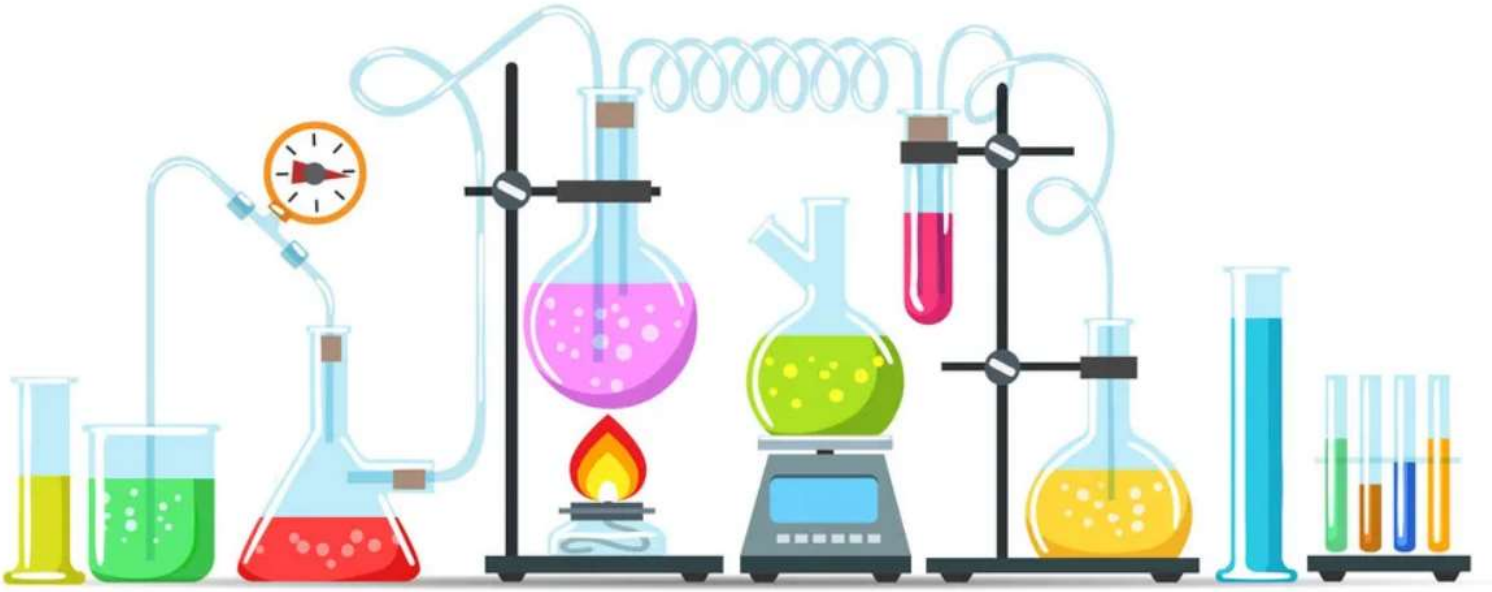
CHEMISTRY



THE p-BLOCK ELEMENTS

Sulphur and its Compounds

Allotropic Forms of Sulphur

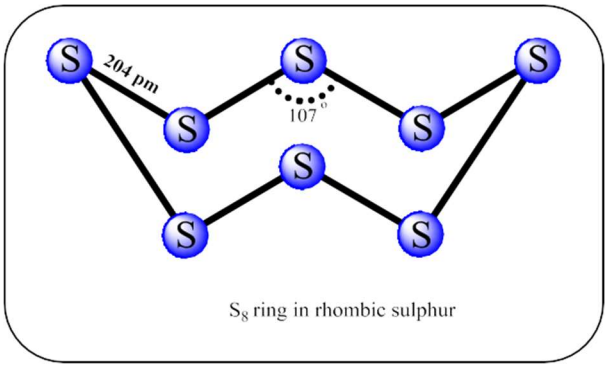
Sulphur forms a variety of allotropes. The most common allotropes are yellow rhombic and monoclinic sulphur. Rhombic sulphur is more stable at room temperature. It gets transformed to monoclinic sulphurwhen heated above 369 K.

Rhombic Sulphur

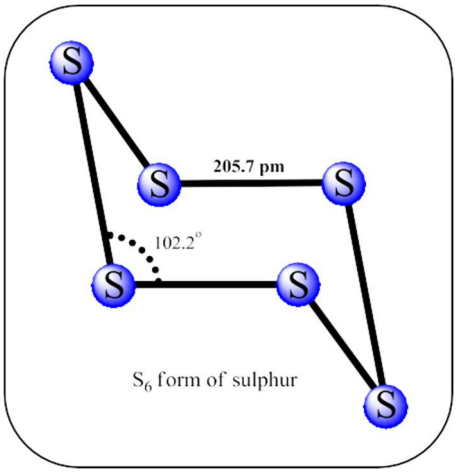
- This allotrope is yellow in colour. Its melting point is about 385.8 K and specific gravity is 2.06.
- Rhombic sulphur crystals are formed when the solution of roll sulphur in CS_2 is evaporated.
- It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is more solublein CS_2.

Monoclinic Sulphur

- Its melting point is 393 K and its specific gravity is 1.98. It is soluble in CS_2.
- This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till a crust isformed.
- Two holes are made in the crust and the remaining liquid is poured out. After removing the crust,colourless needle-shaped crystals of sulphur are formed.
- It is stable above 369 K and transforms into sulphur below 369 K.
- Also, we can say that the sulphur is stable below 369 K and transforms into sulphur above this. At 369 K, both forms are stable. This temperature is called transition temperature.
- Rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both forms is puckered and has a crown shape.



- In the cyclo-S_6 form, the molecule is in the chair shape.



- At very high temperatures (~1000 K); S_2 is paramagnetic like O_2.

