

- 1. **p-Block elements:** Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.
- 2. General electronic configuration of p-block elements: The p-block elements: The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.
- 3. **Representative elements:** Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.
- 4. **Inert pair effect:** The tendency of ns² electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.
- 5. Nitrogen family: The elements of group 15 nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns² np³.
- 6. Oxygen family: Group 16 of periodic table consists of five elements oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their general electronic configuration is ns²np⁴.
- 7. The halogen family: Group 17 elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), belong to halogen family. Their general electronic configuration is ns²np⁵.
- 8. Group 18 elements: Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are Group 18 elements. They are also called noble gases. Their general electronic configuration is ns²np⁶ except helium which has electronic configuration 1s². They are called noble gases because they show very low chemical reactivity.

GROUP 15 ELEMENTS

9. Atomic and ionic radii: Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

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10. **Ionisation energy**: It goes on decreasing down the group due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.

11. **Allotropy**: All elements of Group 15 except nitrogen show allotropy. Catenation: Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group. 13. Oxidation states: The common oxidation states are +3, +5, -3. The tendency shows -3 oxidation state decreases down the group due to decrease in electronegativity which is due to increase in atomic size. The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect. Nitrogen shows oxidation states from -3 to +5. Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionate.

 $3 \text{ HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2 \text{ NO}$

12. **Reactivity towards hydrogen**: All group 15 elements from trihydrides, MH₃. Hybridisation - sp³

The <u>stability of hydrides decrease</u> down the group due to decrease in bond dissociation energy down the group.

 $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Boiling point: PH₃ < AsH₃ < NH₃ < SbH₃ < BiH₃

Boiling point increases with increase in size due to increase in van der Waals forces. Boiling point of NH3 is more because of hydrogen bonding.

Bond angle: NH_3 (107.8°) > PH_3 (99.5°) > AsH_3 (91.8°) \approx SbH_3 (91.3°) > BiH_3 (90°)

<u>Electronegativity</u> of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs.

Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.

Basicity decreases as NH3 > PH3 > AsH3 > SbH3 < BiH3.

This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH₃. It will decrease down the group as the electronegativity decreases down the group.

The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

13. Reactivity towards oxygen: All group 15 elements from trioxides (M_2O_3) and pentoxides (M_2O_5) .

Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H+ ions easily. As we move down the group, the atomic size increases. Hence, the acidic character of oxides decreases and basicity increases as we move down the group.

14. **Reactivity towards halogen**: Group 15 elements form trihalides and pentahalides.

<u>Trihalides</u> – covalent compounds and become ionic down the group. sp^3 hybridisation, pyramidal shape

Pentahalides - sp³d hybridisation, TBP shape

They are lewis acids because of the presence of vacant d – orbitals.

 $PCl_5 + Cl^- \rightarrow [PCl6]^-$

PCl₅ is ionic in solid state and exist as [PCl₄] ⁺ [PCl₆]⁻

In PCl₅, there are three equatorial bonds and two axial bonds.

The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.

Nitrogen does not form pentahalides due to absence of d- orbitals.

15. **Reactivity towards metals**: All elements react with metals to form binary compounds in –3 oxidation state.

16. **Anomalous behaviour of nitrogen**: The behaviour of nitrogen differs from rest of the elements.

Reason:

i. It has a small size.

ii. It does not have d – orbitals

iii. It has high electronegativity

iv. It has high ionization enthalpy

17. Dinitrogen:

Preparation:

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

$$(NH_4)_2 Cr_2O_7 \xrightarrow{heat} N_2 + 4H_2O + Cr_2O_3$$

 $Ba(N_3)_2 \xrightarrow{heat} Ba + 3 N_2$ Properties:

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It is a colouless, odourless, tasteless and non – toxic gas. It is chemically un-reactive at ordinary temperature due to triple bond in . $N \equiv N$ which has high bond dissociation energy.

18. Ammonia: Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp³ hybridised. Preparation:

Haber's process: $N_2(g)+3H_2(g) \Longrightarrow 2 NH_3(g)$ $\Delta_f H^\circ = -46.1 \text{ kJ mol}^{-1}$ Pr essure = 200 × 10⁵ Pa Temperature = 773 K Catalyst is FeO with small amounts of K₂O and Al₂O₃

19. Nitric Acid: a. Ostwald Process: $4NH_3 + 5O_2 \xrightarrow{Pt/Rhgauge}{500 \text{ K},9\text{ bar}} 4NO + 6H_2O \dots(i)$

 $2 \text{ NO} + \text{O}_2 \Longrightarrow 2 \text{ NO}_2 \dots$ (ii)

 $3NO_2(g) + H_2O(I) \rightarrow 2HNO_3(aq) + NO(g) \dots(iii)$

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 .

Nitric acid is strong oxidizing agent in the concentrated as well as in the dilute state.

