DEPARTMENT OF EDUCATION (S)
Government of Manipur

Unit 7: The P-Block Elements

P-Block elements: Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.

General electronic configuration of p-block elements:

The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.

Representative elements: Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.

Inert pair effect:

- The tendency of ns^2 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.

Major Groups in P-Block (XII Syllabus)

1. Nitrogen family: The elements of group 15 – nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Their electronic configuration is ns^2np^3.

2. 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 ns^2np^4.

3. 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 ns^2np^5.

4. 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 ns^2np^6 except helium which has electronic configuration $1s^2$. They are called noble gases because they show very low chemical reactivity.

GROUP 15 ELEMENTS

Characteristic Features:

1. **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.
2. **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.
3. **Allotropy:** All elements of Group 15 except nitrogen show allotropy.
4. **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.
5. **General Electronic Configuration :**

→ General electronic configuration $[\mathrm{NG}]ns^2np^3$

N(7) → $1s^2 2s^2 2p^3$ or $[\mathrm{He}]2s^2 2p^3$
P(15) →$[\mathrm{Ne}]\ 3s^2 3p^3$
As(33) → $[\mathrm{Ar}]\ 3d^{10} 4s^2 4p^3$
Sb(51)→$[\mathrm{Kr}]\ 4d^{10} 5s^2 5p^3$
Bi(83) → $[\mathrm{Xe}]\ 4f^{14} 5d^{10} 6s^2 6p^3$
Mc(289) →

6. Oxidation states:

- The common oxidation states are +3, +5, –3. The tendency to show –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 disproportionation.

eg. $3\ HNO_2 \rightarrow HNO_3 + H_2O + 2\ NO$

7. Reactivity towards hydrogen: All group 15 elements from trihydrides, MH_3. Hybridisation- sp^3

- Stability: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

  The stability of hydrides decreases down the group due to decrease in bond dissociation energy down the group.

- Boiling point: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

  Boiling point increases with increase in size due to increase in van der Waal's forces. Boiling point of NH_3 is more because of hydrogen bonding.

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

  Electronegativity 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: Basicity decreases as $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$.

  This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3. It will decrease down the group as the electronegativity decreases down the group.

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

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

- Acidity: Acidic character of oxides decreases and basicity increases down the group. This is because the size incereases down the group.
- Oxides of Nitrogen have high acidic character. 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.

9. Reactivity towards halogen: Group 15 elements form trihalides (MX_3) and pentahalides (MX_5).

- Trihalides – They are covalent compounds and become ionic down the group. The central atom is undergoing sp^3 hybridisation and they have pyramidal shape.

- Pentahalides – They are more covalent than trihalides and undergo sp^3d hybridisation. Shape is triangular bipyramidal.

  They are lewis acids due to presence of vacant d – orbitals.

  $$PCl_5 + Cl^- \rightarrow [PCl_6]^-$$

  PCl_5 is ionic in solid state and exist as $[PCl_4]^+ [PCl_6]^-$
- In PCl_5, 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.

10. Reactivity towards metals: All elements react with metals to form binary compounds in –3 oxidation state such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2(magnesium bismuthide).

11. Anomalous behaviour of nitrogen: This is due to the following reason -

a) It has a small size.
b) It does not have d – orbitals
c) It can form pπ-pπ bond
d) It has high electronegativity and high ionization enthalpy

NITROGEN

Some common compounds of Nitrogen are

1. **Dinitrogen:**

It is a diatomic molecule form by combining two nitrogen atoms forming triple covalent bond.

Preparation:

a) $NH_4CI(aq) + NaNO_2(aq) \rightarrow 2N_2(g) + 2H_2O(l) + NaCl\ (aq)$
b) $(NH_4)_2Cr_2O_7 \xrightarrow{Heat} 2N_2 + 4H_2O + Cr_2O_3$
c) $Ba(N_3)_2 \rightarrow Ba + 3N_2$

