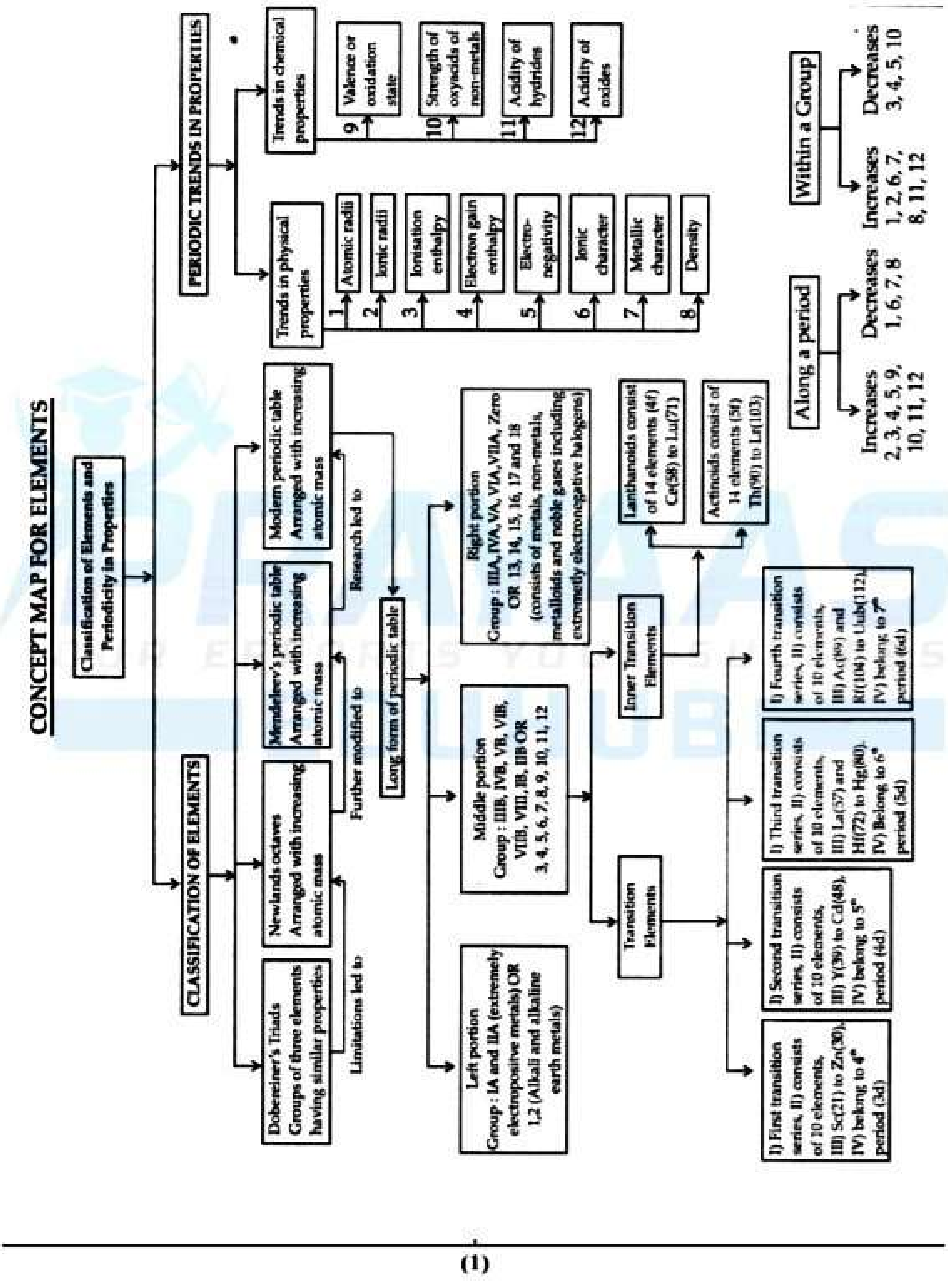
7 p-Block Elements



p-block elements

- **Definition:**

  The elements in which last electron goes to p-orbital of ultimate shell i.e. np orbitals are called p-block elements.

  Valence shell electronic configuration: $ns^2\ np^{1-6}$.

- **Position in P.T. :**

1. TWY are placed in groups 13 to 18 of periodic table and all periods.
2. They are placed at right hand side of periodic table.

GROUP 15 ELEMENTS

- **Valence shell electronic configuration:**

  $ns^2\ np^3$. They are called phicogens (offensive smell)

Sr.	Elements	N	P	As	Sb	Bi	Trend
1.	Name g Properties i	Nitrogen	Phosphorous	Arsenic	Antimony (Stibnite)	Bismuth	-
2.	Discovered by	D. Rutherford	Brand(1669) (1250)	A.Maanus (1604)	B.Valeitine (1953)	GGeoffre)	-
3.	State	Gas	Waxy solid	Solid	Solid	Solid	-
4.	Atomic number	7	15	33	51	83	Increases
5.	Atomic mass (g mol^{-1})	14.01	30.97	74.92	121.75	209.00	Increases
6.	Valence shell c.c.	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$Ss^2 Sp^3$	$6s^2 6p^3$	-
7.	Abundance (ppm (in earth crust)	19	1120	1.8	0.2	0.008	Increases
8.	Atomicity	Diatomic	Tetraatomic atomic	Tetra atomic	Tetra atomic	Mono	-
9.	Covalent radius (pm)	70	110	120	140	150	Increases
10.	Ionic radius (pm)	717 (N^{3-})	212(P^{3-})	222(As^{3-})	76(Sb^{3+})	108(Bi^{3+})	
11.	Atomic volume						
12.	Density (g $mol.^{-1}$)	0.879 at 63 K	1.823 (grey/ $\propto$ form)	5.778	6.580	9.808	Increases
13.	Melting point (K)	63	317.1 (white P)	1087.5 (grey/ $\propto$ form)	904	544	Increases
14.	Boiling point (K)	77.2	554 (white P)	883	1653	1813	Increases
15.	Ionization enthalpy (kJ mol^{-1})	1402	1012	947	834	703	Decreases
16.	Electronegativity	3.00	2.10	2.20	1.82	1.67	Decreases
17.	Electron gain enthalpy (kJ mol^{-1})						-
18.	Metallic nature	Non-metal	Non-metal	Metalloid	Metalloid	Metal	Increases

19.	Conductivity	Bad	Bad	Poor	Moderate	Good	Increases
20.	Allotropy	α (Cubic crystal) and β (Hexagonal)	White, red, black (a, (3) explosive	yellow, grey, (metallic)	yellow, grey,	-	-
21.	Catenation	upto 3 atoms	several atoms two	one or two	one or	No	-
22.	Bond energy (kJ mol^{-1})	N-N 163.8	P-P 201.6	As-As 147.4	Sb-Sb -	Bi-Bi -	-
23.	CommonO.S. -3, -2, -1, 0, +1 +2, +3, +4, +5 Stabilitv of +3 increases, but +S decreases.	Covalency 4	+3, +4, +5, -3	+3, +5,-3	+3, +5, -3	+3, -3	-
24.	Conc.HNO_3	-	H_3PO_4+NO_2	H_3AsO_4 +NO_2	S_4O_{10} +NO_2	$Bi(NO_3)$ +NO_2	Decreases
25.	Conc.H_2SO_4	-	H_3PO_4 +SO_2	H_3AsO_4 +SO_2	$Sb_2(SO_4)_3$ +SO_2	$Bi(SO_4)_3$ +SO_2	-
26.	NaOH		PH+NaH_2PO_2	Na_3AsO_3 +H_2	Na_3SbO_3 +H_2	-	
27.	Metals	Metal nitrides (Mg_3N_2)	Phosphides (Mg_3P_2)	Arsenides (Na_3As_2)	Antimonides (Zn_3Sb_2)	Bismuthide (Mg_3Bi_2)	-
28.	Hydrides	NH_3	PH_3	AsH_3	SbH_3	BiH_3	-
(a).	E-H distance(pm)	101.7	141.9	151.9	170.7	-	Increases
(b).	H-E-Hangle	107.8°	93.6°	91.8°	91.3°	-	Decreases
(c).	Colour	colourless		colourless	colourless	colourless	colourless -
(d).	Stability	most stable →					Decreases
(e).	B.pt.(volatility)	B.Pt. →					Decreases
(f).	Basic nature Decreases	Basic		Weak base	donot show basic properties		
(g).	Poisonous nature	From NH_3 to BiH_3 →					Decreases
(h).	Tendency to form H bonds	strong tendency	No	No	No	No	Decreases
(i)	Decomposition temperature	1573 K	673K	553K	423K	unstable	Decreases
(j)	Thermal stability Decreases	NH_3 > PH_3 > AsH_3	> SbH_3 > BiH_3				
(k)	Dipole moment	→					Decreases
(1)	Reducing property	Weakest	mild	good	strong	strongest	Increases
(m)	Solubility in wate	highly soluble	Solubility →				Decreases
29.	Halides (a) EX_3	NX_3 except	13	PX_3	AsX_3	SbX_3	BiX_3
	(b) EX_5	-	PX_5 except PI_5	AsF_5	SbF_5l ssct,	BiF_5	
30.	Oxides (a) + 5	N_2O_5		P_4O_{10}	As_2O_5	Sb_2O_5	Bi_2F_5
	(b) + 4	NO_2 or N_2O_4	P_4O_8	-		-	-
	(c) + 3	N_2O_3	P_4O_6	As_2O_3	Sb_2O_3	Bi_2O_3	

	(d) + 2	NO(neutral)	-	-	-	-	
	(e) + 1	N_2O(neutral)	-	-	-	-	
	Acidic nature	$\longrightarrow$					Decreases
31.	Oxoacids (a) + 1	$H_2N_2O_2$		H_3PO_2	-	They do not form stable oxoacids	
	(b) + 2	$H_4N_2O_4$		H_3PO_3	-		
	(c) + 3	HNO_2		$H_4P_2O_6$	H_3AsO_3		
	(d) + 5	HNO_3		H_3PO_4 $H_4P_2O_7$	H_3AsO_4		
	(e) + 7	HNO_4		-			

- Anamalous behaviour of nitrogen: Nitrogen shows different properties than the other elements of same group because

i) small size

ii) High ionisation energy

iii) High electronegativity

iv) absence of' d' orbitals.