20. Phosphorus:

a. It shows the property of catenation to maximum extent due to most stable P - P bond.

b. It has many allotropes, the important ones are :

i. White phosphorus

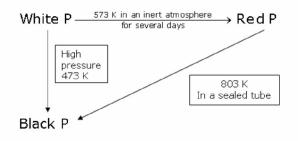
ii. Red phosphorus

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iii. Black phosphorus

White phosphorus	Red phosphorus	Black phosphorus
Discrete tetrahedral P4 molecules	Polymeric structure consisting of chains of P ₄ units linked together	Exists in two forms - α black P and β black P
Very reactive	Less reactive than white P	Very less reactive
Glows in dark	Does not glow in dark	-
Translucent waxy solid	Has an iron grey luster	Has an opaque monoclinic or rhombohedral crystals
Soluble in CS ₂ but insoluble in water	Insoluble in water as well as CS2	-
It has low ignition temperature, therefore, kept under water	-	-

Preparation:



21. Phosphine:

i. $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ $\begin{pmatrix} calcium \\ phosphide \end{pmatrix} (water) \begin{pmatrix} calcium \\ hydroxide \end{pmatrix} phosphine$ $Ca_3P_2 + 6HCI \rightarrow 3CaCl_2 + 2PH_3$ (phosphine)

Phosphine is highly poisonous, colourless gas and has a smell of rotten fish.

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ii. P_4 + 3NaOH + $3H_2O \rightarrow 3NaH_2PO_2 + PH_3$ (sodium hypophosphite) (phosphine)

22. Chlorides of Phosphorous:

PCI ₃	PCI ₅
Colourless oily liquid	Yellowish white powder
$P_4 + 6 Cl_2 \rightarrow 4 PCl_3$	$P_4 + 10 Cl_2 \rightarrow 4 PCl_5$
$P_4 + 8 \operatorname{SOCI}_2 \rightarrow 4 \operatorname{PCI}_3 + 4 \operatorname{SO}_2 + 2 \operatorname{S}_2 \operatorname{CI}_2$	$P_4 + 10 SO_2Cl_2 \rightarrow 4 PCl_5 + 10 SO_2$
Is hydrolysed in the presence of moisture $PCI_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCI$	$PCI_{5} + H_{2}O \longrightarrow POCI_{3} + 2 HCI$ $POCI_{3} + 3 H_{2}O \longrightarrow H_{3}PO_{4} + 3 HCI$
3 CH ₃ COOH + PCl ₃ \rightarrow 3 CH ₃ COCl + H ₃ PO ₃	3 $CH_3COOH + PCl_5 \rightarrow CH_3COCI + POCl_3 + HCl$
$3 C_2H_5OH + PCI_3 \rightarrow 3 C_2H_5CI + H_3PO_3$	$C_2H_5OH + PCI_5 \rightarrow C_2H_5CI + POCI_3 + HCI$
Pyramidal shape, sp ³ hybridisation	TBP geometry, sp ³ d hybridisation
-	$2Ag + PCI_5 \rightarrow 2 AgCI + PCI_3$
	$Sn + 2 PCl_5 \rightarrow SnCl_4 + 2 PCl_3$

GROUP 16 ELEMENTS

23. Oxidation states: They show -2, +2, +4, +6 oxidation states. Oxygen does not show +6 oxidation state due to absence of d – orbitals. Po does not show +6 oxidation state due to inert pair effect.

The stability of -2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity.

Oxygen shows -2 oxidation state in general except in OF, and O₂F,

The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.

24. **Ionisation enthalpy:** Ionisation enthalpy of elements of group 16 is lower than group 15 due to half filled p-orbitals in group 15 which are more stable. However, ionization enthalpy decreases down the group.

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25. **Electron gain enthalpy:** Oxygen has less negative electron gain enthalpy than S because of small size of O. From S to Po electron gain enthalpy becomes less negative to Po because of increase in atomic size.

26. Melting and boiling point: It increases with increase in atomic number. Oxygen has much lower melting and boiling points than sulphur because oxygen is diatomic (O_2) and sulphur is octatomic (S_8) .

27. Reactivity with hydrogen:

All group 16 elements form hydrides. Bent shape

Bond angle: $H_2O > H_2S < H_2Se < H_2Te$

373K 213K 232K 269K

Intermolecular increase in van der Waals forces H bonding

Acidic nature: $H_2O < H_2S < H_2Se < H_2Te$

This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Thermal stability: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

Reducing character: $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

This is because the H-E bond length increases down the group. Therefore, the bond dissociation enthalpy decreases down the group.

28. **Reactivity with oxygen:** EO_2 and EO_3 Reducing character of dioxides decreases down the group because oxygen has a strong positive field which attracts the hydroxyl group and removal of H^+ becomes easy.

Acidity also decreases down the group.

 SO_2 is a gas whereas SeO_2 is solid. This is because SeO_2 has a chain polymeric structure whereas SO_2 forms discrete units.

29. Reactivity with halogens: $EX_2 EX_4$ and EX_6 The stability of halides decreases in the order F > Cl > Br > I. This is because E-X bond length increases with increase in size.

Among hexa halides, fluorides are the most stable because of steric reasons.

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Dihalides are sp³ hybridised, are tetrahedral in shape.

Hexafluorides are only stable halides which are gaseous and have $sp^{3}d^{2}$ hybridisation and octahedral structure.

 H_2O is a liquid while H_2S is a gas. This is because strong hydrogen bonding is present in water. This is due to small size and high electronegativity of O.

30. Oxygen: Preparation:

$$2 \text{ KCIO}_3 \xrightarrow{\text{heat}} 2 \text{ KCI} + 3 \text{ O}_2$$

$$2 \text{ H}_2 \text{ O}_2(aq) \xrightarrow{\text{finely divided metals}} 2 \text{ H}_2 \text{ O}(\text{I}) + \text{ O}_2(\text{g})$$

$$2Ag_2O(s) \xrightarrow{\text{heat}} 4Ag(s) + O_2(g)$$

$$2 \text{HgO}(s) \xrightarrow{\Delta} 2 \text{HgO}(l) + O_2(g)$$

$$2Pb_{3}O_{4}(s) \xrightarrow{\Delta} 6PbO(s) + O_{2}(g)$$
(Red lead)
$$2PbO_{2}(s) \xrightarrow{\Delta} 2PbO(s) + O_{2}(g)$$

31. Oxides: The compounds of oxygen and other elements are called oxides.

Types of oxides:

a. Acidic oxides: Non- metallic oxides are usually acidic in nature.

