Chapter: The p-Block Elements.

Trends in properties of p block

Question 1

Among group 15 elements and group 14 elements which one have the higher ionisation energy and why?

Ans.

Group 15 elements have the higher ionisation energy due to the increase in nuclear charge and extra stable electronic configurations. The electronic configuration is stable due to the presence of half filled p-orbitals in their valence shells.

Question 2

Why fluorine does not show variable valency while other halogens show variable valency?

Ans.

The electronic configuration of fluorine is $1s^2$, $2s^2$, $2px^2$, $2py^2$, $2pz^1$. It has only one half filled orbital and there is no d- orbital available for the excitation of electrons.

Fluorine is also the most electronegative element so it shows the oxidation state of -1 only. But in all other halogens the d-orbitals are available for excitation of electrons so they can combine with more electronegative elements and show variable positive oxidation states.

Question 3

Give reasons for the following:

(i) Fluorine atom is more electronegative than iodine atom but HF has lower acidic strength than HI.

(ii) The electron affinity of fluorine is less than that of chlorine but the oxidizing power of fluorine is greater than that of chlorine.

Ans.

(i) The Fluorine atom is small in size so the bond dissociation energy of H-F molecule is very high as compared to the bond dissociation energy of H-I molecule.

(ii) The oxidizing power of fluorine is greater than the oxidizing power of chlorine because the reduction potential of fluorine is greater than the reduction potential of chlorine.

Question 4

Among noble gases and group 16 elements which one has higher ionisation enthalpy and why?

Ans.

Among noble gases and group 16 elements, the noble gases have a higher ionisation enthalpy because they have stable electronic configurations i.e., they have eight electrons in their valence shell.

Question 5

Halogens have maximum negative electron gain enthalpy in their respective periods of the periodic table. Explain.

Ans.

The halogens have a strong tendency to accept electrons due to their small size and effective nuclear charge so they have maximum negative electron gain enthalpy in their respective periods of the periodic table.

Question 6

The boiling point of NH_3 is higher than the boiling point of PH_3. Explain.

Ans.

In NH_3 the nitrogen atom is highly electronegative due to its small size so it undergoes hydrogen bonding and exists as an associated liquid where as PH_3 molecule does not form hydrogen bonds due to the large size of phosphorus atom.

Question 7

Write the order of thermal stability of hydrides of group 16 elements.

Ans.

The thermal stability of hydrides decreases down the group because of increase in size of the atoms as a result of which the strength of E-H bond decreases.

Question 8

Name the factors on which the metallic character of an element depends?

Ans.

The metallic character of an element depends upon the size of atoms and the ionisation energy of the element.

Question 9

Name two factors on which the electronegativity of an atom depend?

Ans.

The electronegativity of an atom depends upon the size of an atom and the electrons needed to complete the valence shell.

Question 10

What is the value of electron affinities of group 18 elements?

Ans.

The elements of group 18 (noble gases) have zero electron affinities due to stable electronic configuration.

Nitrogen and its compounds

Question 1

Why does NO_2 dimerise?

Ans.

NO_2 contains odd number of valence electrons. It behaves as an odd electron molecule and therefore undergoes dimerisation to form stable N_2O_4 molecule with even number of electrons.

Question 2

(a) Draw the molecular structures of following compounds:

(i) XeF_6

(ii) $H_2S_2O_8$

(b) Explain the following observations:

(i) The molecules NH_3 and NF_3 have dipole moments which are of opposite direction.

(ii) All the bonds in PCl_5 molecule are not equivalent.

(iii) Sulphur in vapor state exhibits paramagnetism.

OR

(a) Complete the following chemical equations:

(i) $XeF_4 + SbF_5 \rightarrow$

(ii) $Cl_2 + F_2$ (exces) $\rightarrow$

(b) Explain each the following:

(i) Nitrogen is much less reactive than phosphorus.

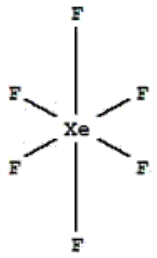
(ii) The stability of +5 oxidation state decreases down group 15.

(iii) The bond angles (O – N – O) are not of the same value in NO_2 and NO_2.

Ans.

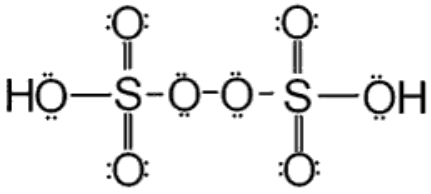
(a) Molecular structure are:

(i) XeF_6



(ii) $H_2S_2O_8$

$H_2S_2O_8$



(b)

(i) The dipole is a vector quantity represented by arrow with tail at more electropositive element and head pointing towards less electropositive element. In case of NF_3 fluoride is more electropositive than nitrogen therefore the arrow is from nitrogen to fluoride whereas in case of NH3 nitrogen is more electronegative than hydrogen. Thus the arrow moves from hydrogen towards nitrogen. Thus the dipole moment in molecules is in opposite direction.

(ii) PCl_5 has five valence electrons. It forms five bond with five F atoms. Since five electrons pair around the phosphorus therefore it has trigonal bipyramidal geometry. The bonds are not equal as three electron pairs are in the same plane at an angle of 120° are called equatorial bond while other two are perpendicular to the plane both making an angle of 90^O with the plane are called axial bond. Thus the bonds are not equivalent.

(iii) In vapour state it exist as S_2 molecule and has two unpaired electrons in antibonding orbitals. Thus sulphur exhibit paramagnetism.

OR

(a)

(i) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$

(ii) $Cl_2 + 3F_2(\text{excess}) \xrightarrow{573K} 2ClF_3$

(b)

(i) Due to presence of triple bond in nitrogen its reactivity decreases. Hence nitrogen is less reactive than phosphorus.

(ii) Due to inert pair effect the stability of +5 oxidation state decreases down group

Question 3

Give chemical reactions involved in brown ring test to confirm nitrates.

Ans.

The brown ring tests depend on the ability of ferrous ion to reduce nitrates to nitric oxide, which reacts with ferrous ion to form a brown colored complex.