Sulphur Dioxide

Preparation

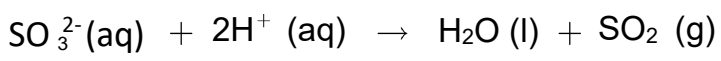
- It can be prepared in the laboratory with the action of metallic sulphate on a dilute acid.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_3SO_4 + H_2O + SO_2$$

- Sulphur dioxide is formed together with a trace amount of sulphur trioxide (6–8%) when sulphur isburnt in air or oxygen:

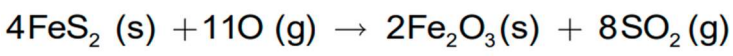
$$S(s) + O_2(g) \rightarrow SO_2\ (g)$$

- In the laboratory, sulphite is treated with dilute sulphuric acid to give sulphur dioxide.



$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g)$$

- It is also produced as a by-product of the roasting of sulphide ores.



$$4FeS_2(s) + 11O(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

- The gas is first dried and is liquefied under pressure and stored in steel cylinders.

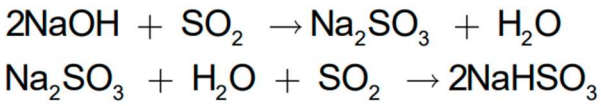
Properties

Physical Properties

- Sulphur dioxide is one of the gases which can be easily liquefied.
- Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.
- It liquefies at room temperature under a pressure of 2 atmospheres and boils at 263 K.
- When sulphur dioxide is passed through water, it forms a solution of sulphurous acid.

Chemical Properties

- It reacts with sodium hydroxide solution to give sodium sulphite, which then reacts with excess ofsulphur dioxide to form sodium hydrogen sulphite.



$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

- When sulphur dioxide reacts with water or alkali, its behaviour is similar to that of carbon dioxide.

- Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to givesulphuryl chloride SO_2Cl_2.

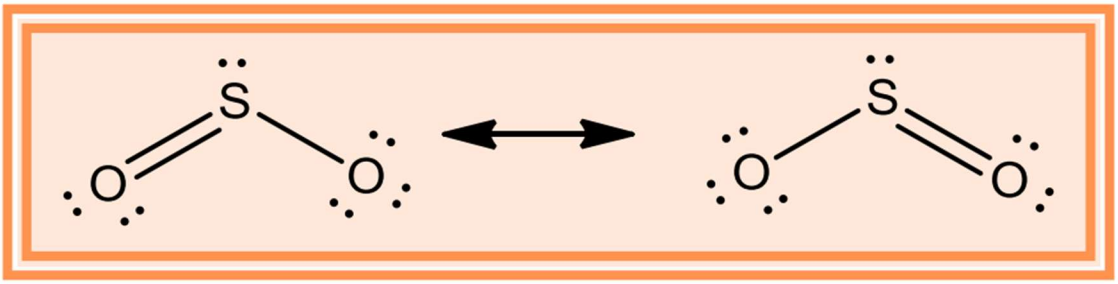
- It is oxidised to sulphur trioxide by oxygen in the presence of vanadium (V) oxide catalyst.

$$SO_2\ g + Cl_2\ g \rightarrow SO_2Cl_2\ l$$

$$2SO_2\ g + O_2\ g \xrightarrow{V_2O_5} SO_3\ g$$

- Under moist conditions, sulphur dioxide behaves as a reducing agent. For example, it converts iron (III) ions to iron (II) ions and decolourises acidified potassium permanganate (VII) solution.

- The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



Uses

- As a bleaching agent
- In refining petroleum and sugar
- In bleaching wool and silk
- As an anti-chlor, disinfectant and preservative
- In the manufacture of sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite(industrial chemicals)
- Liquid SO_2 is used as a solvent to dissolve several organic and inorganic chemical

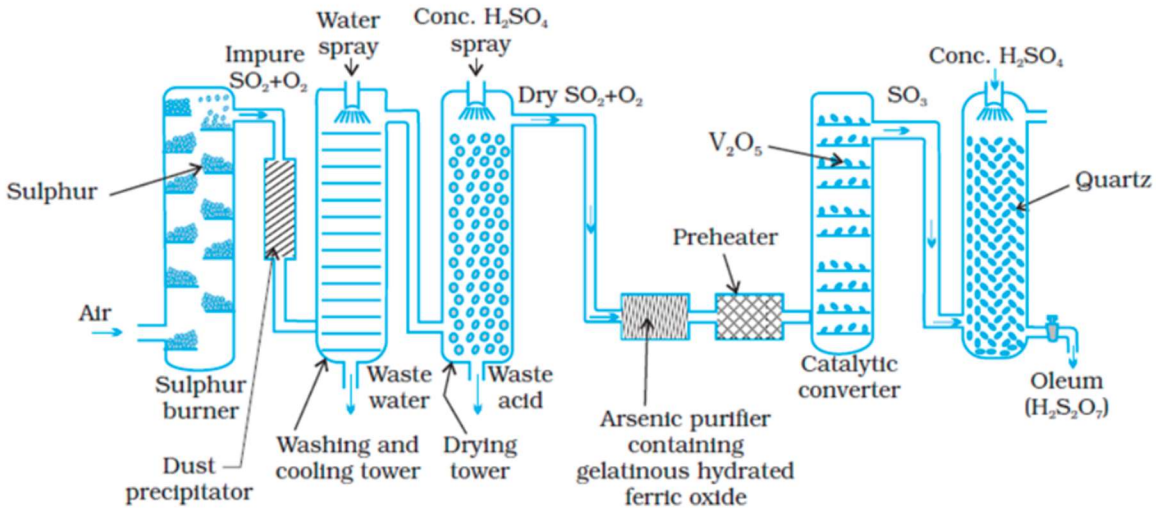
Oxoacids of Sulphur

- Sulphur dioxide is a strong oxidising agent.
- Sulphur forms several oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2−5), H_2SO_4,$H_2S_2O_7$, H_2SO_5 and $H_2S_2O_8$.
- Some of these acids are unstable and cannot be isolated.
- They commonly occur in the form of an aqueous solution or in the form of their salts.

Sulphuric Acid

Preparation

- Sulphuric acid is one of the most important industrial chemicals.
- Sulphuric acid is manufactured by the contact process which involves three steps:
  - Burning of sulphur or sulphide ores in air to generate SO_2
  - Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5)
  - Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$)



Flow diagram for the manufacture of sulphuric acid

- SO_2 produced by this process is purified by removing dust and other impurities such as arseniccompounds.
- The major step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 inthe presence of V_2O_5 (catalyst).

