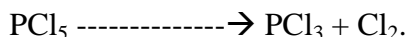


GROUP 15 ELEMENTS

Q. 1. Give chemical reaction in support of the statement that all the bonds in PCl_5 molecule are not equivalent.

Ans. Due to greater bond pair-bond pair repulsions, the two axial P — Cl bonds are less stable than the three equatorial P — Cl bonds. It is because of this reason that when PCl_5 is heated, the less stable axial bonds are broken to form Cl_2 .



Q. 2. The tendency for catenation decreases down the group 14.

Or Why carbon shows catenation but silicon does not

Ans. As we move down the group 14, the atomic size increases and hence the strength of M—M bond decreases steadily. Consequently the tendency for catenation decreases down the group.

Q. 3. PCl_5 is known but NCl_5 is not known. Explain.

Ans. Electronic configuration of P is $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$. Thus phosphorus has empty 3d orbitals in which the electron of the 3s-orbital can be excited but nitrogen has no d-orbitals as its electronic configuration is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$.

Q. 4. Why molecular nitrogen is not reactive ?

Ans. The bond dissociation energy for the triple bond in $\text{N} = \text{N}$ is very high because of small size of N-atoms and hence small internuclear distance.

Q.5. H_3PO_3 is diprotic (or)dibasic. Why?

Ans. Since it has only two ionisable H – atoms which are present as OH groups.

Q. 6. Nitrogen exists as diatomic molecule, N_2 , whereas phosphorus exists a tetraatomic molecule P_4 . Explain.

Ans. Nitrogen atom being small in size forms multiple bonds with another nitrogen atom but phosphorus being large in size forms only single bonds with other P-atoms.

Q. 7. Phosphine is a weaker base than NH_3 . Explain.

Ans. Due to bigger size of P than N, P—H bond is much weaker than N—H bond. As a result, PH_3 has less tendency than N to donate its lone pair of electrons to a proton. Consequently, PH_3 is a weaker base than NH_3 .

Q. 8. NO (Nitric oxide) is paramagnetic in the gaseous state but diamagnetic in the liquid and solid states. Why?

Ans. NO has an odd number of electrons (11 valence electrons) and hence is paramagnetic in the gaseous state. But in liquid and solid states, it exists as a symmetrical or asymmetrical dimer and hence is diamagnetic in these states.

Q. 9. Nitrogen ($\text{N} \equiv \text{N}$), carbon monoxide ($\text{C}=\text{O}$) and cyanide ion ($^-\text{C} = \text{N}$) are isoelectronic, yet CO and $^-\text{C}=\text{N}$ are reactive but N_2 is not. Explain why.

Ans. N_2 is non-polar and has very high ionization energy.

Q. 10. $NC1_3$ gets readily hydrolysed while NF_3 does not. Why ?

Ans. In $NC1_3$, Cl has vacant d-orbitals to accept lone pair of electrons donated by O-atom of H_2O molecule but in NF_3 , F does not have d-orbitals.

Q. 11. Oxides of nitrogen have open chain structures while those of phosphorus have closed chain or cage structures. Why is it so? Illustrate with one structural example for each type of oxides.

Ans. Nitrogen because of its small size and higher electronegativity than phosphorus, has a strong tendency to form $p\pi - p\pi$ multiple bonds. As a result, nitrogen forms multiple bonds with oxygen and hence the oxides of nitrogen have open chain structures. Phosphorus, on the other hand, because of its large size does not form $p\pi - p\pi$ multiple bonds with oxygen atoms but instead prefers to form single bonds. As a result, oxides of phosphorus have closed chain or cage structures.

Q. 12. Write balanced chemical equations for the following reactions :

(a) $Ca_3P_2 + H_2O \longrightarrow ?$ (b) $P_4O_{10} + H_2O \longrightarrow ?$ (c) $As_4 + Cl_2$ (excess) $\longrightarrow ?$ (d) $P_4 + KOH + H_2O \longrightarrow ?$

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

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

(c) $As_4 + 10 Cl_2$ (excess) $\longrightarrow 4 AsCl_5$

(d) $P_4 + 3 KOH + 3 H_2O \longrightarrow PH_3 + 3 KH_2PO_2$.

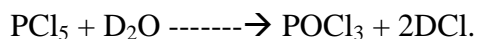
Q. 13. What is the oxidation state of phosphorus in the following:

(a) H_3PO_3 (b) PCl_5 (c) Ca_3P_2 (d) Na_3PO_4 (e) POF_3 .