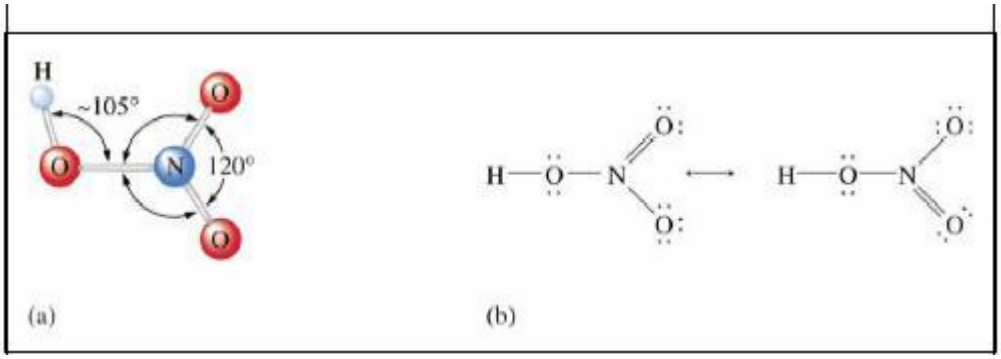
$$NO_3^{-1} + 3Fe^{2+} + 4H^+ \rightarrow NO + 3\,Fe^{3+} + 2H_2O$$

$$\left[Fe(H_2O)_6\right]^{2+} + NO \rightarrow \left[Fe(H_2O)_5(NO)\right]^{2+} + H_2O$$

Question 4

Give the structure of nitric acid.

Ans.



Question 5

Give equations in each step of oswald's process

Ans.

Nitric acid is produced industrially by the Ostwald Process, which involves three steps:

Step 1: Catalytic oxidation of ammonia

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

Step 2: Oxidation of nitric oxide

$$2NO + O_2 \longrightarrow 2NO_2$$

Step 3: Reaction with water and oxygen to form nitric acid:

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Question 6

Give flow chart for preparation of ammonia by Haber's process.

Ans.

nitrogen + hydrogen ⟶ ammonia (+ heat)

The process operates continuously and the recycling of the unreacted nitrogen and hydrogen, gives overall conversion of about 98%.

Question 7

Explain preparation of nitrogen.

Ans.

Air is liquefied, and the oxygen which is about 20.9% gets boiled off at -183^{o}C, leaving liquid nitrogen behind, which boils at -196^{o}C .This process is known as Fractional distillation. Nitrogen can also be made by heating NaN_3 to 300 degrees C. Annual worldwide production is around 44,000,000 tons.

Question 8

Why do chromium and aluminium not react with the most oxidizing agent?

Ans.

These elements form a passive layer of oxide on the surface and prevent the metal to react with nitric acid.

Question 9

Name the oxides of nitrogen and give oxidation number of each oxide.

Ans.

The common oxides of nitrogen include examples of nitrogen with every oxidation number from +1 to +5

N as +1: N_2O

N as +2: NO

N as +3: N_2O_3

N as +4: NO_2

N as +5: N_2O_5

Question 10

Give conditions which favors formation of ammonia as it is a reversible reaction.

Ans.

The reaction is reversible. Only about 15-20 % of the reactants are converted into products.The forward reaction) is exothermic.

Amount of product or yield from a reversible reaction depends on temperature, pressure and catalyst Decreasing the temperature favors exothermic reactions.

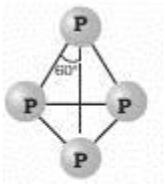
Increasing the pressure favors smaller volume.
Using a catalyst gives the equilibrium conditions more quickly.

Question 11
What is nitrogen fixation? Give an example.
Ans.
When nitrogen is converted into compounds usable by plants, the process is called nitrogen fixation. In plants nitrogen fixing bacteria in the root nodules of legumes convert N_2 to NH_3.

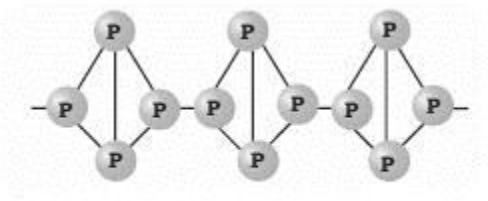
Question 12
Give reasons that nitrogen is different than the other member of its group.
Ans.
Nitrogen of group 15 differs substantially from its other group members in its high electronegativity, small size, ability to form multiple bonds and lack of usable d orbitals. Strong triple bonds in N make it very stable.

Phosphorus and its compounds

Question 1
Draw the structures of white phosphorus and red phosphorus. Which one of these two types of phosphorus is more reactive and why?
Ans.



Red phosphorus

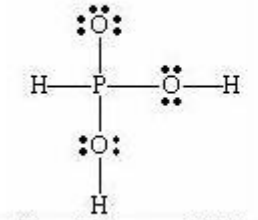


Red phosphorus

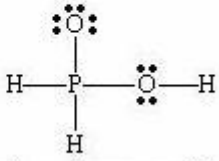
White phosphorus is less stable and therefore, more reactive than the red phosphorus under normal conditions because of angular strain in the P_4 molecule where the angles are 60° only.

Question 2
Which oxoacids of phosphorus are reducing in nature?
Ans.

All acid which have P-H bond are reducing in nature.
Example



Phosphorous acid, H_3PO_3

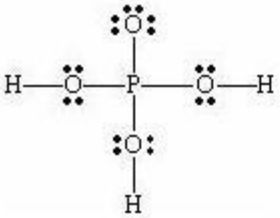


Hyphosphorous acid, H_3PO_3

Question 3

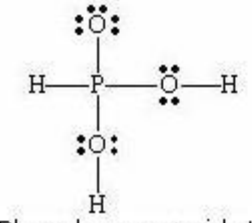
Why is phosphorus acid diprotic and phosphoric acid triprotic in spite 3 hydrogens in both?
Ans.

Structure of phosphoric acid is



Phosphoric acid, H_3PO_4

and has 3 ionisable hydrogens.
In phosphorus acid there are 2 ionisable hydrogens the third one is bonded to phosphorus.

