Date: 23/10/2021

Q1. How is the presence of SO_2 detected?

Q2. Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Q3. Write main differences between the properties of white phosphorus and red phosphorus.

Q4. Why are halogens strong oxidising agents?

Q5. What are the oxidation states of phosphorus in the following?
(a) H_3PO_3 (b) PCl_3 (c) Ca_3P_2 (d) Na_3PO_4 (e) POF_3

Q6. What inspired Neil Barlett for carrying out reaction between Xe and PtF_6?

Q7. Knowing the electron gain enthalpy values for $O \rightarrow O^{\ominus}$ and $O \rightarrow O_2$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having $O^{2\ominus}$ species and not $O^{\ominus}$?

Q8. Which aerosols deplete ozone?

Q9. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation, state and hydride formation.

Q10. Comment the following:
(a) NO_2 readily forms a dimer, explain.
(b) H_3PO_3 is diprotic, explain.
(c) How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

Q11. Account the following:
(a) Give reason SF_6 is not easily hydrolysed though thermodynamically it should be, why?
(b) The bond energy of F_2 is less than Cl_2, explain.
(c) Draw the structure of XeO_3.
(d) Complete the reaction $XeF_6 + KF \longrightarrow$
(e) Arrange the following decreasing boiling point H_2O, H_2S, H_2Se and H_2Te.

Q12. (a) Write the chemical equations involved in the preparation of the following:
(i) XeF_4 (ii) H_3PO_3
(b) Account for the following:
(i) Thermal stability of water is much higher than that of H_2S.
(ii) White phosphorous is more reactive than red phosphorus.
(c) Draw the structure of $XeOF_4$.

Q13. Account the following
(a) Xenon show Fluorides but Xenon chloride not known, explain.
(b) How are XeF_2 and XeF_4 prepared.
(c) Give shape and hybridization of $XeOF_2$ and XeO_2F_2.

Q14. Account the following

- **(a) Give equation to Lab. preparation of dioxygen.**
- **(b) Give equation to Lab preparation of PH_3.**
- **(c) Name two compounds in which oxygen has oxidation state different from – 2. Given oxidation state also.**
- **(d) Oxygen molecule has formula O_2 whilest sulphur is S_8. Explain why?**
- **(e) SF_6 is known but SH_6 is not known.**

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S1. SO_2 is pungent smelling gas. Following two tests can be performed to detect SO_2.

(a) SO_2 turns the pinck violet colour of $KMnO_4$ solution to colourless due to reduction of $MnO_4^{\ominus}$ to $Mn^{2\oplus}$ ions.

$$\begin{aligned} SO_2 + 2H_2O &\longrightarrow SO_4^{2\ominus} + 4H^{\oplus} + e^{\ominus}] \times 5 \\ MNO_4^{\ominus} + 8H^{\oplus} + 5e^{\ominus} &\longrightarrow Mn^{2\oplus} + 4H_2O] \times 2 \\ \hline \underset{\text{(pink violet)}}{2MnO_4^{\ominus}} + 5SO_2 + 2H_2O &\longrightarrow \underset{\text{(colourless)}}{2Mn^{2\oplus}} + 5SO_4^{2\ominus} + 4H^{\oplus} \end{aligned}$$

(b) SO_2 turns acidified $K_2Cr_2O_7$ solution green due to reduction of $Cr_2O_7^{2\ominus}$ to $Cr^{3\oplus}$ ions.

$$\begin{aligned} SO_2 + 2H_2O &\longrightarrow SO_4^{2\ominus} + 4H^{\oplus} + 2e^{\ominus}] \times 3 \\ Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} &\longrightarrow 2Cr^{3\oplus} + 7H_2O \\ \hline \underset{\text{(orange)}}{Cr_2O_7^{2\ominus}} + 3SO_2 + 2H^{\oplus} &\longrightarrow \underset{\text{(green)}}{2Cr^{3\oplus}} + 3SO_4^{2\ominus} + H_2O \end{aligned}$$