Ans. (a) +3 (b) +5 (c) -3 (d) +5 (e) +5

Q. 39. Suggest a method for the laboratory preparation of DCl . Write a balanced equation for the reaction.

Ans. Hydrolysis of PCl_5 with heavy water (D_2O) gives DCl .



Q. 40. Unlike phosphorus, nitrogen shows little tendency for catenation ?

Ans. Due to smaller size, the lone pair of electrons on the N-atoms repel the bond pair of N—N bond. In contrast, because of comparatively larger size of P, the lone pair of electrons on P atoms do not repel the bond pair of the P—P bond to the same extent. As a result, N—N single bond is weaker than P—P single bond.

Consequently nitrogen shows little tendency for catenation while P has a distinct tendency for catenation.

Q. 41. Give the chemical reaction to support that +5 oxidation state of Bi is less stable than +3 state.

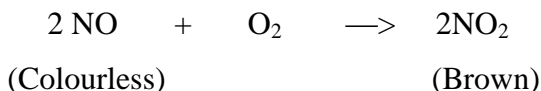
Ans. Due to inert pair effect, Bi can show +3 and +5 oxidation states. Since the inert pair effect is maximum in case of Bi, therefore, its +5 oxidation state is less stable than +3 oxidation state. This is evident from the observation that $BiCl_3$ even on prolonged heating with Cl_2 does not form $BiCl_5$.

Q. 42. Give reasons for the following :

(i) Nitric oxide becomes brown when released in air. (ii) PCl_5 is ionic in the solid state

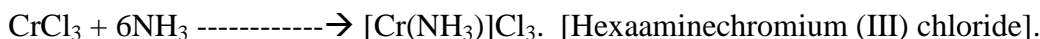
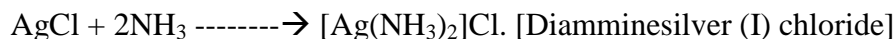
(iii) Ammonia is a good complexing agent.

Ans. (i) Nitric oxide readily combines with O_2 of the air to form nitrogen dioxide (NO_2) which has brown colour.



(ii) PCl_5 is ionic in the solid state because it exists as $[\text{PCl}_4]^+ [\text{PCl}_6]^-$ in which the cation is tetrahedral and the anion is octahedral.

(iii) Due to presence of a lone pair of electrons on N, NH_3 acts as a complexing agent. As a result, it combines with transition metal cations to form complexes. For example :



GROUP 16 ELEMENTS

Q. 43. Oxygen forms diatomic molecules (O_2) while sulphur forms octaatomic molecules (S_8). Explain.

Or Why O_2 is a gas but S_8 is solid. Justify.

Ans. Due to small size of oxygen, the non-bonding electrons on the two oxygen atoms in O—O bond strongly repel each other while such repulsions are much less in S—S bond. As a result, O—O bond dissociation energy is much less than S—S bond dissociation energy. In other words, sulphur has much higher tendency for catenation than oxygen. Further, oxygen because of its small size has a high tendency to form $p\pi - p\pi$ multiple bonds but sulphur because of its bigger size normally does not form $p\pi - p\pi$ multiple bonds.

Oxygen because of its less tendency for catenation and higher tendency for $p\pi - p\pi$ multiple bonds, forms stable diatomic molecules (O_2) whereas sulphur because of its higher tendency for catenation and lesser tendency for $p\pi - P\pi$. multiple bonds forms octaatomic (S_8) molecules having eight membered puckered ring structure.

Q. 44. H_2S acts only as a reducing agent but SO_2 acts both as a reducing agent as well as an oxidising agent. Why ?

Ans. The minimum oxidation number (O.N.) of S is -2 while its maximum O.N. is $+6$. In SO_2 , the O.N. is $+4$. therefore, it can not only increase its O.N. by losing electrons but can also reduce its O.N. by gaining electrons. As a result, it acts both as a reducing agent as well as an oxidising agent. On the other hand, in H_2S , S has an O.N. of -2 . As a result, it can only increase its O.N. by losing electrons and hence acts only as a reducing agent.

Q. 45. Oxygen generally exhibits an oxidation state of -2 only whereas other members of its family show oxidation states of $+2$, $+4$ and $+6$ as well. Explain why.

Ans. The electronic configuration of oxygen is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$, i.e., it has two half-filled orbitals and also there are no d-orbitals available for excitation of electrons. Therefore, it can show an oxidation state of either - 2 or

+ 2. Since, oxygen is the most electronegative element of its family, therefore, it shows an oxidation state of —2 only. Other elements of this family like sulphur have d-orbitals available for excitation thereby giving four and six half-filled orbitals for bonding. Furthermore they can combine with more electronegative elements.

