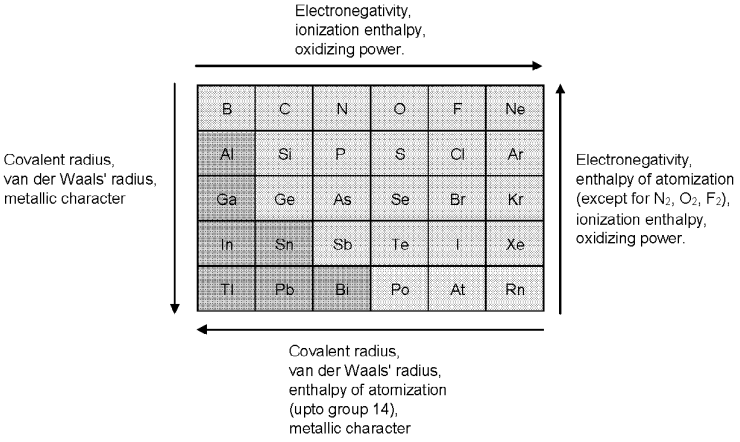
p-BLOCK ELEMENTS & THEIR COMPOUNDS

TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.



(A) GROUP 13 ELEMENTS : THE BORON FAMILY

Oxidation state and trends in chemical reactivity :

General Oxidation State = + 3.

Reactivity towards acids and alkalies

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2Na^{+}[Al(OH)_4]^{-}(aq) + 3H_2(g)$$

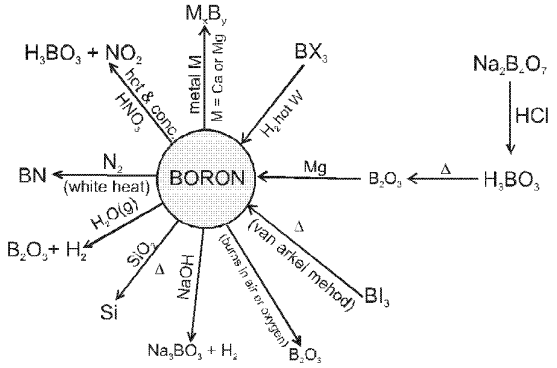
Sodium tetrahydroxoaluminate (III)

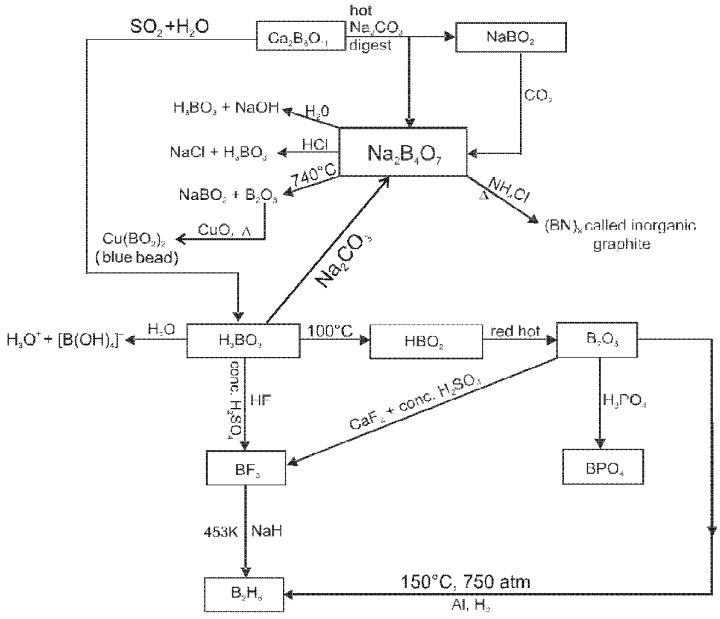
Reactivity towards halogens

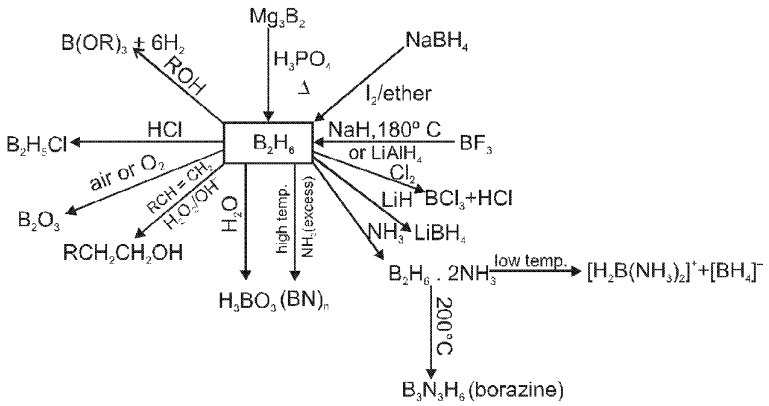
$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s) \qquad (X = F, Cl\ Br, I)$$

BORON (B):

Some Important Reactions of Boron and its compounds :







- Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.
  $B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [BH_4]^-$
- Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.
  $2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$
- $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\ atm} 2BH_3CO$ (borane carbonyl)

(B) GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Electronic Configuration = $ns^2 np^2$.

