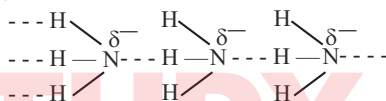


2. Why does the reactivity of nitrogen differ from phosphorous?

Sol. N_2 exist as a diatomic molecule containing triple bond between two N-atoms. Due to the presence of triple bond between the two N-atoms, the bond dissociation energy is large ($941.4 \text{ kJ mol}^{-1}$). As a result of this, N_2 is inert and unreactive, whereas phosphorus exists as a tetraatomic molecule, containing P–P single bond. Due to the presence of single bond, the bond dissociation energy is weaker (213 kJ mol^{-1}) than $N \equiv N$ triple bond ($941.4 \text{ kJ mol}^{-1}$). As a result of this, phosphorus is much more reactive than nitrogen.

4. Why does NH_3 form hydrogen bonds but PH_3 does not?

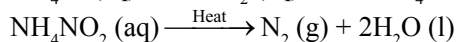
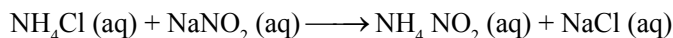
Sol. Nitrogen has an electronegativity value 3.0, which is much higher than that of H (2.1). As a result, N–H bond is quite polar and hence, NH_3 undergoes intermolecular H–bonding.



Phosphorus have an electronegativity value 2.1. Thus, P–H bond is not polar and hence, PH_3 does not undergo H–bonding.

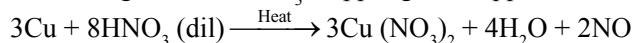
5. How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

Sol. In laboratory, nitrogen is prepared by heating an equimolar aqueous solution of ammonium chloride and sodium nitrite. As a result of double decomposition reaction, ammonium nitrite is formed. Ammonium nitrite is unstable and decomposes to form nitrogen gas.

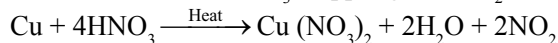


7. Illustrate, how copper metal can give different products on reaction with HNO_3 .

Sol. On heating with dil HNO_3 , copper gives copper nitrate and nitric oxide.



With concentrated HNO_3 , copper gives NO_2 instead of NO .

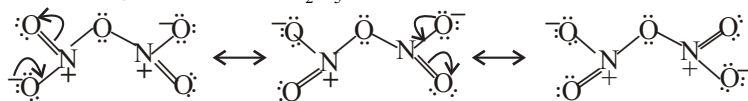


8. Give the resonating structures of NO_2 and N_2O_5 .

Sol. Resonating structures of NO_2 are:



Resonating structures of N_2O_5 are:



9. The HNH angle value is higher than HPH, HAsH and HSbH angles. Why?

Sol. In all these cases, the central atom is sp^3 hybridised. Three of the four sp^3 orbitals form three σ -bonds, while the fourth contains the lone pair of electrons. Since lone pair bond pair repulsions are stronger than the bond pair–bond pair repulsions, therefore, in case of NH_3 , the bond angle decreases from 109.28° to 107.8° . On moving down from N to P to As and to Sb, the electronegativity of the central atom goes on decreasing. As a result of this, bond pairs of electrons lie away and away from the central atom. This is because of the force of repulsion between the adjacent bond pairs goes on decreasing and the bond angles keep on decreasing from NH_3 to SbH_3 . Thus, bond angles are in the order:



10. Why does $R_3P=O$ exist but $R_3N=O$ does not (R=alkyl group)?

Sol. Nitrogen does not contain d -orbitals. As a result, it cannot expand its covalency beyond four to form $p\pi-d\pi$ multiple bonds. In contrast, P contains the d -orbitals, and can expand its covalency beyond 4 to form $p\pi-d\pi$ multiple bonds. Hence, $R_3P=O$ exist but $R_3N=O$ does not.

