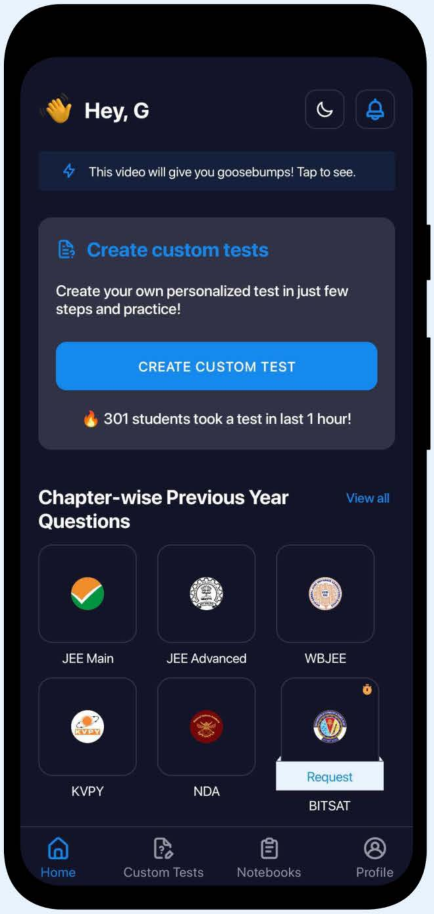

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Chapter-wise Previous Year Questions

# P-BLOCK ELEMENT

# P-BLOCK ELEMENTS

## Introduction :

The right side of the periodic table having group number 13, 14, 15, 16, 17 and 18 are known as p-block elements. These elements have 3, 4, 5, 6, 7 and 8 electrons in their outer most shell, respectively. The last electron of these groups' elements occupies the position in p-sub shell that is why they are called as p-block elements. Their general configuration is $ns^2np^{1-6}$.

## Some Important Properties of P-Block

### 1. Electron affinity :

Electron affinity increase from left to right along the period amongst the p-block elements and it decreases from top to bottom. But group 15 is having exceptionally low values of electron affinity and is due to extra stability because of the presence of exactly half filled orbital in their valence shell. Similarly, elements of group 18 (noble gases) have zero affinities due to presence of complete octet which provides them stability.

### 2. Metallic Character

The metallic character is governed by

(i) Size of atoms and

(ii) Ionization energy.

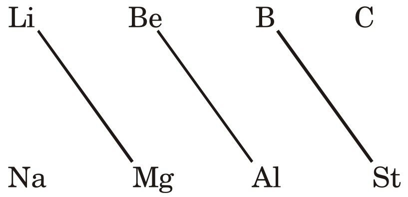
The elements having bigger size and low ionization energy has a greater metallic character. After combining both above mentioned factors we observe that the elements with above two properties are located in left corner of p-block and strong non-metallic elements are located at right corner and a diagonal strip of elements thus two, having in between properties are called as metalloids.

### 3. Oxidation state

The p-block elements shows variety of oxidation states both positive and negative. Some of the p-block elements show different oxidation state due to inert – pair effect, where the lower oxidation state is more predominant.

### 4. Diagonal relationship

On moving diagonally across the periodic table the element show certain simplarities.



**Note :** Elements of 2nd period differ from their own group elements in some of the properties. This is due to the following reasons :

(a) Small size

(b) Absence of vacant d-orbital

(c) High IP

### Some Important Characteristics of P–Block In Tabular Form

| Sr. No. | Property | Along period (left to right) | Along group (top to bottom) |
|---|---|---|---|
| 1. | Atomic radii | Decreases | Increases |
| 2. | Ionization potential | Increases | Decreases |
| 3. | Electron affinity | Increases | Decreases |
| 4. | Electro negativity | Increases | Decreases |
| 5. | Metallic character | Decreases | Increases |
| 6. | Oxidizing property | Increases | Decreases |
| 7. | Reducing property | Decreases | Increases |

## GROUP 13 ELEMENTS

**Elements :** B, Al, Ga, In, TI.

Group 13 elements are boron (B), aluminium (Al), Gallium (Ga), Indium (In) and thallium (TI).

Boron is the only non-metal in this group others are metal. Non-metallic character of boron is due to its small size and high ionization energy. The general valence shell electronic configuration of these elements is $ns^2np^1$.

### General Trends in Physical Properties

| Sr.No. | Property | Boron | Aluminium | Gallium | Indium | Thallium |
|---|---|---|---|---|---|---|
| 1. | Configuration | $[He]2s^22p^1$ | $[Ne]3s^23p^1$ | $[Ar]4s^24p^1$ | $[Kr]5s^25p^2$ | $[Xe]6s^26p^1$ |
| 2. | Common oxidation state | + 3 | + 3 | + 3 | + 3 | + 3, + 1 |
| 3. | Atomic radius (pm) | 83 | 143 | 135 | 167 | 170 |
| 4. | First ionization energy (KJ/mol) | 801 | 578 | 579 | 558 | 589 |
| 5. | Electro negativity | 2.0 | 1.5 | 1.6 | 1.7 | 1.8 |

**1. Density**

Generally increases down the group but aluminium has an exceptionally low density.

**2. Melting point and Boiling point**

B to Ga decrease then Ga to TI increase Ga has lowest M.P. (29.8 C) and therefore liquid at room temperature.

**3. Atomic radii and ionic radii**

On moving from B to TI the size increases due to addition of new energy shells at each step down the group but Ga is smaller than Al.

**4. Ionization energy**

Generally IE decreases down the group but Ga has higher IE than Al exceptionally due to smaller in size as compared to Al.

**5. Metallic character**

Electropositive character increases down the group hence metalic character also increase down the group but aluminium is having high metallic character than Gallium due to low IE than Ga.

**6. Inter Pair Effect**

When we go down the group in p block element, stable positive valency decreases by a factor of 2. This effect is known as inert pair effect. It arises mainly due to poor shielding effect 3d and 4d series element. This result into increase in effective nuclear charge and greater hold on valence S electrons by nucleus. These s electrons can't be pulled easily out which decreases the valency by a factor of 2.

e.g. In 14th group while carbon & silicon show + 4 valency, while Pb is mostly stable in +2 state.

**7. Oxidation states and nature of bond**

The group – 13 elements show variable oxidation states of + 3 and + 1. For lighter members + 3 state is more stable than + 1. Thus for Tl, + 1 state is more stable than + 3. It is due to inert pair effect. The $6s^2$ pair does not prefer to form bonds and is called inert pair. The basic reason for such an effect is bond energy. The M–Cl bond energy in $MCl_3$ compounds are as follows :

| $MCl_3$ | M–Cl, energy (KJ $mol^{-1}$) |
|---|---|
| Ga | 242 |
| In | 206 |
| TI | 153 |

The ionisation energies of B is very high. It is, therefore, covalent in its compounds, always tricovalent ($2s^2 2p^1$ electrons).