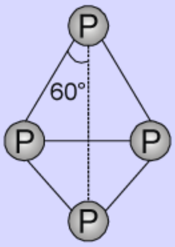
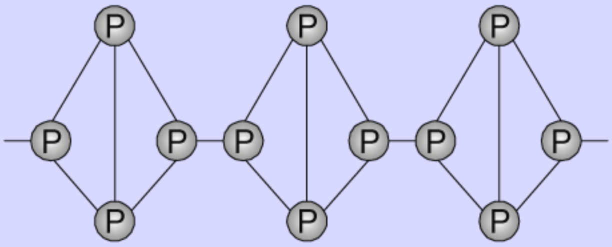
S2. H_2SO_4 is a dibasic acid, it ionises in two stages and hence has low dissociation constants as given below :

(a) $H_2SO_4\,(aq) + H_2O\,(l) \longrightarrow H_3O^{\oplus}\,(aq) + HSO_4^{\ominus}\,(aq);\ K_{a_1} > 10$

(b) $HSO_4^{\ominus}\,(aq)\ H_2O\,(l) \longrightarrow H_3O^{\oplus}\,(aq) + SO_4^{2\ominus}\,(aq);\ K_{a_2} = 1.2 \times 10^{\ominus 2}$

K_{a_2} is less then K_{a_1} *i.e.*, tendency to move towards the products is much less in (ii) than (i). This is because the negativity charged $HSO_3^{\ominus}$ ion has much less tendency to donate a proton to H_2O as compared to neutral H_2SO_4.

S3. Differences between properties of white and red phosphorus.

White phosphorus	Red phosphorus
1. White phosphorus has the structure as given below :  It consists of discrete tetrahedral P_4 soluble.	Red phosphorus has the structure as given below :  It is polymeric, consisting chains of P_4 tetrahedra linked together.
2. It is poisonous, insoluble in water but soluble in carbon disulphide.	2. It is odourless, non-poisonous, insoluble in water as well as carbon disulphide.
3. It glows in the dark (chemiluminiscence).	3. It does not glow in the dark.
4. It is more reactive. It catches fire in the air to give dense white fumes of P_4O_{10}. $P_4 + 5O_2 \longrightarrow P_4O_{10}$	4. It is much less reactive.

S4. Due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy, halogens have a strong tendency to accept electrons and thus get reduced.

$$X + e^{\ominus} \longrightarrow X^{\ominus}$$

In other words, halogens act as strong oxidising agents. Their oxidizing power, however, decreases from F_2 to I_2 as evident from their electrode potentials :

$$E^\circ_{F_2/F^\ominus} = +2.87\text{ V}, \qquad E^\circ_{Cl_2/Cl^\ominus} = +1.36\text{ V},$$

$$E^\circ_{Br_2/Br^\ominus} = +1.09\text{ V} \quad \text{and} \quad E^\circ_{I_2/I^\ominus} = +0.54\text{ V}$$

Thus, F_2 is the strongest while I_2 is the weakest oxidizing agent.

S5. Let the oxidation state of P be taken as *x*. Substituting the oxidation states of other elements, we can calculate the oxidation state of P as done below :

(a) $\overset{+1}{H_3}\ \overset{x}{P}\ \overset{-2}{O_3}$ or $3(+1) + x + 3(-2) = 0$ or $x = +3$

(b) $\overset{x}{P}\ \overset{-1}{Cl_3}$ or $x + 3(-1) = 0$ or $x = +3$

(c) $\overset{+2}{Ca_3}\ \overset{x}{P_2}$ or $3(+2) + 2 \times x = 0$ or $x = -3$

(d) $\overset{+1}{Na_3}\ \overset{x}{P}\ \overset{-2}{O_4}$ or $3\,(+1) + x + 4\,(-2) = 0$ or $x = +5$

(e) $\overset{x}{P}\ \overset{-2}{O}\ \overset{-1}{F_3}$ or $x + 1\,(-2) + 3\,(-1) = 0$ or $x = +5$.

S6. Neil Bartlett observed that PtF_6 reacts with O_2 to yield an ionic solid, $O_2^{\oplus}$, $PtF_6^{\ominus}$.

$O_2\,(g) + PtF_6\,(g) \longrightarrow O_2^{\oplus}\,[PtF_6]^{\ominus}$

In this reaction, O_2 gets oxidised to $O_2^{\oplus}$ by PtF_6.