 $SO_2 + H_2O \longrightarrow H_2SO_3$ (sulphurous acid)

b. Basic oxides: Metallic oxides are mostly basic in nature. Basic oxides dissolve in water forming bases e.g.,

 $Na_2O + H_2O \longrightarrow 2NaOH$ $K_2O + H_2O \longrightarrow 2KOH$

 $CaO + H_2O \longrightarrow Ca(OH)_2$

c. Amphoteric oxides: They show characteristics of both acidic as well as basic $Al_2O_3 + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O$

oxides. $Al_2O_3 + 6NaOH(aq) + 3H_2O(l) \longrightarrow 2Na_3[AI(OH)_6](aq)$

d. Neutral oxides: These oxides are neither acidic nor basic.

Example: CO, NO and N₂O

32. Ozone: Preparation:

i. It is prepared by passing silent electric discharge through pure and dry oxygen 10 - 15 % oxygen is converted to ozone.

 $3O_2(g) \longrightarrow 2O_3(g); \Delta H = +142 \text{ kJ mol}^{-1}$

Structure of Ozone: Ozone has angular structure. Both O = O bonds are of equal bond length due to resonance.

33. Sulphur:

Sulphur exhibits allotropy:

a. Yellow Rhombic (α - sulphur):

b. Monoclinic (β - sulphur):

 α – Sulphur $\xrightarrow{369 \text{ K}} \beta$ – Sulphur

At 369 K both forms are stable. It is called transition temperature.

Both of them have S_8 molecules. The ring is puckered and has a crown shape.

Another allotrope of sulphur – cyclo S_6 ring adopts a chair form.

 S_2 is formed at high temperature (~ 1000 K). It is paramagnetic because of 2 unpaired electrons present in anti bonding π^* orbitals like O_2

34. Sulphuric acid: Preparation: By contact process

$$\frac{1}{8}S_8 + O_2 \longrightarrow SO_2$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5}{2bar} 2SO_3(g) \qquad \Delta H^{\theta} = -196.6 \text{ kJ mol}^{-1}$$

Exothermic reaction and therefore low temperature and high pressure are favorable

 $SO_3(g) + H_2SO_4 \longrightarrow H_2S_2O_7$ (Oleum)

 $H_2S_2O_7 + H_2O \longrightarrow 2 H_2SO_4$ (96-98%)

It is dibasic acid or diprotic acid. It is a strong dehydrating agent. It is a moderately strong oxidizing agent.

GROUP 17 ELEMENTS

- 35. Atomic and ionic radii: Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.
- 36. **Ionisation enthalpy:** They have very high ionization enthalpy because of small size as compared to other groups.
- 37. Electron gain enthalpy: Halogens have maximum negative electron gain enthalpy because these elements have only one electron less than stable noble gas configuration.

Electron gain enthalpy becomes less negative down the group because atomic size increases down the group.

38. **Eelctronegativity:** These elements are highly electronegative and electronegativity decreases down the group. They have high effective nuclear charge.

39. Bond dissociation enthalpy:

Bond dissociation enthalpy follows the order $Cl_2 > Br_2 > F_2 > I_2$ This is because as the size increases bond length increases.

Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2 .

- 40. **Colour:** All halogens are coloured because of absorption of radiations in visible region which results in the excitation of outer electrons to higher energy levels.
- 41. Oxidising power: All halogens are strong oxidizing agents because they have a strong tendency to accept electrons. Order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$
- 42. Reactivity with H₂:

Acidic strength: HF < HCl < HBr < HI Stability: HF > HCl > HBr > HI This is because of decrease in bond dissociation enthalpy. Boiling point: HCl < HBr < HI < HF HF has strong intermolecular H bonding As the size increases, van der Waals forces increases and hence boiling point increases.

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% Ionic character: HF > HCl > HBr > HI Dipole moment: HF > HCl > HBr > HI Electronegativity decreases down the group. Reducing power: HF < HCl < HBr < HI

43. Reactivity with metals: Halogens react with metals to form halides.

Ionic character: MF > MCl > MBr > MI

Halides in higher oxidation state will be more covalent than the one in the lower oxidation state.

44. Interhalogen compounds: Reactivity of halogens towards other halogens:

Binary compounds of two different halogen atoms of general formula X X'_n are called interhalogen compounds where n = 1, 3, 5, or 7

These are covalent compounds.

Interhalogen compounds are more reactive than halogens because X-X' is a more polar bond than X-X bond.

All are diamagnetic.

Their melting point is little higher than halogens.

XX' (CIF, BrF, BrCl, ICl, IBr, IF) (Linear shape)

XX'₃ (CIF₃, BrF₃, IF₃, ICl₃) (Bent T- shape)

 XX'_{5} – CIF₅, BrF₅, IF₅, (square pyramidal shape)

 $XX'_7 - IF_7$ (Pentagonal bipyramidal shape)

45. Oxoacids of halogens:

Fluorine forms only one oxoacid HOF (Fluoric (I) acid or hypofluorous acid) due to high electronegativity. Acid strength: $HOCl < HClO_2 < HClO_3 < HClO_4$ Reason: $HClO_4 \rightarrow H^+ + ClO_4^-$ most stable Acid strength: HOF > HOCl > HOBr > HOIThis is because Fluorine is most electronegative.