In + 3 oxidation state Al has very high charge to radius ratio (~ 6.0). So, it is also covalent in its anhydrous compounds. However, in aq. solution tricovalent Al (e.g. $AlCl_3$) becomes ionic due to high hydration energy of $Al^{+3}$ (4665 KJ $mol^{-1}$) $[Al(OH_2)_6]^{3+}.3Cl^-$. The soluble compounds are quite acidic due to hydrolysis (high charge to radius ratio of $Al^{+3}$).

$$[Al(OH_2)_6]^{+3} + H_2O \longrightarrow H_3O^+ + [Al(H_2O)_5OH]^{+2}$$

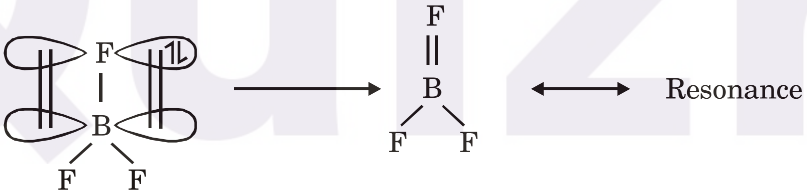
TI is ionic in + 1 oxidation state, TICl ionic. The $TI^+$ ion resembles $K^+$ and $Rb^+$. It is because radii of the ions are comparable ($K^+$ ~ 1.38 Å, TI ~ 1.5 Å, Rb ~ 1.52 Å). Therefore, TIOH is a strong base like group – 1 hydroxides. Tricovalent compounds, $MX_3$, are electron deficient as octet around the central atom is not complete.

(Six electrons around B or Al)

Such compounds remove their electron deficiency by :

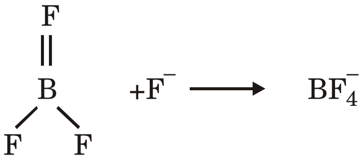
(i) Back – bonding

In $BX_3$, B is $sp^2$ and has a vacant p-orbital perpendicular at the triangular plane. X-atom has filled p-orbital. The overlap resulting into π–bonding.



(ii) Coordination with Lewis bases

B has vacant orbital which accepts electron pair from $F^-$.



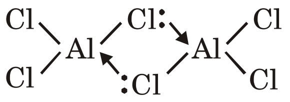
$$Al(OH)_3 + HO^- \longrightarrow Al(OH)_4^-$$

(iii) Polymerisation

$AlCl_3$ removes electron deficiency by dimerisation.

$$2AlCl \longrightarrow Al_2Cl_6$$

Dimer is made easily because Cl has lp and Al has vacant orbital.

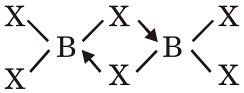


$AlCl_3$ is not stabilized by back bonding. It is due to the following facts :

(i) p-orbital of Al is large, so p–p overlap is not effective.

(ii) 8 electron core in Al causes larger repulsion (8e – 8e) destabilizing back bonding effective.

$BX_3$ can not stabilize by dimerisation. B is small in size. The dimer will have small ring.



So, it is not stable.

## REACTIONS OF ELEMENTS

Pure crystalline boron is very unreactive. However, it is attacked at high temperatures by strong oxidising agents such as a mixture of hot concentrated $H_2SO_4$ and $HNO_3$ or $Na_2O_2$.

$$2B(s) + 6HNO_3\ (aq) \longrightarrow 2H_3BO_3(aq) + 6NO_2(g)$$

In contrast, finely divided amorphous boron (containing about 2–5% impurities) is more reactive. Reactions are summarised in Table below

**Reactions of Group 13 (IIIA) Elements**

| Reaction | Comment |
|---|---|
| • $4M + 3O_2 \longrightarrow 2M_2O_3$ | Reaction at high temperature; with Al exotohermic, a protective oxide layer is formed and TI also forms $TI_2O$. |
| • $2M + N_2 \longrightarrow 2MN$ | Only Al and (B) form nitrides BN, a slippery white solid with layer structure similar to graphite. |
| • $2M + 3X_2 \longrightarrow 2MX_3$ | All form $MX_3$, Tl also form TlX. Iodide of $Tl^{3+}$ ($TlI_3$) is not formed; but TlI reacts with $I_2$ forming $TlI_3$ ($Tl^+$, $I_3^-$) |
| • $2M + 2NaOH + 2H_2O \longrightarrow$ $2NaMO_2 + 3H_2$ | B, Al and Ga only form $NaMO_2$ |
| • $2M + 6NH_3 \longrightarrow 2M(NH_2)_3 + 3H_2$<br>$2B + 2NH_3 \longrightarrow 2BN + 3H_2$ | All form amides except B which forms BN. |
| • $2M + 6H^+ \longrightarrow 2M^{3+}\ 3H_2$ | Metals liberate $H_2$, but $HNO_3$ makes Al passive. |

- Boron reacts directly with elements forming borides which are hard and refractory.

$$3Mg + 2B \longrightarrow Mg_3B_2$$

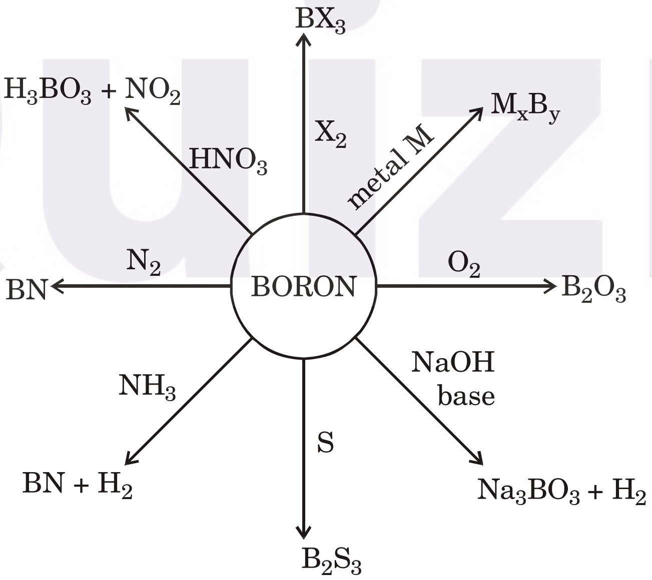
Borides are decomposed by acids forming boranes

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + \underset{\text{diborane}}{B_2H_6}$$

- Aluminium is far more reactive than boron but in air and water it is stable. It is due to the formation of aluminium oxide, $Al_2O_3$ layer, that makes it passive for further attack. $HNO_3$ also makes Al passive by oxide layer formation.
- Reaction of Al with $O_2$ is exothermic and is called thermite reaction.

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s), \qquad \Delta H = -1670 \text{ kJ}$$

The thermite reaction involves so much energy that it can be dangerous. The Al becomes white hot and often causes fires. For this precise reason, mixture of Al and an oxide such as $Fe_2O_3$ or $SiO_2$ (a source of oxygen) were used to make incendiary bombs during World War II.