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{V_2O_5} 2SO_3\ (g)\ \Delta_r H^{\ominus} = -196.6\ kJmol^{-1}$$

- The reaction is exothermic and reversible. The forward reaction leads to a decrease in volume.
- Low temperature and high pressure are favourable conditions for maximum yield.
- But the temperature should not be very low; otherwise the rate of reaction will become slow.
- In actual practice, the plant is operated at a pressure of 2 bar and 720 K.
- SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilutionof oleum with water gives H_2SO_4 of the required concentration.
- In the industry, two steps are carried out simultaneously to make the process a

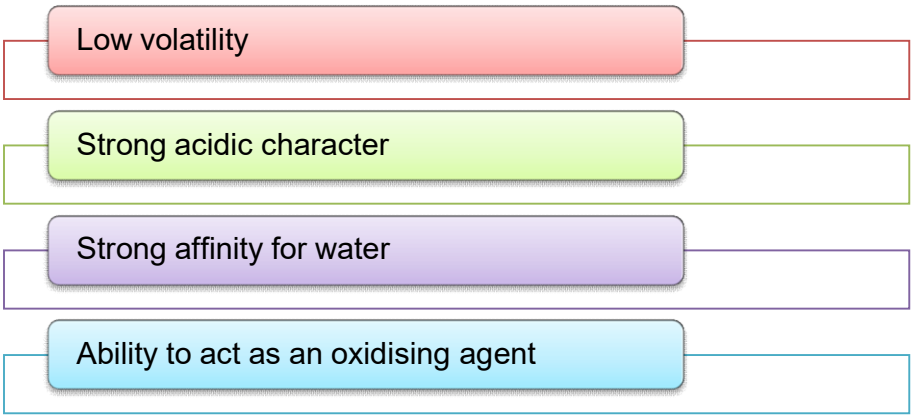
continuous one andto reduce the cost.

$$SO_3 + H_2SO_4 \rightarrow \underset{\text{Oleum}}{H_2S_2O_7}$$

- Sulphuric acid obtained by the contact process is 96–98% pure.

Properties

- Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.
- The acid freezes at 283 K and boils at 611 K.
- It is highly exothermic in the presence of water. It dissolves in water with the evolution of a largequantity of heat.
- Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid.
- The concentrated acid must be added slowly into water with constant stirring.
- Chemical reactions of sulphuric acid are as a result of the following characteristics:



- In an aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4\ aq + H_2O\ l \rightarrow H_3O^+\ aq + HSO_4^-\ aq\ ;\ K_{a_1} = \text{very large}\quad K_{a_1} > 10$$

$$HSO_4^-\ aq + H_2O\ l \rightarrow H_3O^+\ aq + SO_4^{2-}\ aq\ ;\ K_{a_2} = 1.2 \times 10^{-2}$$

- The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and

HSO_4.

- Greater the value of the dissociation constant (Ka), the stronger is the acid.
- The acid forms two series of salts—normal sulphates (sodium sulphate and copper sulphate) andacid sulphates (sodium hydrogen sulphate).
- Sulphuric acid can be used to manufacture more volatile acids from their corresponding saltsbecause of its low volatility.

$$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4 \ (X = F, Cl, NO_3)$$

- Concentrated sulphuric acid is a strong dehydrating agent.
- Many wet gases can be dried by passing them through sulphuric acid, provided the gases do notreact with the acid.
- Sulphuric acid removes water from organic compounds; it is evident by its charring action oncarbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12\,C + 11\,H_2O$$

- Hot concentrated sulphuric acid is a moderately strong oxidising agent.
- In this respect, it is intermediate between phosphoric acid and nitric acid.
- Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2\,H_2SO_4 \text{ conc.} \rightarrow CuSO_4 + SO_2 + 2\,H_2O$$
$$S + 2\,H_2SO_4 \text{ conc.} \rightarrow 3\,SO_2 + 2\,H_2O$$
$$C + 2\,H_2SO_4 \text{ conc.} \rightarrow CO_2 + 2\,SO_2 + 2\,H_2O$$

Uses

- Sulphuric acid is a very important industrial chemical as many other chemicals can be prepared from it.
- Primary use of sulphuric acid is in the synthesis of fertilisers.
- The industrial strength can be judged by the quantity of sulphuric acid it produces and

consumes.

- It is needed for the manufacture of hundreds of other compounds and in many industrial processes.
- Bulk of sulphuric acid produced is used in the manufacture of fertilisers (ammonium sulphate and superphosphate).

MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 7

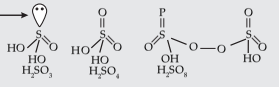
The p- Block Elements

Group 18 Elements

- **Occurrence :** All except radon occur in atmosphere
- **Electronic configuration :** $ns^2 np^6$ except He
- **IE :** High
- **Atomic radii :** Increases down group
- **Electron gain enthalpy :** Largely positive
- **Physical properties :** Monoatmic, colourless, odorless and tasteless. Sparingly soluble in water.
- **M.P. and B.P. :** Low
- **Chemical properties :** Least reactive xenonefluorine compound : XeF_2, XeF_4 and XeF_6.
- **Xenone oxygen compounds :** XeO_3, $XeOF_2$, $XeOF_4$

Group 16 Elements

- Electronic configuration : ns^2np^4
- Atomic and ionic radii : Increase down the group
- IE : Decreases down the group
- Electron Gain enthalpy : O hass less–ve than S.
- Electro-negativity : Decreases with increase in atomic number
- Physical properties : O and S are non metals, Se and Te metalloids whereas Po is a metal. All exhibit allotropy
- M.P. and B.P. : Increases down the group
- Chemical properties : variable
  - ✓ Reactivity with hydrogen : stable hydrides
  - ✓ Reactivity with halogens : $F^- > Cl^- > Br^- > I^-$
- Oxoacids of S :
- Dioxygen (O_2) :



Preparation : $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

Properties : Colourless and odourless gas

$2Ca + O_2 \longrightarrow 2CaO$; $4Al + 3O_2 \longrightarrow 2AlO_3$

$2SO_2 + O_2 \xrightarrow[V_2O_5]{} 2SO_3$; $4HCl + O_2 \xrightarrow{CuCl} 2Cl + 2H_2O$

