



CHAPTER

12

The p-Block Elements

15th-Group Elements

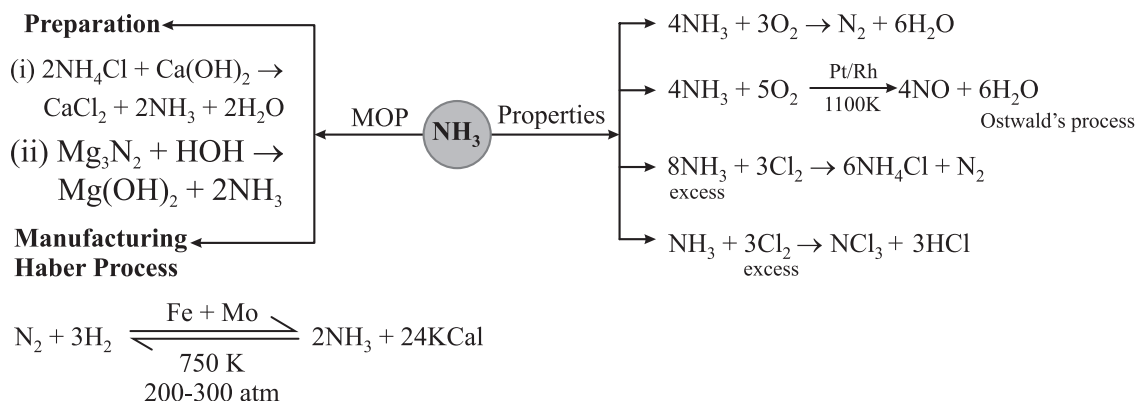
Nitrogen Family

- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. for example,
(i) $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$
- In case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid.

Compounds of Nitrogen Family

Ammonia (NH_3)

Colorless, Pungent Smell, basic in nature liquified easily, uses as coolant



Nitric Acid (HNO_3)

Preparation

Ostwald's process

- $4\text{NH}_3(\text{g}) \xrightarrow[500 \text{ K, } 9 \text{ bar}]{\text{Pt/Rh - gauze catalyst}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$

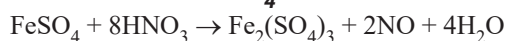
Properties

HNO_3 , nitric acid was earlier called as aqua fortis (meaning strong water).

It usually acquires yellow colour. Due to its decomposition by sunlight into NO_2 .

It acts as a strong oxidising agent.

Reaction with FeSO_4



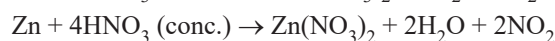
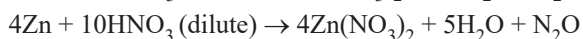
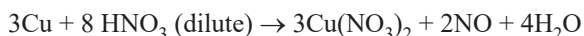
Reaction with non-metals

Non-metals converted into highest oxyacids by hot and conc.

$\text{HNO}_3 \cdot \text{NO}_2$ gas is evolved (S to H_2SO_4 ; P to H_3PO_4 ; C to H_2CO_3 ; I₂ to HIO_3 ; As to H_3AsO_4 ; Sb to H_3SbO_4 and Sn to H_2SnO_3). Most of the

metals except noble metals are attacked by HNO_3 . It plays double role in action on metals, i.e., it acts as an acids as well as an oxidising agent.

Reaction with Metals



Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O + metal nitrate
	Pb, Cu, Ag	NO + metal nitrate
Conc. HNO_3	Sn	$\text{NO}_2 + \text{H}_2\text{SnO}_3$ (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

Phosphine (PH₃)

Preparation

- (i) $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$
- (ii) $\text{PH}_4\text{I} + \text{NaOH} \rightarrow \text{NaI} + \text{H}_2\text{O} + \text{PH}_3$

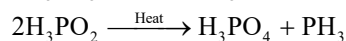
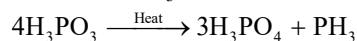
Physical Properties

Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

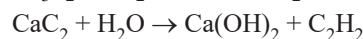
Chemical Properties

- (i) $2\text{PH}_3 + 4\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$
- (ii) $4\text{PH}_3 \xrightarrow{713\text{ K}} \text{P}_4 + 6\text{H}_2$
- (iii) $\text{PH}_3 + 4\text{Cl}_2 \rightarrow \text{PCl}_5 + 3\text{HCl}$

- ❖ On heating, phosphorus acid, H_3PO_3 decomposes into phosphine (PH_3) and phosphoric acid (H_3PO_4).