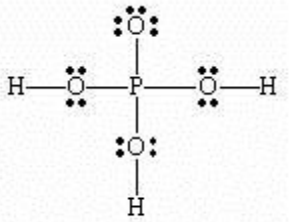


Phosphorous acid, H_3PO_3

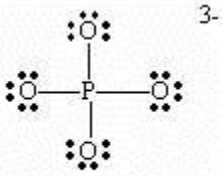
Question 4

Give the structure of oxy acids of phosphorus and list the anions formed.
Ans.

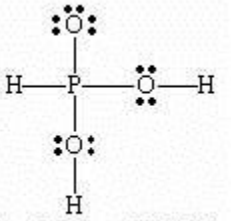
OXYACID	OXYANION



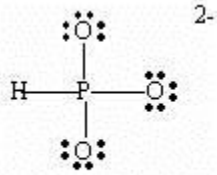
Phosphoric acid, H_3PO_4



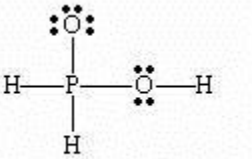
Phosphate, PO_4^{3-}



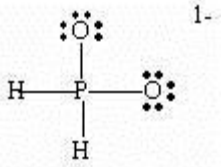
Phosphorous acid, H_3PO_3



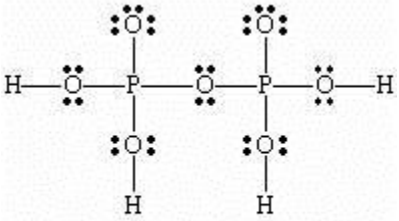
Phosphite, HPO_3^{2-}



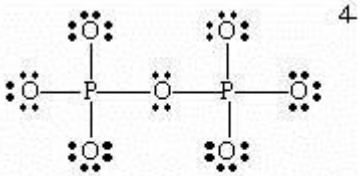
Hypophosphorous acid, H_3PO_2



Hypophosphite, $H_2PO_2^-$



Diphosphoric acid, $H_4P_2O_7$
(pyrophosphoric acid)



Diphosphate, $P_2O_7^{4-}$
(pyrophosphate)

Question 5

Why does PCl_3 fume in moisture?

Ans.

It hydrolyses in moisture giving fumes of HCl.

$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Question 6

Show that PH_3 is basic in nature.

Ans.

PH_3 has a lone pair of electron and readily reacts with acids like HI and forms.

$PH_3 + HI \rightarrow PH_4I$.

Question 7

Give reason that NCl_5 is not formed but PCl_5 is formed.

Ans.

Nitrogen does not have usable d orbitals and cannot expand its octet. Phosphorus can expand its valence shell to hold more than eight electrons, but nitrogen cannot.

Question 8

What are the anhydrides of phosphorus and phosphoric acid?

Ans.

The oxides P_4O_6 and P_4O_{10} are the acid anhydrides of phosphorous acid and phosphoric acid.

Question 9

Name the allotropes of phosphorus.

Ans.

Phosphorus exists in three main allotropic forms ordinary (or white) phosphorus, red phosphorus, and black phosphorus.

When heated to between 230° and 300°C (446° and 572°F) in the absence of air, white phosphorus is converted into the red form.

Question 10

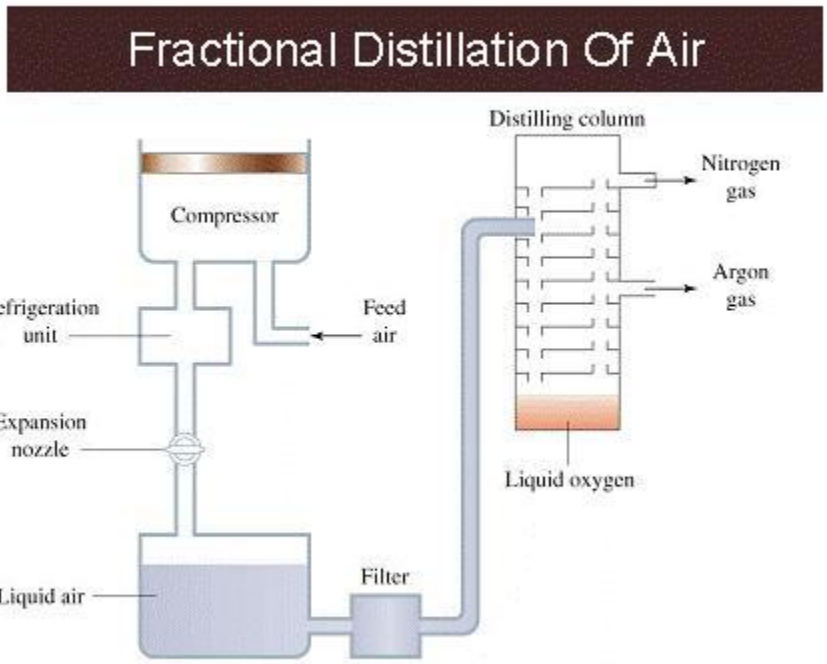
NH_3 is soluble in water but PH_3 is not soluble. Give reasons.
Ans.
Ammonia forms hydrogen bonds but phosphorus does not form hydrogen bonds with water as a result ammonia does dissolve in water.

Question 11
What are the other elements of group 15? How is phosphorus different from nitrogen?
Ans.
Nitrogen, arsenic, antimony and bismuth. Nitrogen-nitrogen triple bonds are much stronger than phosphorus-phosphorus triple bonds. P-P single bonds are stronger than N-N single bonds. Phosphorus can expand its valence shell to hold more than eight electrons, but nitrogen cannot. P_4 is less electronegative, than nitrogen and phosphorus is more likely to exhibit positive oxidation numbers. Common Oxidation Numbers of Phosphorus are -3, +3, and +5.

Oxygen

Question 1
How is oxygen prepared industrially and in the laboratory?
Ans.