Sr.NO.	Properties	Nitrogen	Other elements of 15 group
1.	State	Gas	Solids
2.	Atomicity	Diatomic (N_2)	Tetraatomic (As_4, Sb_4, P_4 etc.)
3.	Oxidation state	From –3 to +5	Limited oxidation state
4.	Hydrogen bond formation	Strong tendency	Do not formed
5.	Multiple bond formation	pπ-pπ multiple bond	dπ-dπ multiple bond
6.	Co-ordination compound formation	Does not formed	Formed
7.	Hydrides	Stable and basic	Less stable and less basic
8.	Trihalides	Unstable except NF_3	–
9.	Pentahalides	Does not formed	Formed

I. DINITROGEN:

Discovered by :

Daniel Rutherford

Occurence :

In air, 78% by volume.

A. Preparation:

i. Laboratory method:

By action of ammonium chloride or $NaNO_2$.

ii. Commercial method:

Fractional distillation of liquid air. Due low boiling point (77.2 K) liquid N_2 distills out first left behind liquid oxygen (b.pt.90 K)

iii. From different compounds:

Thermal decomposition of ammonium dichromate, sodium or barium azide, bleaching powder with NH_3, liberates N_2.

B. Properties:

i. State:

Colourless, odourless, tasteless, chemically inert, non-toxic in nature.

ii. Solubility in water:

Slightly soluble.

iii. **F.pt. and B.pt:**

Low freezing point (195.3 K) and low boiling point (239.6K)

iv. **Isotopes :**

$^{14}_{7}N$ and $^{15}_{7}N$

II. AMMONIA (NH_3) :

A. Preparation:

i. **Laboratory method:**

Heating a mixture of NH_4Cl and $Ca(OH)_2$ and moist NH_3 gas is dried over quick lime (CaO).

ii. **Haber process: (Manufacturing process):**

Process:

Direct combination of N_2 and H_2 in 1:3 proportion.

Reaction:

$N_2 + 3H_2 \rightleftharpoons 2NH_{3(g)}$, $\Delta_f H^o = -46.1$ kJ mol^{-1}

Experimental condition:

At 200 atm pressure and at 700 K.

Catalyst:

Finely divided Fe(iron) with promoter molybdenum (Md).

B. Properties:

i. **State:**

Colourless gas with a pungent smell.

ii. **Fpt and B pt:**

Freezing point of NH_3 is 198.4 K and boiling point 293 K.

iii. **Solubility:**

Highly soluble in water due to the formation of hydrogen bonding.

C. Reactions:

i. **Action of air:**

Gives N_2 and H_2O,

ii. **Action of air in presence of platinum:**

Liberates NO.

iii. **Action of halogens:**

With Cl_2 gives NCl_3 with Br_2 gives NH_4Br and with I_2 gives NH_4I.

iv. **Action of Na, K metals:**

Gives amides ($NaNH_2$, KNH_2 etc.)

v. **Action of sodium hypochloride (NaOCl) :**

Gives hydrazine (NH_2, NH_2)

vi. **Formation of co-ordination compounds:**

$[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]Cl$ etc.

D. Test of ammonium radical (NH_4) :

Ammonia or ammonium salt when treated with Nesseler's reagent (an alkaline solution of K_2HgI_4) gives brown precipitate of Millions base.

$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2N - Hg - O - HgI + 7KI + H_2O$

(Iodide of Millions base)

It is used to detect presence of NH_4^+ radical.

E. Structure of H_3:

Trigonal pyramidal with H-N-H bond angle is 10~5'.

H–H–H bond length = 101.7 PM

III. NITRIC ACID (HNO_3) :

A. Preparation:

i. Laboratory method:

By distillation of sodium nitrite with cone. H_2SO_4.

ii. Commercial method:

Ostwald process:

$$NH_{3(g)} \xrightarrow[Pt,\ 500K,\ 9\ Bar]{O_2} NO_{(g)} \xrightarrow{O_2} NO_{2(g)} \xrightarrow{H_2O} HNO_{3(l)} \text{ (68\% by mass)}$$

Further on dehydration with cone. H_2S0_4, it is concentrated upto 98% called aqua-fortis.

B. Properties:

i. State:

Colourless liquid.

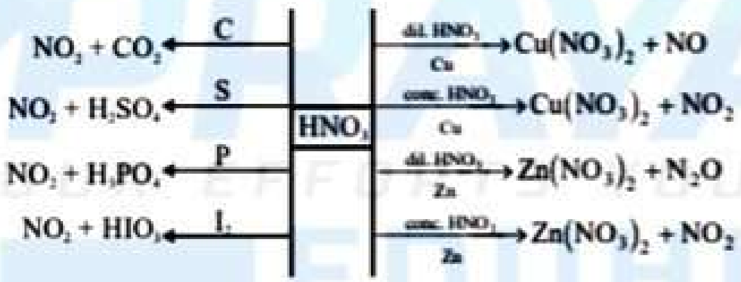
ii. FPt and BPt:

Freezing point of HNO_3 is 231.4 K and boiling point 355.6 K.

iii. Density:

LR grade nitric acid contains 6 % of HNO_3, by mass has a specific gravity 1.504 g/cm³.

C. Reactions:



D. Action on Gold and Platinum:

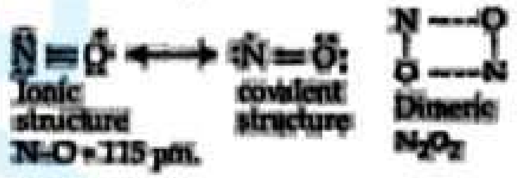
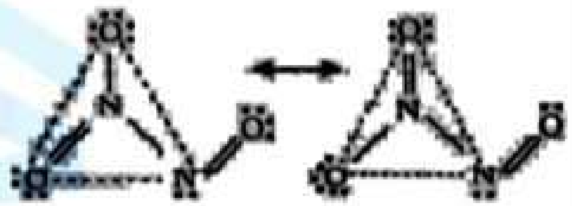
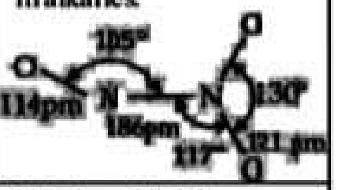
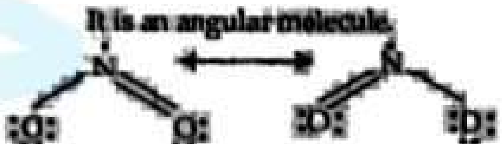
$$3HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2[Cl]$$

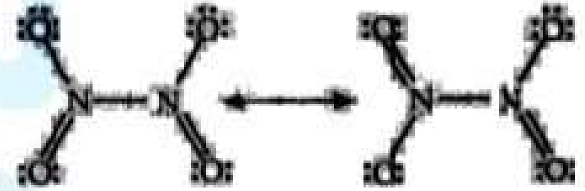
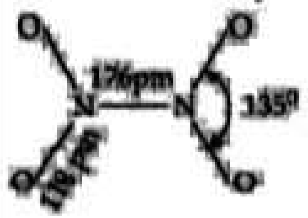
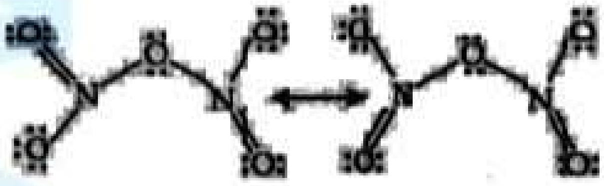
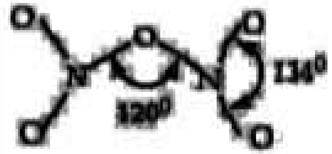
a. $Au + 3[Cl] \rightarrow AuCl_3 \xrightarrow{HCl} HAuCl_4$

b. $Pt + 4[Cl] \rightarrow PtCl_4 \xrightarrow{2HCl} H_2PtCl_6$

E. Brown ring test:

To detect presence of NO_3 (nitrate ions). Brown ring is of $[Fe(H_2O)_5NO]^{2+}$ complex.

