, H,Te, H,O, H,S bond angle
  - (c) Br<sup>o</sup>, I<sup>o</sup>, F<sup>o</sup>, CI<sup>o</sup> enthalpy of hydration of X<sup>o</sup> ion
- Q52. Arrange the following according to given trend
  - (a) M Br, M I, M F, M Cl ionic character of M X bond
  - (b)  $Cl_2O_7$ ,  $Cl_2O_6$ ,  $Cl_2O$ ,  $ClO_2$  oxidising power of oxides
  - (c) CIO<sup>⊙</sup>, CIO<sup>⊙</sup>, CIO<sup>⊙</sup>, CIO<sup>⊙</sup> basic strength of conjugate base
- Q53. Arrange the following according to given trend:
  - (a) HCI, HBr, HI, HF thermal stability
- (b) HCI, HF, HI, HBr acidic strength
- A A, HCI (c) F<sup>o</sup>, I<sup>o</sup>, Br<sup>o</sup>, Cl<sup>o</sup> conjugate base strength
  - (d) HF, HBr, HI, HCI reducing property
- WWW.sinartachilevers.in (e) HBr, HI, HF, HCI dipole moment

**CHEMISTRY - XII** 

**Ascending and Descending NCERT-Solution** 

SIRARITING PVK. Lita.

Date: 22/10/2021

**S1.** 
$$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$$

**S2.** 
$$N_2O_3 > P_2O_3 > As_2O_3$$

**S3.** 
$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

**S4.** 
$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

**S5.** 
$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

**S6.** 
$$N_2O_5 > Bi_2O_5 > Sb_2O_5 > As_2O_5 > P_2O_5$$

**S7.** 
$$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$$

**S8.** 
$$NCI_3 > PCI_3 > AsCI_3 > SbCI_3 > BiCI_3$$

**S9.** 
$$NF_3 > PCI_3 > AsCI_3 > SbCI_3$$

**\$10.** 
$$NF_3 > NCI_3 > NBr_3$$

**S12.** 
$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

**S13.** 
$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

**S14.** 
$$PCl_3 > AsCl_3 > SbCl_3$$

**S16.** 
$$H_2O > H_2Te > H_2Se > H_2S$$

**S19.** 
$$SO < SO_2 < SO_3$$

**\$20.** 
$$SO_2 > SeO_2 > TeO_2 > PoO_2$$

**S21.** 
$$SF_6 > SeF_6 > TeF_6$$

**S22.** 
$$H_2O > H_2S > H_2Se > H_2Te$$

- **S23.**  $H_2O > H_2S > H_2Se > H_2Te$
- **\$24.**  $H_2S < H_2Se < H_2Te$
- **S25.**  $H_2O > H_2S > H_2Se > H_2Te$
- **S26.**  $F^{\ominus} > CI^{\ominus} > Br^{\ominus} > I^{\ominus}$
- **S27.**  $F_2 > Cl_2 > Br_2 > l_2$
- **S28.**  $F_2 > Cl_2 > Br_2 > l_2$
- **S29.**  $F_2 < Cl_2 < Br_2 < l_2$
- **S30.**  $Cl_2 > Br_2 > F_2 > I_2$
- **S31.**  $SO_2 > TeO_2 > SeO_2 > PoO_2$
- **S32.**  $I^{\odot} > Br^{\odot} > CI^{\odot} > F^{\odot}$
- **S33.** M F > M CI > M Br > M I
- **S34.** F > CI > Br > I
- **\$35.** HCI < HBr < HI < HF
- S36. HF < HCI < HBr < HI
- **S37.**  $I^{\odot}$  < Br $^{\odot}$  < Cl $^{\odot}$  < F $^{\odot}$
- **\$38.** HI > HBr > HCI > HF
- **\$39.** HF > HCI > HBr > HI
- S40. HF > HCI > HBr > HI
- JEVERS IFARMING RVI. TRA **S41.**  $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$  (decreasing order)
- **S42.**  $HCIO < HCIO_2 < HCIO_3 < HCIO_4$
- $\mathbf{S43.}\ \mathsf{HCIO} > \mathsf{HCIO}_2 > \mathsf{HCIO}_3 > \mathsf{HCIO}_4$
- **S44.**  $CIO^{\odot} > CIO_2^{\odot} > CIO_3^{\odot} > CIO_4^{\odot}$
- **S45.**  $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$
- **S46.**  $CIO^{\odot} < CIO_2^{\odot} < CIO_3^{\odot} < CIO_4^{\odot}$
- **S47.** (a)  $HCIO_4 > HCIO_3 > HCIO_2 > HCIO$ 
  - HCIO > HCIO<sub>2</sub> > HCIO<sub>3</sub> > HCIO<sub>4</sub>