Group 17 Elements

- Occurrence : F and Cl are fairly abundant while Br and I less so
- Electronic configuration : ns^2np^5
- Atomic Ionic radii : Smallest in periods but increases from F to I
- IE : Decreases down the group
- Electron gain enthalpy : Less –ve down the group
- Electro-negativity : High, decreases down the group
- Physical properties : F and Cl are gases, Br is liquid and I solid
- M.P. and B.P. : Increases with atomic number
- Chemical properties

All exhibit – 1 oxidation state Cl, Br and I exhibit + 1, + 3, + 5 and + 7.O.N
Reactivity towards hydrogen : H – F > H – Cl > H – Br > H – I
Reactivity towards oxygen : F form OF_2 (stable) and O_2F_2
Reactivity towards metals : MF > MCl > MBr > MI
Reactivity towards other halogens : Forms XX', XX'_3, XX'_5 and XX'_7.

Chlorine

Preparation : $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

Deacon's process : $4HCl + O_2 \xrightarrow[CuCl_2]{} 2Cl_2 + 2H_2O$

Properties : Greenish yellow gas with pungent and suffocating odour. Heavier than air

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$

$H_2 + Cl_2 \longrightarrow 2HCl$

$H_2S + Cl_2 \longrightarrow 2HCl + S$

$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
(cold and dilute)

$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$

$C_2H_4 + Cl_2 \xrightarrow{RT} C_2H_4Cl_2$

$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$

$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$

$Cl_2 + H_2O \longrightarrow 2HCl + 0$

Inter-halogen compounds: XX'– sp^3(linear), $XX'_3 sp^3d$ (T–shaped), XX'_5 sp^3d^2 (square pyramidal), XX'_7 sp^3d^3 (Pentagonal bipyramidal)

Group 15 Elements

- Electronic configuration : ns^2np^3
- Elements : $_7N$, $_{15}P$, $_{33}As$, $_{51}Sb$, $_{83}Bi$
- Atomic and Ionic radii : Increase in size down the group.
- Ionization enthalpy : Decreases down the group due to gradual increase in atomic size.
- Electro-negativity : Decreases down the group with increasing atomic size.
- Physical properties : Polyatomic, metallic character increases down the group. N and P are non-metals, As and Sb metalloids and Bi metal. B.P increases top to bottom and M.P. increases upto As and then decreases upto Bi. Except Ni all show allotropy
- Chemical properties : Common O.N : –3, +3 and +5. Nitrogen shows anomalous behaviour.

Ammonia Preparation

$NH_4CO\,NH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons$
$2NH_3 + H_2O + CO_2$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\Delta_f H° = -46.1$ kJ mol^{-1}

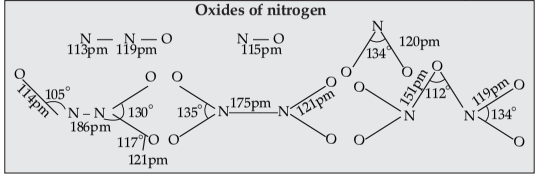
Properties :
Colourless with pungent odour, soluble in water

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$ZnSO_4 + 2NH_4OH \longrightarrow Zn(OH)_2 + (NH_4)SO_4$
(white ppt)

$FeCl_3 + NH_4OH \longrightarrow Fe_2O_3.xH_2O + NH_4Cl$
(Brown ppt)

Oxides of nitrogen



Dinitrogen preparation

- **In laboratory :**
  $NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$
- **Thermal decomposition :**
  $(NH_4)_2Cr_2O_7 \xrightarrow{Heat} N_2 + 4H_2O + Cr_2O_3$
  $Ba(N_3)_2 \longrightarrow Ba + 3N_2$
- **Properties :**
  Colourless, odourless, tasteless and non-toxic gas

$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$

$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$

$N_2 + 3H_2 \xrightarrow{773K} 2NH_3\,\Delta_f H° = 46.1$ KJ mol^{-1}

$N_2 + O_2 \xrightarrow{\Delta} 2NO$

Oxides of nitrogen

N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5

Important Questions

Multiple Choice questions-

1. H_2S is more acidic than H_2O because
(a) oxygen is more electronegative than sulphur.
(b) atomic number of sulphur is higher than oxygen.
(c) H — S bond dissociation energy is less as compared to H — O bond.
(d) H — O bond dissociation energy is less also compared to H — S bond.

2. The boiling points of hydrides of group 16 are in the order
(a) $H_2O > H_2Te > H_2S > H_2Se$
(b) $H_2O > H_2S > H_2Se > H_2Te$
(c) $H_2O > H_2Te > H_2Se > H_2S$
(d) None of these

3. In the manufacture of sulphuric acid by contact process Tyndall box is used to
(a) convert SO_2 and SO_3
(b) test the presence of dust particles
(c) filter dust particles
(d) remove impurities

4. Fluorine differs from rest of the halogens in some of its properties. This is due to
(a) its smaller size and high electronegativity.
(b) lack of d-orbitals.
(c) low bond dissociation energy.
(d) All of the these.

5. The set with correct order of acidity is
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

6. When chlorine reacts with cold and dilute solution of sodium hydroxide, it forms
(a) Cl^- and ClO^-
(b) Cl^- and ClO_2^-
(c) Cl^- and ClO_3^-
(d) Cl^- and ClO_4^-

7. The formation of $O_2^+ [PtF_6]^-$ is the basis for the formation of first xenon compound. This is because
(a) O_2 and Xe have different sizes.
(b) both O_2 and Xe are gases.
(c) O_2 and Xe have comparable electro-negativities.
(d) O_2 and Xe have comparable ionisation enthalpies.