Oxidation states and trends in chemical reactivity

Common oxidation states = +4 and +2. Carbon also exhibits negative oxidation states. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb.

(i) Reactivity towards oxygen :

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively.

(ii) Reactivity towards water :

Tin decomposes steam to form dioxide and dihydrogen gas.

(iii) Reactivity towards halogen :

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl Br, I). Stability of dihalides increases down the group.

ANOMALOUS BEHAVIOUR OF CARBON :

Catenation :

The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation. Due to the property of catenation and pπ-pπ bonds formation, carbon is able to show allotropic forms.

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C—C	348	Si—Si	297
Ge—Ge	260	Sn—Sn	240

Allotropes of Carbon

Diamond :

Crystalline lattice sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral manner. The C–C bond length is 154 pm. and produces a rigid three dimensional network of carbon atoms.

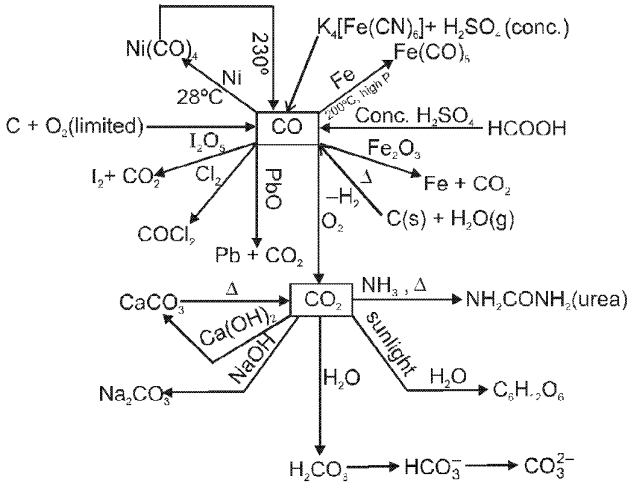
Graphite :

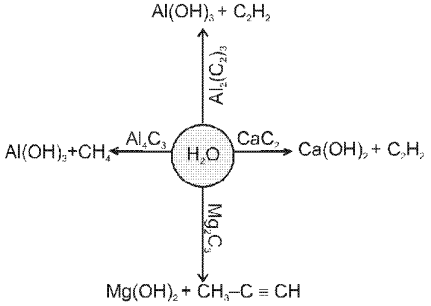
Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

Fullerenes :

C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene.** It contains twenty six -membered rings and twelve five membered rings. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively.

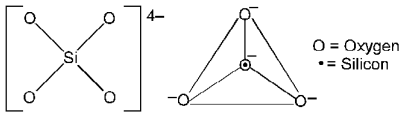
SOME IMPORTANT REACTIONS OF CO, CO_2 AND METAL CARBIDES :



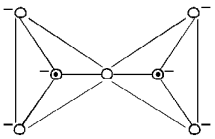


● CLASSIFICATION OF SILICATES :

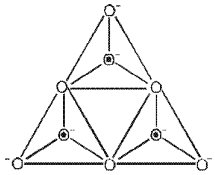
(A) Orthosilicates :

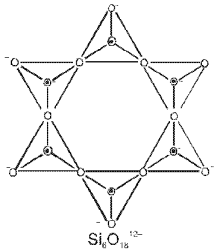


(B) Pyrosilicate :

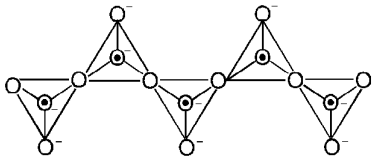


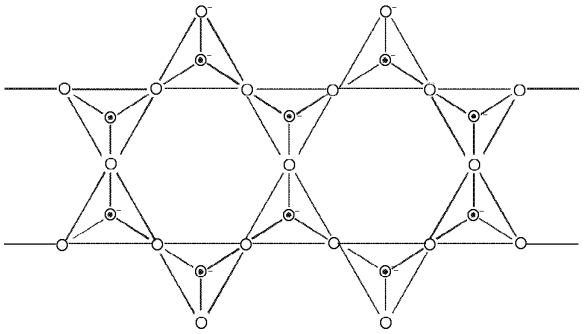
(C) Cyclic silicates :





(D) Chain silicates :





(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

(F) Three dimenstional sheet silicates :

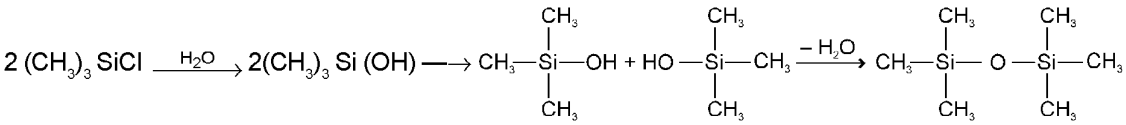
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

● SILICONES :

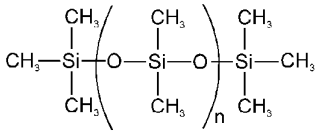
☞ Silicones can be prepared from the following types of compounds only.