Properties:

a) It is a colourless, odourless, tasteless and non-toxic gas.
b) It is chemically unreactive at ordinary temperature due to triple bond in $N \equiv N$ which has high bond dissociation energy.
c) At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

   i) $6Li + N_2 \xrightarrow{Heat} 2Li_3N$

   ii) $3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$

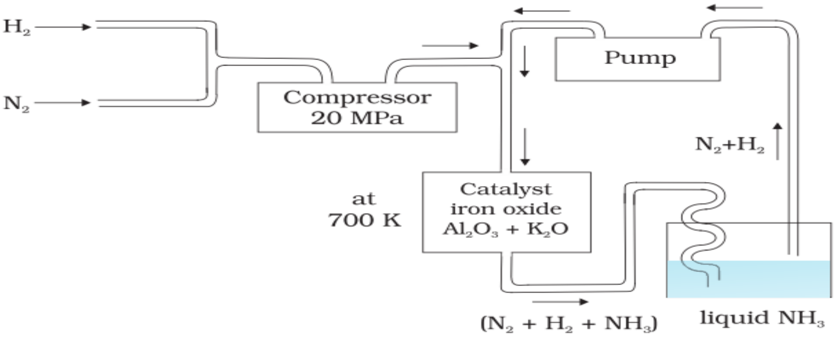
2. **Ammonia:**

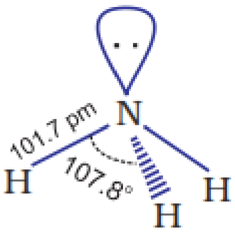
Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp^3 hybridised.

Preparation:

Nitrogen combines with hydrogen at about 773 K in the presence of a catalyst to form ammonia (NH_3) by the process called Haber's Process.

$N_2(g) + 3H_2(g) \xrightarrow{773\ K} 2NH_3(g); \Delta_f H^o = -46.1\ kJmol^{-1}$, Pressure = 200×10^5Pa, catalyst is FeO with small amounts of K_2O and Al_2O_3





NH_3

Properties:

a) It is a colourless gas with pungent odour.

b) It is highly soluble in water and its aqueous solution is weakly basic due to the formation of OH^- ions.

c) Due to the presence of lone pair of electrons on nitrogen atom, it is a Lewis base.

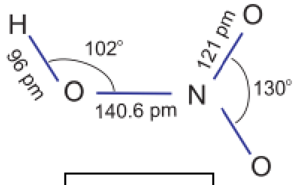
3. **Nitric Acid:**

Preparation: It is prepared by Ostwald's process.

$$4NH_3 + 5O_2 \xrightarrow[500\ K,9bar]{Pt/Rhgauge} 4NO + 6H_2O\ ......(i)$$

$$2NO + O_2 \rightleftharpoons 2NO_2\ ......(ii)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)\ ......(iii)$$



HNO_3

- 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.

PHOSPHORUS:

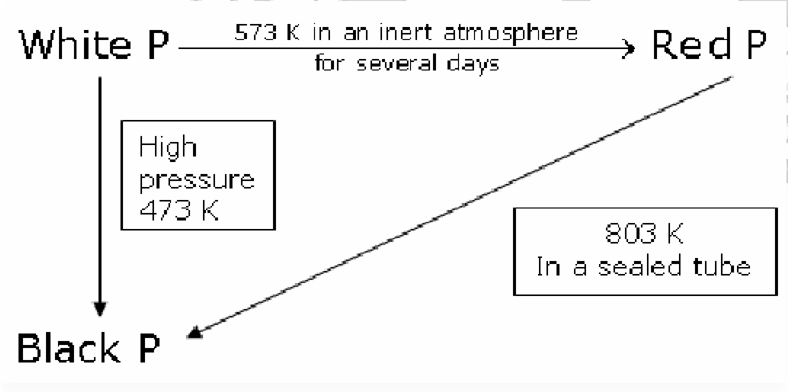
a. It shows the property of catenation to maximum extent due to most stable P – P bond.

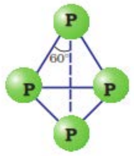
b. It has many allotropes, the important ones are :

i. White phosphorus
ii. Red phosphorus
iii. Black phosphorus

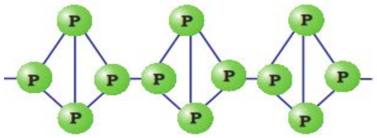
White phosphorus	Red phosphorus	Black phosphorus
Discrete tetrahedral P_4 molecules	Polymeric structure consisting of chains of P_4 units linked together	Exists in two forms - α black P and β black P
Very reactive	Less reactive than white P	Very less reactive
Glows in dark	Does not glow in dark	-
Translucent waxy solid	Has an iron grey lustre	Has an opaque monoclinic or rhombohedral crystals
Soluble in CS_2 but insoluble in water	Insoluble in water as well as CS_2	-
It has low ignition temperature, therefore, kept under water	-	-

Preparation:





White Phosphorus



Red Phosphorus

1. Phosphine (PH_3):

Preparation:

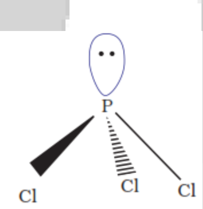
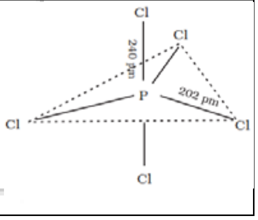
(i) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

(ii) $P_4 + 3NaOH \rightarrow 3NaH_2PO_2 + PH_3$

Ca_3P_2 (Calcium Phosphide), NaH_2PO_2 (Sodium Hypophosphide), $CaCl_2$ (Calcium Chloride)
Phosphine is highly poisonous, colourless gas and has a smell of rotten fish.

2. Chlorides of Phosphorous:

Phosphorus Trichloride PCl_3	**Phosphorus Pentachloride PCl_5**
1. It is a colourless oily liquid	1. It is a yellowish white powder
2. It is obtained by passing dry chlorine over heated white phosphorus. $P_4 + 6Cl_2 \rightarrow 4PCl_3$	2. It is prepared by the reaction of white phosphorus with excess of dry chlorine. $P_4 + 10Cl_2 \rightarrow 4PCl_5$
3. It is hydrolysed in the presence of water as $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$	3. It is hydrolysed in the presence of water as $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$
4. The shape is pyramidal as Phosphorus is SP^3 hybridisation. 	5. The shaped is trigonal bipyramidal 

Oxoacids of Phosphorus.
Some noteworthy points are:

i) In phosphorus acids, phosphorus is present in the lower oxidation state (+1 or +3) while in phosphoric acids, phosphorus is present in the higher oxidation state (+5).

ii) Nomenclature:
  a) If one O-atom is removed, the prefix hypo is added
  b) If one H_2O molecule is removed, the prefix meta is added
  c) If from two molecules, one H_2O molecule is removed, the prefix pyro is added.

iii) All of oxoacids are based on tetrahedral four coordinated phosphorus containing at least one P=O unit and one P-OH group. The OH group is ionizable but H atom linked directly to P is non-ionizable. Thus the number of OH groups present decides the basicity of the acid.

iv) The acids in +3+ oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophosphorus acid (or phosphorus acid) dispropor-tionates on heating to give orthophosphoric acid (or phosphoric acid) and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

v) The acids which contain P-H bond have strong reducing properties. Thus, hypophosphorus acid is a good reducing agent as it contains two P-H bonds and reduces, e.g., $AgNO_3$ to metallic silver.

$$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

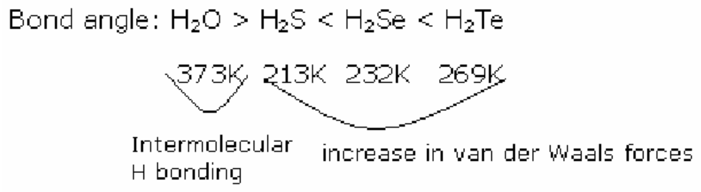
GROUP 16 ELEMENTS

Characteristic Features

1. **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_2 and O_2F_2.
   - The stability of +6 oxidation state decreases and +4 oxidation state increases due to inert pair effect.
2. **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.
3. **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.
4. **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).

5. **Reactivity with hydrogen:**

All group 16 elements form hydrides.



- <u>Acidic nature</u> : $H_2O < H_2S < H_2Se < H_2Te$

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

- <u>Thermal stability</u> : $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

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

- <u>Reducing character</u> : $H_2O < H_2S < H_2Se < H_2Te < H_2Po$

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

6. 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 has discrete units.

7. Reactivity with halogens: They form halides of the form – 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.
- Dihalides are sp^3 hybridised, are tetrahedral in shape.
- Hexafluorides are only stable halides which are gaseous and have sp^3d^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.

OXYGEN:

Preparation: It is exist as dioxygen (O_2).