Name of oxide	Formula	O.S. of N	Common method of preparation	Resonating Structures	Physical properties
Nitrous oxide or Dinitrogen oxide or Nitrogen (I) oxide (Laughing gas)	N_2O	+1	$NH_4NO_3 \xrightarrow{\Delta} N_20 + H_2O$ $NH_4OH + HNO_3$ g $N_2O + 3H_2O$	It has linear structure. 	Colourless gas, neutral, heavier than air, insoluble in water. It is dimagnetic. It is called laughing gas.
Nitric oxide or nitrogen monoxide Nitrogen (II) oxide	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4$ g $Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$ $3Cu + 8$ dil.HNO_3 g $3Cu(NO_3)_2 + 4H_2O + 2NO$	It has covalent as well as ionic structure. NO has one unpaired which may on N or O 	Colourless gas, neutral, slightly heavier than air, partly soluble in water. It is paramagnetic. It is dimerises in liquid and solid state.
Dinitrogen trioxide or Nitrogen (III) oxide or Nitrogen sesquioxide	N_2O_3	+3		It is a planar molecule with one planar N and one angular N-atom.(Planer N in NO_2 and angular N in NO) 	Blue coloured solid, acidic in nature. It is partly soluble in water but soluble in alkalies. 
Nitrogen dioxide or Nitrogen (IV) oxide	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + PbO + O_2$ $Cu + 4HNO_{3\,(conc.)} \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$	It is an angular molecule.  $2NO_2 \rightleftharpoons N_2O_4$	NO_2 is reddish brown gas. paramagnetic. N_2O_4 is colourless solid, dimagnetic. It is acts as an oxidising agent. 

Name of oxide	Formula	O.S. of N	Common method of preparation	Resonating Structures	Physical properties
Dinitrogen tetroxide or Nitrogen (IV) oxide	N_2O_4	+4	$2NO_2 \underset{heat}{\overset{cool}{\rightleftharpoons}} N_2O_4$ N_2O_4 is formed by dimerisation of NO_2	It is planar molecule. Both N → Sp^2 hybridisation.  The N-N bond is formed by two unpaired electrons in two Sp^2 hybridised orbitals of two N atoms.	Colourless solid/liquid. It is acidic in nature. It is formed by dimersation of NO_2 
Dinitrogen pentoxide or Nitrogen (V) oxide	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$ (N_2O_5 is considered as anhydride of HNO_3) It is also formed by combustion of NO_2 molecules.	It is symmetrical and linear molecule. Each N is sp^3 hybridised. 	Colourless ionic solid. It is unstable acidic oxide. It is an excellent oxidizing agent. 

PHOSPHOROUS

Alltropic forms:

Sr. No.	Properties	White or Yellow	Red P	Black P
1.	Colour	White or yellow	Reddish violet	Black
2.	Solubility in CS_2	Soluble	Insoluble	In oluble
3.	Action of air	Chemiluminescence	No chemiluminescence	-
4.	MP	317K	above 773 K	
5.	Action of hot NaOH	Forms phosphine	No phosphine formed	-
6.	Physiological effect	Poisonous	Non-poisonous	-
7.	Structure	4-P atoms are present at the corners of regular tetrahedron	Polymeric due to covalent linkage between adjacent P_4 molecules.	Puckere layers composed of pyramidal trigonal 3-cordinate P atoms.
8.	LP-P-P	60°	60°	99°
9.	Conductivity	Bad	Bad	Good
10.	Preparation	$P_4O_{10} + 10C g P_4 + 10CO$	$\text{White P} \xrightarrow[CO_2]{540-570K} \text{Red P}$	$\text{White P} \xrightarrow[4000-12000atm]{470K} \text{Black P}$

- **Types of Black phosphorous:**

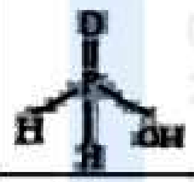
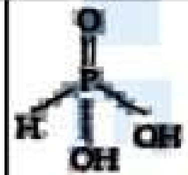
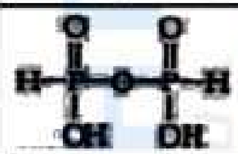
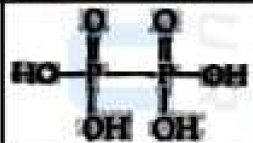
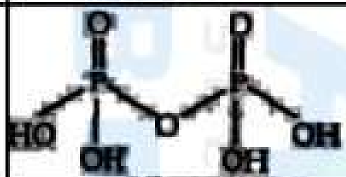
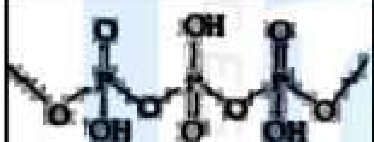
  α- black phosphorous:

  It is prepared by heating red P in sealed tube at 803 K.

  β- black phosphorous:

  It is prepared by heating white P at 453 K under high pressure.

III. OXYACIDS OF PHOSPHOROUS

Sr. No.	Oxyacid	Formula	Oxidation State	Structure	Types of bonds	Preparation	Properties
1.	Hypophospborous acid (Phosphinic acid)	H_3PO_2	(+1)		One P - OH bond, Two P - H bonds One P = O bond	$3Ba(OH)_2 + 8P + 6H_2O$ g $3Ba(H_2PO_2)_2 + 2PH_3$ (ppt.zmonebasic) $Ba(H_2PO_2)_2 + H_2SO_4$ g $BaSO_4 \downarrow + 2H_3PO_2$	It is monobasic acid
2.	Orthophosjhorous acid (Phosphoric acid)	H_3PO_3	(+3)		Two P - OH bond, One P - H bonds One P = O bond	$P_2O_3 + 3H_2O$ g $2H_3PO_3$	It is dibasicadd and act sreducing agents.
3.	Orthophosp horic acid	H_3PO_4	(+5)		Three P-OH bonds, One P = 0 bonds	$P_4O_{10} + 6H_2O$ g $4H_3PO_4$	It is tribasic acid
4.	Pyrophosph orous acid	$H_4P_2O_5$	(+3)		Two P - OH bonds, Two P - H bonds Two P = O bond One P - 0 - P bond	$P_4O_6 + 4H_2O$ g $2H_4P_2O_5$	It is dibasic acid
5.	Hypophosphoric acid	$H_4P_2O_6$	(+4)		Four P-OH bonds, Two P = 0 bonds One P–P bond	Red P + Alkali g $H_4P_2O_6$	It is tetrabasic acid
6.	Pyrophosphoric acid	$H_4P_2O_7$	(+5)		Four P -OH bonds, Two P = 0 bonds One P - 0 - P bond	$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7 + H_2O$	It is tetrabasic acid. On boiling with water it changes to ortho - phosphoric acid.
7.	Polymetaphosph - oric acid OR glacial phosphonic acid	$(HPO_3)_n$	(+5)		Three P-OH bonds, Three P = O bonds Two P–O–P bonds	$H_3PO_3 \xrightarrow[\Delta(\text{sealed tube})]{Br_2} (HPO_3)_n$	It acts as a strong reducing agent.

- **COMPOUND OF PHOSPHOROUS:**

(I) PHOSPHINE (PH_3)

A. Preparation : $P_4 + 3NaOH + 3H_2O$ g $PH_3 + 3NaH_2PO_2$ (Sodium hypophosphite)

i. Laboratory method : 1. $Ca_3P_2 + 6HCl$ g $3CaCl_2 + 2PH_3$ h and

ii. From metal phosphide : 2. $2AlP + 3H_2SO_4$ g $Al_2(SO_4)_3 + 2PH_3$ h

iii. From phosphonium iodide : $PH_4I + KOH$ g $KI + PH_3 + H_2O$

B. Properties:

i. Colour:

Colourless gas with the odour of rotten fish, highly poisonous, sparingl soluble in water.

ii. Action on halognes : $PH_3 + 4Cl_2$ g $PCl_5 + 3HCl$

iii. Action on salt : 1. $3\ CuSO_4 + 2\ PH_3$ g $Cu_3P_2 + 3\ H_2SO_4$ and

2. $3HgCl_2 + 2PH_3$ g $Hg_3P_2 + 6HCl$

iv. Action of heat : $4PH_3 \xrightarrow{600K} P_4 + 6H_2$

v. Action in acid : $PH_3 + HBr$ g PH_4Br

D Uses:

i. Phosphine in combination with acetylene is used in preparing Holme's signals for ships.

ii. It is used as a powerful reducing agent.

iii. It is used to prepared smoke screens.

II. PHOSPHOROUS HALIDES:

Phosphorous forms two types of halides with general formula.

PX_3(X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

1. Phosphorous trichloride (pa$_3$) :

A. Preparation :

i. From chlorine : $P_4 + 6Cl_2$ g $4PCl_3$

ii. From $SOCl_2$: $P_4 + 8SOCl_2$ g $4PCl_3 + 2S_2Cl_2 + 4SO_2$

B. Properties:

i. Colour : It is a colourless oily liquid with pecific gravity 1.6 glee.

ii. Action of water : $PCl_3 + 3\ H_2O$ g $H_3PO_3 + 3\ HCl$

iii. Actionof chlorine : $PCl_3 + Cl_2$ g pels

iv. Action on alcohol : $3\ C_2H_5OH + PCl_3$ g $3\ C_2H_5Cl + H_3PO_3$

v. Action on carboxylic acid : $3\ CH_3COOH + PCl_3$ g $3\ CH_3COCl + H_3PO_3$

vi. Action on silver cyanide : $3\ AgCN + PCl_3$ g $P(CN)_3 + 3\ AgCl$

C. Structure of PCl_3 :

In PCl_3, the P-atom undergoes sp^3 hybridization and P carries lone pair of electrons

Thus it has pyramidal shape.