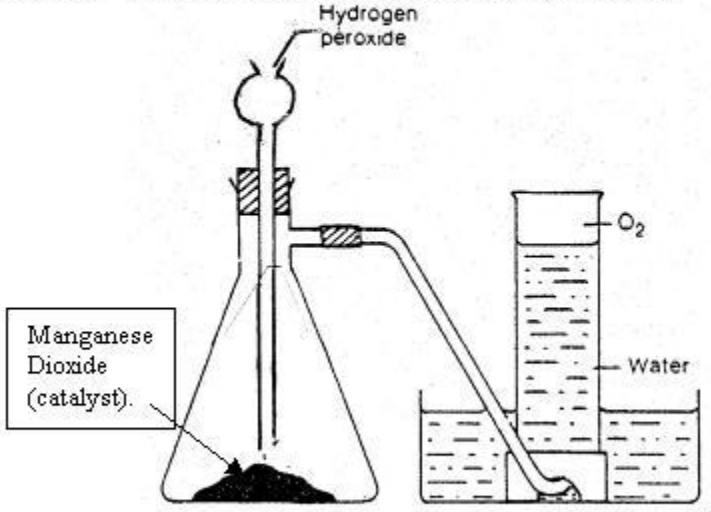
Oxygen is prepared industrially, together with nitrogen, by fractional distillation of air.



Oxygen may be prepared in small quantities by heating potassium chlorate, $KClO_3$ with manganese dioxide, MnO_2 as catalyst:

$2\ KClO_3(s) \longrightarrow 2\ KCl\ (S) + 3O_2(g)$

In the laboratory it can also be prepared by the electrolysis of water or by adding manganese(IV) oxide as a catalyst to aqueous hydrogen peroxide.



Catalyst

Hydrogen peroxide	=	Water	+	Oxygen
$2H_2O_2$	=	$2H_2O$	+	O_2

Question 2

Give physical properties and one test of oxygen.

Ans.

Colourless odourless gas. Slightly soluble in water (hence fish can breathe in it). Many substances, both elements and compound burn in oxygen (and in air which is one fifth oxygen).
Test : Oxygen relights a glowing splint.

Question 3

Show that hydrogen peroxide behaves both as an oxidizing and reducing agent.

Ans.

It produces oxygen and acts as a oxidizing agent in both acid and basic medium:
$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^-$
As a reducing agent $HOCl + H_2O_2 \rightarrow H_2O + Cl^- + O_2$

Question 4

Give general electronic configuration of group 16: oxygen family and comment on the metallic trend in the group.

Ans.

The group VI elements have an outer electron arrangement of ns^2, np^4 .The group VI elements have an outer electron arrangement of ns^2, np^4.
As we descend the group there is a clear trend from non-metals to metals. As we go down the group Sulphur, selenium and tellurium are able to form relatively long chains or catenate whereas oxygen is not.

Question 5

Write short note on the various types of oxides formed by oxygen.

Ans.

Oxygen forms oxides as well as peroxide and super oxides. In peroxides, the two extra electrons go into antibonding orbitals, reducing the bond order to one. The peroxide can be viewed as an oxygen molcules with two extra electrons. Metals that can form ionic peroxides include the alkali metals, calcium, barium, and strontium.
The superoxide molecule can be viewed as an oxygen molecule with an extra single electron and has a bond order of one and a half. Metals that can form ionic superoxides include potassium, rubidium, and cesium.

Question 6

List the anomalus behavior of water and give reason for each.

Ans.

1. Water has higher melting point due to extensive H-bonding.
2. Density of solid water is LESS than liquid state due to open cage structure of H-bonds.
3. Excellent solvent for ionic compounds due to high polarity.

Question 7

Water is an oxide of hydrogen. Comment on its nature.

Ans.

Water is a fascinating compound. It is amphoteric in nature. Hence, it can donate and accept protons. It behaves both Bronsted acid and Bronsted base. It can act as both oxidizing and reducing agent. It also acts as Lewis base due to unshared electron pair on oxygen.

Question 8

Is the boiling point of hydrogen peroxide higher or lower than water?

Ans.

H_2O_2 has two oxygen atoms, hence more extensive H-bonding is present in H_2O_2 than in H_2O this leads to a higher B.P of H_2O_2.

Question 9

Give reason H_2S is a gas and H_2O is liquid.

Ans.

H_2S is a gas as S is not electronegative enough to form H-bonding. In H_2O oxygen protonates hydrogen that it forms an electrostatic force of attraction with other oxygen atoms and this bond is called H-bonding. So the molecules are linked to each other by strong Hydrogen - bonds and so they have a high boiling.

Question 10

Name the two isotopes of oxygen. What is the environment disturbance caused by oxygen and its isotope?

Ans.

Oxygen normally exists as a diatomic molecule O_2, but its allotropic form called ozone O_3 is produced in the upper atmosphere. This acts as a shield protecting life from harmful ultraviolet rays. The destruction of this ozone layer by chemicals called CFC's (chlorinated fluorocarbons - now banned in several countries) is a major cause for concern.

Sulphur and its compounds

Question 1

State reasons for each of the following:

(i) The N – O bond is NO_2^- is shorter than the N – O bond in NO_3^-

(ii) SF_6 is kinetically an inert substance.

OR

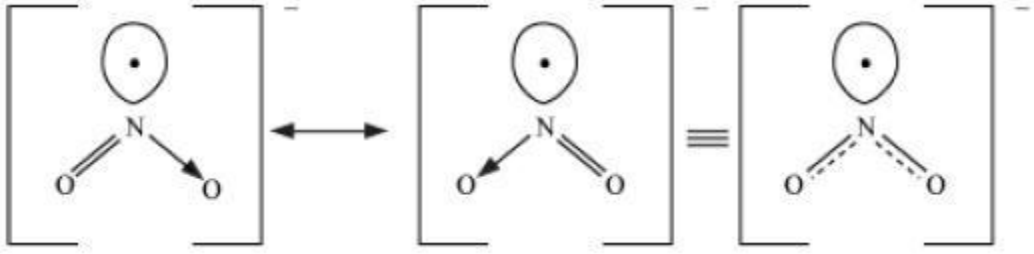
State reason for the each of the following:

(i) All the bonds in PCl_5 molecule are not equivalent.