(i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$

☞ Silicones from the hydrolysis of $(CH_3)_3SiCl$



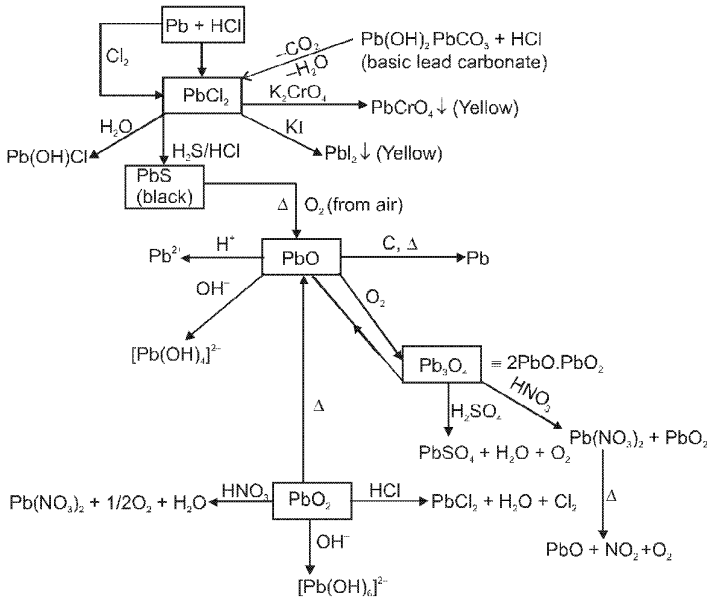
☞ Silicones from the hydrolysis of a mixture of $(CH_3)_3SiCl$ & $(CH_3)_2SiCl_2$



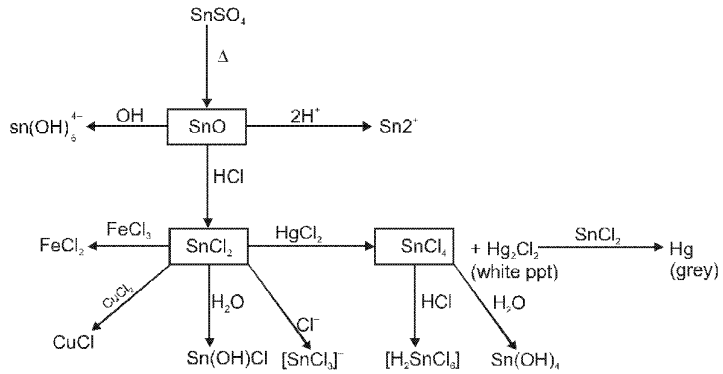
☞ When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained.

☞ The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

COMPOUNDS OF LEAD :



COMPOUNDS OF TIN :



(C) GROUP 15 ELEMENTS : *THE NITROGEN FAMILY*

Electronic Configuration : $ns^2\ np^3$.

Atomic and Ionic Radii : Covalent and ionic (in a particular state) radii increase in size down the group.

Physical Properties:

All the elements of this group are polyatomic. Metallic character increases down the group. The boiling points , in general , increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen , all the elements show allotropy.

Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are –3, +3 and +5. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group ; $Bi^{3+} > Sb^{3+} > As^{3+}$; $Bi^{5+} < Sb^{5+} < As^{5+}$ Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

Anomalous properties of nitrogen :

(i) The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently , the reducing character of the hydrides increases. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point / K	195.2	139.5	156.7	185	–
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	–
HEH angle (^{0})	107.8	93.6	91.8	91.3	–
$\Delta_f H^-$ / kJ mol^{-1}	– 46.1	13.4	66.4	145.1	278
$\Delta_{diss} H^-$(E – H) / kJ mol^{-1}	389	322	297	255	–

(ii) The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

(iii) Nitrogen does not form pentahalide due to non – availability of the d-orbitals in its valence shell. Pentahalides are more covalent than trihalides. Halides are hydrolysed in water forming oxyacids or oxychlorides.