Hence they show oxidation states of +2, +4 and +6 also.

Q. 46. Name two compounds in which oxygen has oxidation state different from —2. Give oxidation states also.

Ans. (i) OF_2 , oxidation state of O = +2 (ii) H_2O_2 , oxidation state of O = —1.

Q. 47. The tendency to show —2 oxidation state diminishes from sulphur to polonium. Why ?

Ans. As we move down the group from sulphur to polonium, the electronegativity decreases.

Q. 48. Why H_2O is a liquid while H_2S is a gas?

Ans. There is H—bonding in H_2O due to high electronegativity and small size of O-atom but there is no H-bonding in H_2S .

Q. 49. Why H_2S is acidic while H_2O is neutral ?

Ans. The S—H bond is weaker than O—H bond because size of S-atom is bigger than that of O-atom. Hence H_2S can dissociate to give H^+ ions in aqueous solution.

Q. 50. SF_6 is known but SH_6 is not known. Explain.

Ans. In the highest oxidation state, sulphur can combine only with highly electronegative elements like oxygen and fluorine.

Q. 51. Why the compounds of fluorine with oxygen are called fluorides of oxygen and not the oxides of fluorine?

Ans. This is because fluorine is more electronegative than oxygen.

Q. 52. Starting from elemental sulphur, how would you prepare (a) H_2SO_4 (b) SCl_2 and (c) SF_6 ?

V_2O_5 , 720 K; 2 Bar pressure

Ans. (a) $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$; $\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5, 720 \text{ K; 2 Bar pressure}} 2 \text{SO}_3$
 $\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$; $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \longrightarrow 2 \text{H}_2\text{SO}_4$.

(b) Heating S and Cl_2 gives S_2Cl_2 which upon saturation with Cl_2 gives SCl_2 .

Heat

$\text{S}_8 + 4 \text{Cl}_2 \longrightarrow 4 \text{S}_2\text{Cl}_2$

$\text{S}_2\text{Cl}_2 + \text{Cl}_2 \longrightarrow 2 \text{SCl}_2$.

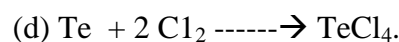
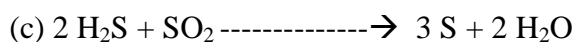
(c) $\text{S}_8 + 24 \text{F}_2 \longrightarrow 8 \text{SF}_6$.

Q. 53. Write balanced equations for the following reactions : Catalysyt

(a) $\text{Cu} + \text{con. H}_2\text{SO}_4 \longrightarrow$ (b) $\text{SF}_4 + \text{H}_2\text{O} \longrightarrow ?$ (c) $\text{H}_2\text{S} + \text{SO}_2 \longrightarrow ?$ (d) $\text{Te} + \text{Cl}_2 \longrightarrow ?$

Ans. (a) $\text{Cu} + 2 \text{con. H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2 \text{H}_2\text{O}$. (b) $\text{SF}_4 + 2 \text{H}_2\text{O} \longrightarrow \text{SO}_2 + 4 \text{HF}$.

catalyst



Q. 54. Why does sulphur in vapour state exhibit paramagnetic behaviour ?

Ans. In vapour state, sulphur partly exists as S_2 molecules which like O_2 has two unpaired electrons in the antibonding molecular orbitals ($2 \pi_x^*$ and $2 \pi_y^*$) and hence exhibits paramagnetism.

Q. 55. Among the hydrides of group 16, water shows unusual physical properties.

Ans. Due to high electronegativity of O, the O—H in H_2O forms strong intermolecular H-bonds. As a result, water exists as an associated molecule while other hydrides of group 16 do not form H-bonds and hence exist as monomers. As a result, water shows unusual physical properties, i.e. high b.p., high thermal stability and weaker acidic character as compared to other hydrides of group 16.

Q. 56. Give reasons for the following observations:

(i) SF_6 is not easily hydrolysed though thermodynamically it should be.

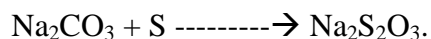
(ii) Sulphur exhibits greater tendency for catenation than selenium.

Ans. (i) in SF_6 , S is sterically protected by six F atoms and hence does not allow H_2O molecules to attack the S atom. Furthermore, F does not have f-orbitals to accept the electrons donated by H_2O molecules. As a result of these two reasons, SF_6 does not undergo hydrolysis. In contrast, in SF_4 , S is not sterically protected since it is surrounded by only four F-atoms. As a result, attack of H_2O molecules can take place easily and hence hydrolysis occurs.