## Boron : Extraction

- $Na_2\ B_4O_7.10H_2O \xrightarrow{\text{acid}} \underset{\text{orthoboric acid}}{H_3BO_3} \xrightarrow{\Delta} H_2O + B_2O_3$

$B_2O_3 + 6Na \xrightarrow{\Delta} 2B + 3Na_2O$

$B_2O_3 + 3Mg \xrightarrow{\Delta} 2B + 3MgO$

- $2BCl_3 + 3H_2 \xrightarrow[\text{filament}]{\text{red hot}} 2B + 6HCl$
- Pyrolysis of $BI_3$

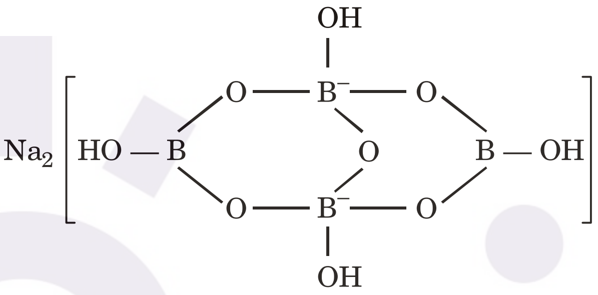
  $2BI_3 \xrightarrow[\text{filament}]{\text{red hot}} 2B + 3I_2$
- thermal decomposition of $B_2H_6$

  $B_2H_6 \xrightarrow{\Delta} 2B + 3H_2$

## Compounds of Boron

### 1. Borax ($Na_2B_4O_7.10H_2O$)

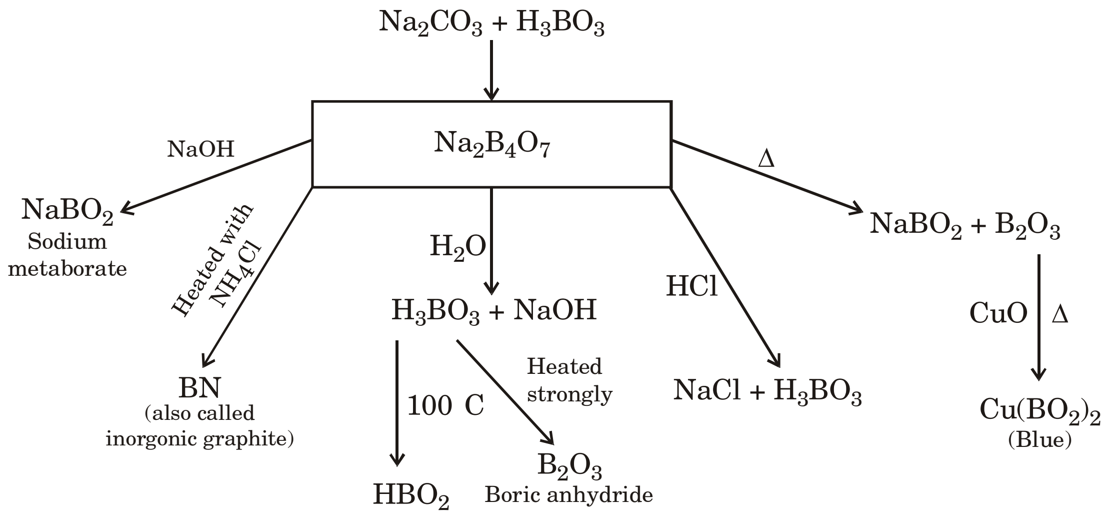
- The actual formula is $Na_2[B_4O_5(OH)_4].8H_2O$



- Action of heat

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\text{Heat}} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{\underset{\text{sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydrid}}{B_2O_3}}_{\text{Glassy mass}}$$

- Various reactions of borax



- Solution of Borax is alkaline in nature. This is due to hydrolysis

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong alkali}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

## 2. Boric acids and oxides

(i) $H_3BO_3$ or $B(OH)_3$ orthoboric acid

(ii) $HBO_2$ metaboric acid

(iii) $H_2B_4O_7$ pyroboric acid

$$\begin{tikzcd} H_3BO_3 \arrow[r, "100\ C"] & HBO_2 \arrow[r, "140\ C"] & H_2B_4O_7 \arrow[d, "\text{red hot}"] \\ & & B_2O_3 \end{tikzcd}$$

## 3. Boron Trioxide, $B_2O_3$

- $2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$

  It is a white hygroscopic solid. It absorbs moisture and converted into boric acid.

  $B_2O_3 + H_2O \longrightarrow 2HBO_2$

  $HBO_2 + H_2O \longrightarrow H_3BO_3$

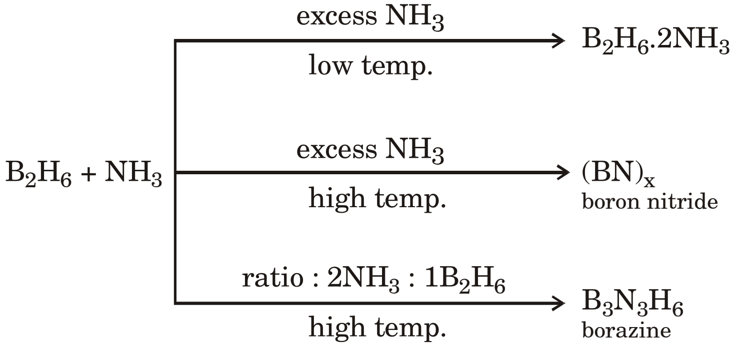
- $2B_2O_3 + P_4O_{10} \longrightarrow 4BPO_4$
- It is reduced by magnesium

  $B_2O_3 + 3Mg \xrightarrow{\text{Heated}} 2B + 3MgO$

## 4. Boron halide

$$\begin{tikzcd} \boxed{CaF_2 + H_2SO_4 + H_3BO_3(\text{or } B_2O_3)} \arrow[d, "\Delta"] & \\ \boxed{BF_3} \arrow[r, "H_2O"] \arrow[d, "NaH", "180\ C"'] & H_3BO_3 + BF_4^- \\ \boxed{B_2H_6} & \end{tikzcd}$$

## 5. Boron Hydrides

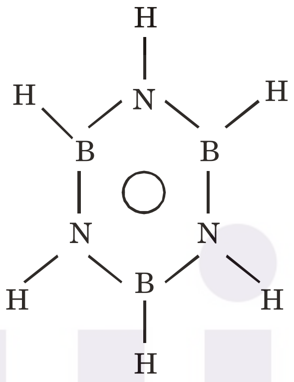


$$B_2H_6 + NH_3 \xrightarrow[\text{low temp.}]{\text{excess } NH_3} B_2H_6.2NH_3$$

$$B_2H_6 + NH_3 \xrightarrow[\text{high temp.}]{\text{excess } NH_3} (BN)_x \text{ boron nitride}$$

$$B_2H_6 + NH_3 \xrightarrow[\text{high temp.}]{\text{ratio} : 2NH_3 : 1B_2H_6} B_3N_3H_6 \text{ borazine}$$

- $B_2H_6 . 2NH_3$ is ionic and forms borazine on heating. Borazine is called inorganic benzene.