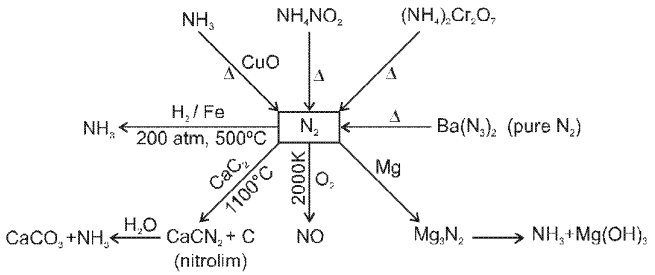
$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$;

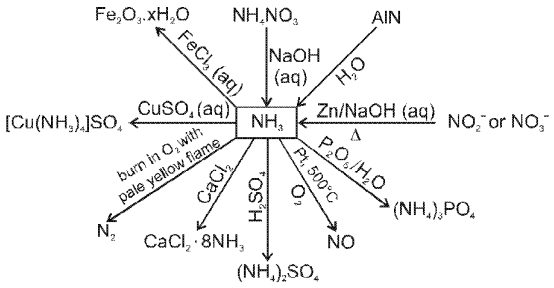
$SbCl_3 + H_2O \longrightarrow SbOCl\downarrow$ (orange) + 2HCl ;

$BiCl_3 + H_2O \longrightarrow BiOCl\downarrow$ (white) + 2HCl

(iv) These elements react with metals to form their binary compounds exhibiting –3 oxidation state , such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide) and Na_3As_2 (sodium arsenide).

NITROGEN (N) AND ITS COMPOUNDS :

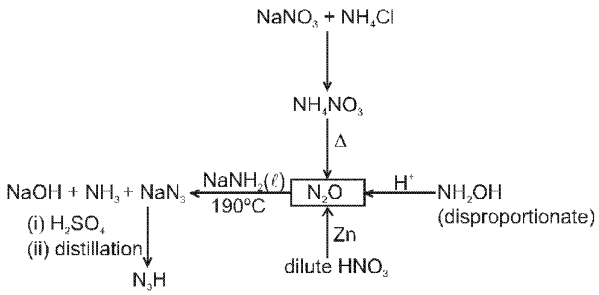


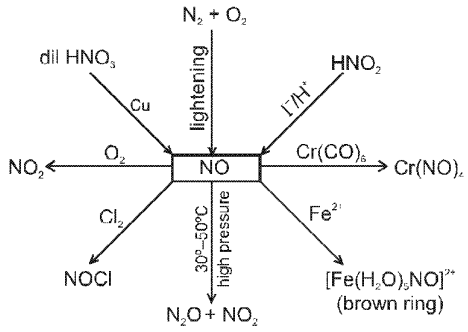


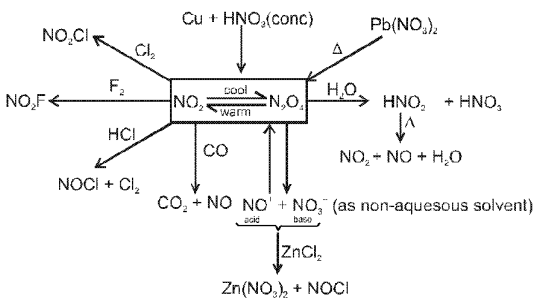
$CaO + H_2O \rightarrow Ca(OH)_2$; used for drying of NH_3

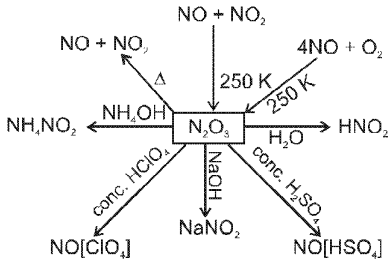
Oxides of Nitrogen

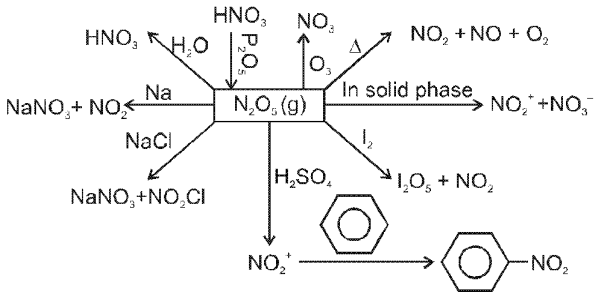
Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2\,H_2O$	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide] (Nitric acid)	NO	+ 2	$2\,NaNO_2 + 2\,FeSO_4 + 3\,H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2\,NaHSO_4 + 2\,H_2O + 2\,NO$	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide] (Nitrogen sesquioxide)	N_2O_3	+ 3	$2\,NO + N_2O_4 \xrightarrow{250\,K} 2\,N_2O_3$	blue solid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\,Pb(NO_3)_2 \xrightarrow{673\,K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetraoxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\,NO_2 \underset{\text{Heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(IV) oxide]	N_2O_5	+ 5	$4\,HNO_3 + P_4O_{10} \longrightarrow 4\,HPO_3 + 2\,N_2O_5$	colourless solid, acidic