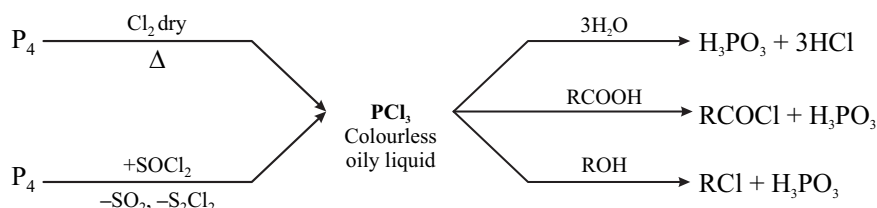


- ❖ **Holme's signals:** A mixture of Ca_3P_2 and CaC_2 on treatment with H_2O forms PH_3 and P_2H_4 along with C_2H_2 . The mixture burns with a bright light

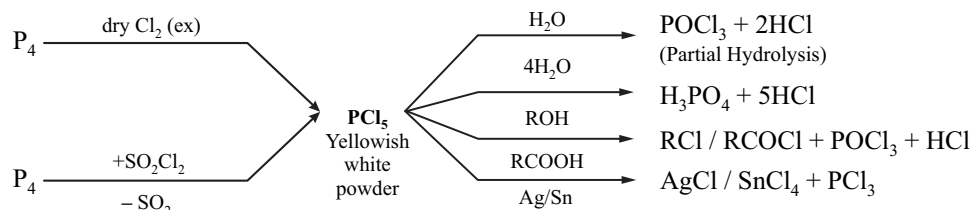


- ❖ Smoke screens, involve the use of calcium phosphide, Ca_3P_2 . The PH_3 gas obtained from Ca_3P_2 catches fire to give the needed smoke.

PCl₃



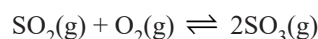
PCl₅



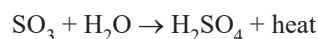
16th-Group Elements

- ❖ Sulphur trioxides (SO_3) is a white crystalline solid with melting point 290 K and boiling point 318 K.
- ❖ SO_3 is prepared by the direct oxidation of SO_2 with atmospheric oxygen in presence of finely divided Pt or V_2O_5 at a pressure of 2 bar and temperature 720 K.

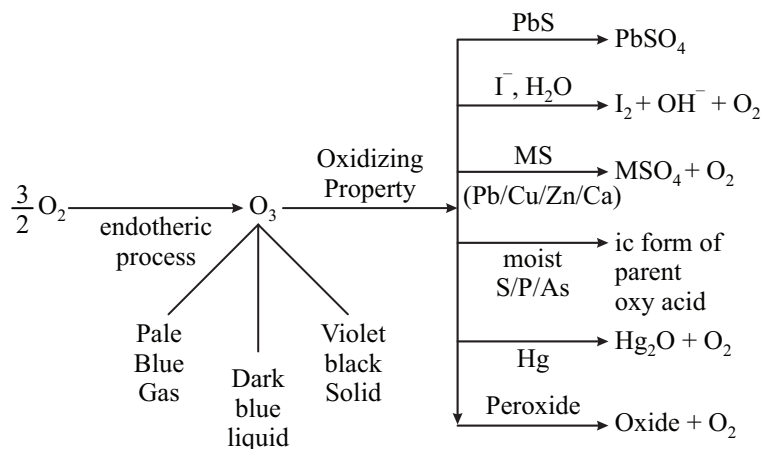
- ❖ SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



SO_3 reacts with water to produce H_2SO_4 and large amount of heat is evolved.