**Similarity between Boron and Silicon (Diagonal Relationship)**

- Both form volatile hydrides (called boranes and silanes) which spontaneously catch fire on exposure to air and are easily hydrolysed.
- Halides of both (except $BF_3$) are easily hydrolysed :

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$$

- Boron forms binary compounds with several metals–these are called borides. Silicon form silicides. Borides and silicides are hydrolysed by $H_2O$ forming boranes and silanes :

$$Mg_3B_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + B_2H_6$$

$$Al_4Si_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3SiH_4$$

- $B_2O_3$ and $SiO_2$ are acidic in nature and are important constituents of glass. Borate and silicates have tetrahedral $BO_4$ and $SiO_4$ structural units, respectively.
- Both are semi-conductors.

- Boric acid ($H_3BO_3$) and silicic acids ($H_4SiO_4$) are weak crystalline.
- They do not dissolve in cold dilute acids but do so in alkalies–boron only in fused alkalies and silicon in both fused and aqueous alkalies.

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

---

## Compounds of Aluminium

### 1. Aluminium oxide or Alumina, $Al_2O_3$

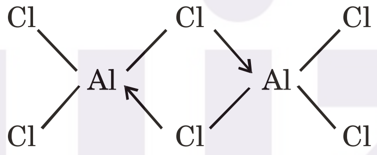
$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

$$Al_2(SO_4)_3 \longrightarrow Al_2O_3 + 3SO_3$$

$$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$$

### 2. Aluminium Chloride

$AlCl_3$ exists as a dimer, thus attaining an octet of elections.



However, when the halides dissolve in $H_2O$, the high enthalpy of hydration is sufficient to break the covalent dimer into $[M(H_2O)_6]^{3+}$ and $3X^-$ ions.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

### 3. Alums

Alums have general formula

$$M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$$

where M stands for monovalent basic radicals such as $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ag^+$ etc. and M´ for trivalent basic radicals such as $Al^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Mn^{3+}$, $Co^{3+}$

Some examples of alums are :

| | |
|---|---|
| Potash Alum | $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ |
| Ferric alum | $(NH_4)_2SO_4 . Fe_2(SO_4)_3$ |

Alums are crystalline compounds. In alums each metal ion is surrounded by six water molecules and the crystals of alums consists of $[M(H_2O)_6]^+$, $[M'(H_2O)_6]^{3+}$ and $SO_4^{2-}$ ions.

## GROUP–14

Elements of this group are p-block element. Carbon and Si are non-metals (Si slightly metallic), Ge is metalloid, Sn and Pb are metals.

Carbon has three isotopes, they are :

| Isotope | No. of neutron | Abundance | Nature |
|---|---|---|---|
| $^{12}C$ | 6 | 98.9% | Stable isotopes |
| $^{13}C$ | 7 | 1.1% | |
| $^{14}C$ | 8 | Trace | Radioactive<br>$t_{1/2}$ = 5770 yrs |

**Physical properties of group–14 elements**

| Property | C | Si | Ge | Sn | Pb |
|---|---|---|---|---|---|
| Atomic no. | 6 | 14 | 32 | 50 | 82 |
| Electronic structure | – $2s^2 2p^2$ | – $3s^2 3p^2$ | $3d^{10} 4s^2 4p^2$ | $4d^{10} 5s^2 5p^2$ | $4f^{14} 5d^{10} 6s^2 6p^2$ |
| Atomic radius (A) [covalent radius] | 0.77 | 1.17 | 1.22 | 1.40 | 1.44 |
| Ionic radius (A) | 0.15 | 0.41 | 0.53 | 0.71 | 0.84 |
| Metallic radius (Å) | -- | -- | 1.37 | 1.62 | 1.75 |
| Ionisation energy (ev) [I] | 11.3 | 8.2 | 7.8 | 7.3 | 7.4 |
| [II] | 24.4 | 16.3 | 15.9 | 14.6 | 15.0 |
| Electronegativity | 2.5 | 1.9 | 1.8 | 1.7 | 1.7 |
| mp ( C) | > 3550 | 1410 | 937 | 232 | 327 |
| bp ( C) | 4827 | 2355 | 2830 | 2260 | 1744 |

{The values are not to be remembered, these are given to show the variations}

**Note :**

(i) The radii of Si and Ge are very similar due to d-block contraction. Also Sn and Pb have almost similar radii due to lanthanide contraction.

(ii) Ionisation energy vary as C > Si ~ Ge > Sn < Pb. Silicon and Ge have comparable IE due to similarity in their radii.

The radius of Sn is smaller than Pb but Pb has higher IE than Sn. It is due to higher Z* for Pb as F – orbital is least shielding.

## Oxidation states and Bonding

Group–14 elements show variable oxidation states of + 2 and + 4. The stability of + 2 state is very stable for Pb. It is due to inert pair effect.

| | +4 | +2 |
|---|---|---|
| C | | |
| Si | | |
| Ge | | |
| Sn | | |
| Pb | ↓ | ↓ |
| | Stability decreases | Stability increases |

Carbon and Si have high ionisation energy. Therefore, they are covalent in their compounds.

Tin and Pb form ionic compounds having appreciable covalent nature. It is because Sn and Pb are not very large and have 18e core.

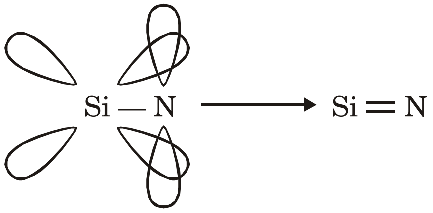
Carbon and Si differ widely in their bonding pattern. It is because of the following reasons :

| Property | C | Si |
|---|---|---|
| Valence orbitals and electrons | $2s^2 2p^2$ | $3s^2 3p^2$ $(3d^0)$ |
| Number of bonds or coordination number | 4 only | More than 4 (5 or 6) |
| $\pi$-bonding | Very effective (p–p) $\pi$ bonding | No (p-p) $\pi$ bonding but (p – d) $\pi$ bonding. Using vacant 3d orbitals |
| C–C bond energy | 356 KJ $mol^{-1}$ | 226 KJ $mol^{-1}$ |
| Catenation property | Very high | Low, however, heterocatenation is pronounced due to strong Si – O bond (368 KJ $mol^{-1}$) |

The features of certain Si compounds having Si – O and Si – N bonds are explained by (d – p) $\pi$ bonding. For example,

| | |
|---|---|
| $(CH_3)_3N$ | triangular Pyramidal |
| $(SiH_3)_3N$ | triangular Planar |
| $(SiH_3)_2O$ | $<$ (Si – O – Si) $\approx$ 144 |

Trisilylamine, $(SiH_3)_3N$, is trogonal planar due to (d – p) $\pi$ bonding involving filled N $2p_z$ orbital and vacant Si $3d_{xy}$ orbitals.



The large angles at O of disilyl ethers $(R_3Si)_2O$, is due both to electronic and steric factors.