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow{Heat, MnO_2} 2KCl + 3O_2$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$; $2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$; $2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$$

1. 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.

$$SO_2 + H_2O \rightarrow H_2SO_3 \text{ (sulphurous acid)}$$

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

$$CaO + H_2O \rightarrow Ca(OH)_2 \text{(Calcium hydroxide)}$$

c) Amphoteric oxides: They show characteristics of both acidic aswell as basic oxides.

$$Al_2O_3 + 6HCl \rightarrow 2\,AlCl_3 + 3H_2O$$

$$Al_2O_3 + 6NaOH + 3H_2O \rightarrow 2Na_3[Al(OH)_6]$$

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

Example: CO, NO, H_2O and N_2O

2. Ozone:

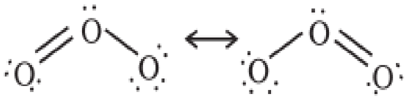
Preparation:

It is prepared by passing silent electric discharge through pure and dry oxygen (10 – 15 %).

Oxygen is converted to ozone as–

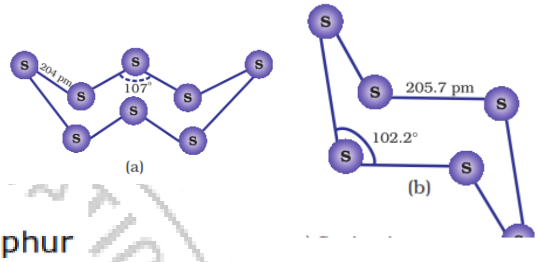
$$3O_2(g) \rightarrow 2O_3(g);\ \Delta H = +142 \text{ kJ mol}^{-1}$$

Structure of Ozone:



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

Allotropic forms of Sulphur :



- Sulphur exhibits allotropy:
  - a. Yellow Rhombic (α - sulphur):
  - b. Monoclinic (β- sulphur):

$$\alpha - \text{Sulphur} \underset{}{\overset{369\ K}{\rightleftharpoons}} \beta - \text{Sulphur}$$

- 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 likeO_2.

Sulphur dioxide SO_2 :

(i) By burning sulphur in air :

$$S + O_2 \rightarrow SO_2$$

$$2S + 3O_2 \rightarrow 2SO_3$$

(ii) By roasting sulphides, e.g., Zinc sulphide, iron pyrites (as by-product in extraction)

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

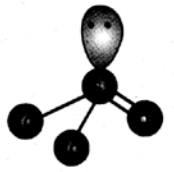
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

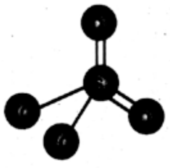
(iii) Laboratory preparation. By treating a sulphite with dilute sulphuric acid.

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

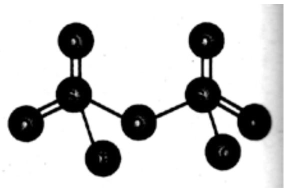
Oxacids of Sulphur :

Sulphur forms a number of oxoacids such as H2SO3, H2S2O3, H2S2O4, H2SO5, H2SxO6 (x = 2 to 5), H2SO4, H2SO5, H2S2O8. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown.


Sulphurous acid
(H_2SO_3)


Sulphuric acid
(H_2SO_4)


Peroxodisulphuric acid
($H_2S_2O_8$)


Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

Properties of Sulphur Dioxide

(a) Physical Properties

(i) Sulphur dioxide is a colourless gas with a pungent smell. It is poisonous in nature.

(ii) It is very soluble in water and its solution in water is called sulphurous acid.

(b) Chemical Properties

(1) **Thermal dissociation :** It dissociates on strong heating to form sulphur trioxide and sulphur trioxide and sulphur.

$$3SO_2 \rightarrow S + 2SO_3$$

Under the action of electric discharge at low pressure. It dissociates into sulphur monoxide and oxygen.

$$4SO_2 \rightleftharpoons 2S_2O + 3O_2$$

(2) **Acidic Nature :** Sulphur dioxide dissolves in water to give sulphurous acid, which ionizes as follows :

$$\underset{\text{Sulphorous anhydride}}{SO_2(g) + H_2O(l)} \rightleftharpoons \underset{\text{Sulphorous acid}}{H_2SO_3(aq)} \rightleftharpoons 2H^+(aq) + SO_3^{2-}\ (aq)$$

It is, therefore, called sulphorous anhydride. It turns blue litmus red, neutralizes alkalis and decomposes carbonates forming two series of salts, sulphites and bisulphites.

$$2NaOH + SO_2 \rightarrow NaHSO_3$$

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

(3) **Addition Reactions :** Sulphur is hexavalent but in sulphur dioxide (SO_2) only four valencies are satisfied by two atoms of oxygen. Sulphur dioxide thus gives addition products.