(ii) Sulphur has greater tendency for catenation than oxygen.

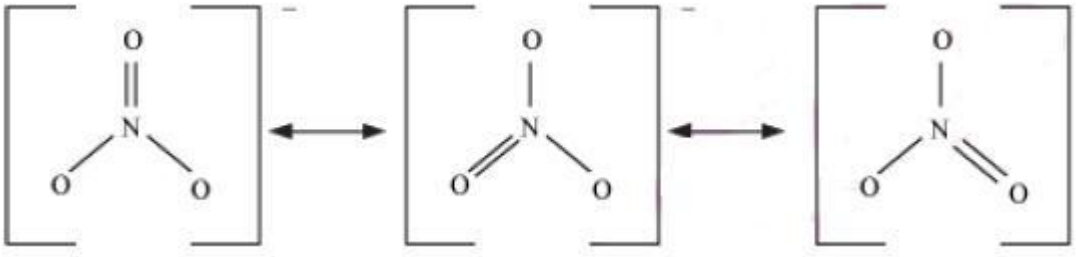
Ans.

The Shorter N – O bond in NO_2^- is due to the existence of resonance in NO_2^-. The resonating structure can be drawn as follows.



Due to resonance in NO_2^-, the two bonds are equivalent. This leads to a decrease in bond length. Thus, the N – O bond length in NO_2^- resembles a double bond.

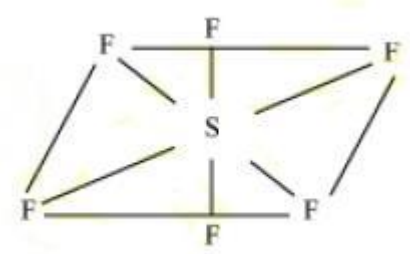
Now, the resonating structure for NO_3^- can be drawn as:



As seen from the above resonating structure of NO_3^-, the three oxygen atoms are sharing two single bonds and one double bond. So the real N-O bond length resembles a single bond closely.

This explains the existence of shorter bond length of the N-O bond in NO_2^- than in NO_3^-.

(ii) The kinetic inertness of SF_6 can be explained on the basis of its structure.



As seen from the above structure, the six fluorine (F) atoms protect the sulphur atom from attack by the regents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur.

OR

(i) In gaseous and liquid state, PCl_5 has a trigonal bipyramidal structure. In this structure, the two axial PCl bonds are longer and less stable than the three equatorial PCl bonds. This is because of the greater bond pair – bond pair repulsion in then axial bonds. Hence, all the bonds in PCl_5 are not equivalent.

(ii) Because of stronger S-S bonds as compared to O-O bonds, sulphur has a greater tendency for catenation than oxygen.

Question 2

PH_3 and H_2S which is more acidic and why?

Ans.

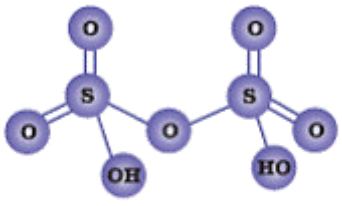
H_2S is more acidic than PH_3 because S is more electronegative than P. This results in the S-H bond to become more polar than a P-H bond and thus easier to remove. Once removed, the more electronegative S is more able to stabilize the negative charge, leading to a more stable conjugate base.

Question 3

What is oleum? Draw its structure

Ans.

Oleum is a oxoacid of sulphur and is a pyrosulphuric acid.- $H_2S_2O_7$



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Question 4

How SO_2 is formed and discuss its state at room temperature. Why SO_2 is a more powerful reducing agent in an alkaline medium than in an acidic medium.

Ans.

Sulphur when burnt in air forms dioxides, SO_2 is a gas at room temperature and has a bent structure with a bond angle of 119°

SO_2 is a strong reducing agent undergoes the following reaction

$$SO_2 + 2OH^- \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

The reaction proceeds in the forward direction with increase in the OH^- ions concentration.

Question 5

What happens when sulphur is passed through conc. H_2SO_4 solution and SO_2 is passed through an aqueous solution of Fe(III) salt?

Ans.

When sulphur is passed through conc H_2SO_4 solution it forms SO_2

$$3S + 2H_2SO_4 \text{ (conc.)} \longrightarrow 3SO_2 + 2H_2O$$

When SO_2 is passed through an aqueous solution of Fe(III) salt, it converts Fe(III) ions to Fe(II)

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

Question 6

What happens when SO_2 is treated with O_2 in presence of V_2O_5 catalyst. Draw the structure of the product formed in the gaseous state.

Ans.

When SO_2 is treated with O_2 in presence of V_2O_5 catalyst it forms SO_3

$$SO_2 + O_2 \xrightarrow{V_2O_5} SO_3.$$

Structure of SO_3(Gaseous state)

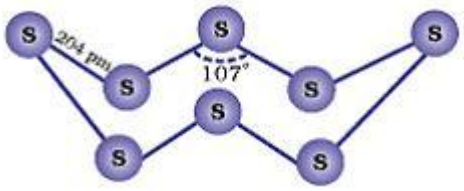
SO_3 exists as planar triangular molecule in the gaseous state and in the solid state it exists as a cyclic trimer.

Question 7

Draw the structure of rhombic sulphur.

Ans.

Both orthrombic and monoclinic sulphur have S_8 molecules which are puckered and crown shaped.



Question 8

Write the steps involved in the manufacture of sulphuric acid by contact process?

Ans.

Sulphuric acid is prepared by the contact process which involves burning of sulphide ores in air to generate SO_2, this is followed by conversion of SO_2 to SO_3 by the reaction with oxygen in presence of V_2O_5 catalyst and finally SO_3 is absorbed in H_2SO_4 to give oleum i.e. $H_2S_2O_7$.