(ii) As we move from S to Se, the atomic size increases and hence the strength of M—M bond decreases. As a result, S—S bond is much stronger than Se—Se bond and consequently, S shows greater tendency for catenation than selenium.

Q. 57. Sulphur disappears when boiled with an aqueous solution of sodium sulphite.

Ans. S reacts with Na_2SO_3 to form sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) and hence S disappears.



GROUP 17 ELEMENTS

Q. 58. The bond energy of F_2 is less than that of Cl_2

Ans. Due to smaller size, the lone pairs of electrons on the F-atoms repel the bond pair of the F—F bond. In contrast, because of comparatively larger size of Cl atoms, the lone pairs of Cl do not repel the bond pair of Cl—Cl bond. As a result, F—F bond energy is lower than that of Cl—Cl bond energy.

Q. 59. Fluorine does not undergo disproportionation reactions but other halogens do. Explain.

Ans. Disproportionation means simultaneous oxidation-reduction. F being the most electronegative element undergoes only reduction but not oxidation. As a result, it shows only —1 oxidation state while other halogens show both negative (—1) and positive (+1, +3, +5, +7) oxidation states. Thus, F does not show disproportionation reactions while other halogens do.

Q.60. Write an example of a neutral molecule which is isoelectronic with ClO^- .

Ans. ClO^- ion has $17 + 8 + 1 = 26$ electrons. A neutral molecule with 26 electrons is OF_2 ($8 + 2 \times 9 = 26$). Thus OF_2 is isoelectronic with ClO^- .

Q.61. Both NO and ClO_2 are odd electron species whereas NO dimerises but ClO_2 does not. Why?

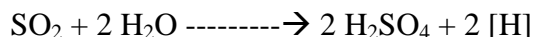
Ans. In NO , the odd electron on N is attracted by only one O-atom but in ClO_2 , the odd electron on Cl is attracted by two O-atoms. As a result, the odd electron on N in NO is localized while the odd electron on Cl in ClO_2 is delocalized. Consequently, NO has a tendency to dimerize but ClO_2 does not.

Q.62. Bleaching of flowers by chlorine is permanent while that by sulphur dioxide is temporary. Explain.

Ans. Cl_2 bleaches coloured material by oxidation : $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + [\text{O}]$
 $\text{Coloured material} + [\text{O}] \rightarrow \text{Colourless}$

and hence bleaching is permanent.

On the other hand, SO_2 bleaches coloured material by reduction and hence bleaching is temporary since when the bleached colourless material is exposed to air, it gets oxidised and the colour is restored.



Aerial oxidation

$\text{Coloured material} + [\text{H}] \rightarrow \text{Colourless material} \rightarrow \text{Coloured material}$

Q. 63. Why fluorine shows an oxidation state of—1 only while other halogens show oxidation states of +1, +3, +5 and +7 as well ? Or Why fluorine does not show variable valency while other halogens exhibit variable valency ?

Ans. Electronic configuration of fluorine is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. It has only one half-filled orbital and there is no d-orbital available for excitation of electrons. Therefore, it can show oxidation state of either +1 or -1. Since, it is the most electronegative element, therefore, it shows oxidation state of—1 only. In all other halogens, d-orbitals are available for excitation of electrons. Moreover they can combine with the more electronegative element, oxygen. Hence they show variable positive oxidation states.

Q. 64. F-atom is more electronegative than I-atom, yet HF has lower acid strength than HI . Explain.

Or Hydrogen fluoride is a much weaker acid than HCl in aqueous solution.

Ans. F atom being small in size, the bond dissociation energy of H—F is very high as compared to that of H—I bond because I-atom is very large in size.

Q. 65. Why F_2 is a stronger oxidizing agent than Cl_2 while electron affinity of fluorine is less than that of chlorine ?

Ans. F_2 is a stronger oxidizing agent than Cl_2 because electrode potential of F_2 (+ 2.87 V) is much higher than that of Cl_2 (+ 1.36 V). As a result, F_2 is more readily reduced than Cl_2 and hence F_2 is a stronger oxidising agent than Cl_2 .

Q. 66. OF_2 should be called oxygen difluoride and not fluorine oxide. Why ?

Ans. Because F is more electronegative than oxygen.

Q. 67. Iodine is more soluble in KI than in water. Why?

Ans. Iodine combines with KI to form the soluble complex, KI_3 ($\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$).

Q. 68. Arrange HClO , HBrO and HIO in order of decreasing acidic strength giving reason.

Ans. $\text{H—O—Cl} > \text{H—O—Br} > \text{H—O—I}$. This is because electro negativities decrease in the order $\text{Cl} > \text{Br} > \text{I}$.