Ozone



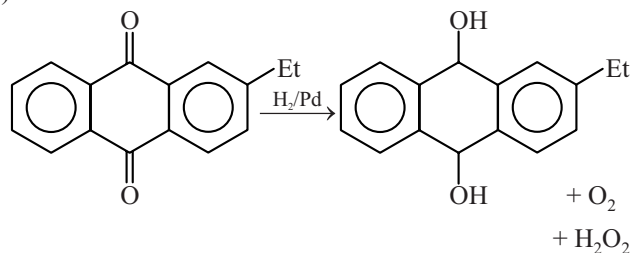
*** Fishy odour, Highly toxic.**

Gases	Absorbent
O ₃	Turpentine Oil/Oil of cinnamon.
NO	FeSO ₄
SO ₂	NaOH
CO	Cu ₂ Cl ₂
O ₂	Pyrogallol

Hydrogen Peroxide

Preparation

- (i) $\text{Na}_2\text{O}_2 + \text{H}_2\text{O (icecold)} \rightarrow \text{NaOH} + \text{H}_2\text{O}_2$
- (ii) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
(Now a day conc. H_3PO_4 is used)
- (iii) $2\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + 2\text{HSO}_4^-$
Anode : $2\text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$
Cathod : $2\text{H}^+ + \text{e}^- \rightarrow \text{H}_2$
 $\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$
- (iv)



Properties

Oxidizing Property

- (i) $\text{H}_2\text{O}_2 \xrightarrow{\text{PbS}} \text{PbSO}_4$
- (ii) $\text{H}_2\text{O}_2 \xrightarrow{\text{BaSO}_3} \text{BaSO}_4 + \text{H}_2\text{O}$
- (iii) $\text{H}_2\text{O}_2 \xrightarrow{\text{H}_2\text{S}/\text{HI}} \text{S}/\text{I}_2 + \text{H}_2\text{O}$
- (iv) $\text{H}_2\text{O}_2 \xrightarrow{\text{Fe}^{+2}/\text{H}^-} \text{Fe}^{+3} + \text{H}_2\text{O}$
- (v) $\text{H}_2\text{O}_2 \xrightarrow{\text{Cr}^{+3}/\text{OH}^-} \text{Cr}^{+6} + \text{H}_2\text{O}$

Reducing Property

- (i) $\text{H}_2\text{O}_2 \xrightarrow{\text{Fe}^{+3}/\text{OH}^-} \text{Fe}^{+2} + \text{O}_2$
- (ii) $\text{H}_2\text{O}_2 \xrightarrow{\text{Pb}^+ \text{ Grids}} \text{PbO}$
- (iii) $\text{H}_2\text{O}_2 \xrightarrow{\text{Cl}_2/\text{Br}_2} \text{HCl} + \text{O}_2$
- (iv) $\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_4^-/\text{OH}^-} \text{MnO}_2 + \text{O}_2$
- (v) $\text{H}_2\text{O}_2 \xrightarrow{\text{MnO}_4^-/\text{H}^+} \text{Mn}^{+2} + \text{O}_2$
- (vi) $\text{H}_2\text{O}_2 \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} \text{Cr}^{+3} + \text{O}_2$
- ❖ Tailing of mercury is due to the formation of mercury oxide when Hg reacts with ozone.
- $2\text{Hg} + \text{O}_3 \rightarrow \text{Hg}_2\text{O} + \text{O}_2$

As a result of it, mercury loses its meniscus and starts sticking to the glass.

- ❖ The bleaching action of Ozone and H_2O_2 is permanent and is due to oxidation while that of SO_2 is temporary and is due to reduction.
- ❖ H_2O_2 is used to restore the colour of old lead paintings which have been blackened due to the formation of PbS by the action of H_2S present in the air.
- $$\underset{\text{Black}}{\text{PbS}} + 4\text{H}_2\text{O}_2 \rightarrow \underset{\text{White}}{\text{PbSO}_4} + 4\text{H}_2\text{O}$$
- ❖ Antichlor action of H_2O_2 is due to its tendency to reduce the excess of chlorine from bleaching powder to HCl .
- $\Rightarrow \text{NH}_2 \cdot \text{NH}_2 + \text{H}_2\text{O}_2$ as rocket propellant.
- \Rightarrow Storage:

Sulphuric Acid (H_2SO_4)

It is also known as oil of vitriol and king of chemicals.