11. Explain why NH_3 is basic while BiH_3 is only feebly basic.

Sol. In both NH_3 and BiH_3 , N and Bi have a lone pair of electrons on the central atom and hence, should behave as Lewis bases. But NH_3 is much more basic than BiH_3 . Since the atomic size of N (70 pm) is much smaller than that of Bi (148 pm), therefore, electron density on N-atom is much higher than that on Bi-atom. Thus, the tendency of N in NH_3 to donate electron density is much higher than that on Bi-atom. Hence, NH_3 is more basic than BiH_3 .

12. Nitrogen exists as diatomic molecule and phosphorus as P_4 . Why?

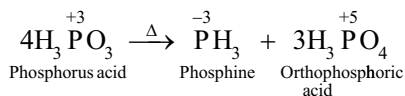
Sol. Nitrogen exists as a diatomic molecule having a triple bond between the two N-atoms. This is due to its small size and high electronegativity, that it forms $p\pi-p\pi$ multiple bonds. On the other hand, phosphorus due to its larger size and lower electronegativity usually does not form multiple $p\pi-p\pi$ bonds. It prefers to form P–P single bonds and hence, it exists as tetrahedral P_4 molecule.

14. Why does nitrogen show catenation properties less than phosphorus?

Sol. The extent of catenation depends upon the strength of the element – element bond. The N–N bond strength (159 kJ mol^{-1}) is weaker than P–P bond strength (213 kJ mol^{-1}). Thus, nitrogen shows less catenation properties than phosphorus.

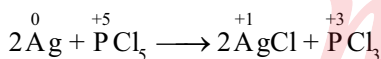
15. Give the disproportionation reaction of H_3PO_3 .

Sol. On heating, H_3PO_3 undergoes self-oxidation reduction (i.e. disproportionation to form PH_3).



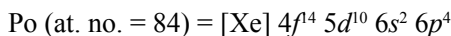
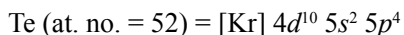
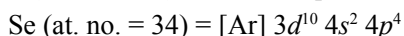
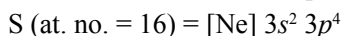
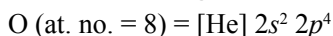
16. Can PCl_5 act as an oxidising as well as reducing agent. Justify.

Sol. The oxidation state of P in PCl_5 is + 5. Since P has five electrons in its valence shell, therefore, it cannot donate electron and cannot increase its oxidation state beyond + 5. Thus, PCl_5 cannot act as a reducing agent.



17. 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.

Sol. (1) **Electronic configuration:**



Thus, all these elements have the same $ns^2 np^4$ ($n = 2-6$) valence shell electronic configuration, hence are justified to be placed in group 16 of the Periodic Table.

(2) **Oxidation states:** Two more electrons are needed to acquire the nearest noble gas configuration. Thus, the minimum oxidation state of these elements should be -2 . O and to some extent S show -2 oxidation state. Other element being more electropositive than O and S, do not show negative oxidation state. As these contain six electrons, thus, maximum oxidation state shown by them is $+6$. Other

oxidation state shown by them are +2 and +4. O do not show +4 and +6 oxidation state, due to the absence of *d*-orbitals.

Thus, on the basis of maximum and minimum oxidation states, these elements are justified to be placed in the same group 14 of the Periodic Table.

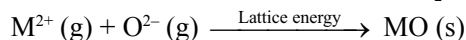
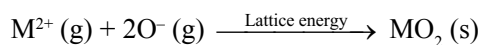
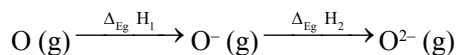
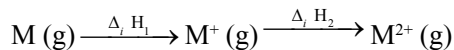
- (3) **Hydride formation:** All these elements share two of their valence electrons with *1s*-orbital of hydrogen to form hydrides of the general formula EH_2 (i.e. H_2O , H_2S , H_2Se , H_2Te and H_2Po). Thus, on the basis of hydride formation, these elements are justified to be placed in the same group 14 of the Periodic Table.