He thought since the first ionisation enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecule (1175 kJ mol^{-1}), PtF_6 should also oxidise Xe to $Xe^{\oplus}$. This inspired Barlett to carry out the reaction between Xe and PtF_6. When Xe and PtF_6 were mixed, actually a rapid reaction took place and a red solid with the formula, $Xe^{\oplus}\,PtF_6^{\ominus}$ was obtained.

$Xe + PtF_6 \xrightarrow{278\text{ K}} \underset{\text{red}}{Xe^{\oplus}\,[PtF_6]^{\ominus}}$

S7. Consider the reaction of a divalent metal (M) with oxygen. The formation of M_2O and MO involves the following steps:

$$M(g) \xrightarrow{\Delta_i H_1} M^{\oplus}\,(g) \xrightarrow{\Delta_i H_2} M^{2\oplus}\,(g)$$

$\Delta_i H_1$ and $\Delta_i H_2$ are first and second ionisation enthalpies of the metal M.

$$O\,(g) \xrightarrow{\Delta_{eg} H_1} O^{\ominus}\,(g) \xrightarrow{\Delta_{eg} H_2} O^{2\ominus}\,(g)$$

$\Delta_{eg} H_1$ and $\Delta_{eg} H_2$ are first and second electron gain enthalpies

$$2M^{\oplus}(g) + O^{\ominus}(g) \xrightarrow{\text{Lattice energy}} M_2O(s)$$

$$M^{2\oplus}(g) + O_2^{\ominus}(g) \xrightarrow{\text{Lattice energy}} MO\,(s)$$

Although $\Delta_i H_2$ is much more than $\Delta_i H_1$ and $\Delta_{eg} H_2$ is much higher than $\Delta_{eg} H_1$, yet the lattice energy of formation of MO (s) due to higher charges is much more than that of M_2O (s). In other words, formation MO is energetically more favourable than M_2O. It is due to this reason that oxygen forms preferably oxides having the $O_2^{\ominus}$ species and not $O^{\ominus}$.

S8. Aerosols such as chlorofluorocarbons (CFC's) depletes the O_3 layer by supplying Cl free radical which convert O_3 to O_2 in the following sequence of reactions :

$$\underset{\text{Freon}}{Cl_2CF_2\,(g)} \xrightarrow{hv} \bullet Cl\,(g) + \bullet CClF_2\,(g)$$

$$\bullet Cl(g) + O_3\,(g) \longrightarrow ClO\bullet\,(g) + O_2\,(g)$$

$$ClO\bullet\,(g) \longrightarrow Cl\bullet\,(g) + \bullet O\,(g)$$

$$ClO\bullet\,(g) + \bullet O\,(g) \longrightarrow \bullet Cl\,(g) + O_2\,(g)$$

S9. (a) ***Electronic configuration:*** All these elements have the common ns^2np^4 (n = 2 to 6) valence shell electronic configuration.

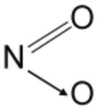
$${}_{8}O = [He]2s^2\,2p^4;\quad {}_{16}S = [Ne]\,3s^2\,3p^4;\quad {}_{34}Se = [Ar]\,3d^{10}\,4s^2\,4p^4$$

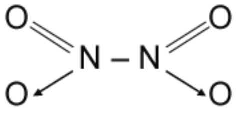
$${}_{52}Te = [Kr]\,4d^{10}\,5s^2\,5p^4 \quad \text{and} \quad {}_{84}Po = [Xe]\,4f^{14}\,5d^{10}\,6s^2\,6p^4$$

Hence, it is justified to place them in Group 16 of the periodic table.

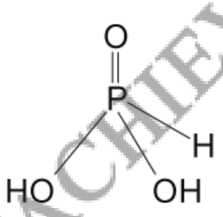
(b) ***Oxidation states:*** They need two more electrons to form dinegative ions and acquire the nearest inert gas configuration. Thus, the minimum oxidation state of these elements should be –2. Oxygen, sulphur being electronegative show an oxidation state of –2. Other elements of this group, being more electropositive than O and S, do not show negative oxidation states. Since these elements have six electrons in the valence shell, therefore, at the maximum they can show an oxidation state +6. Other positive oxidation states shown by these elements are +2 and +4. However, due to the absence of *d*-orbitals, oxygen does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group.