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

$$SO_2 + Cl_2 \xrightarrow[\text{camphor}]{\text{sunlight or}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$$

(4) **Reducing Character :** In presence of moisture, it can liberate nascent hydrogen or in presence of an oxidizing agent it can easily take an atom of oxygen. In both these cases, it acts as a strong reducing agent.

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

Following reactions illustrate the reducing character of sulphur dioxide.

(i) Acidified potassium permanganate is decolorized.

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

(ii) Acidified potassium dichromate is turned green.

$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+}$

(iii) Halogens are reduced to halogen acids.

$I_2 + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2l^- + 4H^+$

(iv) Ferric salts are reduced to ferrous salts.

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

(5) **Bleaching and Disinfecting Properties :** In the presence of moisture, SO^2 reduces the vegetable colouring matter to colourless reduction product. It is thus often used as a bleaching agent. On standing in air, the colourless product is reoxidized by atmosphere oxygen to the original colour. Therefore, bleaching with sulphur dioxide is of a temporary nature.

(6) **Oxidizing Nature :** Its reaction with hydrogen sulphide, sodium, potassium, magnesium and iron shows that sulphur dioxide acts as an oxidizing agent also.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$
$$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$$
$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

Uses : Some of the important uses of sulphur dioxide are :

(i) For the manufacture of sulphuric acid and sulphites, e.g., calcium bisulphite which is extensively used in the paper industry.
(ii) For bleaching delicate articles and for refining sugar
(iii) As a disinfectant and household fumigation.
(iv) Liquid sulphur dioxide is used as an inorganic solvent.
(v) Sulphur dioxide is used as the refrigerant.

1. **Sulphuric acid:**

Preparation: It is prepared by contact process which involved three steps-

i) Conversion of sulphur to sulphur dioxide (SO_2)

$S_8 + 4O_2 \rightarrow 8SO_2$

ii) Conversion of SO_2 to SO_3 in the presence of catalyst

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$; $\Delta H^0 = -196.6\ kJmol^{-1}$

It is exothermic reaction and therefore low temperature and high pressure are favourable.

iii) Formation of Oleum

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum)

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

Thus, from oleum we can get desire strength of H_2SO_4 acid by diluting it with water.

Properties of Sulphuric Acid :

Sulphuric acid dissolves in water with evolution of a large amount of heat. Hence sulphuric acid solution is prepared by slowly adding concentrated acid to water.

Chemical Properties of Sulphuric Acid :

(A) Ionic Reactions : Sulphuric acid is a dibasic acid and and ionizes in solution in two steps

$$H_2SO_4\ (aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)\ K1 = \text{very large } (> 10)$$

$$HSO_4\text{-}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)\ K2 = 1.2 \times 10^{-2}$$

First dissociation constant being large, sulphuric acid is a strong acid.

(B) Affinity for water : Sulphuric acid is a strong dehydrating agent. It removes water from organic compounds as shown by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$$

(C) Action on metals :

(i) Metals like iron, zinc, aluminium, tin and manganese react with dil. Acid to liberate hydrogen;

(ii) Metals like lead, copper, mercury and silver react with hot concentrated sulphuric acid to produce sulphur dioxide; while

(iii) Noble metals like gold and platinum do not react at all.

$$Zn + 2H_3O^+ \rightarrow Zn_2 + H_2 + 2H_2O$$

In dil. acid

$$Cu+SO_4^{2-} + 4H^+ \rightarrow Cu^2+ + SO_2 + 2H_2O$$

From hot conc. acid

(D) Action on salts : It is a strong acid and decomposes the salts of the more volatile acids, e.g. chlorides, nitrates, sulphites, carbonates, etc. The corresponding acid is liberated.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

(E) Oxidizing action : It acts as an active oxidizing agent.

$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$

(i) It oxidizes carbon and sulphur to their corresponding oxides.

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

(ii) It oxidizes hydrobromic and hydriodic acids to bromine and iodine respectively.

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

$$2Hl + 2H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$$

GROUP 17 ELEMENTS

Characteristic Features

1. **Atomic and ionic radii:** Halogens have the smallest atomic radii in their respective periods because of maximum effective nuclear charge.

2. **Ionisation enthalpy:** They have very high ionization enthalpy because of small size as compared to other groups.

3. **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.