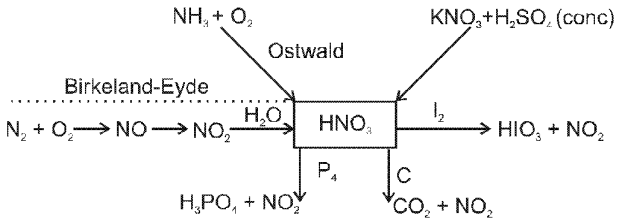


Sn (a) dilute NH_4NO_3 $4Sn+10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

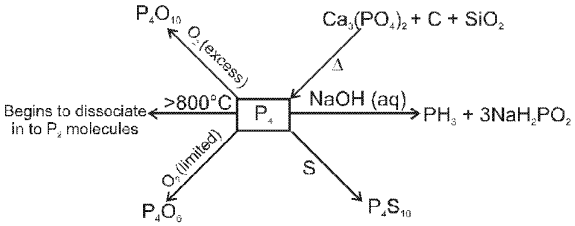
(b) concentrated NO_2 $Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$

meta stannic acid

antimonic acid

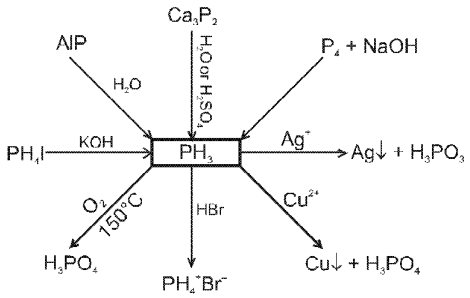


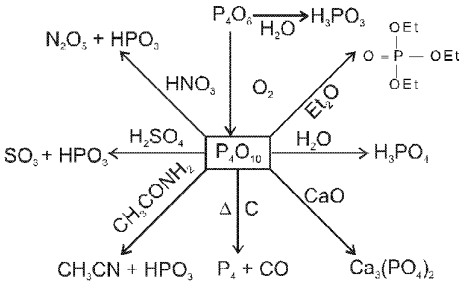
PHOSPHORUS (P) AND ITS COMPOUNDS :



When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is produced. α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. β-black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

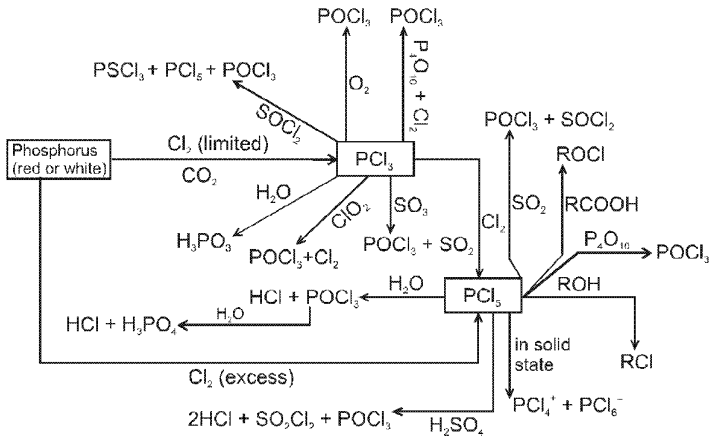
Order of thermodynamic stability of various allotropes of phosphorus : black > red > white





Oxoacids of Phosphorus

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous	H_3PO_2	+ 1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous	H_3PO_3	+ 3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P – OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric	$(HPO_3)_3$	+ 5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2 , heat in sealed tube



(D) GROUP 16 ELEMENTS : THE OXYGEN FAMILY

Electronic Configuration : $ns^2\ np^4$.

Atomic and Ionic Radii :

Due to increase in the number of shells , atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

Physical Properties :

Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). The melting and boiling points increase with an increase in atomic number down the group.

Catenation :

Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

Chemical Properties

Oxidation states and trends in chemical reactivity :

Elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen is due to its small size and high electronegativity. The absence of d orbitals in oxygen limits its covalency to four.

(i) Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be understood in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group , the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this property increases from H_2S to H_2Te.

PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS

Property	H_2O	H_2S	H_2Se	H_2Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	-286	-20	73	100
Δ_{diss} H (H-E)/kJ mol^{-1}	463	347	276	238
Dissociation constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

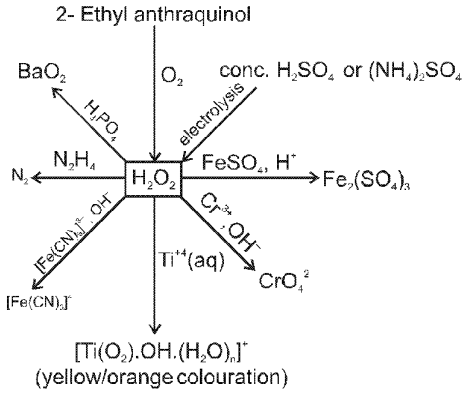
(ii) Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Oxides are generally acidic in nature.