- **\$48.** (a) SO<sub>2</sub> > SeO<sub>2</sub> > TeO<sub>2</sub> > PoO<sub>3</sub>
  - (b)  $Cl_2 > Br_2 > F_2 > I_2$
- **S49.** (a) HCIO < HCIO<sub>2</sub> < HCIO<sub>3</sub> < HCIO<sub>4</sub>
  - (b)  $CIO^{\odot} < CIO_{2}^{\odot} < CIO_{3}^{\odot} < CIO_{4}^{\odot}$
- **\$50.** (a)  $H_2SO_4 > H_2SO_3 > H_2S_2O_3 > H_2SO_5$ 
  - (b) HCIO<sub>4</sub> > HCIO<sub>3</sub> > HCIO<sub>2</sub> > HCIO
  - (c)  $NH_3 > PH_3 > ASH_3 > SbH_3 > BiH_3$
- **\$51.** (a)  $H_2O > H_2S > H_2Se > H_2Te$ 
  - (b)  $H_2O > H_2S > H_2Se > H_2Te$
  - (c) F > Cl > Br > l
- **S52.** (a) M F > M CI > M Br > M I
- SMARTA CHILIFATE SIE ARRIVED THE STATE OF TH (b)  $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$  (decreasing order)
  - (c)  $CIO > CIO_2^{\odot} > CIO_3^{\odot} > CIO_4^{\odot}$ WWW.SIRARIACHIEVERS.IR
- **\$53.** (a) HF > HCI > HBr > HI
  - (b) HI > HBr > HCl > HF
  - (c) I < Br < Cl < F
  - (d) HF < HCl < HBr < HI
  - (e) HF > HCI > HBr > HI

**CHEMISTRY - XII** 

**Lab of Industrial Preparation NCERT** 

Date: 23/10/2021

- Q1. How HNO<sub>3</sub> is prepared in the laboratory?
- Q2. Explain the Industrial preparation of ammonia (Haber's process).
- Q3. Explain Ostwald's process to prepare HNO<sub>3</sub>.
- Q4. Describe the manufacture of H<sub>2</sub>SO<sub>4</sub> by contact process.



### **SMART ACHIEVERS**

Nurturing Success...

**CHEMISTRY - XII** 

**Lab of Industrial Preparation NCERT-Solution** 

Date: 23/10/2021

**S1.** Laboratory Preparation: Nitric acid is prepared by heating metallic nitrate (usually solid sodium or potassium nitrate) with concentrated sulphuric acid in a glass retort. The vapours evolved are cooled in a receiver when a yellow liquid is obtained.

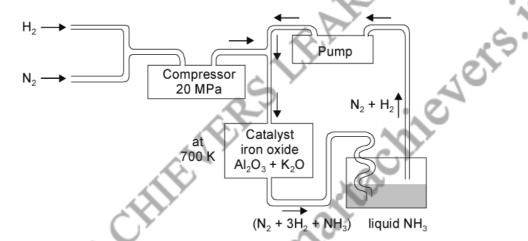
$$\mathsf{KNO}_3(s) + \mathsf{H}_2\mathsf{SO}_4 \longrightarrow \mathsf{KHSO}_4(s) + \mathsf{HNO}_3(g)$$
  
Potassium Sulphuric Potassium   
Nitrate Acid Bisulphate

**S2.** Industrial preparation of ammonia (Haber's process). Haber's process involves the direct combination of dihydrogen with dinitrogen to form ammonia as follows:

$$N_2(g) + 3H_2(g) \implies 2NH_3(g) : \Delta H = -46.1 \text{ kJ/mol}.$$

This reaction is reversible, exothermic and is accompanied by decrease in volume. Therefore, the most favourable conditions for maximum yield according to Le Chatelier's principle are:

- (a) Low temperature: The optimum temperature has been found to be nearly 700 K.
- (b) High pressure: The optimum pressure is nearly 200 atm.
- (c) Catalyst: Finely divided iron with molybdenum as promoter is used as catalyst. The flow chart for the production of ammonia is shown.