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

5. **Bond dissociation enthalpy:**
   - Bond dissociation enthalpy follows the order
     $Cl_2 > Br_2 > F_2 > I_2$
   - Bond dissociation enthalpy of Cl_2 is more than F_2 because there are large electronic repulsions of lone pairs present in F_2.
6. **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.
7. **Oxidising power:** All halogens are strong oxidising agents because they have a strong tendency to accept electrons.
   Order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$
8. **Reactivity with H_2:**
   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 Waal’s forces increases and hence boiling point increases.
   Percentage ionic character: HF > HCl > HBr > HI
   Dipole moment: HF > HCl > HBr > HI; Electronegativity decreases down the group.
   Reducing power: HF < HCl < HBr < HI
9. **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.

10. Chlorine : Chlorine can be prepared by the oxidation hydrochloric acid with any of the following oxidizing agents :

(i) Manganese dioxide.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

Or

$$MnO_2 + 4H^+ + 2C^{l-} \rightarrow Cl_2 + Mn^{2+} + 2H_2O$$

(ii) Potassium permanganate or dichromate

$$2KMnO_4 + 16\ HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

Or

$$2MnO_4^- + 15H+ + 10Cl- \rightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$

(iii) Bleaching powder or a hypochlorite like sodium hypochlorite, NaOCl,

$$CaOCl_2 + 2HCl \rightarrow CaCl_2 + Cl_2 + H_2O$$

$$NaOCl + 2HCl \rightarrow NaCl + H_2O + Cl_2$$

Or

$$OCl^- + Cl^- + 2H^+ \rightarrow H_2O + Cl_2\uparrow$$

Manufacrture of Chlorine :

(i) Deacon's process which involves oxidation of hydrogen chloride gas by atmosphere oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) Electrolytic Process which involves electrolysis of concentrated NaCl solution. Reactions involved in the process are :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$\left.\begin{array}{c} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ Na^+ + OH^- \rightarrow NaOH \end{array}\right]$$

$$\left.\begin{array}{c} Cl^- - e^- \rightarrow Cl \\ Cl + Cl \rightarrow Cl_2 \end{array}\right]$$

Chlorine is also obtained as a by-product in many chemical industries.

Properties of Chlorine

(a) Physical

(i) It is a greenish-yellow, pungent smelling gas.
(ii) It is poisonous in nature.
(iii) It dissolves in water to give chlorine water.
(iv) It can be easily liquefied by cooling under pressure to a yellow liquid.

(b) Chemical

(i) Combination with Elements.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

$Cu + Cl_2 \rightarrow CuCl_3$

$H_2 + Cl_2 \rightarrow 2HCl$

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

(ii) **Affinity for Hydrogen :** Chlorine reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$
$$H_2S + Cl_2 \rightarrow 2HCl + S$$
$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

(iii) **Reaction with ammonia :** With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen, trichloride (explosive) is formed.

$$2NH_3 + 3Cl_2 \rightarrow 5NH_4Cl + N_2$$
$$NH_3 + 3Cl_2 \rightarrow NC_{l3} + 3HCl$$

(iv) **Reaction with alkalies** : With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$
$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

With dry slaked lime it gives bleaching powder.

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

The composition of bleaching powder is $Ca(OCl)_2 + CaCl_2Ca(OH)_2.2H_2O$.

(v) **Reaction with hydrocarbons :** Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.

For Example.

$CH_4 + Cl_2$ ¾$\overset{uv}{¾}$® $CH_3Cl + HCl$ (Substitution)

$C_2H_4 + Cl_2$ $C_2H_4Cl_2$ (Addition)

(vi) **Oxidizing, Bleaching and Disinfecting action of Chlorine :** Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so produced has a tendency to lose nascent oxygen which is responsible for the oxidizing and bleaching action of chlorine.

$$Cl_2 + H_2O \rightarrow HCl + HClO$$
$$HClO \rightarrow HCl + O$$

Or Chlorine is an oxidizing agent since it can take electrons.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

(vii) It oxidizes ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

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

$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2 (SO_4)_3 + H_2O$$

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

$$\text{Or} \quad 2Fe_2+ + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HlO_3 + 10\ HCl$$

(viii) It is a powerful bleaching agent; bleaching action is due to oxidation

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

$$\text{Coloured Substance} + O \rightarrow \text{Colourless substance}$$

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent because there is no reducing agent in the atmosphere to convert the colourless matter back to coloured matter.