8. Partial hydrolysis of XeF_4 gives
(a) XeO_3
(b) $XeOF_2$
(c) $XeOF_4$
(d) XeF_2

9. Helium is preferred to be used in balloons instead of hydrogen because it is
(a) incombustible
(b) lighter than hydrogen
(c) more abundant than hydrogen
(d) non polarizable

10. The increasing order of reducing power of the halogen acids is
(a) HF < HCl < HBr < HI
(b) HI < HBr < HCl < HF
(c) HBr < HCl < HF < HI
(d) HCl < HBr < HF < HI

Very Short Questions-

1. Write the elements of group 15?
2. Write chemical name & formulae of
a) Chile saltpetre
b) Indian saltpetre
3. What is special about the valence configuration of Group 15?
4. The atomic radii increases considerably from N to P but very little increase is observed from As to Bi. why?
5. Give reason for the following- the first ionization enthalpy of 15^{th} group elements is higher than 16^{th} group elements?
6. How does metallic character vary down the 15 group & why?
7. What are the common oxidation states of this group?
8. What is the maximum covalence shown by N?
9. Bi (v) is a stronger oxidizing agent than Bi (III). Why?
10. Give an example showing disproportionation of oxidation state of nitrogen?

Short Questions-

1. Write the various steps for preparation of sulphuric acid by contact process?
2. Name different sulphates formed by sulphuric acid?
3. Why are pentahalides more covalent than trihalides?
4. Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements?
5. Why is N_2 less reactive at room temperature?
6. How does ammonia react with a solution of Cu^{2+}?
7. What is the covalence of nitrogen in N_2O_5?
8. What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2?
9. Write a balanced equation for the hydrolytic reaction of PCl_5 in heavy water.
10. What happens when PCl_5 is heated?

Long Questions-

1. Give reasons: -

(a) Oxygen molecule is diatomic whereas sulphur molecule is polyatomic.

(b) The most common oxidation state of oxygen is -2.

(c) H_2O is liquid whereas H_2S is gas at room temperature.

(d) The increasing order of acidic character in 16th group hydrides is $H_2O < H_2Se < H_2Te$.

(e) SF_6 is exceptionally stable, SH_6 does not exist.

2. Discuss the different types of oxides.
3. Bond angle in PH_4^+ is higher than that in PH_3. Why?
4. Comment on the nature of two S-O bonds formed in SO_2 molecule. Are the two S-O bonds in this molecule equal?
5. Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.
6. Discuss the trends in chemical reactivity of group 15 elements.
7. Write main differences between the properties of white phosphorus and red phosphorus.
9. Describe the manufacture of H_2SO_4 by contact process?
10. How is SO_2 an air pollutant?

Assertion and Reason Questions-

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Caro's acid has S atom in +6 oxidation state.

Reason: Caro's acid contains one peroxo O_2^{2} – group.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: HOF bond angle in HFO is higher than HOCl bond angle in HClO.

Reason: Oxygen is more electronegative than all halogens except fluorine.

Case Study Questions-

1. Read the passage given below and answer the following questions:

Chlorine is a greenish yellow gas with pungent and suffocating odour. With dry slaked lime, it gives bleaching powder. Bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride:

$[Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O]$.

The amount of chlorine obtained from a sample of bleaching powder by the treatment with excess of dilute acids or CO_2 is called available chlorine. Chlorine is a powerful bleaching agent. Bleaching effect of chlorine is permanent.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Chlorine gas reacts with _____ to form bleaching powder.

a) $Ca(OH)_2$
b) $CaCl_2$

c) $CaSO_4$
d) dry CaO

(ii) Chlorine reacts with cold and dilute alkali to form:

a) Chloride
b) Hypochlorite
c) Chlorate
d) Both (a) and (b)

(iii) Which of the following is produced on the reaction of bleaching powder with a few drops of cone. HCl?

a) Hypochlorous acid
b) Oxygen
c) Chlorine
d) Calcium oxide

(iv) Chlorine is used as a bleaching agent. The bleaching action is due to.

a) Oxidation
b) Chlorination
c) Hydrogenation
d) Reduction

(v) Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is:

a) Cl_2O
b) Cl_2O_7
c) ClO_2
d) Cl_2O_6

2. Read the passage given below and answer the following questions:

Noble gases are inert gases with general electronic configuration of ns^2np^6. These are monoatomic, colourless, odourless and tasteless gases. The first compound of noble gases was obtained by the reaction of Xe with PtF_6. A large number of compounds of Xe and fluorine have been prepared till now. The structure of these compounds can be explained on the basis of VSEPR theory as well as concept of hybridisation. The compounds of krypton are fewer. Only the diftuoride of krypton (KrF_2) has been studied in detail. Compounds of radon have not isolated but only identified by radio tracer technique. However, no true compounds of helium, neon or argon are yet known.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The formula of the compound when Xe and PtF_6 are mixed, is:

a) XeF_6
b) XeF_4
c) Xe_2PtF_6
d) $Xe^+[PtF_6]^-$

(ii) The shape and hybridisation of some xenon oxy-fluoride and fluoride compounds are given below. Find the incorrect one.

a) $XeOF_2$ - T-shape - sy^3d
b) $XeOF_4$ - square pyramidal - sp^3d^2
c) XeF_2 - linear - sp^3d
d) XeF_6 - square planar - dsp^2

(iii) Which of the following is not formed by Xe?

a) XeF_5
b) XeF
c) XeF_3
d) All of these.

(iv) The number oflone pairs and bond pairs of electrons around Xe in $XeOF_4$ respectively are,

a) 0 and 5
b) 1 and 5
c) 1 and 4
d) 2 and 3

(v) Which of the following compounds has more than one lone pair of electrons around central atom?

a) XeO_3
b) XeF_2
c) $XeOF_4$
d) XeO_2F_2

MCQ Answers-

1. Answer: b

2. Answer: b
3. Answer: b
4. Answer: b
5. Answer: b
6. Answer: a
7. Answer: d
8. Answer: b
9. Answer: a
10. Answer: a

Very Short Answers-

1. **Ans.** The elements of group 15 are Nitrogen (N), Phosphorous (P) , Arsenic (As) , Antimony (Sb) and Bismuth (Bi).

2. **Ans. (**a) Chile saltpetre – Sodium nitrate – $NaNO_3$
(b) Indian saltpetre – Potassium nitrate – KNO_3

3. **Ans.** The valence configuration of 15 group is ns^2np^3 the s-orbital is completely filled, and p-orbital is half filled. This half-filled orbital gives extra stability to elements of this group.