Manufacture of Sulphuric Acid

Lead chamber process

The various steps involved are :

- (a) Production of SO_2 : By burning S or iron pyrites.
- $\text{S} + \text{O}_2 \xrightarrow{\Delta} \text{SO}_2$
- $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
- (b) Production of catalyst : Oxides of nitrogen.
- $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$
- $2\text{HNO}_3 \xrightarrow{\Delta} \text{H}_2\text{O} + \text{NO} + \text{NO}_2 + \text{O}_2$
- (c) Reaction in lead chamber
- $\text{SO}_2 + \text{NO}_2 \longrightarrow \text{SO}_3 + \text{NO}$
- $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$
- $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ (used again)

Contact Process

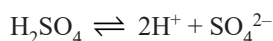
The steps involved are:

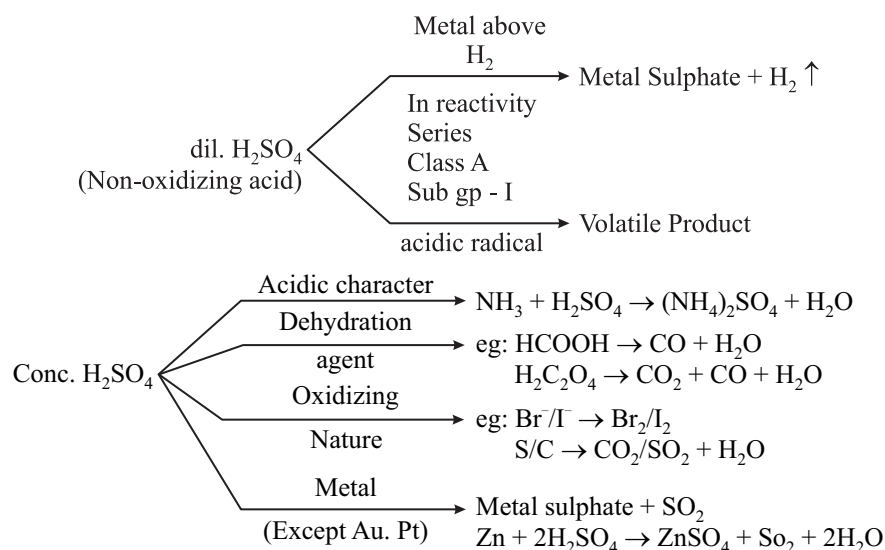
- (a) **Production of SO_2** : It is produced by burning sulphur or iron pyrites and purified by treating with steam to remove dust particles.
- (b) **Conversion of SO_2 to SO_3** : It is done in container or catalyst chamber after being pre-heated to 450°C .
- $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 + x \text{ cal}$
- Catalyst** : Formerly, platinised asbestos was used which is costly and easily poisoned. These days V_2O_5 is used.
- (c) SO_3 is absorbed by conc. H_2SO_4 and then water is added to produce the acid of desired concentration.
- $\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{H}_2\text{S}_2\text{O}_7$
- $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$

Properties

Its specific gravity is 1.8 and it is 98% by weight.

It is strong dibasic acid.





Uses

In lead storage batteries.

In manufacture of paints and pigments.

In metallurgy for electrolytic refining of metals.

17th-Group Elements

- All halogens are coloured. For example, F_2 has yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid.
- They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
- In general, a halogen oxidises halide ions of higher atomic number.
 $\text{F}_2 + 2\text{X}^- \rightarrow 2\text{F}^- + \text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$ or I)
 $\text{Cl}_2 + 2\text{X}^- \rightarrow 2\text{Cl}^- + \text{X}_2$ ($\text{X} = \text{Br}$ or I)
 $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$
- O_2F_2 oxidises plutonium to PuF_6 and the reaction is issued in removing plutonium as PuF_6 from spent nuclear fuel.
- I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Interhalogen Compounds

These compounds are regarded as halides of more electropositive (i.e. less electronegative) halogens.