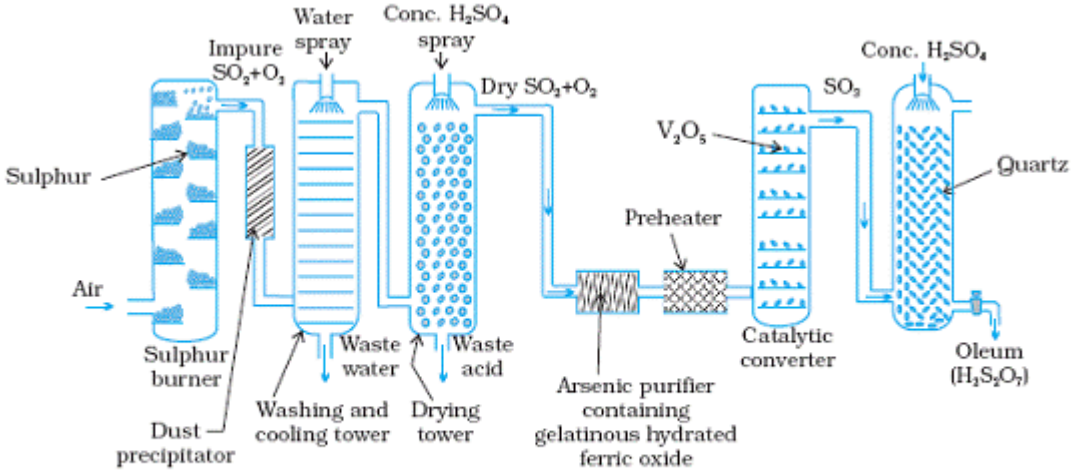


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid

Sulphuric acid -a bulk of it is used in the manufacture of fertilizers e.g ammonium sulphate, superphosphate and also in petroleum refining, manufacture of pigments, paints and dye stuff intermediates, in the detergent industry, in the metallurgical applications -electroplating and galvanizing. It is also used in the storage batteries and as a lab reagent.

Question 9

How to get an increased yield of sulphuric acid in Contact process.Draw the flow diagram for the manufacture of sulphuric acid.

Ans.

Catalytic oxidation of SO_2 with O_2 to give SO_3 in presence of V_2O_5 at a low temperature and high pressure are the favourable conditions for maximum yield in Contact process and finally SO_3 is absorped in H_2SO_4 .

$$SO_2 + O_2 \xrightarrow{V_2O_5} SO_3.$$

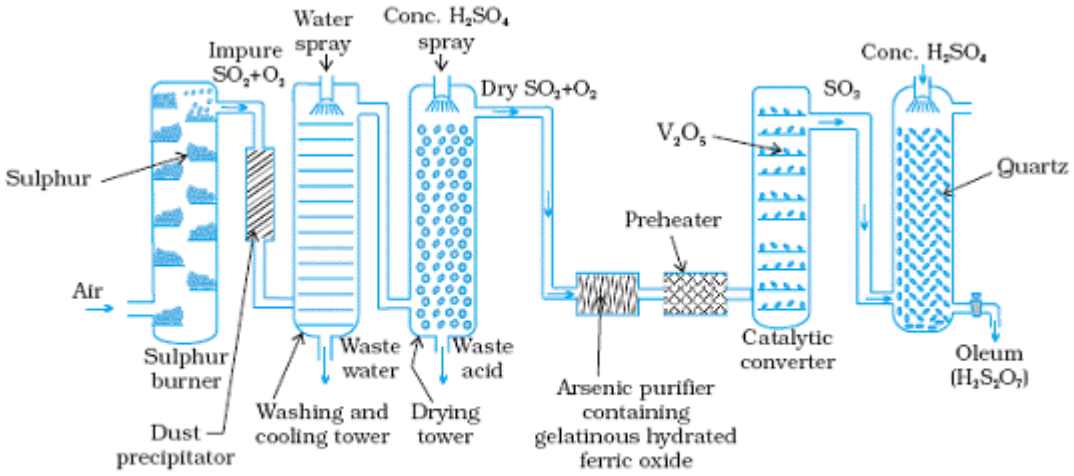
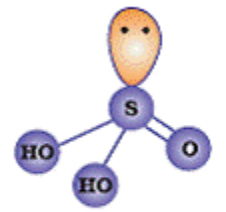


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid

Question 10

Draw the structure of Sulphurous acid.

Ans.



Sulphurous acid (H_2SO_3)

Question 11

Mention some of the uses of sulphuric acid.

Ans.

Sulphuric acid –a bulk of it is used in the manufacture of fertilizers e.g ammonium sulphate,superphosphate and also in petroleum refining, manufacture of pigments, paints and dyestuffintermediates, in the detergent industry, in the metallurgical applications – electroplating and galvanizing .It is also used in the storage batteries and as a lab reagent.

Question 12

What are the allotropic forms of sulphur?

Ans.

Sulphur forms two allotropic forms: These are rhombic-alpha sulphur and monoclinic sulphur-Beta sulphur.

Halogens

Question 1

(a) Explain the following:

(i) NF_3 is an exothermic compound whereas NCl_3 is not.

(ii) F_2 is most reactive of all the four common halogens.

(b) Compete the following chemical equations:

(i) $C + H_2SO_4\,(conc) \longrightarrow$

(ii) $P_4 + NaOH + H_2O \longrightarrow$

(iii) $Cl_2 + \underset{(excess)}{F_2} \longrightarrow$

OR

(a) Account for the following:

(i) The acidic strength decreases in the order $HCl > H_2S > PH_3$

(ii) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(b) Complete the following chemical equations:

(i) $P_4 + SO_2Cl_2 \longrightarrow$

(ii) $XeF_2 + H_2O \longrightarrow$

(iii) $I_2 + \underset{(conc)}{HNO_3} \longrightarrow$

Ans.

(a)

(i) As we move down the group 17, the size of the atom increases from fluorine to chlorine. The larger difference in the size of N and Cl results in the weakness of strength of N – Cl bond. On the other hand, the difference in size of N and F is small; consequently the N – F bond is quite strong. As a result, NF_3 is an exothermic compound.