4. **Ans.** There is a considerable increase in size from N to P as expected but due to the presence of completely filled d- orbitals which have very poor shielding effects, the increase in size is very little from As to Bi.

5. **Ans.** Due to extra stability of half-filled configuration, the first Ionisation enthalpy of 15^{th} group elements is higher than 16^{th} group configuration ns^2np^3

6. **Ans.** The metallic character increases down the group due to decrease in ionization

enthalpy and increase in size of atom.

7. **Ans.** The common oxidation states of the group are -3, +3 & +5.

8. **Ans.** Nitrogen shows a maximum covalence of +4 because only four orbitals, one S and three P- orbitals are available for bonding in Nitrogen.

9. **Ans.** Bi is more stable in +3 oxidation state in comparison to +5 due to inert pair effect therefore Bi (v) has a strong tendency to act as oxidizing agent.

10. **Ans.**

$$\underset{+3}{3HNO_2} \rightarrow \underset{+5}{HNO_3} + H_2O + \underset{+2}{2NO}$$

Here Nitrogen is getting oxidized to a higher oxidation state as well as reduced to a lower oxidation state.

Short Answers-

Ans 1. Contact process for sulphuric acid: -

Step 1: Burning of sulphur in air to give SO_2.

$S + O_2 SO_2$

Step 2: Conversion of $SO_2 \text{ to } SO_3$ by reacting it with oxygen in presence of V_2O_5.

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

Step 3: Absorption of SO_3 in H_2SO_4 to give of oleum $(H_2S_2O_7)$

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7\,(oleum)$

Step 4: Dilution of oleum with water to get H_2SO_4 of desired concentration

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Ans 2. The two type of sulphates are –

(i) Normal sulphate eg. $Na_2SO_4,\ CuSO_4$

(ii) acid sulphate eg. $NaHSO_4$.

Ans 3. In pentahalides, the oxidation state is +5 and in trihalides, the oxidation state is +3. Since the metal ion with a high charge has more polarizing power, pentahalides are more covalent than trihalides.

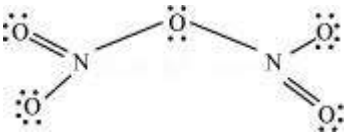
Ans 4. As we move down a group, the atomic size increases and the stability of the hydrides of group 15 elements decreases. Since the stability of hydrides decreases on moving from NH_3 to BiH_3, the reducing character of the hydrides increases on moving from NH_3 to BiH_3.

Ans 5. The two N atoms in N_2 are bonded to each other by very strong triple covalent bonds. The bond dissociation energy of this bond is very high. As a result, N_2 is less reactive at room temperature.

Ans 6. NH_3 acts as a Lewis base. It donates its electron pair and forms a linkage with metal ion.

$$\underset{\text{Blue}}{Cu^{2+}_{(aq)}} + 4NH_{3(aq)} \leftrightarrow \underset{\text{Deep Blue}}{\left[Cu(NH_3)_4\right]^{2+}_{(aq)}}$$

Ans 7.



From the structure of N_2O_5, it is evident that the covalence of nitrogen is 4.

Ans 8. White phosphorous dissolves in boiling NaOH solution (in a CO_2 atmosphere) to give phosphine, PH_3.

$$PH_3.P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

Ans 9. All the bonds that are present in PCl_5 are not similar. It has three equatorial and two axial bonds. The equatorial bonds are stronger are stronger than the axial ones. Therefore, when PCl_5 is heated strongly, it decomposes to form PCl_3.

Ans 10.

$PCl_5 + D_2O \rightarrow POCl_3 + 2DCl_2$

$POCl_3 + 3D_2O \rightarrow D_3PO_4 + 3DCl$

Therefore, the net reaction can be written as

$PCl_5 + 4D_2O \rightarrow D_3PO_4 + 5DCl$

Long Answers-

Ans 1. (a) Oxygen being small in size forms effective and strong P π-P π bonds with other oxygen atom. Therefore, oxygen molecule is diatomic and discrete whereas Sulphur due to its larger size, its orbitals cannot overlap effectively to form P π-P π bonds & completes valency by forming σ bonds with many sulphur, atom. Therefore, sulphur molecule is polyatomic solid.

(b) Since oxygen is highly electronegative, it has little tendency to give electrons. Therefore, its most common oxidation state is -2.

(c) H_2O is liquid at room temperature due to presence of intermolecular Hydrogen bonding which is absent in H_2S.

(d) As we move down the group, the size of atom increases this make the bond of the element with hydrogen weak. Due to weaker bonds, the bond dissociation enthalpy decreases making the molecule more acidic. Therefore, the order of acidic strength is.

$H_2O < H_2S < H_2Se < H_2Te$

(e) SF_6 is exceptionally stable due to steric reasons. Hydrogen being electropositive or less electronegative than fluorine cannot make the s- electrons of sulphur to participate in bonding. Therefore SF_6 does not exist.

Ans 2. A binary compound of oxygen with another element is called oxide. Oxides can be simple or mixed. Simple oxides can be classified as acidic, basic Amphoteric or neutral.

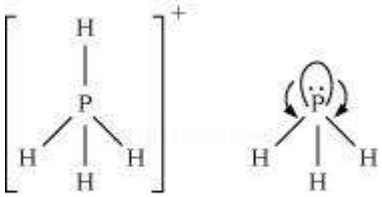
An oxide that combines with water to give an acid is termed acidic oxide e.g. CO_2, SO_2 etc.

An oxide that combines with water to give a base is called basic oxide e.g. Na_2O, CaO, BaO etc.

An **oxide** that shows characteristics of both acids and bases is Amphoteric oxide e.g. Al_2O_3.

An oxide that shows characteristic of neither acid nor base is called neutral oxide e.g. CO, NO and N_2O.

Ans 3. In PH_3, P is sp_3 hybridized. Three orbitals are involved in bonding with three hydrogen atoms and the fourth one contains a lone pair. As lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the tetrahedral shape associated with *sp*3bonding is changed to pyramidal. PH_3 combines with a proton to form PH_4^+ in which the lone pair is absent. Due to the absence of lone pair in PH_4^+, there is no lone pair-bond pair repulsion. Hence, the bond angle in PH_4^+ is higher than the bond angle in PH_3.