2. Phosphorous pentachloride (PCl_5)

A. Preparation:

i. From chlorine : $P_4 + 10\ Cl_2$ g 4 PCls

ii. From SO_2Cl_2 : $P_4 + 10SO_2Cl_2$ g $4PCl_5 + 10SO_2$

iii. From PCl_3 : $PCl_3 + Cl_2$ g PCl_5

B Properties:

i. Colour : PC ls is yellowish white powder having sharp odour and sub lines below 373 K.

ii. Action of water : $PCl_5 + H_2O$ g $POCl_3 + 2HCl$ and $POCl_3 + 3H_2O$ g $H_3PO_4 + 3HCl$

iii. Action of heat : $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$

iv. Action on alcohol : $C_2H_5OH + PCl_5$ g $C_2H_5Cl + POCl_3 + HCl$

v. Action on carboxylic acid : $CH_3COOH + PCl$ g $CH_3COCl + POCl_3 + HCl$

vi. Action on silver and tin : 2Ag + PCls g 2 AgCl + PCl_3 and Sn + $2PCl_5$ g $SnCl_4 + 2PCl_3$

C. Uses:

i. PCl_5 is used in the synthesis of some organic compounds i.e. C_2H_5Cl, CH_3COCl .

ii. It is also used as a chlorinating agent.

D. Structure of PCl_5:

i. In PCl_5, the P-atom undergoes sp3d hybridization. Thus PCls trigonal bipyramidal structure.

ii. In this, there are total 5 bonds. The three equatorial P-Cl bonds are equivalent, while two axial bonds are longer than equatorial bonds. Because the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.

GROUP 16 ELEMENTS

Group 16 consists of oxygen, sulphur, selenium, tellurium and polonium.

Valence Shell: ns^2np^4(n = 2 to 7). They are called chalcogens (ore forming).

Sr.	Element g	O	S	Se	Te	Po	Trend
1.	Name g Properties ↓	Oxygen	Sulphur	Selenium	Tellurium	Polonium	
2.	Discovered by	Lavosier (1774) Salvert (sanskrit)	Lavosier (1777) Moon	Berzelius (1817) (1782) Tellus	MullerVon Reichensteins (1898)	Marie currie (Polond)	
3.	State	Gas	Solid	Solid	Solid	Solid	-
4.	Atomic number	8	16	34	51	83	Increases
5.	Atomic mass (g mol^{-1})	16	32.06	77.96	127.60	210	Increases
6.	Valence shell e.c.	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^2\ 4p^4$	$[Kr]\ 4d^{10}\ 5s^25P^4$	[Xe]5d 10 $6s^2\ 6P^4$	-
7.	Abundance (ppm) in earth crust	455000	340	0.05	0.001	-	-
8.	Atomicity	Diatomic	Octaatomic	Octaatomic	Octaatomic	Monoatomic	-
9.	Covalent radius (pm)	74	104	117	137	140	Increases
10.	Ionic radius (M^{2-})pm	140	184	198	221	230 (app.)	Increases

11. Atomic volume(Cm^3)	14.0	15.5	16.5	20.5	22.7	Increases
12. Density (gcm^{-3}) at 298 K	1.32	2.06	4.19	6.25	-	Increases
13. Melting point (K)	55	386	490	723	-27	Increases
14. Boiling point (K)	90	718	958	1263	1233	Increases
15. Ionisation enthalpy (kJ mol^{-1})	1310	1000	941	870	812	Decreases
16. Electro-negativity	3.50	2.5	2.48	2.1	2.0	Decreases
17. Electron gain enthalpy (kJ mol^{-1})	-141	- 200	-195	-190	-183	Decreases
18. Metallic nature	Non-metal	Non-metal	metalloid	Metalloid	Metal	Increases
19. Conductivity	Bad	Bad	Poor	Moderate	Good	Increases
20. Allotropy	O_2 & O_3	α, β, γ, plastic etc.	Red monoclinic Grey metallic Dark brown, Red amphorous	Metallic and Nonmetalic	α and B	-
21. Catenation	Little atoms	Several	Do not show	Do not show	Do not	how -
22. common oxidation state	–2 peroxide(–1) OF2(+2), O_2F_2(+1)	–2,+2,+4,+6	–2, +2,+4,+6,	–1,+2,+4,+6	+2,+4	
	stability of + 4 oxidation state increases while + 6 decreases →					
23. Hydrides	H_2O	H_2S	H_2Se	H2Te	H_2Po	-
a. E-H distance (pm)	96	132	147	173	-	Increases
b. H-E-H bond angle	104.5°	92.1°	91°	90°	-	Decreases
c. State	liquid	gas	gas	gas →	→	Decreases
d. Stability	Most stable					Decreases
e. B.pt.(K) (volatile)	373	213	232	269	-	
f. Acidic nature	Amphoteric	Weakly acidic	Weakly acidic →	Moderate	-	Increases

g. Poisonous Nature			from H_2O to H_2Te			Increases
h. Tendency to form H-bonds	strong	weak tendency	No	No	-	Decreases
i. Bond dissociation energy ($kJ\ mol^{-1}$)	463	347	276	238	-	Decreases
j. Heat of formation ($kJ\ mol^{-1}$)	- 246	- 20	+ 81	+ 154	-	Increases
k. Dipole moment		→				Decreases
l. Reducing property		$H_2O < H_2S < H_2Se < H_2Te$				Decreases
24. Halides						
a) preparation						
i) With F_2	OF_2	S_2F_2, SF_2 SF_4, SF_6	Se_2F_2, SF_4 SeF6	TeF_4, TeF_6		-
ii) With Cl_2 Cl_2O_7	$Cl_2O, ClO,$ SCl_4	$S_2Cl_2, SCl_2,$ $SeCl_4$	Se_2Cl_2, $SeCl_2$,	$TeCl_2$, $TeCl_4$	$PoCl_2$, $PoCl_4$	-
iii) With Br_2	Br_2O	$S_2Br_2, 5Br_2$	$SeBr_2, 5eBr_4$	$TeBr_2$, $TeBr_4$	$PoBr_2$, $PoBr_4$	-
iv) With I_2	I_2O_5	S_2I_2	-	TeI_4	PoI_4	-
b. Stability			$F^- > Cl^- > Br^- > I^-$			Decreases
c. Degree of hydrolysis	-	$5F_6 < SeF_6 < TeF_6$ →				Increases
25. Oxides						
a) O.S. + 4	-	SO_2	SeO_2	TeO_2	PoO_2	
+5	-	SO_3	SeO_3	TeO_3	-	-
b) Thermal Stability	-	$SO_3 < SeO_3 < TeO_3$ →				Increases
c) Nature	-	Acidic	Weakly acidic	Amphoteric	Basic	Basic nature Increases
d) Reducing property	-	Reducing property →				Decreases
26. Oxoacids						
a) O.S. (+4)	-	H_2SO_3	$HeSeO_3$	H_2TeO_3	-	-
(+6)	-	H_2SO_4	H_2SeO_4	H_2TeO_4	-	-
b) Acidic strength	-	H_2SO_4	H_2SeO_4	H_2TeO_4 →		Decreases

- **Anamalous behaviour of oxygen:**

  Anamalous nature of oxygen is due to its -

i. small size

ii. high ionisation enthalpy

iii. high electronegativity and

iv. the absence of d-orbital

The main points of difference between oxygen and other group 16 element :

S.No.	Propertiess	Oxygen	Other elements of 16 group
1.	State	Gas	solids
2.	Atomicity	Diatomic (O_2)	Polyatomic (S_8,Se_8)
3.	Oxidation state	–2	-2, +2, +4, +6
4.	Hydrogen bond formation	Strong tendency	Do not formed
5.	Multiple bond formation	pα-pα multiple bond	Do not formed
6.	Magnetic behaviour	Paramagnetic	Diamagnetic
7.	Hydrides	Stable and liquid	Less stable and gases
8.	Nature of compounds	More ionic	Less ionic

DIOXYGEN (O_2)

Occurence:

In free state oxygen occurs to an extent of 23.2% by weight or 20% by volume - air.

A. Preparation:

i. Laboratory method:

Mixture of $KClO_3$(4parts) and MnO_2(I part) (acts as catalyst, when is heated in a hard glass tube to 420 K gives dioxygen gas. The gas may collected by the downward dis lacement of water.

$$2KClO_3 \xrightarrow[MnO_2]{420K} 2KCl + 3O_2$$

ii. Manufacture of O_2:

Commercial preparation of O_2 is done by two methods.

a. From water:

Electrolysis of acidified water gives H_2 at the cathode and and O_2 at the anode.

b. From air On a large scale, dioxygen is generally prepared by the fractional distillation of liquid air. On distillation, liquid dinitrogen (lower B.P.) distils out leaving behind liquid dioxygen (higher B.P.)

iii. General methods:

a. By the thermal decomposition of oxygen rich salts

b. By the thermal decomposition of metallic oxides

c. By the action of water or acidified potassium permangnate on odi m pero ide.

B. Properties of dioxygen :

i. State :

It is colourless, odourless and ta tele gas. It is heavier than air.

ii. Solubility :

Its solubility in water is to the e tent of 30 $m^3 L^{-1}$ (3.0 cm^3 of water) at 293 K(S.T.P.)

iii. M.pt and B.pt :

It can be liquefied under pressure of a pale blue liquid (B.P.90.2K) and on cooling.