Types of interhalogen compound:

AB type : ClF , BrF , BrCl , ICl , IBr

AB_3 type : ClF_3 , BrF_3 , ICl_3

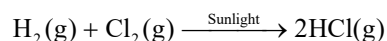
AB_5 type : BrF_5 , IF_5

AB_7 type : IF_7

Hydrochloric Acid, (HCl)

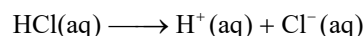
Preparation: By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

By the direct combination of hydrogen and chlorine.



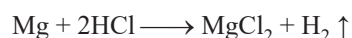
Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.

Properties: Hydrogen chloride is a covalent compound but when dissolved in water it ionizes to form hydrogen ions and chloride ions.



Thus, anhydrous HCl does not show acidic properties. Only aqueous HCl or in pressure of moisture, HCl behaves as an acid.

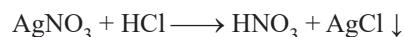
Metal + Hydrochloric acid → Metal chloride + Hydrogen



It react with bases and basic oxides or hydroxides to form their respective chlorides and water.



It reacts with metal carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites, etc, to form their respective chlorides.



Reducing property: HCl is a strong reducing agent.



Uses

In the production of dyes, paints, photographic chemicals, etc.

Used in the preparation of chlorides, chlorine, aquaregia, etc.

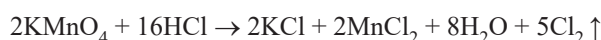
Used as a laboratory reagent.

Pseudo Halides

Pseudo halides are uninegative group which show certain characteristics of halide ions. For example Cyanide (CN^-), Cyanate (OCN^-), Thiocyanate (SCN^-), Selenocyanate (SeCN^-), Azide (N_3^-), Azidothio carbonate (SCSN_3^-) and isocyanate (ONC^-).

Chlorine (Cl_2)

Preparation: By oxidation of conc. HCl.



Manufacture:

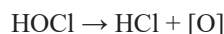
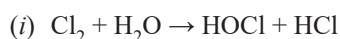
Weldon's process: By heating pyrolusite with conc. HCl.



Deacon process: $2\text{HCl} + \text{O}_2 \xrightarrow{\text{CuCl}_2} \text{Cl}_2 \uparrow + \text{H}_2\text{O}$

Properties: It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$.

Bleaching action and oxidising property

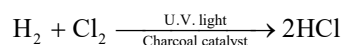


Coloured matter + nascent : $[\text{O}] \rightarrow$ Colourless matter

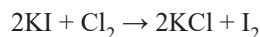
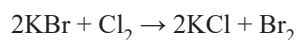
The bleaching action of chlorine is permanent and is due to its oxidising nature.



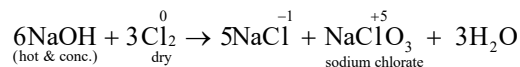
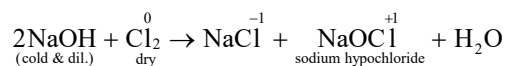
Action of hydrogen:



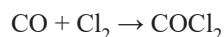
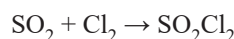
Displacement reactions :



Action of NaOH :



Addition reactions:

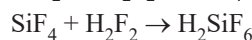
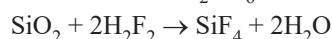


❖ **Test for chlorine:**

- It is a greenish yellow gas with irritating smell.
- It turns starch iodide paper blue.
- It bleaches litmus paper and indigo solution.

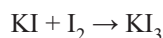
Key Note

- Action of silica and glass :** Strong solution of HF attacks readily forming silicon fluoride which gives complex fluosilicic acid, H_2SiF_6 with excess HF.



This is called etching of glass.

- Iodine is slightly soluble in water but much more soluble in KI due to the formation of KI_3 .

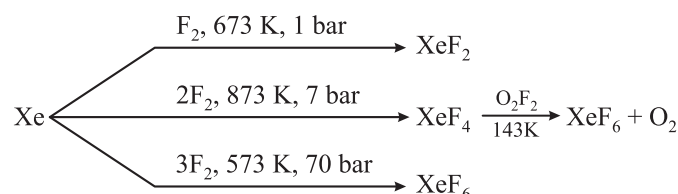


The solution behaves as a simple mixture of KI and I_2 .