GROUP 18 ELEMENTS:

- 46. Ionisation enthalpy: They have very high ionization enthalpy because of completely filled orbitals.Ionisation enthalpy decreases down the group because of increase in size.
- 47. Atomic radii: Increases down the group because number of shells increases down the group.

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- 48. **Electron gain enthalpy:** They have large electron gain enthalpy because of stable electronic configuration.
- 49. Melting and boiling point: Low melting and boiling point because only weak dispersion forces are present.
- 50. XeF_2 is linear, XeF_4 is square planar and XeF_6 is distorted octahedral. KrF_2 is known but no true compound of He Ne and Ar are known.

51. Compounds of Xe and F:

 $Xe + F_2 \xrightarrow{673 \text{ K, 1bar}} XeF_2$

$$Xe + 2F_2 \xrightarrow{873 \text{ K}} XeF_4$$

$$Xe + 3F_2 \xrightarrow{573 \text{ K}} XeF_6$$

 $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

 XeF_2 , XeF_4 and XeF_6 are powerful fluorinating agents.

52. Compounds of Xe and O

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

 $XeF_6 + 3 H_2O \longrightarrow XeO_3 + 6 HF$

Conceptual questions and answers

Q1) Why penthalides more covalent than trihalides

Ans) Higher the positive oxidation state of central atom, more will be its polarizing power. Which it turns increases the covalent character of bond formed between the central atom and the other atom

Q2) Why is BiH_3 the strong reducing agent amongst all the hydrides of group 15 elements

Ans) Because BiH_3 is the least stable amongst the hydrides of group 15. Bi - H bond is the weakest amongst the hydrides of elements of group 15.

Q3) Why does the reactivity of nitrogen differs from Phosphorous?

Ans) Nitrogen forms $p\pi - p\pi$ multiple bonds with itself where as phosphorous does not form $p\pi - p\pi$ multiple bonds. Thus nitrogen exists as s diatomic molecule with a triple bond (N=N) between the two atoms, consequently, its bond enthalpy is very high. Therefore nitrogen is inert and unreactive in its elemental state. In contrast, phosphorous forms single bonds and exists as P₄ molecule. Since P-P single bond is much weaker than N=N triple bond, therefore, phosphorous is much more reactive than nitrogen.

Q4) Why does NH₃ forms hydrogen bond but PH₃ does not? Ans) The electro negativity of Nitrogen is much higher than that of phosphorous, as a result, N-H bond is quite polar and hence NH₃ undergoes intermolecular H-bonding where as P-H bond is less polar and hence PH₃ does not undergo H – bonding.

Q5) PH₃ has lower boiling point than NH₃ why?

Ans) N3 undergoes extensive intermolecular H-bonding and hence it exists as an associated molecule. On the other hand, PH₃ does not undergo H-bonding and thus exists as discrete molecules. Therefore PH3 has lower boiling point than NH₃

Q6) Why does NH₃ act as a Lewis base? Nitrogen atom in NH₃ has lone pair of electrons which is available for donation. Therefore, it acts as Lewis base.

Q7) Give reason for anomalous property of Nitrogen Ans) Nitrogen differs from the rest of the members of group 15 due to its smaller size, high electro negativity, higher ionization enthalpy and nonavailability of d-orbitals

Q8) Write the reaction for thermal decomposition of Sodium azide Ans) $2NaN_3 \rightarrow 2Na+3N_2$

Q9) Nitrogen exists as diatomic molecule and phosphorous as P₄ why? Ans) Nitrogen because of its small size and higher electro negativity forms $p\pi - p\pi$ multiple bonds with itself. Therefore it exists as a diatomic molecule having a triple bond between two Nitrogen atoms. Phosphorous, on the other hand, due to its large size and lower electro negativity does not form $p\pi - p\pi$ multiple bonds with itself. Instead it prefers to form P-P single bonds and hence exists as P₄ molecules

Q10) Nitrogen exists in gaseous state whereas Phosphorous in solid state why? Ans) Refer Q9

Q11) Explain why NH₃ is basic while BiH₃ is only feebly basic? Ans) N in NH₃ and Bi in BiH₃ have a lone pair of electrons on the central atoms and hence should behave as Lewis base. Since atomic size of 'N' is much smaller than that of Bi therefore, electron density on the N-atom is much higher than that of Bi atom. Consequently, the tendency of N in NH₃ to donate its pair of electrons is much higher than BiH₃

Q12) Why does R₃P=O exist but R₃N=0 does not (R = alkyl group) Ans) Nitrogen due to the absence of d-orbital's cannot form $p\pi - d\pi$ multiple bonds and hence cannot expand its covalency beyond 4. Therefore N cannot form R₃N=0 in which the covalency of N is 5. In contrast, P due to the presence of d-orbitals forms $p\pi - d\pi$ multiple bonds and hence can expand its covalency beyond 4. Therefore P forms R₃P+o in which the covalency of P is 5

Q13) What is the covalency of Nitrogen in N_2O_5 The covalency of nitrogen in $N_2 O_5$ is four

Q14) Name the various oxides of Nitrogen. Mention their oxidation states. Give their preparation