Uses of Chlorine : Chlorine is used :

(i) For bleaching wood pulp, cotton and linen textiles.
(ii) For purification of drinking water.
(iii) In organic chemical industry it is used for the manufacture of chloroform ($CHCl_3$); carbon tetrachloride (CCl_4) and ethylene chloride ($C_2H_4Cl_2$), solvents, refrigerants, DDT, synthetic plastics, rubbers, anti-knock compounds etc.
(iv) In inorganic chemical industry it is used for the manufacture of bleaching powder hypochlorides, chlorate, perchlorates, bromine and hydrochloric acid.
(v) For extraction of metals like gold and platinum.
(vi) In warfare for the manufacture of poisonous gases e.g.
  (a) Phosgene, $COCl_2$, (b) Tear gas, $CCl_3\ NO_2$ (c) Mustard gas, ClC_2H_4 –S-C_2-H_4Cl.

11. Hydrogen Chloride :

Hydrochloric acid gas is prepared in the laboratory by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4\ NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl\ Na_2SO_4 + HCl$$

Hydrochloric acid gas may be dried by passing through concentrated sulphuric acid.

Properties of Hydrochloric Acid :

(a) Physical

(i) HCl gas is a colourless, pungent smelling gas with acidic taste.
(ii) It fumes in moist air and is extremely soluble in water.
(iii) It can be easily liquefied to a colourless liquid (b.p. 190K) and frozen to a while crystalline solid (m.p. 160K).

(b) Chemical

(i) Acidic Properties :

(1) It is a typical acid but when perfectly dry does not affect litmus. In most state or in solution. It turns blue litmus red.

(2) It reacts with metals, their oxides, hydroxides or carbonates to give chlorides, e.g.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

(ii) Action with Ammonia : Hydrochloric acid gas gives thick while fumes of ammonium chloride with ammonia.

$$HCl + NH_3 \rightarrow NH_4Cl$$

(iii) Aqua Regia : A mixture of three parts of concentrated hydrochloric acid with one part of concentrated nitric acid called aqua regia is used for dissolving noble metals, gold and platinum as their chlorides. Aqua regia liberates nascent chlorine which dissolves Au of Pt.

$$Au+4H+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$
$$3Pt + 16H+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-}\ 4NO + 8H_2O$$

(iv) Action on Salts : Hydrochloric acid decomposes salts of weaker acids e.g., carbonates, bicarbonates, sulphides and nitrites. This is used as a test for these acid radicals.

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2\uparrow + H_2O$$
$$Na2SO_3 + 2HCl \rightarrow 2NaCl + SO_2\uparrow + H_2O$$
$$2NaNO_2 + 2HCl \rightarrow 2NaCl + NO\uparrow + NO_2\uparrow + H_2O$$

Uses of Hydrochloric Acid :

(i) For the manufacture of chlorine and chlorides, e.g., ammonium chloride.
(ii) In the manufacture of glucose from corn starch.
(iii) For extracting glue from bones and purifying bone black.
(iv) As a constituent of aqua regia, which is used for dissolving noble metals.
(v) It is also used in medicine and as a reagent in the laboratory.

12. 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 > HOI; this is because Fluorine is most electronegative.

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

- Binary compounds of two different halogen atoms of general formula XX'_n are called interhalogen compounds where n = 1, 3, 5, or 7
- All these are covalent compounds.
- Interhalogen compounds are more reactive than halogens because XX’ 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 (ClF_3, BrF, IF3, ICl_3) (Bent T- shape)
  - XX'_5(ClF_5, BrF_5, IF_5) (Square Pyramidal Shape)
  - XX'_7 (IF_7) (Pentagonal bipyramidal shape

GROUP 18 ELEMENTS:

Characteristic Features

1. **Ionisation enthalpy:**

- They have very high ionization enthalpy because of completely filled orbitals.
- Ionisation enthalpy decreases down the group because of increase in size.

2. **Atomic radii:** Increases down the group because numbers of shells increases down the group.

3. **Electron gain enthalpy:** They have large electron gain enthalpy because of stable electronic configuration.

4. **Melting and boiling point:** Low melting and boiling point because only weak dispersion forces are present.

5. General Introduction of Group 18 Elements :

The group 18 of the periodic table consists of six monoatomic gases i.e., helium (He), neon (Ne), argon (Ar), kypton (Kr), xenon (Xe) and radon (Rn). Except radon, all other gases are present in the atmosphere in very small quantities and hence they are known as rare gases of the atmosphere. These gases are also sometimes referred to as aerogens (present is the air).

All these gases do not show any chemical reactivity at ordinary temperature and nature they were earlier called inert gases. However, later a number of compounds of these gases, particularly those of xenon and krypton, have been prepared. This suggests that these gases are not completely inert. Consequently, these gases are now called noble gases on analogy with noble metals like gold and platinum which show reluctance to react rather than complete inertness.