It can be solidified into a light blue solid (M.P.54.4 K).

iv. **Magnetic property :**

It is paramagnetic in nature.

v. **Isotopes :**

Oxygen atom has three stable isotopes ^{16}O, ^{17}O, ^{18}O.

C. **Chemical properties:**

1. **Support of combustion :**

Dioxygen is not combustible but support combustion.

2. **Reaction with metals :**

Metals combine with dioxygen under different conductions to form then oxides.

3. **Reaction with non-metals :**

Non metals burn brightly in dioxygen and form their respective oxides

4. **Reaction with ammonia :**

$$4NH_3 + 5O_2 \xrightarrow{1073LK} 4NO + 6H_2O$$

5. **Reaction with hydrogen chloride :**

$$4HCl_{(g)} + O_{2(g)} \xrightarrow[Pt]{725K} 2H_2O + 2Cl_2$$

6. **Reaction with sulphur dioxide :**

$$2SO_2 + O_2 \xrightarrow[Pt]{725K} 2SO_3$$

7. **Reaction with carbon disulphide :**

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$$

8. **Reaction with metal sulphide :**

$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ and $2MgS + 3O_2 \longrightarrow 2MgO + 2SO_2$

9. **Reaction with hydocarbons :**

All saturated, unsaturated and aromatic hydrocarbons when burn in excess of dioxygen (or in air) to form carbon dioxide and water with liberation of heat.

E. **Classification of oxides:**

1. **Acidic oxides:**

The oxide which combines with water to give an acid is called as acidic oxide.

Ex.

CO_2, B_2O_3 (boron trioxide), N_2O_5 (Nitrogen pentoxide), SO2 (Sulphur dioxide), SO_3 (Sulphur trioxide), Cl_2O_7 (Chlorine heptoxide).

2. **Basic oxides:**

The oxide which combines with water to form a base is termed oxide.

Ex.

CaO (Calcium oxide), Na20 (sodium oxide), K_2O (potassium oxide), MgO (magnesium oxide).

3. **Amphoteric oxides:**

The oxides which show both acidic and basic characteristics i.e. The oxides react with acids as well as bases to form salts are called amphoteric oxides.

Ex.

$A1_2O_3$, SiO_2, ZnO, PbO, SnO etc.

4. **Neutral oxides:**

The oxides which are neither acidic nor basic are called natural oxides.

Ex.

NO, CO, N_2O etc.

OZONE (O_3)

- **History:**

  Ozone was first noticed by Van Murum (1785). Name ozone is derived from Green word 'ozein' meaining to smell proposed by Schenbien Soret (1866).

- **Ozone umbrella:**

  The stratopheric pool of ozone is commonly known as ozonosphere or the ozone umbrella, which filters out the Sun's harmful radiations like ultraviolet rays and helps to sustain life on earth.

A. Preparation:

Ozone is produced by the action of ultraviolet radiation ondioxygen.

1. Atmospheric method:

Step I : Formation of excited oxygen atom (O*) :

$$O_2 \xrightarrow[175nm]{hv} O + O^*$$

Step II : Formation of moleuclar oxygen (O_2) :

$O^* + O_2 \longrightarrow O + O2$

Step III : Formation of excited ozone (O_3*) :

$O + O2 \longrightarrow O_3^*$

Step IV : Formation of ozone (O_3)

$O_3^* + M^- \longrightarrow O3 + M$

where M can be O_2 or N_2 or an other inert molecule.

2. Laboratory preparation:

Ozone is produced by the action of silent electrical discharge on dioxygen.

The product is known as ozonised oxygen.

B. Properties:

1. State:

Gaseous ozone is blue, liquid ozone is blue black and solid ozone is violet black. It has pungent odour.

2. Decomposition of ozone:

Decomposition of ozone into oxygen liberates heat (–ΔH) and increases entropy (+ΔS). Due to this it results into a large negative Gibb's energy change (–ΔG) to convert ozone to oxygen.

3. Oxidizine agent:

Ex.

i. $PbS_{(s)} + 4O_3(g) \longrightarrow PbSO_{4(s)} + 4O_{2(g)}$

ii. $2KI_{(aq)} + H_2O + O_{3(g)} \longrightarrow 2KOH_{(aq)} + I_{2(s)} + O_{2(g)}$

ii. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

4. Reducing agent:

i. $BaO_2 + O_3 \longrightarrow BaO + 2O_2$

ii. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

4. Structure of ozone:

Ozone molecule is angular with O–O–O bond angle as 1170 and O–O bonds are identical having bond length 128 pm.

SULPHUR

A. Occurance :

Sulphur occurs in native state (free state) as well as in the combined state.

1. Sulphide:

Sulphur is widely distributed as sulphides of metals.

Ex:

Copper pyri es (Cu_2S), Iron pyrines (FeS_2), zinc blende (ZnS)

2. Sulphates :

A large quantity of sulphur is distributed as sulphate in nature.

Ex.

gypsum, ($CaSO_4.2H_2O$),epsum ($MgSO_4.7H_2O$),burytes ($BaSO_4$),Glauber's salt ($Na_2SO_4.10H_2O$) etc.

B. Allotropic forms of Sulphur:

Preparation	**1. Rhombic Sulphur**	**2. Monoclinic sulphur**	**3. Plastic sulphur**
Other name	α-sulphur or octahedral sulphur	β -sulphur or prismatic sulphur	γ -sulphur
Colour	Pale yellow in colour.	Colourless.	Colourless.
Specific gravity	2.06 g/cc.	of 1.98 g/cc.	1.95 g cc
M.Pt.	385.8 K	393 K	No sharp melting point.
Solubility	It is insoluble in water but soluble in carbon disulphide	It is insoluble in water but soluble in carbon disulphide	It is insoluble in water as well as in carbon disulphide
Crystal Structure	It is found to consists of S_8 units, which are formed a pucked ring in a crown shape.	It is found to consists of S_8 units, which are formed a puckred ring in a crown shape.	It has open c:hain structure, in which each sulphur atom is linked to other two sulphur atoms by covalent bonds.
Preparation	It is obtained by melting the sulphur and cooling till crust is formed. On removing this crust, transparent crystals of monoclinic sulphur are formed, which are needle shaped.	It is obtained by melting the sulphur and cooling till crust is formed. On removing this crust, transparent crystals of monoclinic sulphur are formed, which are needle shaped.	It is obtained by boiling the sulphur and cooling in cold water.

- **KEEP IN MIND:**
- **Transition temperature:**

β sulphur is stable above 369 K and get con erted into α-sulphur below 369 K.

Whereas a a-form is stable below 369 K and gets converted into β-form above this temperature.

At 369 K both the forms, β and β sulphur are stable. This temperature is called transition temperature.

4. Milk of sulphur:

Preparation:

From milk of lime and sulphur:

$3\,Ca(OH)_2 + 12S \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$

$2\,CaS_5 + CaS_2O_3 + 6HCl \longrightarrow 3CaCl_2 + 3H_2O\ 12\,S$ (Milk of sulphur)

5. **Colloidal sulphur:**

Preparation:

a. From hydrogen sulphide and nitric acid OR Sodium thiosulphate and conc.HCl

$H_2S + 2HNO_3$ g $2H_2O + 2NO_2 + S$ (Colloidal sulphur) OR

$Na_2S_2O_3 + 2\ HCl$ g $2NaCl + SO_2 + H_2O + S$ (Colloidal sulphur)

b. **From hydrogen sulphide and sulphur dioxide**

$2H_2S + SO2$ g $2H_2O + 3S$ i. (Colloidal sulphur)

- **COMPOUNDS OF SULPHUR:**

I. **SULPHUR DIOXIDE:**

A. **Preparation:**

1. **Laboratory Methogs:**

i. $Cu + 2H_2SO_4$ g $CuSO_4 + SO_2 + 2H_2O$

ii. $Na_2SO_{3(aq)} + 2HCl_{(aq)}$ g $2NaCl_{(aq)} + H_2O_{(l)} + SO_{2(g)}$

2. **Industrial method:**

Pyrites and blendes on roasting gives SO_2 gas. The gas in dried liquefied under pressure and stored in steel cylinders. $4\ FeS_{2(s)} + 11O_{2(g)}$ g $2Fe_2O_{3(s)} + 8SO_{2(g)}$

B. **Properties:**

1. **Nature:**

It is colourless gas, with punugent smell, acidic in nature. It forms discrete molecules even in solid.

2. **Solubility:**

It is soluble in water and it forms H_2SO_3. Hence it is called anhydride of sulphurous acid.

3. **M.pt. and B.pt. :**

It liquefies at room temperature under a pressure of 2 atm. and boils at 263 K.

C. **Reactions:**

1. **Reducing agent:**

It acts as a reducing agent it reduces-

a. $I_2 + SO_2 + 2H_2O$ g $2HI + H_2SO_4$

b. $K_2Cr_2O_7 + 3SO_2 + H_2SO_4$ g $K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

c. $2FeCl_3 + SO_2 + 2H_2O$ g $2FeCl_2 + H_2SO_4 + 2HCl$

d. $5SO_2 + 2KMnO_4 + 2H_2O$ g $K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

2. **Oxidizing agent (Lewis base) :**

It is acts as an oxidizing agent. It oxidises :

$2H_2S + SO_2$ g $2H_2O + 3S$ i. and $4FeCl_2 + SO_2 + 4HCl$ g $4FeCl_3 + 2H_2O + S$ i.