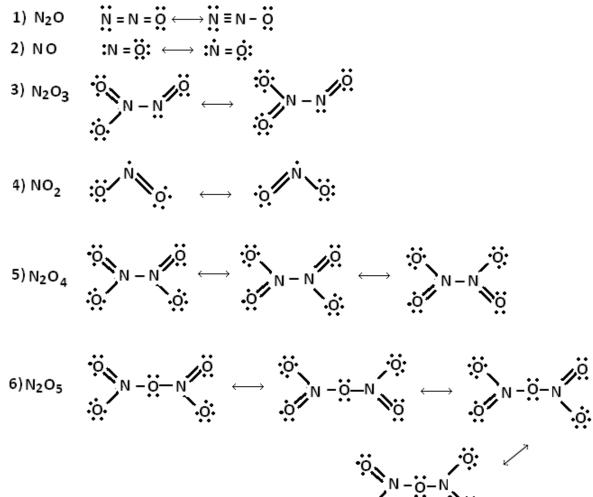
- 1) N₂O , Dintrogen oxide or Nitogen (I)oxide, oxidation State +1 $NH_4 \xrightarrow{heat} N_2O + H_2O$
- 2) NO Nitrogen oxide, oxidation state +2 $NaNO_2 + 2FeSO_4 + 3H_2SO_4 \xrightarrow{heat} NO + Fe_2(SO_4)_3 + 2NaHSO_4$
- 3) N₂O₃ Dintrogen trioxide or Nitrogen (III) oxide, oxidation state +3 $2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$
- 4) NO₂, Nitrogen dioxide or Nitrogen (IV) oxide, oxidation state +4 $Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO$
- 5) N₂O₄ Dinitrogen tetraoxide or Nitrogen (IV) oxide, oxidation state +5 $2NO_2 \xleftarrow{Cool}{Heat} N_2O_4$
- 6) N₂O₅ (Dintrogen pentoxide) or Nitrogen (V) oxide, oxidation state +6 $4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$

Q15) Why does NO₂ dimerise?

Ans) NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation it is converted to stable N_2O_4 molecule with even number of electrons

Q16) Why does nitrogen show catenation property less than Phosphorus? Ans) The property of catenation depends upon the strength of the element – element bond. Since the single N-N bond is weaker than single P-P bond strength, therefore nitrogen shows less catenation properties than phosphorus

Q17) Give resonating structures of following oxides Ans)



Q18) Metals like Cr, Al do not dissolve in concentrated HNO₃ why? Ans) It is because of the formation of passive film of oxide on the surface

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Q19) Bond angle in PH_4^+ is higher than in PH_3 why?

Ans) Both are sp³ hybridised. In PH_4^+ , all the four orbitals are bonded where as in PH_3 , there is a lone pair of electrons on P. Which is responsible for lone pairbond pair repulsion PH_3 reducing the bond angle to less than $109^{\circ}28'$

Q20) What happens when white phosphorous is heated with conc. NaOH solution in an inert atmosphere of CO_2 ?

Ans) White phosphorous reacts with NaOH solution in an inert atmosphere to form Phosphine

 $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$

Q21) Why does the PCl₃ fume in moisture? Ans) PCl₃ hydrolyses in the presence of moisture giving fumes of HCl PCl₃ + $3H_2O \rightarrow H_3PO_3 + 3HCl$

Q22) Are all the five bonds in PCl₅ molecule equivalent? Justify your answer Ans) PCl₅ has a trigonal bipramidal structure and the three equal P-Cl bonds are equivalent, while two axial bonds are different and longer than equatorial bond

Q23) What happens when PCl₅ is heated? Ans) When heated PCl₅ sublimates but decomposes on strong heating $PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$

Q24) Write a balanced chemical equation for the hydrolysis reaction of PCl_5 in heavy water

 $PCl_5 + D_2O \xrightarrow{Heat} POCl_3 + 2DCl$

Q25) how do you account for the reducing behavior of H_3PO_2 , Ans) In H_3PO_2 , Two H atoms are bounded directly to P atom which imports reducing character to the acid.



Q26) What is the basicity of H₃PO₄?

Ans) Since it contains three ionizable H-atoms which are present as OH group, it behaves as a tribasic acid i.e the basicity is three

Q27) H₃PO₃ is a dibasic acid why?

Ans) Since it contains two ionizable H atoms which are present as OH groups, it behaves as a dibasic acid. i.e. the basicity is two

Q28) What happens when H₃PO₂ is a monobasic acid why?

Ans) Since it contains only one ionizable H-atom which is present as OH group it behaves as a monobasic acid i.e basicity is one

Q29) What happens when H₃PO₃ is heated?

Ans) Phosphorous acid on heating disproportionate to give phosphoric acid and phosphine

 $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

Q30) Give an example for reducing property of H_3PO_2 ? Ans) H_3PO_2 reduces AgNO₃ to Ag $4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4 HNO_3 + H_3PO_4$

Q31) NO (nitric oxide) is paramagnetic in the gaseous state but diamagnetic in the liquid and solid state why?