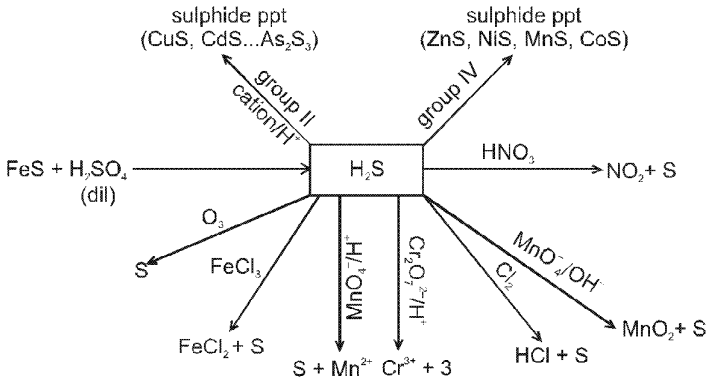
(iii) The stabilities of the halides decrease in the order F > Cl > Br > I. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.

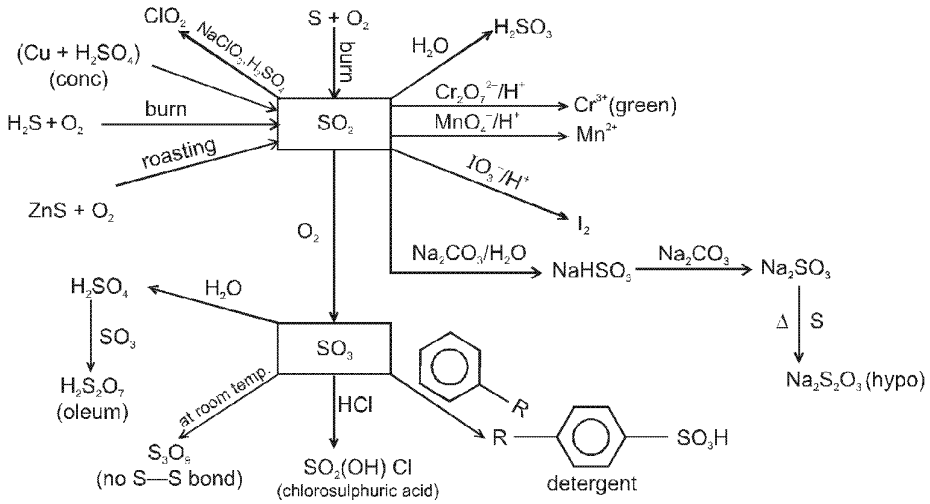
The well known monohalides are dimeric in nature, Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below :

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se.$$

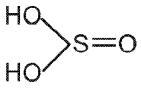
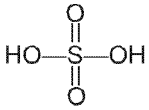
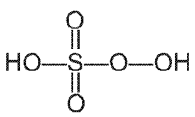
OXYGEN (O_2) AND ITS COMPOUNDS :