**S3.** Ostwald's Process: In this process, conversion of ammonia to nitric acid is done through the following steps.

**Step 1:** Oxidation of ammonia to nitric oxide. Ammonia is oxidized by air in the presence of Pt catalyst to give nitric oxide.

$$4NH_3(g) + 5O_2(g) \stackrel{\text{Pt. Rh guauge catalyst (9 : 1)}}{\underbrace{500 \text{ K. 9 bar}}} 4NO(g) + 6H_2O(g) : ΔH = -90 \text{ kJ}$$

**Step 2:** Oxidation of NO to NO<sub>2</sub>. The nitric oxide is oxidized to nitrogen dioxide (NO<sub>2</sub>) by air at temperature below 100°C.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

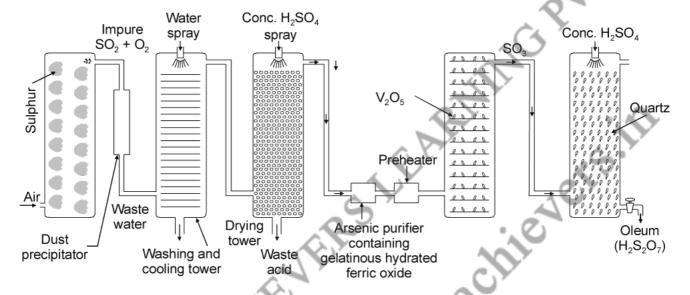
Step 3: Formation of nitric acid. Nitrogen dioxide dissolves on water to give HNO<sub>3</sub>.

$$3NO_2(g) + H_2O(1) \longrightarrow 2HNO_3(aq) + NO(g)$$

NO thus formed is recycled and the aqueous  $HNO_3$  can be concentrated by distillation upto — 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated  $H_2SO_4$ .

- **S4.** Manufacture of sulphuric acid by contact process involves three steps:
  - (a) Burning of sulphur in air to generate SO<sub>2</sub>.
  - (b) Conversion of SO<sub>2</sub> to SO<sub>3</sub> by oxidation with air in the presence of V<sub>2</sub>O<sub>5</sub> as catalyst.
  - (c) Absorption of SO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> to obtain oleum H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>.

A flow diagram for the manufacture of  $H_2SO_4$  is given below:



SO<sub>2</sub> produced by burning of sulphur is freed from dust and other impurities.

The plant is operated at a pressure of 2 bar and a temperature of 720 K. These are the optimum conditions for the conversion of  $SO_2$  to  $SO_3$ , according to Le Chatelier principle.

 $SO_3$  produced in the catalyst converter is absorbed in concentrated  $H_2SO_4$  to produce oleum. Oleum is diluted with water to obtain  $H_2SO_4$  of desired concentration.

Sulphuric acid obtained as above is 96-98% pure.



### SMART ACHIEV

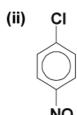
**CHEMISTRY - XII** 

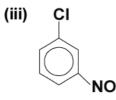
**Mixed Questins NCERT** 

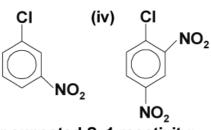
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#### Arrange the following according to reactivity towards nucleophillic substitution reaction.





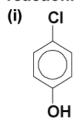


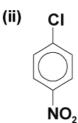


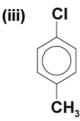
Answer the following in order of their expected S<sub>N</sub>1 reactivity:

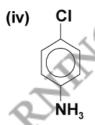
 $CH_3CH(Br)CH_3$ ,  $CH_3CH_2Br$ ,  $CH_2 = CHBr$ ,  $CH_2 = CHCH(Br)CH_3$ 

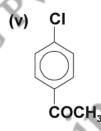
- (c) tert-butyl chloride reacts with aqueous NaOH by  $S_N 1$  mechanism while n-butyl chloride reacts by S<sub>N</sub>2 mechanism, Why?
- Q2. (a) Arrange the following according to reactivity towards nucleophillic substitution reaction.