Ans) NO has an odd number of electrons and hence is paramagnetic in gaseous state, but in the liquid and solid state it exists as dimer and hence diamagnetic in these states

Q32) NCl₃ gets readily hydrolyzed while NF₃ does not. Why? Ans) In NCl₃, Cl has vacant d-orbital to accept the lone pair of electrons donated by O-atom of H₂O molecules but in NF₃, F does not have d-orbital

Q33) PCl_5 is in ionic in nature in the solid state. Give reason Ans) In the solid state it exists as $[PCl_4]^+ [PCl_6]^-$. Therefore PCl_5 is ionic nature in the solid state

Q34) Can PCl₅ act as an oxidizing as well as reducing agent? Justify

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Ans) The oxidation state of P in PCL₅ is +5. Since P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore PCl₅ cannot act as a reducing agent. However, it can decrease its oxidation state from +5 to lower oxidation state, therefore PCl₅ can act as an oxidizing agent

 $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$ Sn + 2PCl_5 \rightarrow SnCl₄ + 2 PCl₃

Q35) H₂S is less acidic than H₂Te. Why?

Ans) H-S bond dissociation energy is higher than that of H-Te bond dissociation energy and hence H-S bond breaks less easily than H-Te bond. Hence H_2S is a weaker acid than H_2 Te

Q36) Why is H₂O is liquid and H₂S a gas?

Ans) Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state. In contrast, H₂S does not undergo H-bonding and exists as discrete molecules. Therefore, H₂S is gas at room temperature

Q37) Give reason for anomalous behavior of Oxygen Ans) Oxygen differs from the rest of members of the group due to its smaller size, high electronegativity and non-availability of d-orbitals

Q38) Which of the following do not reacts with oxygen directly. Zn, Ti, Rt, Fe Ans) Platinum does not reacts with oxygen directly. It is because the sum of first four ionization enthalpy is very large

Q39) Why is dioxygen is a gas while sulphur is solid

Ans) Due to small size and high electronegativity, oxygen form $p\pi$ - $p\pi$ multiple bonds, as a result oxygen exists as diatomic molecules (O₂) and has less intermolecular force of attraction. Therefore, O₂ 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 prefers to form S-S single bond as a result, sulphur exists as octa-atomic (S₈) and has high intermolecular force of attraction. Therefore, sulphur is a solid at room temperature

Q40) What are acidic oxide? Give examples Ans) An oxide which give a acid with water is known as acidic oxides. E.g CO₂, SO_2 , N_2O_5

Q41) What are basic oxides? Give examples

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Ans) An oxide which give a base with water is known as basic oxide. E.g. N_2O , CaO, BaO

Q)42) What are amphoteric oxides? Give example

Ans) Those oxides which shows characteristics of both acidic as well as basic oxides are known as amphoteric oxides . they react with acids as well as bases e.g. Al_2O_3 , ZnO, PbO, SnO

Q43) What are neutral Oxides? Give examples

Ans) Oxides which neither react with acid nor with bases are called as neutral oxides. E.g. No, CO, N_2P

Q44) High concentration of ozone is dangerously explosive. Explain Ans) The decomposition of ozone into oxygen results in the liberation of heat (Δ H is negative) and an increase in entropy (Δ S). these two effects reinforce each other resulting in large negative Gibbs energy change (Δ G is negative) for its conversion into oxygen. Therefore, higher concentrations of ozone is dangerously explosive

Q45) Why does the ozone acts as a power oxidizing agent? Ans) Due to the ease with which it liberates atom of nascent oxygen it acts as powerful oxidizing agent

Q46) How is O₃ estimated quantitatively Ans) When O₃ is treated with excess of KI solution buffered with Borate buffer (pH = 9.2). I₂ is liberated quantitatively which can be titrated against a standard solution of sodium thiosulphate $2I_{(aq)}^{-} + O_3 + H_2O \rightarrow 2OH^{-} + I_{2}(S) + O_{2}(S)$

Q47) Which aerosols deplete ozone? Ans) Freons deplete the ozone layer supplying Cl free radical which converts O_3 to O_2

Q48) Explain how nitrogen oxides deplete ozone layer

An) Nitrogen oxides emitted from the exhaust system of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone in the upper atmosphere

 $\mathrm{NO}_{(g)} + \mathrm{O}_{3(g)} \twoheadrightarrow \mathrm{NO}_{2(g)} + \mathrm{O}_{2(g)}$

Q48) What is meant by transition temperature of sulphur Ans) The temperature at which both α –sulphur and β -sulphur are stable is known as transition temperature. The transition temperature of sulphur is 369K.

Below 369K α –sulphur is stable where as above 369K β -sulphur is stable

Q49) Which form of sulphur shows paramagnetic behavior Ans) In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and hence, exhibits paramagetism

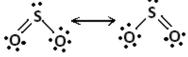
Q50) What happens when SO_2 (sulphur dioxide) is passed through an aqueous solution of Fe(III) salt

Ans) SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe(III) salt to Fe(II) salt

 $2Fe^{+3} + + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

Q51) Comment on the two S-O bonds formed in SO_2 molecule , are the two bonds in this molecule equal

Ans) Both S-O bonds are covalent and have equal strength due to resonating structures



Q52) Why is Ka₂ << Ka₁ for H₂SO₄ in water Ans) H₂SO₄ (aq) + H₂O(l) \rightarrow H₃O⁺(aq) + HSO₄⁻ (aq) , Ka₁ HSO₄⁻_(aq) + H₂O(l) \rightarrow H₃O⁺(aq) + SO₄⁻² (aq) , Ka₂ Ka₂ is less than Ka₁ because the negatively changed HSO₄⁻ ion has much less tendency to donate a proton to H₂O as compared to neutral H₂SO₄ to donate a proton to water

Q53) Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table why

Ans) Halogens have the smallest size in the respective periods and therefore high effective nuclear change. As a consequence they readily accept one electron to acquire noble gas electronic configuration.