## Catenation

The property of self-linking is known as catenation. It depends mainly on bond energy. The C–C bond energy is very high. Therefore, C has maximum catenation property. The bond energy decreases down the group and so also the catenation property, i.e.

$$C >> Si > Ge \approx Sn >> Pb$$

| Bond | Bond Energy (KJ mol$^{-1}$) |
|---|---|
| C – C | 356 |
| Si – Si | 210 – 250 |
| Ge – Ge | 190 – 210 |
| Sn – Sn | 105 – 145 |

Sulphur also shows catenation because S – S bond energy is relatively high. Boron, Si, P shows heterocatenation as B – O, Si – O and P – O bond energies are high.

| Bond | Bond Energy (KJ mol$^{-1}$) |
|---|---|
| S – S | 226 |
| B – O | 560 – 790 |
| Si – O | 368 |
| P – O | ~ 340 |

## Allotropy and structure

All the elements are solid. Carbon and Sn only show allotropy.

Carbon has three crystalline allotropes :

(a) Graphite

(b) Diamond and

(c) Fullerene.

Tin is found as $\alpha - Sn$, and $\beta - Sn$.

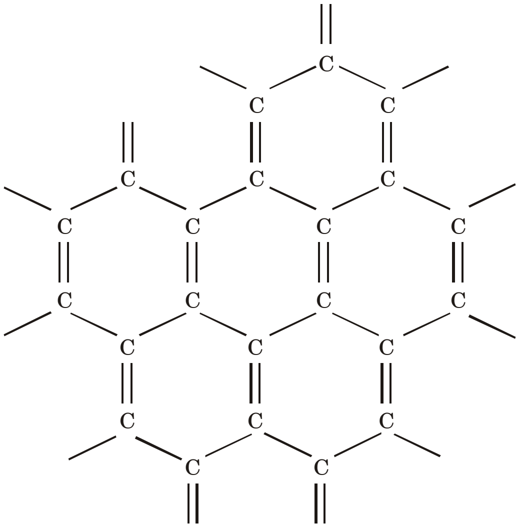
| Element | Allotrope | Structure |
|---|---|---|
| C | Graphite<br>Diamond<br>Fullerence | Layer structure<br>Cubic structure<br>Carbon cluster |
| Si | -- | Diamond structure |
| Ge | -- | Diamond structure |
| Sn | $\alpha - Sn$<br>$\beta - Sn$<br>$\gamma - Sn$ | Diamond structure<br>Cubic structure<br>Simple cubic structure |
| Pb | -- | ccp |

## (a) Graphite

It is soft dull looking greasy substance and is electrical conductor. Graphite has two-dimensional layer structure.

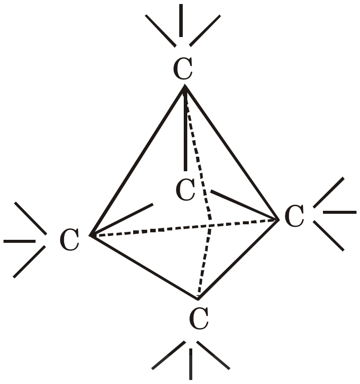
Layers are made up of $sp^2$ hybridized C atoms. Each C is joined with three other C atoms through $\sigma$ – bonds forming hexagonal rings. Each C is left with its fourth valence electron in a p-orbital. They overlap and form $\pi$ bonds. These $\pi$ bonds are delocalized. Therefore, all C – C bond distances in graphite are equal (1.415 Å). Sheet to sheet distance in graphite is 3.35Å. It is known as C – dimension. Layers are joined by weak Van der waals force.

The weak force between layers allows one layer to slide over the other. It imparts softness to graphite. It is, therefore, used in pencils for writing. Due to delocalized $\pi$ electrons graphite is a conductor (though along the sheet not perpendicular to it). Hence, it is used as electrode.



## (b) Diamond

It is colourless transparent hardest substance known and is insulator. Cut diamond is sparkling solid (due to refraction). Diamond has cubic unit cell. Each C is $sp^3$ hybridised and is joined with four other C atoms through σ – bonds.



As C – C bond energy (356 KJ $mol^{-1}$) is very high and diamond has a giant structure, it is very hard. This structure is responsible for its insulator property.

Density of diamond (3.51 g/cc) is greater than graphite (2.22g/cc). This shows that to convert graphite into diamond, pressure must be applied. There is the equilibrium.

$$\text{Graphite} \underset{300\text{ k}}{\overset{15000\text{ atm}}{\rightleftharpoons}} \text{diamond}$$

Graphite can be transformed into diamond at a reasonable rate at high pressure and ~ 300 K in the presence of a transition metal (Fe, Cr, Pt) catalyst.

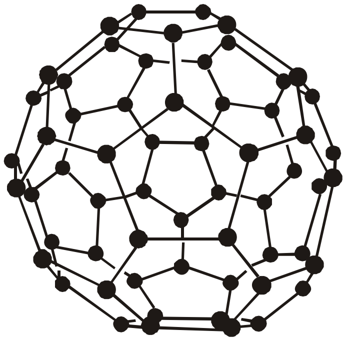
## (c) Fullerenes

Fullerenes are carbon clusters having cage like structures.

Fullerenes $C_{60}$ and $C_{70}$ can be separated by chromatogrphic method over alumina. Many other fullerenes also exist such as $C_{32}$, $C_{50}$, $C_{76}$, $C_{84}$ etc.

The fullerenes $C_{60}$ is well known. It has a soccer ball structure which contains 12 five – membered and 20 six membered rings. The rings are unsaturated. The $C_{60}$ fullerene is called Buckminster fullerene in honour of American architect Robert Buckminster Fuller.

### Structure of $C_{60}$



Silicon exists only in diamond structure. A graphite like structure for Si is not possible because it has no propensity to form (p – p)π bond.

Tin exists in three forms, α – Sn, β – Sn and γ – Sn.

$$\underset{\substack{\text{(Grey)}\\ \text{(Non – metallic}\\ \text{diamond structure)}}}{\alpha \text{ — Sn}} \longrightarrow \underset{\substack{\text{(White)}\\ \text{(Metallic distorted}\\ \text{close packed)}}}{\beta \text{ — Sn}} \longrightarrow \underset{\substack{\text{(Brittle)}\\ \text{(Rhombic)}}}{\gamma \text{ — Sn}}$$

### Semiconductor property of Si and Ge

Silicon and to a less extent Ge are important semiconductor materials. Pure Si and Ge are non-conductor of electricity. However, when they are droped with group – 13 or group – 15 elements, they become semiconductor.