PH_4^+ PH_3

Concept insite: the long pair-bond pair repulsion is more than bond pair-bond pair repulsion.

Ans 4. The electronic configuration of S is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$.

During the formation of

SO_2, one electron from 3*p* orbital goes to the 3*d* orbital and S undergoes sp^2 hybridization. Two of these orbitals form sigma bonds with two oxygen atoms and the third contains a lone pair. *p*-orbital and *d*-orbital contain an unpaired electron each. One of these electrons forms $p\pi - p\pi$ bond with one oxygen atom and the other forms $p\pi : p\pi$ bond with the other oxygen. This is the reason SO_2 has a bent structure. Also, it is a resonance hybrid of structures I and II. Both S-O bonds are equal in length (143 pm) and have a multiple bond character.

Ans 5. General trends in group15 elements

(i) Electronic configuration: All the elements in group 15 have 5 valence electrons. Their general electronic configuration is $ns^2\ np^3$.

(ii) Oxidation states: All these elements have 5 valence electrons and require three more electrons to complete their octets. However, gaining electrons is very difficult as the nucleus will have to attract three more electrons. This can take place only with nitrogen as it is the smallest in size and the distance between the nucleus and the valence shell is relatively small. The remaining elements of this group show a formal oxidation state of -3 in their covalent compounds. In addition to the -3 state, N and P also show -1 and -2 oxidation states.
All the elements present in this group show +3 and +5 oxidation states. However, the stability of +5 oxidation state decreases down a group, whereas the stability of +3 oxidation state increases. This happens because of the inert pair effect.

(iii) Ionization energy and electronegativity
First ionization decreases on moving down a group. This is because of increasing atomic sizes. As we move down a group, electronegativity decreases, owing to an increase in size.

(iv) Atomic size: On moving down a group, the atomic size increases. This increase in the atomic size is attributed to an increase in the number of shells.

Ans 6. General trends in chemical properties of group – 15

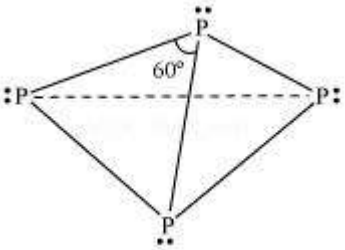
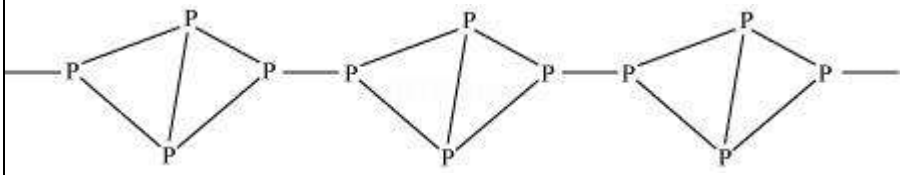
(i) Reactivity towards hydrogen:
The elements of group 15 react with hydrogen to form hydrides of type EH_3, where E = N, P, As, Sb, or Bi. The stability of hydrides decreases on moving down from NH_3 to BiH_3.

(ii) Reactivity towards oxygen:
The elements of group 15 form two types of oxides: E_2O_3 and E_2O_5, where E = N, P, As, Sb, or Bi. The oxide with the element in the higher oxidation state is more acidic than the other. However, the acidic character decreases on moving down a group.

(iii) Reactivity towards halogens: The group 15 elements react with halogens to form two series of salts: EX_3 and EX_5. However, nitrogen does not form NX_5 as it lacks the *d*-orbital. All trihalides (except NX_3) are stable.

(iv) Reactivity towards metals: The group 15 elements react with metals to form binary compounds in which metals exhibit -3 oxidation states.

Ans 7.

White phosphorus	Red Phosphorus
It is a soft and waxy solid. It possesses a garlic smell.	It is a hard and crystalline solid, without any smell.
It is poisonous.	It is non-poisonous.
It is insoluble in water but soluble in carbon disulphide.	It is insoluble in both water and carbon disulphide.
It undergoes spontaneous combustion in air.	It is relatively less reactive.
In both solid and vapour states, it exists as a P4 molecule. 	It exists as a chain of tetrahedral P4 units. 

8. 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.

Ans 8. The elements of group 16 are collectively called chalcogens.

(i) Elements of group 16 have six valence electrons each. The general electronic configuration of these elements is $ns^2\,np^4$, where n varies from 2 to 6.

(ii) Oxidation state:

As these elements have six valence electrons $(ns^2\,np^4)$, they should display an oxidation state of -2. However, only oxygen predominantly shows the oxidation state of -2 owing to its high electronegativity. It also exhibits the oxidation state of -1 (H_2O_2), zero (O_2), and +2 (OF_2).

However, the stability of the -2 oxidation state decreases on moving down a group due to a decrease in the electronegativity of the elements. The heavier elements of the group show an oxidation state of +2, +4, and +6 due to the availability of *d*-orbitals.

(iii) Formation of hydrides:

These elements form hydrides of formula H_2E, where E = O, S, Se, Te, PO. Oxygen and sulphur also form hydrides of type H_2E_2. These hydrides are quite volatile in nature.

Ans 9. Sulphuric acid is manufactured by the contact process. It involves the following steps:

Step (i): Sulphur or sulphide ores are burnt in air to form SO_2.

Step (ii): By a reaction with oxygen, SO_2 is converted into SO_3 in the presence of V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_2 \xrightarrow{V_2O_5} 2SO_{3(g)}$$

Step (iii): SO_3 produced is absorbed on H_2SO_4 to give $H_2S_2O_7$ (oleum).

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

This oleum is then diluted to obtain H_2SO_4 of the desired concentration.
In practice, the plant is operated at 2 bar (pressure) and 720 K (temperature). The sulphuric acid thus obtained is 96-98% pure.

Ans 10. Sulphur dioxide causes harm to the environment in many ways:

1. It combines with water vapour present in the atmosphere to form sulphuric acid. This causes acid rain. Acid rain damages soil, plants, and buildings, especially those made of marble.

2. Even in very low concentrations, SO_2 causes irritation in the respiratory tract. It causes throat and eye irritation and can also affect the larynx to cause breathlessness.