3. **Action on alkali:**

It reacts with NaOH solution as :

$2NaOH + SO_2$ g $Na_2SO_3 + H_2O$ and $Na_2SO_3 + H_20 + SO2$ g $2NaHSO_3$

4. **Action on non-metal (chlorine, oxygen) :**

a. $SO_{2(g)} + Cl_{2(g)}$ g $SO_2C_{l2(l)}$ and

b. $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$

· **Structure of SO_2 molecule:**

1. Sulphur is sp^2 hybridised and the lone pair of electrons of sulphur reduces the angle from 120^0 to 119^0 and bond length 143 pm.
2. In the structure, each oxygen atoms is joined to sulphur by a 'a' and a 'st' bond.
3. The 'a' bonds between Sand O are formed by' sp^2–p , overlap while one of the "n' bonds arises from 'pπ - pπ' overlap and other from pπ - dπ overlap.

II. SULPHURIC ACID (OIL OF VITRIOL)

It is called kind of Chemicals

A. Manufacturing process / Preparation:

There are two manufacturing processes:

a. contact process

b. lead chamber process.

1. Contact process:

This process involves of following important steps.

a. Preparation of SO_2 :

$S(g) + O_{2(g)} \rightarrow SO_{2(g)}$ or $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8\,SO_2$

b. Oxidation of SO_2 to SO_3 (2:3) :

$$2SO_{2(g)} + 2O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_3 \quad \Delta H = -196.6\text{ kJ}$$

c. Dissolution of SO_3 in H_2SO_4 :

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)

d. Dillution of oleum, $H_2S_2O_7$:

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

2. Lead chamber process:

In this process a mixture of SO_2, O and air treated with steam to product H_2S0_4.

Nitric oxide (NO) acts as a catalyst:

$$2SO_{2(g)} + O_{2(g)} + H_2O \xrightarrow{NO} 2H_2SO_4$$

Different steps are:

a. Water reacts with O to give HNO_3 :

$2\,H_2O + NO \rightarrow HNO_3 + 3H^+$

b. Sulphur oxidize to SO_2 in presence of oxygen :

$S + O_2 \rightarrow SO_2$

c. HNO_3 reacts with SO_2 gives SO_3

$2HNO_3 + 2SO_2 \rightarrow H_2O + O + O_2 + 2SO_3$

d. Sulphur trioxide reacts with water to from H_2SO_4 :

$SO_3 + H_2O \rightarrow H_2SO_4$

B) Properties:

1. Nature:

It is a colourless, dense, oily liquid. It has specific gravity of 1.84 at 298 K.

2. Freezing point and boiling point:

Freezing point is 283 K and the boiling point is 611 K.

3. Basicity:

It is a dibasic acid. In aqueous solution sulphuric acid ionizes in two steps.

i. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

ii. $HSO_4^- \rightleftharpoons H^+ + SO_4^-$ $\quad \therefore K_{a_2} = 1.2 \times 10^{-2}$

H_2SO_4 is strong acid because it has high value of dissociation constant (Ka) shows more dissociation into H^+ and HSO_4^- .

4. Dehydrating agent :

a. $(COOH)_2 \xrightarrow{H_2SO_4} CO + CO_2 + H_2O$

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

5. Oxidizing agent:

Cone. H_2SO_4 on heating gives oxygen. Thus hot cone, H_2S0_4 acts as oxidising agent.

6. Sulphonating agent:

Conc. H_2SO_4 acts a sulphonating agent i.e. addition $-SO_3H$ group to the benzene.

7. Action of PCl_5:

HO.SO_2OH + PCls g Cl.SO_2OH + $POCl_3$ + HCl

Chlorosulp huric acid

ClSO_2.OH + PCl_5 g Cl.SO_2Cl + $POCl_3$ + HCl

Sulphuryl chloride

8. Action on $KClO_3$:

$3KClO_3 + 3H_2SO_4$ g $3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

9. Action on salts :

$2MX + H_2SO_4$ g $2HX + M_2SO_4$

(Where X = F^-, Cl^-, NO_3^- and M = Metal)

OXYACIOS OF SULPHUR

These are grouped infjp five series as -

Sr.	Name	Formula	O.S.	Structure	Bonds
A.	**Sulphoxylic acid group**				
1.	Sulphoxylic acid	H_2SO_2	+2	$HO-S-OH$	-
B.	**Sulphurous acid group**				
2.	Sulphurous acid	H_2SO_3	+4	$HO-\overset{\overset{O}{\Vert}}{\underset{\cdot\cdot}{S}}-OH$	One S = O
3.	Thiosulphurous acid	$H_2S_2O_2$	+2, +4	$HO-\overset{\overset{S}{\Vert}}{\underset{\cdot\cdot}{S}}-OH$	One S = S
4.	Dithionus acid (Hydrosulp hurous acid)	$H_2S_2O_4$	+3	$HO-\overset{\overset{O}{\Vert}}{S}-\overset{\overset{O}{\Vert}}{S}-OH$	Two S = O
5.	Pyrosulphurous acid or disulphorous acid	$H_25_2O_5$	+4	$HO-\overset{\overset{O}{\Vert}}{S}-O-\overset{\overset{O}{\Vert}}{S}-OH$	Two S = O and One S-O-S
C.	**Sulphuric acid series**				
6.	Sulphuric acid or oil of vitrol	H_2SO_4	+6	$HO-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-OH$	OneO = S = O
7.	Thisulphuric acid	$H_25_2O_3$	(–2, +6)	$HO-\underset{\underset{O}{\Vert}}{\overset{\overset{S}{\Vert}}{S}}-OH$	One5=5=0
8.	Pyrosulphuric acid or oleum or disulphuric acid	$H_25_2O_7$	+6	$HO-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-O-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-OH$	TwoO=5=0 One5-0-5
D.	**Peroxy Sulphuric acid series**				
9.	Peroxy monosulphuric acid or Caro' s acid (monobasic)	H_2SO_5	+6	$HO-O-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-OH$	OneO = S = O One peroxy group
10.	Peroxy disulphuric acid or Marshall's acid or perdisulphuric acid	$H_2S_2O_5$	+6	$HO-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-O-O-\underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}}-OH$	Two O = S = O One peroxy group

E. Thionic acid series				
11. Dithionic acid	$H_2S_2O_6$	+5	$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$	Two O = S = O One S – O
12. Poly thionic acid	$H_2S_nO_6$ (n = 3 to 6)	(+5, 0)	$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-(S)_n-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$	Two O = S = O

GROUP 17 ELEMENTS (i!ALOGEN FAMILY)

- **General Introduction:**

Group 17 of perodic table contains the elements fluorine (F) chlorine (Br iodine II and astatine (At).

These elements are collectively known as halogens, (halous meaning alts, gene meaning born) i.e. salt producers derived from Greek words.

Valence shell electronic configuration: (n = 2 to 7) $ns^2{}_{np}5$.

Occurence:

1. Fluorine occurs to the extent of 0.07% of the earths crust. The important minerals of fluorine are as follows:

i. fluorspar or fluorite, CaF_2

ii. Cryolite Na_3 AIF_6.

iii. Fluoropatite: $3Ca_3(PO4).CaF_2$.

Sr.	Element g Properties1	F	a	Br	I	At	Trend
1.	Name	Fluorine	Chlorine	Bromine	Iodine	Astatine	-
2.	Discovered by	Davy(1813)	Scheele (1774)	Balard (1826)	Courtios (1811)		
3.	a) State	Gas	Gas	Liquid	Solid	Solid	-
	b) Colour	Pale yellow	Greenish yellow	Reddish	Blackish violet	- -	- -
	c) Greek name	Fluos	Chloros	Broms	Ioeides	-	-
	d) English meaning	To flow	Greenish yellow	Stench (bad smell)	Violet -	- -	- -
	e) Source	KHF_2	MnO_2 +HCl	Sea water	Sea weeds	-	-
4.	Atomic number	9	17	35	53	85	Increases
5.	Atomic mass (g/mol)	19	35.5	80	127	210	Increases
6.	Valence shell e.c.	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10}4s^2 4p^5$	$[Kr]4d^{10}$ $5s^2$ 5p5	$[Xe]5d^{10}6s^2 6p^5$	-
7.	Abundance	0.07%	0.14%	-	-	-	-
8.	Atomicity	diatomic	diatomic	diatomic	diatomic	-	
9.	Covalent radius (pm)	64	99	114	133	-	I creases
10.	Ionic radius (pm)	119	167	182	206	-	Increases
11.	Atomic volume (pm)	72	99	114	133	-	-