(ii) Due to the small size of F atom, the three lone pair of electrons on each F atom F – F molecule repels the bond pair. As a result, F – F is most reactive of all the four common halogens.

(b)

(i) $C + 2H_2SO_4 \longrightarrow 2SO_2 + CO_2 + 2H_2O$

Sulphur dioxide

(ii) $P_4 + 3NaOH + 3H_2O \xrightarrow{CO_2} PH_3 + 3NaH_2PR_2$

Phosphine

(iii) $Cl_2 + 3F_2 \longrightarrow 2ClF_3$

(excess) Chlorine trifluoride

OR

(a)

(i) In a period, the electro negativity decreases in the order Cl > S > P. As a result, the loss of H^+ ions decreases.

Thus, the acidic strength of the hydrides decreases in the following order: $HCl > H_2S > PH_3$

(ii) The tendency to form pentahalides decreases down the group 15 due to inert pair effect i.e., in Bi the s-electrons remain inert and do not take part in bonding.

(b)

(i) $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$

(ii) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$

(iii) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(conc.)

Question 2

(a) Complete the following chemical equations:

(i) NaOH (aq)+ $\xrightarrow{Cl_2(g)}$

(Hot and conc.)

(ii) XeF_6(s) + H_2O(l) $\longrightarrow$

(b) How would you account for the following?

(i) The value of electron gain enthalpy with negative sign for sulphur

is higher than that for oxygen.

(ii) NF_3 is an exothermic compound but NCl_3 is endothermic compound.

(iii) ClF_3 molecule has a T-shaped structure and not a trigonal planar one.

OR

(a) Complete the following chemical reaction equations:

(i) $P_4 + SO_2Cl_2 \longrightarrow$

(ii) $XeF_4 + H_2O \longrightarrow$

(b) Explain the following observations giving appropriate reasons:

(i) The stability of +5 oxidation state decreases down the group in group 15 of the periodic table.

(ii) Solid phosphorus pentachloride behaves as an ionic compound.

(iii) Halogens are strong oxidizing agents.

Ans.

(a)

(i) $6\,NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

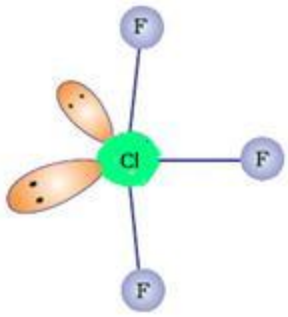
(ii) $XeF_6(s) + 3\,H_2O(l) \rightarrow XeO_3 + 6\,HF$

(b)

(i) This is because oxygen has a smaller size than sulphur. Hence, electron- electron repulsions will be more in the case of oxygen than sulphur.

(ii) This is because NF_3 is a stable compound whereas NCl_3 is an unstable compound. NF_3 is stable because of small difference between the size of N and F which results in stable N-F bond. NCl_3 is unstable because of large difference between the size of N and Cl which results is weak N-Cl bond.

(iii)This is because in ClF_3, Cl is sp^3d hybridised and two lone pairs are present on equatorial positions.



OR

(a)

(i) $P_4 + 10\ SO_2Cl_2 \rightarrow 4\ PCl_5 + 10SO_2$

(ii) $6\ XeF_4 + 12\ H_2O \rightarrow 4Xe + 2XeO_3 + 24\ HF + 3\ O_2$

(b)

(i) This is because of inert pair effect. As we move down the group, due to poor shielding of inner d- electrons, ns electrons are pulled strongly towards the nucleus. Thus, ns electrons are difficult to release and do not participate in bond formation.

(ii) This is because in solid state it exists as $[PCl_4]^+[PCl_6]^-$

(iii)This is because of their high electron affinities that they have a great tendency to take up electrons.

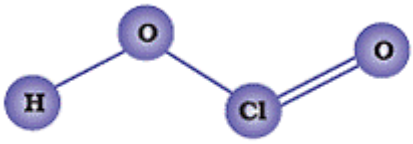
Question 3

Draw the structures of following oxoacids of chlorine

(i) Chlorous acid
(ii) Chloric acid
(iii) Perchloric acid

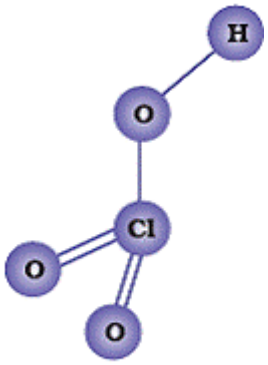
Ans.

(i)



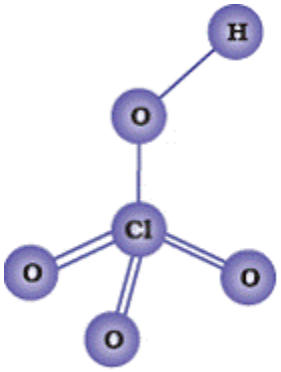
Chlorous acid

(ii)



Chloric acid

(iii)



Perchloric acid

Question 4

Give the balanced reactions when chlorine reacts with

(i) Excess Ammonia
(ii) Hot and conc. NaOH
(iii) Hydrogen sulphide

Ans.

$$\underset{\text{excess}}{8NH_3} + 3Cl_2 \longrightarrow \underset{\substack{\text{Ammonium}\\\text{chloride}}}{6NH_4Cl} + N_2$$

(ii) $6\,NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

(iii) $H_2S + Cl_2 \longrightarrow 2HCl + S$

Question 5

Give the two processes for manufacturing chlorine.
Ans.
(i) **Deacon's process**: Chlorine can be prepared by oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of catalyst $CuCl_2$.

$$4HCl + O_2 \xrightarrow[(ii)723K]{(i)CuCl_2} 2Cl_2 + 2H_2O$$

(ii) **Electrolytic process**: Chlorine is obtained by the electrolysis of concentrated NaCl solution, also called brine. In this process Chlorine is liberated at anode of the electrolytic cell.