Q. 69. Arrange HClO_4 , HClO_3 , HClO_2 , HClO in order of (i) acidic strength (ii) oxidizing power. Same as above.

Ans. Acidic strength: $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

Reason: Stability of $\text{ClO}_4^- > \text{ClO}_3^- > \text{ClO}_2^- > \text{ClO}^-$

Oxidizing power: $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$

Reason: Same as above.

Q. 70. Why interhalogens are more reactive than halogens?

Ans. This is because the bond in the interhalogen (A—X) is weaker than X—X bond in the halogens. This is due to less effective overlapping between orbitals of dissimilar atoms than those between similar atoms.

Q. 71. Why HF acid is stored in wax coated glass bottles?

Ans. This is because HF does not attack wax but reacts with glass. It dissolves SiO_2 present in glass forming hydrofluoro silicic acid. $\text{SiO}_2 + 6 \text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}$

Q. 72. Chlorine vapours are evolved when concentration sulphuric acid is added to a mixture of sodium chloride and manganese dioxide. Write a balanced equation for the reaction.

Ans. $2\text{NaCl} (\text{s}) + 2\text{H}_2\text{SO}_4 (\text{aq}) + 2\text{MnO}_2 (\text{s}) \rightarrow \text{Na}_2\text{SO}_4 (\text{aq}) + \text{MnSO}_4 (\text{aq}) + 2\text{H}_2\text{O}$

Q. 73. Deduce the molecular shape of BrF_3 , on the basis of VSEPR theory.

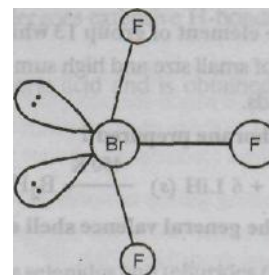
Ans. On the basis of VSEPR theory, a molecule with three bond pairs and two lone pairs must be T-shaped (i.e. distorted bipyramidal) as shown.

The two lone pairs will occupy equatorial positions to minimize lone pair-lone pair and lone pair-bond pair repulsions, which are greater than,

bond pair-bond pair repulsions. Further, the axial F atoms will be slightly

bent towards the equatorial F atom to minimize the lone pair-lone pair

repulsions. Therefore, the shape of BrF_3 would be slightly bent T as shown above.



Q. 74. ClF_3 exists but FCl_3 does not.

Ans. Reasons are :

(i) Cl has vacant d-orbitals and hence can show an oxidation state of +3 but F has no d-orbitals, therefore, it cannot show positive oxidation states. Further, since F can show only -1 oxidation state, therefore, FCl_3 does not exist.

(ii) Because of bigger size, Cl can accommodate three small F atoms around it while F being smaller cannot accommodate three large sized Cl atoms around it.

GROUP 18 ELEMENTS

Q. 75. Helium and neon do not form compounds with fluorine. Why?

Ans. He and Ne do not contain d-orbitals in their valence shell and hence their electrons cannot be promoted to higher energy levels like that in Xe to form bonds. Therefore, He and Ne do not form compounds with fluorine.

Q. 76. Neon is generally used for warning signals. Why?

Ans. Neon lights are visible from long distances even in fog and mist and hence neon is generally used for warning Signals.

Q. 77. Why do noble gases form compounds with fluorine and oxygen only?

Ans. The electro negativity of both fluorine and oxygen is very high. Moreover, fluorine is a highly reactive element.

Q. 78. What prompted Bartlett to the discovery of noble gas compounds.

Ans. Since PtF_6 oxidises O_2 To O_2^+ , Bartlett thought that PtF_6 should also oxidise Xe and Xe^+ because the ionization energies of O_2 (1175 kJ mol^{-1}) and Xe (1170 kJ mol^{-1}) are quite close.

Q. 79. Most of the known noble gas compounds are those of xenon.

Ans. Amongst noble gases, Xe has the lowest ionization enthalpy and hence can be easily oxidised by strong oxidising agents like O_2 and F_2 .

Q. 80. Give reasons:

(i) Xenon does not form fluorides such as XeF_3 and XeF_5 .

(ii) Out of noble gases, only xenon is known to form real chemical compounds.

Ans. (i) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5p-filled orbitals to the 5 d-vacant orbitals will give rise to two, four and six half-filled orbitals. So Xe can combine with even but not odd number of F atoms. Hence, it cannot form XeF_3 and XeF_5 .

(ii) Except radon which is radioactive. Xe has least ionization energy among noble gases and hence it readily forms chemical compounds particularly with O_2 and F_2 .