18. Why is dioxygen a gas but sulphur is a solid?

Sol. Due to the small size and high electronegativity, oxygen forms $p\pi-p\pi$ multiple bonds. As a result, oxygen exists as diatomic (O_2) molecules. These molecules are held together by weak van der Waals forces of attraction which can be overcome by collisions of the molecules at room temperature. Therefore, O_2 is a gas at room temperature. Due to its bigger size and lower electronegativity, sulphur does not form $p\pi-p\pi$ multiple bonds. It prefers to form S-S single bonds. S-S single bond is stronger than O-O single bond. Thus, sulphur has higher tendency for catenation than oxygen. Due to higher tendency for catenation and lower tendency for $p\pi-p\pi$ multiple bonds sulphur exists as octa-atomic (S_8) molecule. Due to bigger size, the force of attraction holding the S_8 molecules together are much stronger which cannot be overcome by collisions of molecules at room temperature. Therefore, sulphur is solid at room temperature.

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

Sol. Consider a direct metal *M* reacting with oxygen. M_2O and MO are formed as follows:

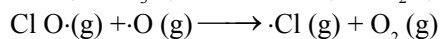
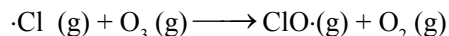
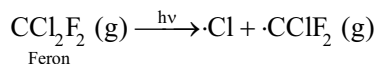


Here, $\Delta_i H_2 > \Delta_i H_1$ and $\Delta_{\text{Eg}} H_2 > \Delta_{\text{Eg}} H_1$, still the lattice energy of formation of MO (s) is than that of $\text{MO}_2 \text{ (s)}$. This is because of higher charges on MO

(s) than that of MO_2 (s). Thus, oxygen forms a large number of oxides having the O^{2-} species and not O^- .

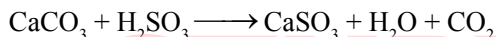
20. Which aerosols deplete ozone?

Sol. Aerosols like chlorofluorocarbons (CFC's) (i.e. freon (CCl_2F_2)), deplete the ozone layer by supplying Cl free radicals which convert O_3 to O_2 .



22. How is SO_2 an air pollutant?

Sol. 1. SO_2 dissolves in moisture present in air to form H_2SO_3 which damages building materials especially marble (acid – rain).



2. It corrodes metals like Fe and steel. It also brings about fading and deterioration of fabrics, leather, paper, etc., and affecting the colour of paints.

3. Even at low concentration (≈ 0.03 ppm), it has damaging effect on the plants. If exposed for a long time, say a few days or weeks, it slows down the formation of chlorophyll (i.e. loss of green colour). This is called chlorosis.

4. It is strongly irritating to the respiratory tract. It cause throat and eye irritation, resulting into cough, tears and redness in eyes. It also cause breathlessness and effects larynx (i.e. voice box).

23. Why are halogens strong oxidising agents?

Sol. The halogens are strong oxidising agents due to low bond dissociation enthalpy, high electronegativity and large negative electron gain enthalpy.

24. Explain why fluorine forms only one oxo-acid, HOF.

Sol. Cl, Br and I form four series of oxo-acids of general formula HOX, HOXO, HOXO₂ and HOXO₃. In these oxo-acids, the oxidation states of halogens are +1, +3, +5, and +7 respectively. However, due to high electronegativity and small size, F does not form oxo-acids with +3, +5 and +7, oxidation states. It just forms one oxo-acid in which the oxidation state of F is +1 (i.e. HOF).

25. Explain, why in spite of nearly the same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Sol. This is because their atomic size (covalent radii) are much different, $\text{O} = 66$ pm and $\text{Cl} = 135$ pm. Consequently, electron density per unit volume

on oxygen atom is much higher than that of a chlorine atom. Thus, oxygen forms hydrogen bonds while chlorine does not, even though both have nearly the same electronegativity.