12.	Density (g/cm^3)	85	239	333	458	-	-
13.	M.Pt.(K)						Increases
14.	B.Pt.						Increases
15.	Ionisation enthalpy ($kJ\ mol^{-1}$)	1681	1255	1140	1008	-	-
16.	Electronega-tivity	4.00	3.0	2.8	2.5	2.2	Decreases
17.	Electron gain enthalpy ($kJ\ mol^{-1}$)	- 328	-349	- 325	- 296	-	Decreases
18.	Metallic Nature	[Non metal	on metal	Non metal	Non metal	Metal	Increases
19.	Conductivity	Bad	Bad	Bad	Bad	-	-
20.	X-X distance in X_2 (pm)	143 (F-F)	199 (Cl-Cl)	228 (Br-Br)	266 (I - I)	-	-
21.	a) Std.R.P(V) b) Oxidising agent c) Reducing agent	 Strongest -	2.87 Stronger Mild	1.40 Mild Stronger	1.05 Very poor Strongest	0.62 - -	- - Decreases Increases
22.	Common O.S.	-1	-1,+ 1,+3,+4 +5,+6,+7	-1,+1,+3,+4 +5,+6,	-1,+1,+3, +5,+7,	-	-
23.	Bond energy ($kJ\ mol^{-1}$)	F-F 158	Cl–Cl 243	Br–Br 193	I – I 151	-	-
24.	Displace-ment of other halogens	All	only Br_2 & I_2	only I_2	-	-	-
25.	Action of NaOH (cold dil.)	$NaF+OF_2 +H_2O$	NaCl+ NaOCl+ H_2O	NaBr+ NaOBr+ H_2O	-	-	-
26.	NaOH (Hotconc.)	NaF + O_2 +H_2O H_2O	NaCl + $NaOCl_3$ + H_2O	NaBr+ NaOBr3 +	forms iodides and iodous acid	-	-
27.	Metals	Fluorides MF_n	Chlorides MCl_n	Bromides MBr_n	Iodides MI_n	-	Decreases M-metal n - valency of metal

28.	Strength M-Xbond						Decreases
29.	**Halides**	HF	HCl	HBr	HI	-	
a)	H-Xbond length(pm)	91.7	127.4	141.4	160.9	-	Increases
b)	State	Liquid	Gas	Gas	Gas	-	-
c)	$\Delta_{diss}H$ (kJ mol^{-1})	574	431.6	362.5	294.6	-	Decreases
d)	Thermal Stability		H - F > H - Cl > H - Br > HI				Decreases
e)	Reducing character	INo	Mild	Strong	Strongest	-	Increases
f)	Solubility in water	Highly soluble	soluble	soluble	soluble	-	Decreases
g)	Tendency to form H bonds	stronger	-	-	-	-	Decreases
30.	Action on non metals and noble gases	combine N_2, O_2 and	-	-	combines only halogens p,As,H_2		
31.	Oxides						
	O.S.–1	OF_2,O_2F_2	-	-	-	-	-
	+1	-	Cl_2O	Br_2O	-	-	-
	+4	-	ClO_2	BrO_2	I_2O_4	-	-
	+5	-	-	-	I_2O_5	-	-
	+6	-	Cl_2O_6	BrO_3	-	-	-
	+7	-	Cl_2O_7	-	I_2O_7	-	-
32.	Oxoacids						
a)	O.S. -1	HOF	HClO	HOBr	HOI	-	-
	-3	-	$HClO_2$	-	-	-	-
	-5	-	$HClO_3$	$HBrO_3$	HIO_3	-	-
	-7	-	$HClO_4$	$HBrO_4$	HIO_4	-	-
b)	Oxidising power						Increases
c)	Thermal stability						I creases

- **Anomalous behaviour of fluroine:**

  Fluorine exhibits anomalous behaviour, it is due to

i. small size

ii. high electronegativity

iii low F-F bond dissociation energy

iv. non availability of d-orbitals

- **The main points of difference between fluorine and other elements of the group are as follow,**

S.No.	Properties	Oxygen	Other elements of group 17
1.	Reactivity	More reactive	less reactive
2.	Oxidation state	-1	- I, + I, + 3, + 5 and + 7
3.	Polyhalides ions	Do not form	Forms, such as I_3^-, Br_3^-, Cl_3^-, etc.
4.	H bond formation	Strong tendency	Do not formed
5.	Behaviour of Hydrogen halide	a) H F is liquid b) H F is weak acid	a) HX are gases (X = ci. Br, I) b) HX are strong acid (X = Cl, Br, I)
6.	Electron gain enthalpy	Less than chlorine	Chlorine has more han fluorine
7.	Nature of compounds	Ionic nature. *Ex :* AlF_3, CsF	Covalent nature. *Ex.:* $AlCl_3$

I. CHLORINE:

A. Occurence :

Chlorine occurs to an extent of 0.14% in the earth crust. Some minerals containing chlorine are as follows:

i. Rock salt: NaCl,

ii. Carnalite: KCl, $MgCl_2$, $6H_2O$

iii. Sylvine : KCl,

iv. Horn.silver : AgCl.

B. Preparation of chlorine:

1. Manufacture of chlorine:

i. Deacon process:

Hydrogen chloride gas is oxidized by atmospheric oxygen in the presence of $CaCl_2$ (catalyst) at 723 K liberates Cl_2. $4HCl + O_2 \xrightarrow{CaCl_2} 2Cl_2 + 2H_2O$

ii. Electrolytic process:

During electrolysis, aq.solution of brine (NaCl), H_2 gas liberates at cathode, whereas Cl_2 gas liberates at anode.

- **General Methods:**

2. by the oxidation of hydrochloric acid:

i. Manganaese dioxide :

$MnO_2 + 4HCl$ g $MnCl_2 + Cl_2 + 2H_2O$

ii. Lead dioxide or red lead :

$PbO_2 + 4HCl$ g $PbCl_2 + Cl_2 + 2H_2O$ and

$Pb_3O_4 + 8HCl$ g $3PbCl_2 + Cl_2 + 4H_2O$

iii. Potassium permagnate :

$2KMnO_4 + 16HCl$ g $2KO + 2MnCl_2 + 8KH_2O + SCl_2$

iv. Potassium dichromate :

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

3. By the action of dilute HCl or dilute H_2SO_4 on bleaching powder ($CaOCl_2$) :

$CaOCl_2$, 2HCl g $CaCl_2 + Cl_2 + H_2O$ and

$CaOCl_2 + H_2SO_4$ g $CaSO_4 + Cl_2 + H_2O$

4. By the action of conc. H_2SO_4 on aCl in the presence of MnO_2 :

$2NaCl + + MnO_2 + 3H_2SO_4$ g $2NaHSO_4 + MnSO_4 + Cl_2 + 2H_2O$

C. Chemical properties:

5. Combustibility:

Chlorine is neither combustible nor a supporter of combustion.

6. Combination with metals:

i. $2Na + Cl_3$ g $2NaO$

ii. $2K + Cl_2$ g $2KCl$

iii. $Ca + Cl_2$ g $CaCl_2$

iv. $Cu + Cl_2$ g $CuCl_2$

3. Reaction with water: Bleaching action:

It bleaches colouring matter. The bleaching action is due to the liberation of nasent oxygen in presence of moisture and form colourless matter. $O_2 + H_2O$ g $2HO + [O]$

Vegetable colouring matter + (O) g Colourless matter.

4. Reaction with non metals:

i. $2As + 3Cl_2 \rightarrow 2AsCl_3$

iii. $2S + Cl_2 \rightarrow S_2Cl_2$

ii. $2Sb + 3Cl_2 \rightarrow 2SbCl_3$

iv. $P_4 + 6Cl_2 \rightarrow 4PCl_3$

5. Reaction with ammonia:

i. $3Cl_2 + 8NH_3 \rightarrow 6NH_4Cl + N_2$
(excess)

ii. $3Cl_2 + NH_3 \rightarrow 3HCl + Cl_3$
(excess) itrogen tri chloride

6. Reaction with CS_2 :

$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2O_2$ and

$2S_2O_2 + 0_2 \rightarrow CCl_4 + 6S$

7. Oxidizing nature of chlorine:

i. It oxidizes ferrous salts to ferric salts :

$2Fe5S_4 + H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$

ii. It oxidizes sulphites to sulphates :

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

iii. It oxidizes H_2S to sulphur :

$O_2 + H_2S \rightarrow S + 2HCl$

iv. It oxidizes SO_2 to H_2SO_4 :

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

8. Formation of addition products :

i. $SO_2 + Cl_2 \xrightarrow{\text{sunlight}} SO_2Cl_2$ (Sulphuryl chloride)

ii. $CO + Cl_2 \xrightarrow{\text{sunlight}} COCl_2$ (Carbonyl chloride) (phosgene)

- **Uses of chlorine:**

1. As a bleaching agent.
2. In the manufacture of bleaching powder of refrigerant such as Freon (i.e.CCl_2F_2), platies (PVC), insecticides (DDT,BHC).
3. In manufacture of pogions gases like mustard gas ($Cl.C_2H_4 - S - C_2H4.Cl$), phosgene ($COCl_2$), tear gas ($CCl.NO_2$)

II. HYDROGEN CHLORIDE (HYDROCHLORIC ACID)

History:

Hydrochloric acid was first prepared by Glauber in 1648. Davy in 1810 showed that the acid is a compound of hydrogen and chlorine.

A. Method of preparation:

1. Laboratory method:

a. Process :

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

$NaHSO_4 + NaCl \xrightarrow{822K} Na_2SO_4 + HCl$

b. Purification:

HCl gas is dried by passing through conc. H_2SO_4 and collected by upward displacement of air.

B. Properties:

1. Nature :

It is a colourless gas with pungent odour.

2. F.pt. & B. pt. :

On liquification HCl gas gives a colourless liquid (b.p. 189 K) which on freezing gives white crystalline solid (m.p. 159 K).

3. Solubility :

It is highly soluble in water and ionizes, giving a strongly acidic solution is called hydrochloric acid.