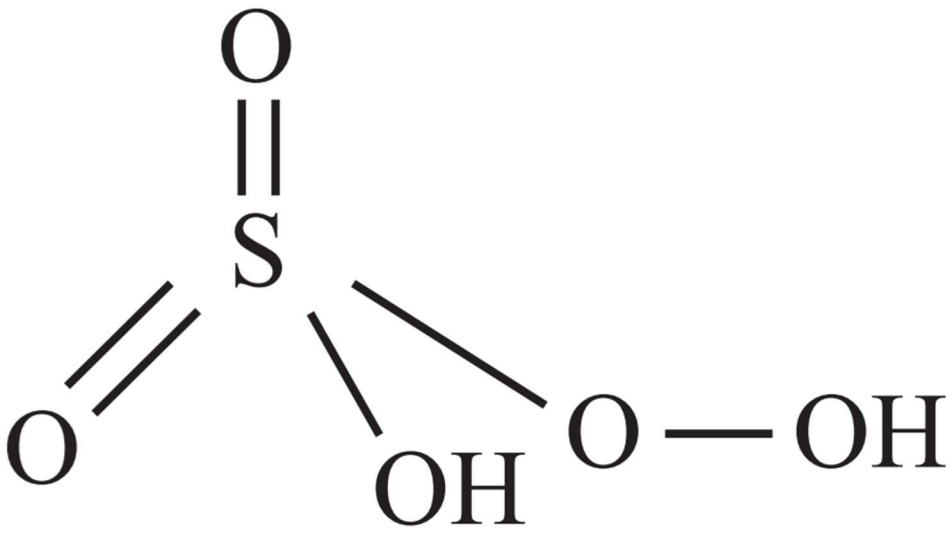
3. It is extremely harmful to plants. Plants exposed to sulphur dioxide for a long time lose colour from their leaves. This condition is known as chlorosis. This happens because the formation of chlorophyll is affected by the presence of sulphur dioxide.

Assertion and Reason Answers-

1. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

This can be explained through structure of caro's acid (peroxomonosulphuric acid).



Oxidation no. of S = x, oxidation no. of H = +1,

Oxidation no. of O in peroxo linkage = -1 (each),

Oxidation no. of other oxygen atoms = -2 (each).

2 + x - 6 - 2 = 0 or x = +6.

2. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

HOF bond angle in HFO is lesser than that of HOCl bond angle in HClO. Oxygen is more electronegative than all halogens except fluorine.

Case Study Answers-

1. Answer :

(i) (a) $Ca(OH)_2$

(ii) (d) Both (a) and (b)

Explanation:

In cold, chlorine reacts with dilute alkalies to form chlorides and hypochlorites.

(iii) (c) Chlorine

(iv) (a) Oxidation

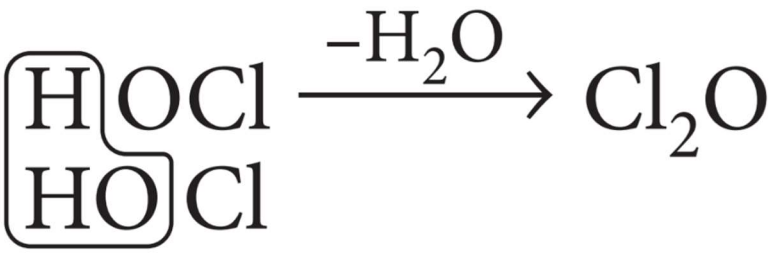
Explanation:

$Cl_2 + H_2O \rightarrow 2HCl + [O]$

(v) (a) Cl_2O

Explanation:

Bleaching powder contains OCl^- ion, hence the oxoacid is HOCl. Anhydride of HOCl is Cl_2O.



2. Answer :

(i) (d) $Xe^+[PtF_6]^-$

(ii) (d) XeF_6 - square planar - dsp^2

Explanation:

XeF_6 has sp^3d^3 hybridisation and distorted octahedral shape.

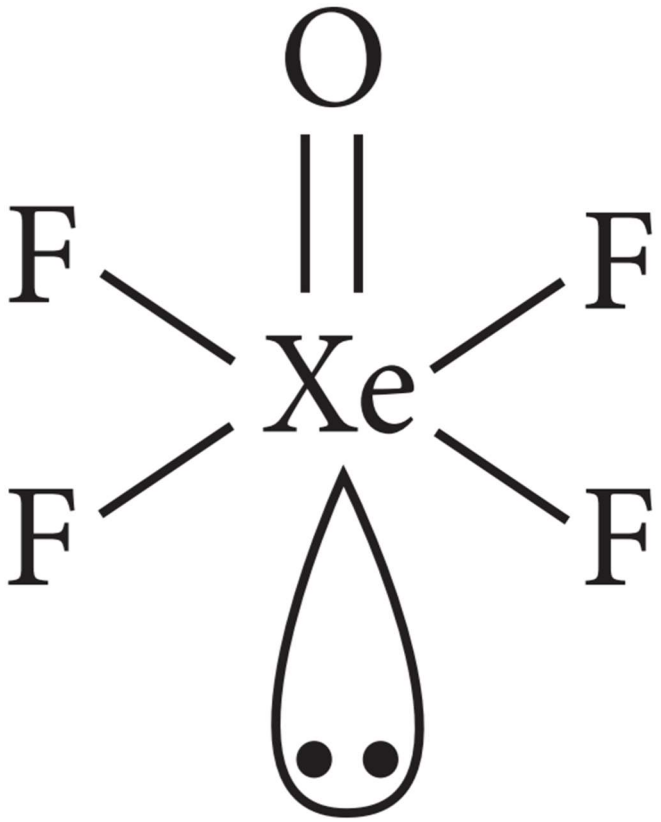
(iii) (d) All of these.

Explanation:

Xe has completely filled 5p-orbital. As a result, when it undergoes bonding with an odd number (1, 3 or 5) of fluorine atoms, it leaves behind one unpaired electron. This causes the molecule to become unstable. As a result, XeF, XeF_3 and XeF_5 do not exist.

(iv) (b) 1 and 5

Explanation:



(v) (b) XeF_2

Explanation:

XeF_2 has 3 lone pairs on Xe atom.