(i) Ge dopped with In

Ge – $4s^2 4sp^2$

In – $5s^2 5p^1$

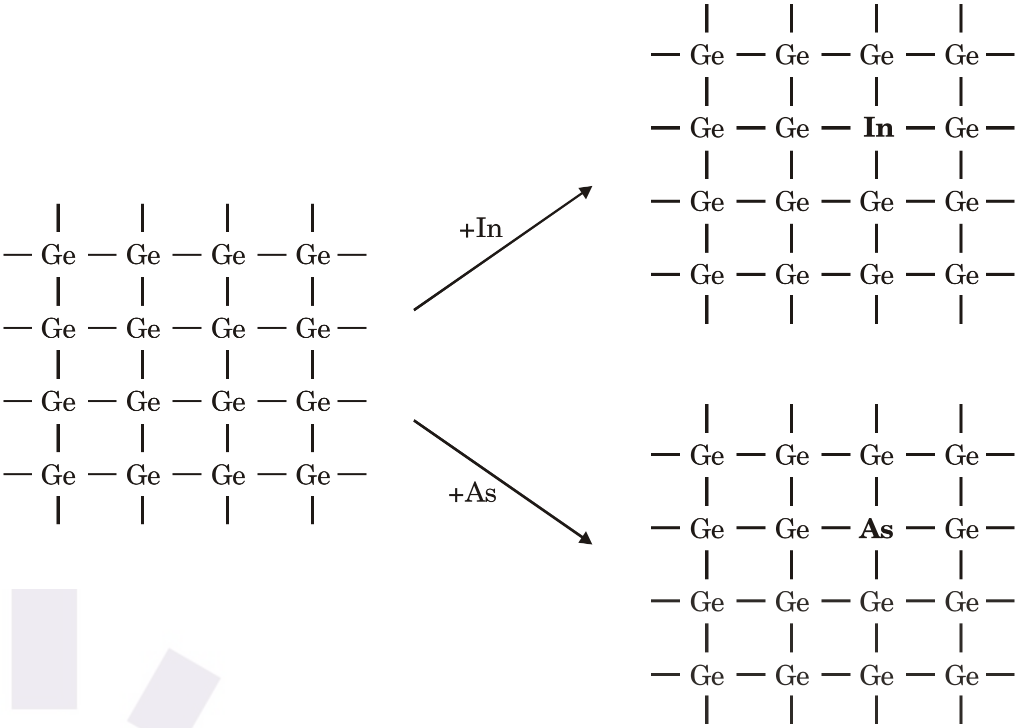
When Ge is dopped with In, there is one electron less at In site. There develops a positive hole in the lattice which makes Ge conducting. Such a semiconductor is called p – type (positive – type) semiconductor.

(ii) Ge dopped with As

Ge – $4s^2 4p^2$

As – $4s^2 4p^3$

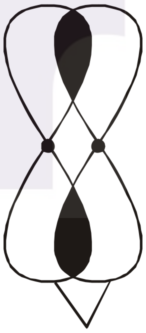
When As is dopped in Ge, there is one electron excess at As site. Due to this excess electron Ge conducts electricity. Such a semiconductor is called n – type (negative type).



## Multiple Bonding

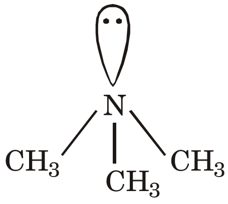
In Group 14, carbon is the only element capable of forming comparatively stable multiple bonds with another C atom and also with N, O etc. Examples are alkenes (> C = C <), alkynes (– C ≡ C –), imines (> C = N –), nitriles (– C ≡ N –), ketones (> C = O), etc. None of the other elements of the group forms stable compounds containing multiple bonds. Recently, some success has been achieved in synthesising compounds with > Si = Si < and Si = C < double bonds, but their details are beyond the scope of this course. Stoichiometric analogues like $SiO_2$, $SnO_2$ and $(Me_2SiO)_n$ are known which are giant macromolecules containing M–O–M linkages.

The tendency of formation of multiple bonds easily, in case of carbon, is because of the high bond energy and a small atomic radius of carbon is compared to other elements of the group. So its p-orbitals can approach the p-orbitals of the other C, O or N atom for an effective overlap essential for π-bond formation.

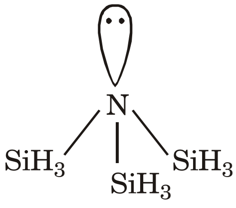


p-orbitals

- Silicon also uses d-orbitals in multiple bonding, **In case of $N(CH_3)_3$, geometry is pyramidal, but in case of $N(SiH_3)_3$ it is planar. It is due to the fact that in the latter, the lone pair of N-atom is transferred to empty d-orbitals of silicon (pπ–dπ overlapping) :**



pyramidal
(no π bonding)



planar
($p_\pi$–$d_\pi$ bonding)

- The normal valency of the elements is four, but apart from carbon, the elements can make more than four bonds. This is because they make use of a set of d-orbitals in bonding. Thus availability of d-orbitals (empty but electrons of $ns^2$ and $np^2$ can be excited into this) is responsible for the ability of the elements, except carbon, to make complex ions such as $SiF_6^{2-}$.

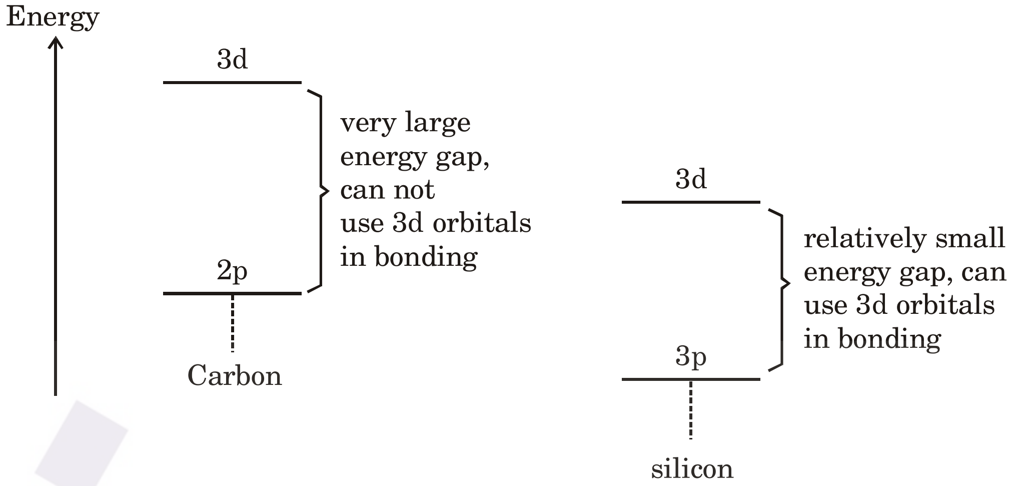


Fig. Energy difference between 2p and 3d energy levels in carbon and between 3p and 3d energy levels in silicon.