18th-Group Elements

- Relative Abundance:
 $\text{Ar} > \text{Ne} > \text{Kr} > \text{He} > \text{Xe} > \text{Rn}$
- Melting and Boiling point:
 $\text{Rn} > \text{Xe} > \text{Kr} > \text{Ar} > \text{Ne} > \text{He}$
- He has the lowest boiling point among all element.
- $\text{O}_2[\text{PtF}_6]$ is the first noble gas compound.
- Ar, Kr and Xe form clathrate compound when pass in ice with high pressure.
 $\text{A} \cdot 6\text{H}_2\text{O}$ ($\text{A} = \text{Ar/Kr/Xe}$)

Preparation of Xe-Fluoride



Properties

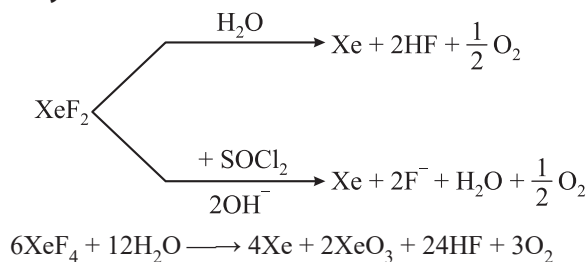
Fluoride donor : Eg. $\text{XeF}_2 + \text{MF}_5 \longrightarrow [\text{XeF}_4]^+ [\text{MF}_6]^-$
($\text{M} = \text{As/Sb/P}$)

Fluoride acceptor : Eg. $\text{XeF}_6 + \text{MF} \longrightarrow \text{M}^+ [\text{XeF}_7]^-$
($\text{M} = \text{Na/K/Rb/Cs}$)

Fluoride agents : Eg. $\text{XeF}_4 \xrightarrow{\text{SF}_4/\text{Pt}} \text{PtF}_4/\text{SF}_6 + \text{Xe}$

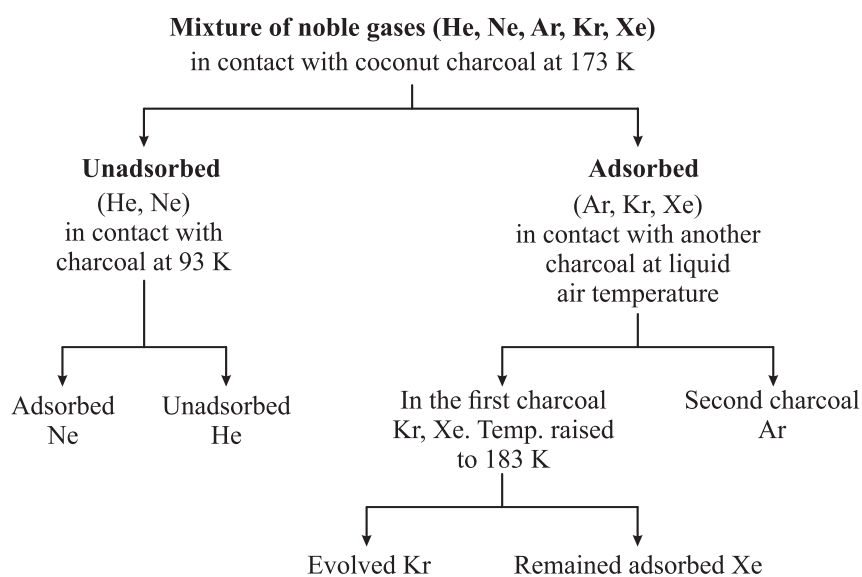
Reaction with SiO_2 : Eg. $2\text{XeF}_6 + \text{SiO}_2 \rightarrow \text{SiF}_4 + \text{XeOF}_4$

Hydrolysis



Noble Gases

In Dewar's method, the separation of noble gases is summarized below:



The viscosity of He is extremely low, about $1/100^{\text{th}}$ of hydrogen gas.