Q54) The electron gain enthalpy of fluorine is less than that of chlorine why? Ans) It is due to small size of fluorine atom. AS a result, there is strong interelectronic repulsion in the relatively small 2p orbitals of fluorine and thus the incoming electron does not experience much attraction

Q55) Although electrogain enthalpy in a stronger oxidizing agent than chlorine why?

Ans) It is due to

- (i) Low enthalpy of dissociation of F-F bond
- (ii) High hydration and enthalpy of F⁻ ion

Q)56) Give two examples to show the anomalous behavior of fluorine? Ans) (i) Fluorine shows only an oxidation state of -1 while other halogens. Show positive oxidation states of +1, +3, +5 and +7 besides oxidation state of -1

(ii) The band dissociation enthalpy of F-F bond is lower than that of Cl-Cl bond

Q57) Explain why fluorine forms only one oxoacid, HOF?

Ans) Fluorine is the most electronegative element and can exhibit only -1 oxidation state. Secondly Fluorine does not have d-orbitals in its valence shell and therefore cannot expand it octet. Hence Fluorine form only one oxoacid

Q58) What are interhalogen compounds? Give examples

Ans) When two different halogens react with each other to form a number of compound called interhalogen compounds. There general formula is XX'_n where X is a less electronegative halogen while X' is a more electronegative halogen (smaller size halogen) and n is its number e.g IF₇, BrF₅ IF₅

Q59) Explain why inspite of nearly same electronegativity oxygen forms hydrogen bonding while chlorine does not

Ans) Oxygen has smaller size than chlorine. As a result electron density per unit volume on oxygen atoms is much higher than that of on chlorine atom. Therefore, oxygen forms H-Bonds while chlorine does not

Q60) Why Halogens are coloured

Ans) All the halogens are coloured. This is due to absorption of radiation in visible region which result in the excitation of outer electrons to higher energy level. While the remaining light is transmitted. The colour of the halogens is actually the colour of this transmitted light. By absorbing different quanta of radiation they display different colours

Q61) Give the bleaching action of Cl_2 Ans) In presence of moisture or in aqueous solution, Cl_2 liberates nascent oxygen which is responsible for bleaching action of Cl_2 $Cl_2 + H_2O \rightarrow 2HCl + O$ (nascent oxygen) The bleaching action of Cl_2 is due to oxidation

Q62) Why is ICl more reactive than I_2 ?

Ans) In general, interhalogen compounds are more reactive than halogen due to weaker X-X' bonding than X-X bond thus ICl is more reactive than I₂

Q63) Why are the elements of Group 18 known as noble gases? Ans) The elements present in Group 18 have their valance shell orbitals completely filled and therefore, react with a few elements only under certain condition. Therefore, they are known as noble gases

Q64) Noble gases have very low boiling points. Why?

Ans) Noble gases being mono-atomic have no inter-atomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling point.

Q65) Noble gases are least reactive. Why?

Ans) It is due to following reasons

- i) The noble gases except helium (1s²) have completely filled ns²np⁶ electronic configuration in their valence shell
- ii) They have higher ionization enthalpy and more positive electron gain enthalpy

Q66) What inspired N. Bartlett for carrying out reaction between Xe and PtF₆? Ans) N.Bartlett observed that PtF₆ reacts with O₂ to yield an ionic solid $O_2^+PtF_6^+$. Since the first ionization enthalpy of molecular oxygen (1175 KJmol⁻¹) is almost identical with that of xenon is (1170 KJmol⁻¹). Bartlett thought that PtF₆ should also Oxidises Xe to Xe⁺. This inspired Bartlett to carry out the reaction between Xe and PtF₆. He prepared X⁺[PtF₆]⁻ mixing PtF₆ and Xe Xe + PtF₆ \rightarrow Xe⁺ [PtF₆]⁻

Q67) Does the hydrolysis of XeF_6 leads to a redox reaction Ans) No, the products of hydrolysis are $XeOF_4$ and $XeO_2 F_2$ where oxidation states of all elements remain the same as it was in the reacting state

Q68) Why is helium used in diving apparatus?

Ans) Because of its low solubility compared to N_2 in blood a mixture of oxygen and helium is used in diving apparatus

Q69) Why has been difficult to study the chemistry of radon? Ans) Radon is radioactive with very short half life which makes the study of chemistry of radon difficult

Q70) With what neutral molecule is ClO⁻ iso-electronic . is that molecule is a Lewis base

Ans) ClF, Yes it is Lewis base due to presence of lone pair of electrons

Q71) Bismuth is a strong oxidizing agent in the pentavalent state. Why? Ans) Due to inter pair effect, +5 oxidation state of Bi is less stable than +3 oxidation state. Therefore, Bismuth in the pentavalent state can easily accept two electrons and this gets reduced to trivalent bismuth $Bi^{+5} + 2e^{-} \rightarrow Bi^{+3}$

Q72) Nitric oxide becomes brown when released in air. Why? Ans) Nitric oxide readily combines with O_2 of the air to form a nitrogen dioxide (NO₂) which has brown colour 2NO + $O_2 \rightarrow 2NO_2$

Q73) H_2S is less acidic than H_2Te . Why? Ans) H-S bond dissociation enthalpy is higher than that of H-Te bond dissociation enthalpy and hence H-Te bond breaks easily than H-S bond. Therefore H_2S is a weaker acid than H_2Te

Q74) H_2S acts only as a reducing agent but SO_2 acts as a reducing agent as well as an oxidizing agent. Why?