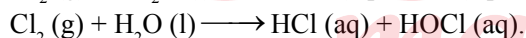
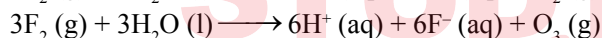
26. Write two uses of ClO_2 .

- Sol.**
- ClO_2 is an excellent bleaching agent. It is 30 times stronger bleaching agent than Cl_2 . It is used to bleach flour to make white bread.
 - ClO_2 is also a powerful oxidising agent and chlorinating agent. It is used for bleaching wood pulp and cellulose. It is used for purifying drinking water.

27. Why are halogens coloured?

Sol. The halogens are coloured because their molecules absorb light in the visible region. As a result of which their electrons get excited to higher energy levels while the remaining light is transmitted.

28. Write the reactions of F_2 and Cl_2 with water.

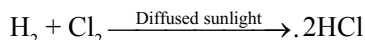


29. How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.



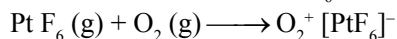
Oxidising
agent

We can also use KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc. in place of MnO_2 .

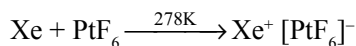


30. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ?

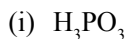
Sol. N. Bartlett observed that PtF_6 reacts with O_2 to give a compound $\text{O}_2^+ \text{PtF}_6^-$.



Since the first ionisation enthalpy of Xe (1170 kJ mol^{-1}) is fairly close to that of O_2 molecule (1175 kJ mol^{-1}), he thought that PtF_6 should also oxidise Xe to Xe^+ . This inspired Bartlett to carry out the reaction between Xe and PtF_6 . When PtF_6 and Xe were made to react, a rapid reaction took place and a red solid, $\text{Xe}^+ \text{PtF}_6^-$ was obtained.



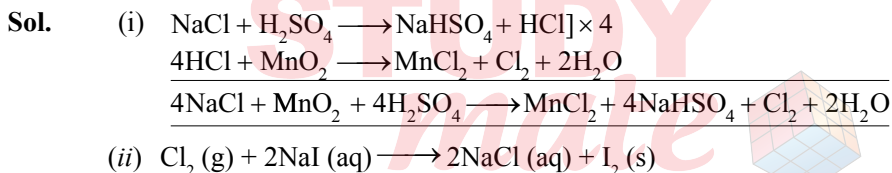
31. What is the oxidation states of phosphorus in the following:



- Sol.** (v) POF_3
 (i) H_3PO_3 $3(+1) + x + 3(-2) = 0$
 $\therefore x = +3$
- (ii) PCl_3
 $x + 3(-1) = 0$
 $x = +3$
- (iii) Ca_3P_2 $3(+2) + 2x = 0$
 $x = -3$
- (iv) Na_3PO_4 $3(+1) + x + 4(-2) = 0$
 $x = +5$
- (v) POF_3
 $x + 1(-2) + 3(-1) = 0$
 $x = +5$

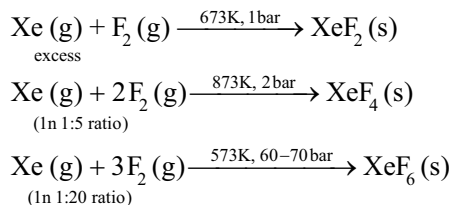
32. Write balanced equations for the following:

- (i) NaCl is heated with sulphuric acid in presence of MnO_2 .
 (ii) Cl_2 gas is passed into a solution of NaI in water.



33. How are XeF_2 , XeF_4 and XeF_6 obtained?

Sol. XeF_2 , XeF_4 and XeF_6 are obtained by direct reaction between Xe and F_2 as follows:



34. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

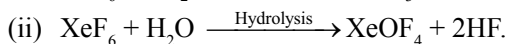
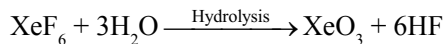
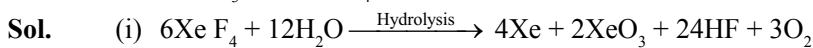
Sol. ClO^- has $17 + 8 + 1 = 26$ electrons.