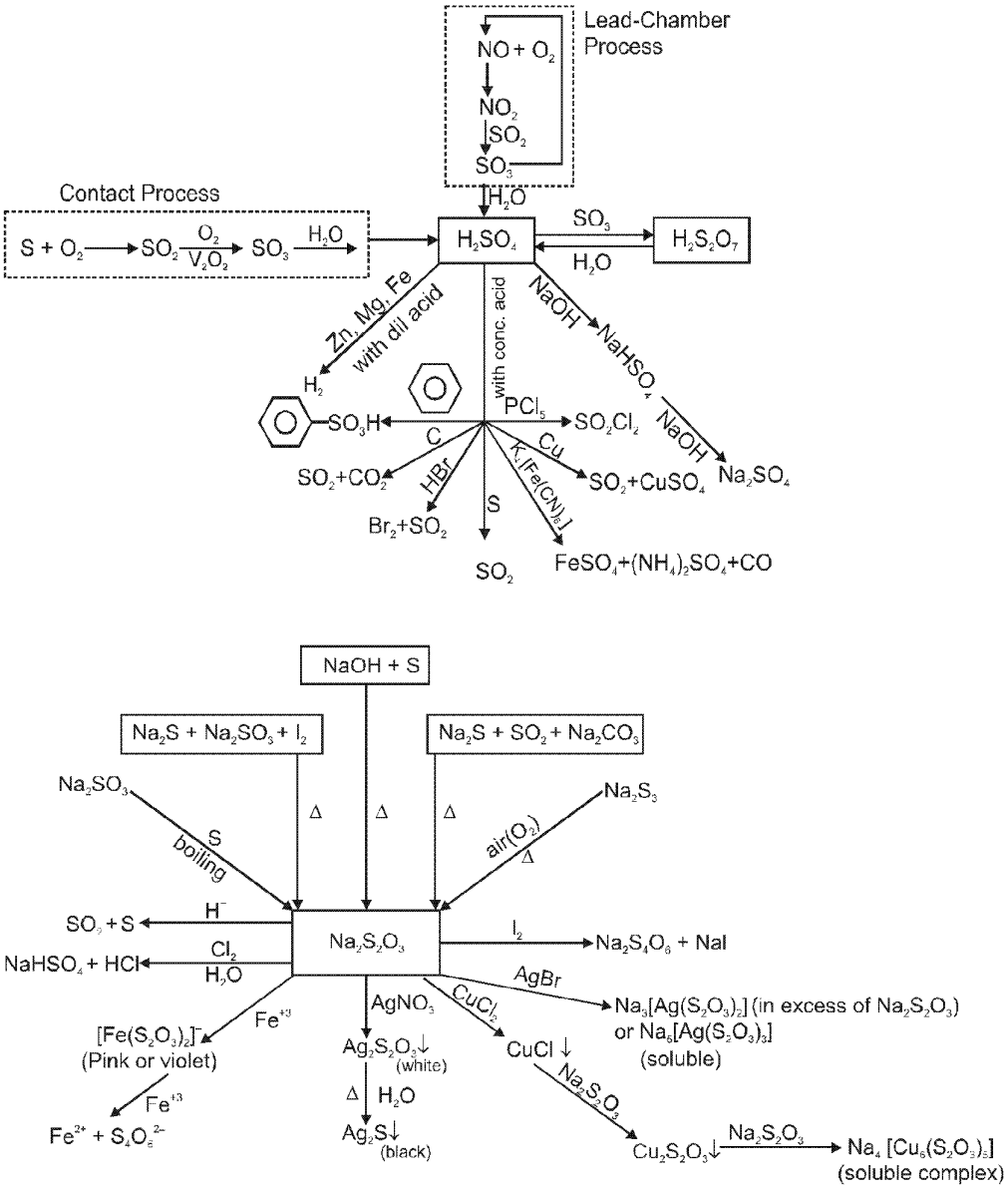






Oxo-acids of Sulphur

1.	**Suplhurous**	**acid series**		
	(a) H_2SO_3	S (IV)	sulphurous acid	
2.	**Sulphuric**	**acid series**		
	(a) H_2SO_4	S (VI)	sulphuric acid	
3.	**Peroxo**	**acid series**		
	(a) H_2SO_5	S (VI)	peroxomonosulphuric acid Caro, acid)	



(E) GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17.

Electronic Configuration : $ns^2 np^5$

Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge .

Physical Properties

Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid. Their melting and boiling points steadily increase with atomic number. The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : Cl – Cl > Br – Br > F – F > I – I.

Chemical Properties

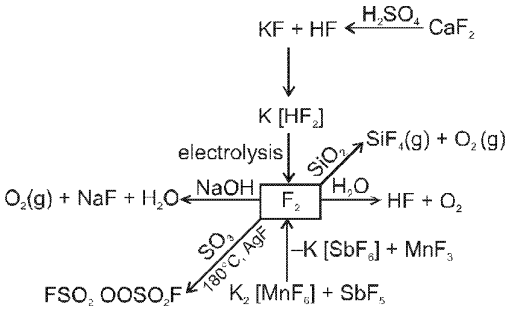
Oxidation states and trends in chemical reactivity

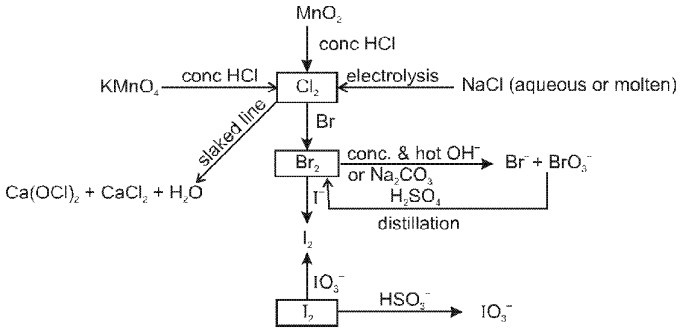
All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also.