(c) ***Formation of hydrides:*** All the elements complete their respective octets by sharing two of their valence electrons with 1*s*-orbital of hydrogen to form hydrides of the general formula EH_2, i.e., H_2O, H_2S, H_2Se, H_2Te and H_2Po. Thus, on the basis of formation of hydrides of the general formula EH_2, these elements are justified to be placed in Group 16 of the period table.

S10.
(a)  has one unpaired electron, therefore, it is unstable and forms dimer, i.e., N_2O_4 whose structure is

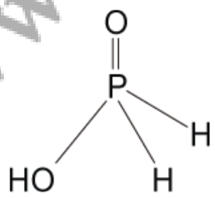


(b) H_3PO_3 has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.



$$H_3PO_3 \rightleftharpoons HPO_3^{2\ominus} + 2H^{\oplus}$$

(c) 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.

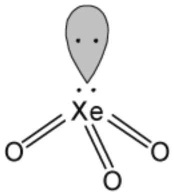
S11. (a) Due to sterically protection of six F atom, which donot allow to water molecules to attack on sulphur and due to steric repulsion of F at SF_6 thermodynamically unstable.

(b) 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 Cl is bigger in size and has less electron-density and has not electron-electron repulsion in Cl_2 and bond length is comparatively shorter than F_2.

(c) Shape of XeO_3

Hybridization sp^3

Shape - Bent pyramidal



(d) $XeF_6 + KF \longrightarrow K^{\oplus}[XeF_7]^{\ominus}$

(e) $H_2O > H_2Te > H_3Se > H_2S$

S12. (a) (i)

$$\underset{1}{Xe(g)} + \underset{5}{2F_2(g)} \xrightarrow[7\text{ bar}]{873\text{ K}} XeF_4(s)$$

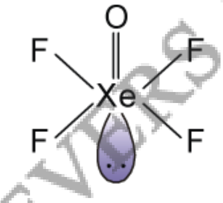
(ii)

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl.$$

(b) (i) Due to high electronegativity of oxygen, the O — H in H_2O forms strong intermolecular H — bonds. While other hydrides of group of 16 like H_2S do not form H — bonds. So, water has high stability as compared to H_2S.

(ii) It is because white phosphorus is a discrete P_4 molecule whereas red phosphorus is polymeric.

(c) Structure $XeOF_4$.



S13. (a) 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.

(b) XeF_2 is prepared in Lab in Nickel tube at 673 and 1 bar pressure.

$$Xe + F_2 \xrightarrow[673\text{ K, 1 bar}]{\text{Nickel tube}} XeF_2$$

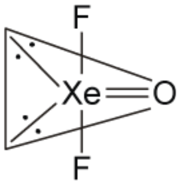
XeF_4 is prepared in Lab in nickel tube at 673 K and 7 bar pressure.

$$Xe + 2F_2 \xrightarrow[673\text{ K, 7 bar}]{\text{Nickel tube}} XeF_4$$

(c) $XeOF_2$

hybridization – sp^3d

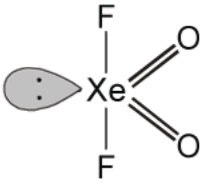
shape – T–shape



$XeOF_2$

XeO_2F_2

hybridization — sp^3d
shape — see-saw shape



XeO_2F_2

S14. (a) $2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$

MnO_2 lower the B.P. of $KClO_3$

(b) $P_4 + 3\,NaOH + 3H_2O \longrightarrow \underset{\text{Sodiumhydrophosphite}}{3\,NaH_2PO_2} + \underset{\text{phosphine}}{PH_3}$

(c) Oxygen Floride OF_2 oxygen has +2 oxidation state. Hydrogen peroxide H_2O_2 oxygen has –1 oxidation state.

(d) Oxygen is smaller in size and has ability to form $P\pi - P\pi$ multiple bond, and satisfy its octate forming (O ═ O) O_2 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_8 molecule.

(e) F is highly electronegative hence F unpair the paired electron of sulphate to form SF_6 while H is electropositive in respect to sulphur and it cannot unpair to paired electron of sulphur to expained S oxidation state.