- The main chemical differences between silicon and carbon are :
  - Si does not form stable double bonds
  - Si does not form very stable Si – Si bonds.
  - Si has vacant 3d-orbitals in its valence shell into which it can accept electrons from donor atoms.
- Some carbon compound are less reactive than the corresponding compounds of the other members of the group. $CCl_4$ has no interaction with $H_2O$ (hydrolysis) whereas $SiCl_4$ does by use of empty 3d-orbitals.
- All the elements give hydrides. Carbon, of course gives an immense number, but silicon and germanium also show a wide variety.

| | |
|---|---|
| $CH_4$ | methane (alkane) |
| $SnH_4$ | Stannane |
| $SiH_4$ | silane |
| $PbH_4$ | plumbane |
| $GeH_4$ | germane |

Carbon hydrides will not ignite in air unless a flame is put to them. Apart from silane, $SiH_4$, the silicon hydrides are less well behaved. $Si_3H_8$ is spontaneously flammable in air :

$$Si_3H_8(l) + 5O_2(g) \longrightarrow 3SiO_2(s) + 4H_2O(l)$$

Alkanes as well as silane are not hydrolysed however, traces of alkali converts silane into hydrated silica $SiO_2 . nH_2O$.

- As we descend the group, acidic nature of the oxides decreases and basic nature of the oxides increases.

| **Oxides** | **Nature** | **Oxides** | **Nature** |
|---|---|---|---|
| $CO, CO_2$ | acidic | $SnO, SnO_2$ | amphoteric |
| $SiO_2$ | acidic | $PbO, PbO_2$ | basic |
| $GeO, GeO_2$ | amphoteric | $Pb_3O_4$ | amphoteric |

Si, Ge, Sn and Pb form oxides $MO_2$ . $SiO_2$ is infinite three-dimensional network solid of silicon and oxygen atoms connected by single covalent bonds. $GeO_2$, $SnO_2$ and $PbO_2$ are all solids and exist in several modifications.

### Example 1

**Why is graphite a better electrical conductor than diamond and why does the conductivity of graphite depend on direction ?**

**Solution :**

Graphite has a two-dimensional sheet like structure in which each carbon atom uses $sp^2$ hybrid orbitals to form trigonal planar $\sigma$ bonds to three neighbouring carbon atoms. In addition, each carbon atom uses its remaining p-orbital, perpendicular to the plane of the sheet, to form a $\pi$ bond. Because each carbon atom must share its $\pi$ bond with its three neighbours, the $\pi$ electrons are delocalised and are free to move in the plane of the sheet. As a result, the electrical conductivity of graphite in a direction parallel to to the sheet is about $10^{20}$ times greater than the conductivity of diamond. The conductivity of graphite perpendicular to the sheets of carbon atoms is lower because electrons must hop from one sheet to the next. The substance or crystal that show different properties in different directions is called **anisotropic.**

### Example 2

**Why elemental silicon does not form graphite like structure as carbon does ? Explain.**

**Solution :**

This is due to the reluctance of silicon to form $p\pi$-$p\pi$ multiple bonds because of large size of silicon atom. Hence Si exists only in diamond form.

## Compounds of Carbon and Silicon

1. **Carbides :** Binary compounds of carbon are called carbides, SiC, $CaC_2$, $Al_4C_3$ etc. Three types are found :
   (i) Ionic or salt like carbides,

(ii) Covalent carbides,

(iii) Interstitial carbides.

**(i) Ionic carbides**

Three types of ionic carbides are found :

(a) Methanides,

(b) Acetylides,

(c) Propynide.

Ionic carbides are decomposed by water (or dil. Acid) at room temperature. The liberated anions are also immediately hydrolysed. It affords a method of classification.

**(a) Methanides : ($C^{-4}$ unit)**

Those carbides which are hydrolysed to give $CH_4$ are called methanide. They are supposed to contain $C^{-4}$ unit.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al\ (OH)_3 + 3CH_4$$

**(b) Acetylides : ($C_2^{-2}$ unit)**

Those which are hydrolysed to $C_2H_2$ are called acetylides. They are common and formed by Group – 1, Group – 2, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Ag, Al and La metals.

| | |
|---|---|
| Gr – 1<br>Cu, Ag | $M_2C_2$ |
| Gr – 2<br>Zn, Cd | $MC_2$ |
| Al, La | $M_2(C_2)_3$ |

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_2(C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C_2H_2$$

**(c) Propynide : ($C_3^{4-}$ unit)**

Such carbides hydrolyse to propyne

$$Mg_2C_3 + H_2O \longrightarrow 2Mg(OH)_2 + CH_3 - C \equiv CH$$

**(ii) Covalent carbides**

Elements which compares with C in size and electronegativity form such carbides, Be, B, Si etc. Boron and Si carbides are more important.

$$SiO_2 + 2C \xrightarrow{\Delta} Si + 2CO$$

$$Si + C \xrightarrow{\text{High temp}} SiC$$

Silicon carbide (SiC) is called carborundum. It is very inert and extremely hard.

$$B_2O_3 + C \xrightarrow{\text{High temp}} B_4C$$

$B_4C$ is a also very hard, infusible and inert. It is used to make bulletproof clothing.

These covalent carbides (or $\alpha - Al_2O_3$) are comparable in hardness to diamond (Moh's scale).

$$\text{Hardness} \longrightarrow \text{Diamond} > B_4C > SiC > \alpha - Al_2O_3$$

**(iii) Interstitial carbides**

Transition metals form such carbides, in which C atoms occupy octahedral voids. Such materials are very hard, electrically conducting and have very high mp. For example : TiC, ZrC, MoC, WC etc.

## 2. Oxides

Electrons of this form oxides of the type MO and $MO_2$. Carbon forms suboxides also, e.g., $C_3O_2$.

| Oxides | C | Si | Ge | Sn | Pb |
|---|---|---|---|---|---|
| MO | CO<br>(neutral) | X | GeO | SnO<br>ampoteric | PbO → |
| $MO_2$ | CO | $SiO_2$ | $GeO_2$ | $SnO_2$<br>ampoteric | $PbO_2$ → |
| | ← acidic → | | | | |

**(a) Carbon monoxide (CO)**

It forms many important gaseous mixtures of industrial use

| | | |
|---|---|---|
| (i) | Water gas or synthesis gas | $CO + H_2$ |
| (ii) | Producer gas | $CO + N_2$ |
| (iii) | Coal gas | $CO + H_2 + CH_4 + CO_2$ |

→ CO is a neutral oxide.

→ Carbon monoxide has a triple bonded C atom, one s and two p bonds (best explained by MO model).

→ CO, however, is a strong ligand towards transition metals and form variety of complexes known as carbonyls, Ni $(CO)_4$, $Fe(CO)_5$ etc. They are stable due to synergic bonding.

→ CO is very toxic and rapidly forms a bright red complex with haemoglobin of blood. Thus preventing haemoglobin to carry oxygen to cells, using oxygen deficiency to unconsciousness and then death.