Question 6
Give the laboratory method for the preparation of hydrochloric acid?
Ans.
In laboratory, HCL can be prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$$

Question 7
Why are halogens coloured?
Ans.
Absorption of radiations in visible region by halogen atoms, results in the excitation of outer electrons to higher energy level. By absorbing radiation of different wavelength, they display different colours. For example, F_2 has yellow, Cl_2 has greenish yellow colour, Br_2 has red colour and I_2 has violet colour.

Question 8
Electron gain enthalpy of the elements of the halogen group becomes less negative down the group. But, why the negative electron gain enthalpy of fluorine is less than that of chlorine?
Ans.
Due to small size of fluorine atom there are strong interelectronic repulsions in the relatively small 2*p* orbitals of fluorine atom and thus, the incoming electron does not experience much attraction. This is why the negative electron gain enthalpy of fluorine is less than that of chlorine.

Question 9

Name two poisonous gases which can be prepared from chlorine gas.

Ans.

(i) Phosgene ($COCl_2$) (ii) Tear gas (CCl_3NO_2).

Question 10

What is aqua regia?

Ans.

Aqua regia is mixture of three part Hydrochloric acid (HCl) and one part nitric acid (HNO_3).

Question 11

What is the chemical composition of bleaching powder?

Ans.

The composition of bleaching powder is $CaOCl_2.CaCl_2.Ca(OH)_2.2H_2O$.

Question 12

Write down the electronic configuration of Chlorine.

Ans.

Cl (17) : $1s^2, 2s^2 2p^6, 3s^2 3p^5$

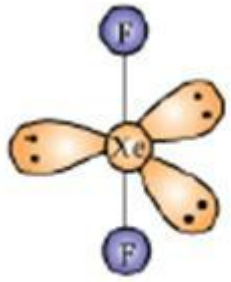
Group 18 elements

Question 1

Draw the structure of XeF_2 molecule.

Ans.

XeF_2 is a linear molecule and adopts the following structure:



Linear

Question 2

Explain the following giving an appropriate reason in each case.

(i) O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.

(ii) Structures of X enon fluorides cannot be explained by Valence Bond approach.

Ans.

(i) The tendency to stabilize highest oxidation state of a metal is maximum in oxygen than the fluorine because oxygen can form multiple bonds but fluorine do not.

(ii) According to valence bond theory valence electron take part in the bonding but since Xenon has completely filled electronic configuration in the valence shell. So structure of Xenon fluoride cannot be explained by valence bond approach.

Question 3

State usefulness of the Noble gases.

Ans.

Helium is a light gas. It is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Xenon and Krypton are also used in light bulbs designed for special purposes.

Question 4

How is xenon difluoride prepared? What happens when it is treated with PF_5?

Ans.

Xenon difluoride is prepared by treating xenon with fluorine at 673 K

$$\underset{\text{(xenon in excess)}}{Xe\ (g) + F_2\ (g)} \xrightarrow{673\,K,\ 1\,bar} XeF_2(s)$$

$$XeF_2 + PF_5 \rightarrow [XeF]^+\ [PF_6]^-;$$

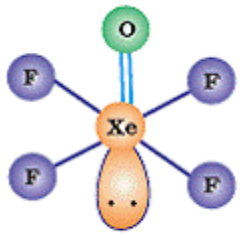
Question 5

Draw the structure of $XeOF_4$. How it is prepared?

Ans.

$XeOF_4$ is having a square pyramidal structure. It is prepared by treating XeF_6 with H_2O

$XeF_6 + H_2O$ ------à $XeOF_4 + 2\ HF$



(d) Square pyramidal

Question 6

Write the products of hydrolysis of XeF6 with 1,2 and 3 moles of water.

Ans.

The products of hydrolysis of XeF_6 with 1,2 and 3 moles of water are:

$XeF_6 + H_2O$ ------à $XeOF_4 + 2\ HF$

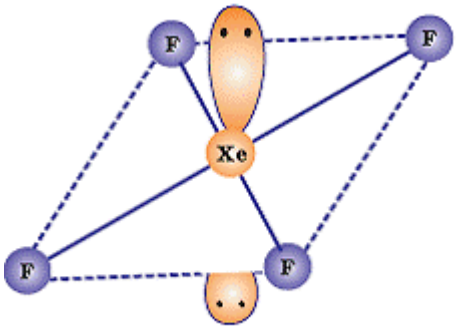
$XeF_6 + 2\ H_2O$ -----à $XeO_2F_2 + 4\ HF$

$XeF_6 + 3\ H_2O$ -----à $XeO_3 + 6\ HF$

Ques 8: Draw the structure of

XeF_4 ? (01/K/S)

Ans: XeF_4 is having a square planar structure.



(b) Square planar

Question 7

Comment on the ionization enthalpy of the inert gases. Discuss the trend that is observed down the group.

Ans.

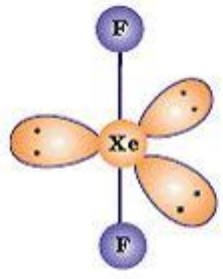
Ionisation enthalpy of inert gases are towards higher side. This is because of there stable inert gases electronic configuration of ns^2np^6.
Down the group with increase in atomic size, i.e. the atomic radii increases and hence ionization enthalpy decreases as the energy required to remove the outermost electron in an atom decreases.

Question 8
What are the binary fluorides of xenon?
Ans.
Xenon forms three binary fluorides: These are XeF_2, XeF_4 and XeF_6.

Question 9
What happens when Xenon reacts with fluorine in the ratio of 1:20?
Ans.
Xenon reacts with fluorine in the ratio of 1:20 ratio to give XeF_6

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

Question 10
Draw the structure of Xenon difluoride.
Ans.
Xenon difluoride is having a linear structure.



Linear

Question 11
Why noble gases have low boiling points?
Ans.

Noble gases have low boiling points as being monoatomic have weak dispersion forces and can be liquefied at low temperature.

Question 12

Why the noble gases are inert in nature?

Ans.

Noble gases are inert in nature as except for He ($1s^2$) as they have completely filled ns^2np^6 electronic configuration in their valence shell. Also they have high ionization enthalpy and more positive electron gain enthalpy.

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