Also, OF_2 has $(8 + 2 \times 9) = 26$ electrons.

and ClF has $(17 + 9) = 26$ electrons.

ClF can combine with F to form ClF_3 , thus, acts as a Lewis base.

35. How are XeO_3 and XeOF_4 prepared?



36. Arrange the following in order of property indicated for each set:

(i) F_2 , Cl_2 , Br_2 , I_2 – Increasing bond dissociation enthalpy.

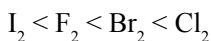
(ii) HF , HCl , HBr , HI – Increasing acid strength.

(iii) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 – Increasing base strength.

Sol. (i) Bond dissociation enthalpy decreases as the bond distance increases from F_2 to I_2 due to increase in the size of the atom, on moving from F to I.

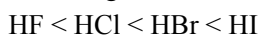
F–F bond dissociation enthalpy is smaller than Cl–Cl and even smaller than Br–Br. This is because F atom is very small and hence, the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in F_2 molecules.

The increasing order of bond dissociation enthalpy is



(ii) Acid strength of HF , HCl , HBr and HI depends upon their bond dissociation enthalpies. The bond dissociation enthalpy of H–X bond decreases from H–F to H–I as the size of atom increases from F to I.

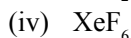
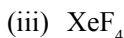
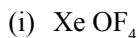
Thus, the acid strength order is



(iii) NH_3 , PH_3 , AsH_3 , SbH_3 and BiH_3 behaves as Lewis bases due to the presence of lone pair of electrons on the central atom. As we move from N to Bi, size of atom increases. Electron density on central atom decreases and hence, the basic strength decreases from NH_3 to BiH_3 . Then the base strength order is



37. Which of the following does not exist and why?



Sol. NeF_2 does not exist. This is because the sum of first and second ionisation enthalpies of Ne are much higher than those of Xe. Consequently, F_2 can oxidise Xe to Xe^{2+} but cannot oxidise Ne to Ne^{2+} .

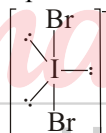
38. Give the formula and describe the structure of a noble gas species which is isostructural with:

- (i) ICl_4^- (ii) IBr_2^-
 (iii) BrO_3^-

Sol. (i) ICl_4^- : In ICl_4^- , central atom I has seven valence electrons and one due to negative charge. Four of these eight electrons are utilised in forming four single bonds with four Cl atoms. Four remaining electrons constitute the two lone pairs. It is arranged in square planar structure. ICl_4^- has 36 valence electrons. A noble gas species having 36 valence electrons is XeF_4 ($8 + 4 \times 7 = 36$). XeF_4 is also square planar.



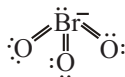
(ii) IBr_2^- : In IBr_2^- , central atom I has eight electrons. Two of these are utilised in forming two single bonds with two Br atom. Six remaining electrons constitutes three lone pairs. It is arranged in linear structure.



IBr_2^- has 22 valence electrons. A noble gas species having 22 valence electrons is XeF_2 ($8 + 2 \times 7 = 22$).

XeF_2 is also linear.

(iii) BrO_3^- : In BrO_3^- , central atom Br has seven electrons. Four of these seven electrons form two double bonds with two oxygen atoms while the fifth electron forms a single bond with O^- ion.



Two remaining electrons form one lone pair. It is arranged in a pyramidal structure. BrO_3^- has 26 valence electrons. A noble gas species having 26 valence electrons is XeO_3 ($8 + 3 \times 6 = 26$).

XeO_3 is also pyramidal.

39. Why do noble gases have comparatively large atomic sizes?

Sol. This is because noble gases have only van der Waals radii while others have covalent radii. Van der Waals radii are larger than covalent radii.