Occurance of Noble Gases :

Except radon which is radioactive element, all other noble gases occur in the elemental state in the atmosphere. Their total percentage in dry air is about 1% by volume of which argon is the major component. Helium is the second most abundant element in the universe (23% as compared to 76% hydrogen) although its terrestrial abundance is very low. Helium is also present in the natural gas to an extent of 2-7%. Helium and sometimes neon are also present, in small quantities, in various radioactive minerals such as clevite, monazite, pitchblende, etc. Helium, neon and argon are also present in trace amounts in some spring waters. The relative abundance of different noble gases in the atmosphere are given below :

Element	**Abundance in Air (% by volume)**	**Element**	**Abundance in Air (% by volume)**
Helium (He)	5.25×10^{-4}	Krypton (Kr)	1.14×10^{-4}
Neon (Ne)	1.82×10^{-3}	Xenon (Xe)	8.7×10^{-6}
Argon (Ar)	0.934	Radon (Rn)	Trace

Electronic Configuration :

The general outer electronic configuration of noble gases in $ns^2\ np^6$. Hence, however, has $1s^2$ configuration. In all these gases, all the orbitals which are occupied by the elements are completely filled. This impacts stability to the atoms of these gases. As a result of this stable arrangement of electrons, the atoms of these gases neither have any tendency to gain electrons nor to lose electrons. Consequently, these gases are almost chemically inert. The electronic configuration of noble gases is given in Table.

Name	Atomic Number	Electronic Configuration	
		Complete	With noble gas core
Helium (He)	2	$1s^2$	-
Neon (Ne)	10	$1s^2 2s^2 2p^6$	[He] $2s^2$
Argon (Ar)	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ne] $3s^2\ 3p^6$
Krypton (Kr)	36	$1s^2 2s^2 2p^6 3s^2 3d^{10} 4s^2 4p^6$	[Ar] $3d^{10}\ 4s^2 4p^6$
Xenon (Xe)	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$	[Kr] $4d^{10} 5s^2 5p^6$
Radon (Rn)	86	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^6$

General Physical Properties of Group 18 Elements :

(i) Low melting points and boiling points because the only type of interatomic interation in these elements is weak dispersion forces.
(ii) Difficult to liquefy.
(iii)Low solubility in water
(iv)Monoatomicity.

(v)Helium has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

General Chemical Properties of Gourp 18 Elements :

The noble gases are chemically inert due to the following reasons :

(i) The noble gases have completely filled ns2np6 electronic configuration in their valence shells.

(ii) The noble gases have high ionization enthalpies.

(iii) The electron gain enthalpies of noble gases are positive.

Noble gases neither have a tendency to lose nor to gain electrons and hence do not enter into chemical combination. Before 1962, it was thought that noble gases do not combine at all and hence no compounds of noble gases were possible.

However, in 1962, Neil Barlett observed that platinum hexafluoride (PtF_6) – a powerful oxidising agent reacts with dioxygen to yield an ionic solid, dioxygenylhexaaafluroplatinate (V), O_2^+ $[PtF_6]^-$

$$O2(g) + PtF6(g) \rightarrow O_2^+ [PtF_6]^-(s)$$

In this reaction O2 has been oxidised to O_2^+ by $[PtF_6]^-$

Since the first ionization enthalpy of xenon (1170kJ mol-1), is fairly, close to that of O2 molecule (1175kJ mol-1), Barlett thought that PtF6 should also oxidise Xe to Xe+. Thus, when Xe and PtF_6were mixed, a rapid reaction occurred and a red solid with the formula Xe+[PtF6-] was obtained.

$$Xe+PtF_6\ Xe+[PtF_6]^-$$

After this discovery, a large number of xenon compounds mainly with most electronegative elements like fluorine and oxygen have been prepared.

6. **Shape:** 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 is known.

7. **Compounds of Xe and F:**

- $Xe + F_2 \xrightarrow{673\,K,\ 1\,bar} XeF_2$
- $Xe + 2F_2 \xrightarrow{873\,K,\ 7\,bar} XeF_4$
- $Xe + 3F_2 \xrightarrow{573\,K,\ 60-70\,bar} XeF_6$
- $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

XeF_2, XeF_4 and XeF_6 are powerful fluorinating agents.

7. **Compounds of Xe and O:**

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