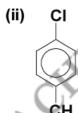


Answer the following in order of their expected S<sub>№</sub>1 reactivity:

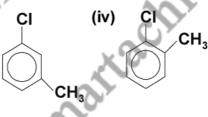
(CH<sub>1</sub>)<sub>3</sub>CCI, C<sub>E</sub>H<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CI, (CH<sub>3</sub>)<sub>3</sub>CHCI, CH<sub>3</sub>CH<sub>2</sub>CI

- Point out the difference between racemic modification and meso compound. (c)
- Arrange the following according to reactivity towards nucleophillic substitution Q3. (a) reaction.









(b) Answer the following in order of their expected S<sub>N</sub>1 reactivity:

 $CICH_{,CH} = CHCH_{,CH_{,1}}$   $CH_{,C}(CI) = CHCH_{,CH_{,1}}$   $CH_{,CH_{,CH_{,CH_{,1}}}}$   $CH_{,CH_{,CH_{,CH_{,1}}}}$  $CH_1CH = CHCH(CI)CH_1$ 

- (c) How will you carry out the following conversions in not more than two steps: 1-chlorobutane to *n*-octane
- (a) How will you carry out the following conversions in not more than two steps: Q4.
  - Benzyl alcohol to phenylethanitrile (ii) But-1-ene to But-2-ene
  - (b) Wurtz reaction fails in case of tert-alkyl halides. Explain.



# SMART ACHIEVERS Nurturing Success...

**CHEMISTRY - XII** 

**Mixed Questins NCERT-Solution** 

Date: 23/10/2021

#### **S1.** (a) (i) > (ii) > (iv)

- (b)  $CH_2 = CHCH(Br)CH_3 > CH_3CH(Br)CH_3 > CH_3CH_2Br > CH_2 = CHBr$
- (c) *tert*-butyl chloride reacts via S<sub>N</sub>1 mechanism because the heterolytic cleavage of C CI bond gives 3° carbocation which is highly stable. While *n*-butyl chloride reacts via S<sub>N</sub>2 because C of C CI bond is less crowded and favourable for nucleophile to attack from back side results in the formation of transition state.
- **S2.** (a) (iv) > (i) > (iii) > (v) > (ii).

- (b)  $CH_3CH_2CH_2CI < (CH_3)_2CHCI < (CH_3)_3CCI < C_6H_5C(CH_3)_2CI$
- (c) Racemic modification and Meso compound:

S. No.	Recemic Modification	Meso compound
1.	It is the mixture of equal proportion of <i>dextro</i> and <i>levo</i> forms is called racemic modification.	It is an optically inactive compound whose molecules are achiral, even thought they contain tetrahedral atoms with four different groups.

**S3.** (a) (iv) > (ii) > (iii) > (i)

- (b)  $CH_3C(CI) = CHCH_2CH_3 < CH_3CH = CHCH_2CH_2CI < CICH_2CH = CHCH_2CH_3$  $< CH_3CH = CHCH(CI)CH_3$
- (c)  $CH_3CH_2CH_2CH_2CH_2$   $\xrightarrow{\text{Na}}$   $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$  1-Chlorobutane n-Octane

**S4.** (a) (i) 
$$\bigcirc$$
  $CH_2OH \xrightarrow{SOCI_2}$   $\bigcirc$   $CH_2CI \xrightarrow{KCN}$   $\bigcirc$   $\bigcirc$   $CH_2CN$  Phenyl ethanenitrile

(ii) 
$$CH_2 = CHCH_2CH_3 \xrightarrow{HBr} CH_3CHCH_2CH_3 \xrightarrow{alc. KOH} CH_3CH = CHCH_3$$
  
But-1-ene Br

(b) *tert*-alkyl halides undergo dehydrohalogenation in presence of sodium metal instead of undergoing Wurtz reaction as shown below:

$$(CH_3)_3C$$
 — Br + 2Na —  $(CH_3)_3C$  — Na<sup>+</sup> + NaBr   
tert-Butyl bromide  $tert$ -Butyl sodium

$$\begin{array}{c} \mathsf{CH_3} \\ | \\ (\mathsf{CH_3})_3 \mathsf{C-Na^+} \ + \ \mathsf{H-CH_2-C-Br} \\ | \\ | \\ \mathsf{CH_3} \end{array} ) \xrightarrow{\mathsf{C}} \ (\mathsf{CH_3})_3 \mathsf{CH} \ + \ \mathsf{CH_2 = C-CH_3} \\ | \\ | \\ \mathsf{Isobutane} \\ \mathsf{CH_3} \end{array}$$

Therefore, 3° alkyl halides fail to undergo Wurtz reaction.