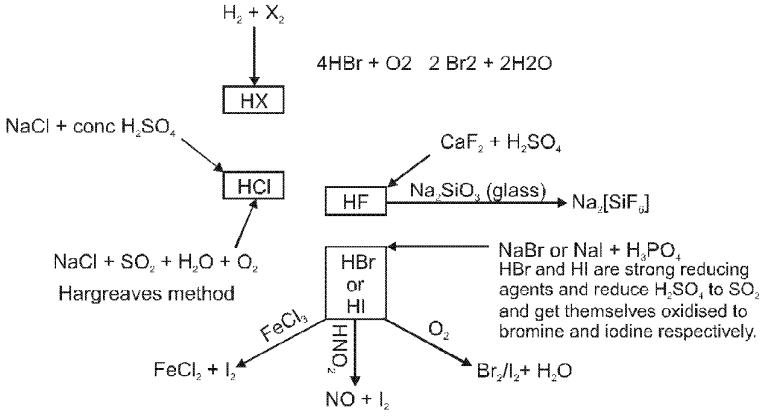
$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

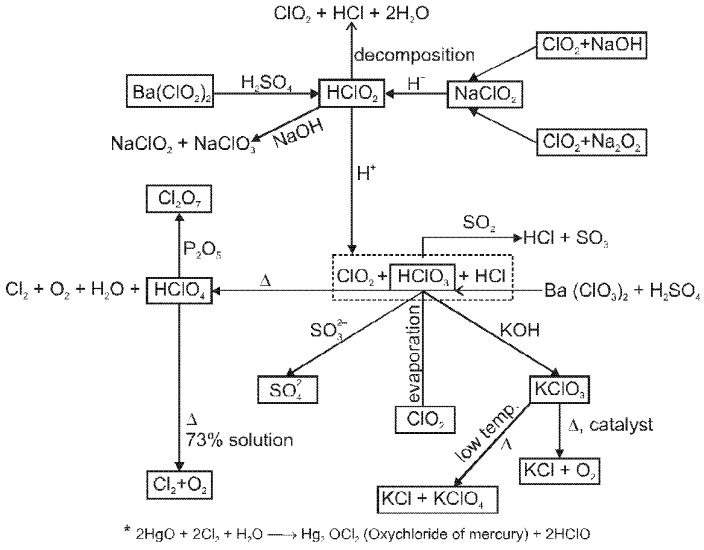
$X_2(g) + H_2O(\ell) \rightarrow HX(aq) + HOX(aq)$; (where X = Cl or Br)

$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(\ell)$

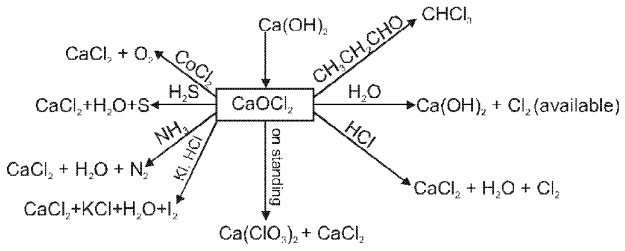




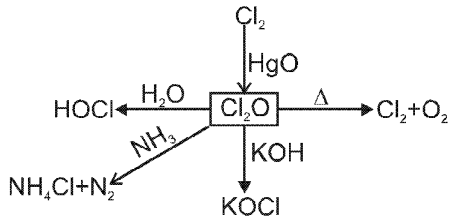


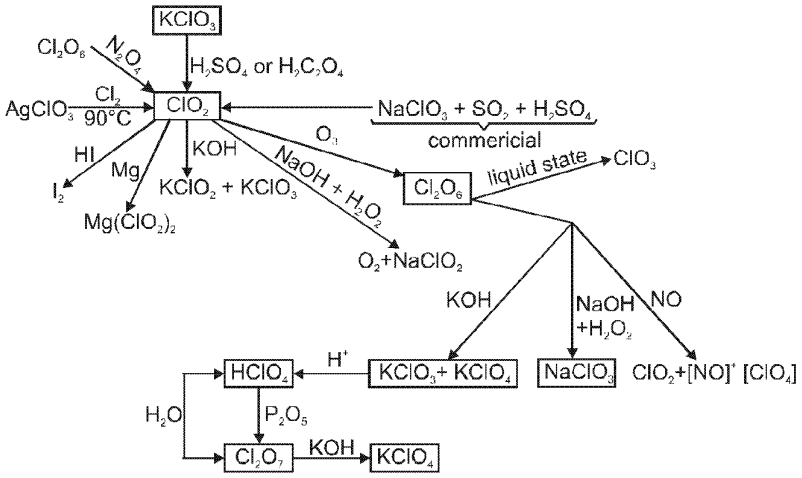


* $2HgO + 2Cl_2 + H_2O \longrightarrow Hg_2OCl_2$ (Oxychloride of mercury) + 2HClO



*The composition of bleaching powder is Ca(OCl)2. CaCl2. Ca(OH)2. 2H2O.





(F) GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

helium, neon, argon, krypton , xenon and radon .

❍ Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Electronic Configuration : ns^2np^6

Atomic Radii

Atomic radii increase down the group with increase in atomic number.

Physical properties

All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,.

Chemical Properties :

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled $ns^2\ np^6$ electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to

force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First , he prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He , then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with $Xe^+ PtF_6^-$ by mixing $Pt F_6$ and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

- If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

CLATHERATE COMPOUNDS :

During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clatherate compounds.
Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.