$HCl_{(g)} + H_2O(l)$ g $H_3O^+_{(aq)} + Cl^-$ (Ka = 10^7)

Ordinary concentrated hydrochloric acid contains about 37% (12 N) acid. This acid fumes in moist air called fuming hydrochloric acid.

4. Reaction with sodium :

$2Na + 2HCl$ g $2NaCl + H_2$ with explosion

5. Reaction with ammonia (NH_3) :

$NH_3 + HCl$ g NH_4Cl (white fumes)

6. Reaction with noble metals like gold, platinum:

A mixture of three parts of conc. HCl and one part of concentrated HNO_3 is known as aquaregia. It is used for dissolving noble metals, like gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

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

7. Reaction with salts:

Hydrochloric acid decomposes salts of weaker acids, e.g. sulphites, carbonates, hydrogen carbonates, etc. and dissolves basic oxides and neutralizes alkalies.

i. $NaHSO_3 + HCl$ g $NaCl + H_2O + SO_2$

iii. $NaHCO_3 + HCl$ g $NaCl + H_2O + CO_2$

ii. $Na_2CO_3 + 2HCl$ g $2NaCl + H_2O + CO_2$

iv. $CaO + 2HCl$ g $CaCl_2 + H_2O$

v. $Mg(OH)_2 + 2HCl$ g $MgCl_2 + 2H_2O$

vi. $NaOH + HCl$ g $NaCl + H_2O$

III. INTERHALOGEN COMPOUNDS:

· **Definition:**

The compounds which are formed when two different halogens combine together called interhalogen compounds.

A. Types of interhalogen compounds:

Type	Example
XX'	ClF, BrF, BrCl, ICl
XX'_3	ClF_3, BrF_3, IF_3, ICl_3(unstable)
XX'_5	IF_5, BrF_5, ClF_5
XX'_7	IF_7

Where X g halogen of large size

X' g halogen of small size

X is more electro positive than X'.

B. Preparation :

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.

1. **Formation of BrF_3 :** It is yellow green liquid. $Cl_2 + F_2 \xrightarrow{437K} 2ClF$

2. **ICl formation:** It is ruby red solid a form and Brown red solid β form. $I_2 + Cl_2 \longrightarrow 2ICl$

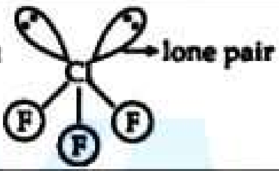
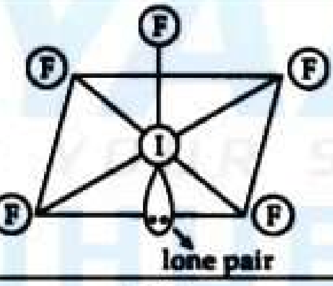
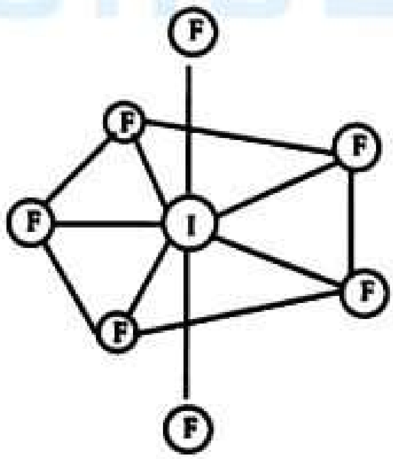
3. **Formation of ClF (Chlorine monofluoride) :** It is yellow powder. $BR_2 + 3F_2 \longrightarrow 2BrF_3$

4. **Formation of C/F$_3$ (CHlorine trifluoride) :** It is colourless gas. $Cl_2 + 3F_2(excess) \xrightarrow{573K} ICl_3$

5. **Formation of Icl3 (Iodine tri chloride) :** It is colour less gas. $I_2 + 3Cl_2(excess) \longrightarrow 2ICl$

6. **Formation of BrF_5 :** It is colourless liquid $Br_2 + 5F_2(excess) \longrightarrow 2BrF_5$

• **Structure of interhalogen compound:**

Type	Hybridisation of X (central atom)	Shape	Mole.	Structure	Excited state
XX'		Linear	Cl_2	Cl–Cl	
XX'3	sp^3d	T-shaped OR trigonal bipyramidal	ClF_3	First 	X atom Cl-F = 1.689 A
XX'_5	sp^3d^2	Square pyramidal	IF_5		Second excited state of X atom
XX'_7	sp^3d^3	Pentagonal pyramidal	IF_7		Third excited state of X atom

Properties of oxyacids :

a. Oxidising power of these oxyacids decreases as oxidation number.
$HClO > HClO_2 > HClO_3 > HClO_4$

b. Thermal stability increases with increase in the oxidation state of halogen.
$HClO < HClO_2 < HClO_3 < HClO_4$

GROUP 18 ELEMENTS (NOBLE GASES)

A. Introduction:

The group 18 consist of helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and redon (Rn)

B. Valence Shell electronic configuration:

The electronic configuration of He is 1s2, while all other noble gases have ns^2np^6 (n = 2 to 7).

Sr. No.	Element Property	He	Ne	Ar	Kr	Xe	Rn	Trend
1.	Name	Helium	Neon	Argaon	Krypton	Xenon	Radon	-
2.	Discovered by	J.C.P. Janseen and N. Lockyer (1868)	W.Ramsay and M-Travers (1898)	W.Ramsay (1894)	W.Ramsay and M.Travers (1898)	W.Ramsay and M.Travers (1898)	E.Rutherford (1899)	-
3.	Atomic number	2	10	18	36	54	86	-
4.	Atomic mass ($g mol^{-1}$)	4.00	20	39.9	83.9	131.3	222	-
5.	Valence shell e.c.	$1s^2$	$2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]$ $3d^{10}4s^24p^6$	$[Kr]$ $4d^{10}5s^25p^6$	$[Xe]4f^{14}$, $5d^{10},6s^26p^6$	-
6.	Abundance in dry air by volume (ppm)	5.24×10^{-4}	18.2×10^{-3}	93.40×10^{-3}	1.14×10^{-3}	8.7×10^{-6}	Traces	-
7.	Atomic radius (pm)	93	112	154	167	-	-	-
8.	Vander Waals radius (pm)	120	160	192	197	217	-	-
9.	Density ($g mol^{-1}$)	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}	Increases
10.	Melting point (K)	3	24	84	116	161	202	Increases
11.	Boiling point (K)	4	27	87	121	165	211	Increases
12.	Ionisation enthalpy ($kJ mol^{-1}$)	2372	2080	1520	1350	1170	1037	Decreases
13.	Electron gain enthalpy ($kJ mol^{-1}$)	48	116	96	96	77	68	Decreases

Trends in physical properties:

1. Liquefication tendency :

Inert gaseous are not easily liquefied.

From He to Rn tendency of liquefication increases.

Atoms of noble gas brought together by vander Waal's force of attraction Since the vander Waal's force present between noble gases are very weak, hence the noble gases have very little tendency to liquefied.

From He to Rn strength of vander Waal's forces increases with increasing atomic size.

Thus tendency to liquefication of these gases increases from He to Rn.

2. Heat of vaporization:

It is measure in forces of holding the atoms together.

From He to Rn heat of vaporization increases, hence tendency to liquefication increases.

3. Ability to diffuse :

All noble gases are able to diffuse through glass, rubber, plastic material and some metals. Hence, they are difficult to handle in the laboratory for low temperature research work.

Decreasing order diffuse ability is, He > Ne > Ar > Kr > Xe > Rn

4. Solubility in water :

Noble gases are slightly soluble in water.

Helium is least soluble. The solubility of noble gases increases from He to Rn.

He < Ne < Ar < Kr < Xe < Rn

The solubility of these element in water is due to **dipole induce dipole interaction (Interaction between polar and non-polar molecule).**

Chemistry of group 18 elements prior to 1962 :

Before 1962, it was believed that noble gases are inert and cannot take part in chemical combination.

Reactivity of element - Bartlett reaction:

Neil Bartlett demonstrated the first chemical reaction of noble gases in 1962. He conducted the reaction between Xe and PtF_6 and separated the first compound of noble gases i.e. $Xe^+PtF_6^-$. It is an orange yellow crystalline solid.

$$Xe + PtF_6 \longrightarrow Xe^+ Ptf_6^-$$

[Xenon hexafluro-platinate (v)]

- **Uses of noble gases:**

1. Helium:

a. It is used for filling ballons and air shaps as it is light and non combustible.

b. It is used in producing inert atmosphere in metallurgical operations and welding of metals.

c. It is also used in gas cooled nuclear reactors.

2. Neon:

a. Neon is largly used for production of neon lights.

b. Neon is also used in television sets, spark plug, warming signals etc.

3. Argon:

a. Argon is used to filling discharge tubes and electric bulbs.

b. It is used to provide inert atmosphere for welding and several metallurgical process.

c. It is used in gas chromatography.

4. Krypton:

a. Krypton is used in filling discharge tubes and electric bulbs.

b. It is also used in high effeiciency miner's cap lamps.

5. Xenon:

a. A mixture of Xe and Kr is used in the flash bulbs used in the high speed photography.

b. Liquid xenon is used in research laboratories for the detection of measons and gamma photons.

6. Radon:

a. It is used in the treatment of cancer by radiotherapy.

b. It is used for photographing the interior of opaque materials like steel castings.

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