Ans) The minimum oxidation state of S is -2 while its maximum oxidation state is +6. In SO₂, the oxidation state of S is +4 therefore, it can not only increase its oxidation state by losing electrons but can also decrease its oxidation state by gaining electrons. As a result, SO₂ acts both as a reducing agent as well as oxidizing agent. On other hand, in H₂S, S has an oxidation state of -2. As a result it can only increase its oxidation state by losing electrons and hence it acts only as a reducing agent

Q75) Why the compounds of Fluorine with oxygen are called fluorides of oxygen (Oxygen fluorides) and not the oxides of fluorine (Fluorine oxide) Ans) This is because fluorine is more electronegative than oxygen

Q76) 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.

Q77) Bleaching by Chlorine is permanent while that by SO₂ is temporary Why? Ans) Cl₂ bleaches coloured material by Oxidation and hence bleaching is permanent. On the other hand, SO₂ bleaches coloured material by reduction and hence is temporary since when the bleached colour material exposed to air, it gets oxidized and the colour is restored.

Q78) Hydrogen iodide is stronger acid than Hydrogen fluoride in aqueous solution. Why?

Ans) Because of larger size of Iodine as compared to fluorine, the bond dissociation enthalpy of H-I bond is much lower than that of H-F bond. As a result, in aqueous solution, H-I bond breaks more easily to form H⁺ ion than H-F bond. Thus HI is strong acid than HF in aqueous solution

Q79) Helium and Neon do not forms compounds with fluorine why? Ans) He and Ne do not contain d-orbitals in their respective valence shells and hence their electrons cannot be promoted to higher energy levels. Therefore, He and Ne do not forms compounds with fluorine

Q80) Neon is generally used for warning signals. Why? Ans) Neon lights are visible from long distance even in fog and Mist and hence Neon is generally used for warning signals

Q81) Xenon does not form fluorides such as XeF_3 and XeF_5 Ans: As all the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5P – filled orbitals to 5d- vacant orbitals will give rise 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

Q82) Out of noble gases, only Xenon is known to form chemical; compounds why?

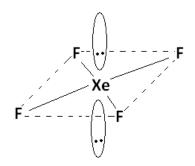
Ans) Except radon, which is radioactive, Xe has least ionization enthalpy among noble gases and hence it readily forms chemical compounds particularly O_2 and F_2

Q83) Knowing the electron gain enthalpy values of $O_2 \rightarrow O^-$ and $O \rightarrow O^{2-}$ as 141 KJ mol⁻ and 700 KJ mol⁻¹ respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^- Ans) It is because lattice energy of Oxides which overcome second electron gain enthalpy that is oxides are formed with O^{2-}

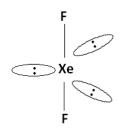
Q84) Give the formula and describe the structure of a noble gas species which is isostructural with (i) ICl_{4}^{-} (ii) $IBr_{2}^{-}3$ BrO_{3}^{-}

Ans (i) ICl₄⁻ is isostructural with XeF₄. XeF₄ has four bonding pair and two loan pairs of electrons. Therefore according to VSER theory XeF₄ has square planar structure.

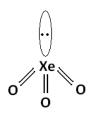
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(II) IBr_2^- : is isostructural with XeF_2 . XeF_2 has two bonding pairs and three lone pairs of electrons. Therefore according to VSEPER theory, XeF_2 has linear shape.



(III) BeO_3^- is isostructural with XeO_3 , XeO_3 has three bonding pairs and one lone pairs of electrons. Therefore according to VSEPR theory, XeO_3 has pyramidal structure



Q85) Deduce the molecular shape of BrF_3 on the basis of VSEPR theory Ans) The central atom Br has seven electrons in the valence shell. Three of these will form electron pair with three fluorine atoms leaving behind four electrons. Thus there are three bond pairs and two loan pairs. According to VSEPR theory, these will occupy the corners of trigonal bipyramid. The two loan pairs will occupy the equatorial position to minimize. Lonepair – lone pair repulsion. Which are greater than the bond pair –bond pair repulsion. In addition the axial Fluorine atom will be bent towards the equatorial fluorine in order to minimize the lone pair –loan pair repulsions. The shape will be that of slightly bent 'T'

Q86) Which one of PCl_4^+ and PCl_4^+ is not likely to exist and why? Ans) PCl_4^- does not exists because octet of "P' is not complete and it is unstable

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Q87) Despite lower value of its electron gain enthalpy with negative sign, fluorine (F_2) is a stronger oxidizing agent than Cl_2 Ans) It is due to higher reduction potential of F_2 which is due to low bond

dissociation energy of F-F bond due to repulsion among small size atoms, high electron gain enthalpy and highest hydration enthalpy

Q88) Which is stronger reducing agent, SbH₃ or BiH₃ and why? Ans) BiH₃ is stronger reducing agent because it has low bond dissociation energy than SbH, due to longer bond length Q89) Fluorine does not exhibit any positive oxidation state. Why?

Ans) Because it is most electronegative element and best oxidizing agent.

Q90) Explain why phosphorus forms PF_5 while nitrogen does not form NF_5 Ans) Phosphorous form PF_5 because it has d-orbitals where as nitrogen does not form NF_5 due to non-availability of d-orbitals

Q91) Why are covalent fluorides more inert than other covalent halides Ans) Covalent fluorides are inert due to strong covalent bonds as compared to other covalent halides in which halogens are bigger in size, therefore, bond formed is weaker



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