**(b) Carbon dioxide ($CO_2$)**

→ $CO_2$ is acidic oxide

→ $CO_2$ is biologically important

(i) Maintains pH of blood, due to the equilibrium

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

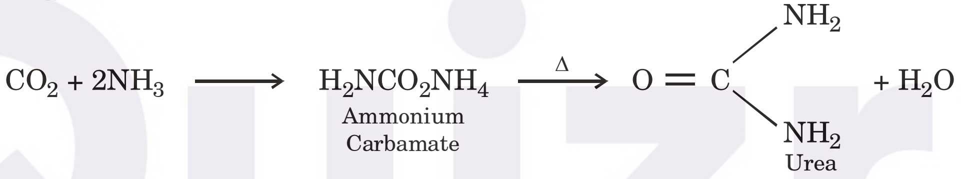
(ii) Main components of photo synthesis

$$6CO_2 + 6H_2O \xrightarrow[\text{Sun light}]{\text{Chlorophyll}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + 6O_2$$

(iii) The reverse process of the above takes place in the process of respiration.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy}$$

→ $CO_2$ is used in the synthesis of urea

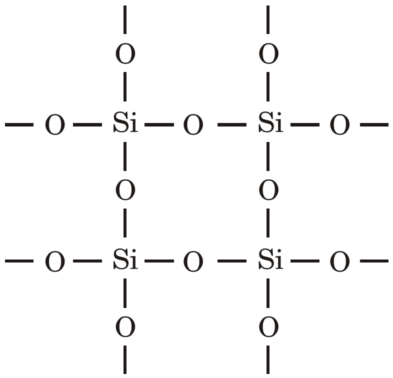


$$CO_2 + 2NH_3 \longrightarrow \underset{\text{Ammonium Carbamate}}{H_2NCO_2NH_4} \xrightarrow{\Delta} \underset{\text{Urea}}{O=C(NH_2)_2} + H_2O$$

→ $CO_2$ is gas at NTP and has the structure O = C = O. The (p – p)π bonding is very effective. Therefore, even in solid state discrete $CO_2$ molecules exist. The intermolecular forces are weak Van der Waals' force.

→ Solid $CO_2$ is called 'dry ice' or 'cardice'.

Silicon dioxide, $SiO_2$, unlike $CO_2$ is a solid. The (p – p) π bonding is not effective in $SiO_2$ like $CO_2$. It is due to larger size of Si and more core electrons (8e) in Si. Therefore, to stabilize; $SiO_2$ contains a continuous lattice of Si and oxygen atoms joined by covalent bonds. Each Si is $sp^3$ and is joined with 4 O + atoms and each O – atom with two Si – atoms. A macromolecule is formed, hence $SiO_2$ is a solid.



## Halides $MX_2$ and $MX_4$

Group – 14 elements form tetrahalides of the type $MX_4$ (X = F, Cl, Br, I) except $PbI_4$.

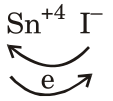
$PbI_4$ does not exist due to strong oxidizing power of $Pb^{+4}$ and reducing nature of $I^-$ ion. The $Pb^{+4}$ is strong oxidizing agent due to greater stability of $Pb^{+2}$ (inert pair effect).

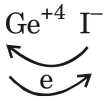
Thus, $MX_4$, [M = C, Si, Ge, Sn, X = F, Cl, Br, I]

Germanium, Sn and Pb also for $MX_2$. The stability of $MX_2$ is maximum for $Pb^{+2}$.

$SnF_2$ is sparingly soluble in water and is used in fluoride containing tooth pastes.

The $MX_4$ halides are all colourless except $GeI_4$ and $SnI_4$ which are bright orange solids. Colour in these halides is due to charge transfer.





All tetrachlorides except $CCl_4$ are hydrolysed by water.

Carbon tetrachloride is not hydrolysed because :

(a) carbon in $CCl_4$ is coordinatively saturated

(b) C – Cl bond is less polar

$X_C = 2.5$, $X_{Cl} = 3.0$, $\Delta\chi = 0.5$

Silicon tetra chloride ($SiCl_4$) is extensively hydrolysed. It is because :

(a) Si – Cl bond is more polar

$X_{Si} = 1.8$, $X_{Cl} = 3.0$, $\Delta\chi = 1.2$

(b) Si in $SiCl_4$ can increase its coordination number by using 3d orbitals

The tetra halides of Si, Ge, Sn and Pb can increase their coordination numbers by using d orbitals and can form haloanions.

$$SiF_4 + 2F^- \longrightarrow SiF_6^{2-}$$

$$SnCl_4 + 2Cl^- \longrightarrow SnCl_6^-$$

The hexacoordinated halo anions are octahedral having $sp^3d^2$ hybridised central atom (Si).

---

### Example 3

**$CCl_4$ can not be hydrolysed but $SiCl_4$ can be. Why ?**

**Solution :**

Vacant d orbital is not present in carbon so it can not extend its configuration like Si. Therefore it can not be hydrolysed.

**Example 4**

**$SiCl_2$ is solid while $SiCl_4$ is liquid at room temperature. Why ?**

**Solution :**

$SiCl_2$ is more ionic than $SiCl_4$ by Fajan's rule. Therefore it has greater m.p. so it is solid at room temperature while $SiCl_4$ is liquid.

---

## Hydrides :

All element of this group form hydrides.

Carbon forms a large number of chain and ring compounds due to high catenation property. They are :

| | |
|---|---|
| Alkanes | $C_nH_{2n+2}$ |
| Alkenes | $C_nH_{2n}$ |
| Alkynes | $C_nH_{2n-2}$ |

Cyclo alkanes and cycloalkynes

Aromatic hydrocarbons ($C_6H_6$)

Silicon (others also) form saturated hydrides only which are called silanes, $Si_nH_{2n+2}$ (Si ~ 8).

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + AlCl_3 + LiCl$$

## Silicons :

They are organosilicon polymers having empirical formula approximately $R_2SiO$. Polymers are very stable due to strong Si – O and Si – C bonds. Silicones can be prepared as oils, resins, plastics etc. They are :

→ Inert

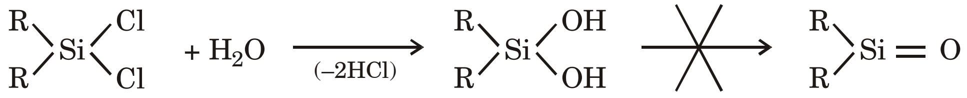
→ Water repellent

→ Heat resistant

→ Electrical insulator

All these properties make silicones very useful.

Hydrolysis of alkyl chlorosilanes produces products having Si – OH bonds. They do not dehydrate like gem diols (of C).

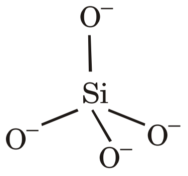


## Silicates

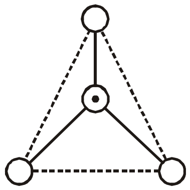
Silicates are solids having Si – O bonds. Most of the rocks and even soil contain silicates. Alkali metal silicates are water soluble. They are made on a large scale as

$$Na_2CO_3 + SiO_2 \xrightarrow{\sim 1500°C} Na_4SiO_4,\ (Na_2SiO_3)_n \text{ etc.} + CO_2\uparrow$$

They are used in detergents. The concentrated aq. solution of $Na_4SiO_4$ is solid like and as known as water glass. Variety of silicates are found but in all the basic unit is the $SiO_4$ tetrahedron.



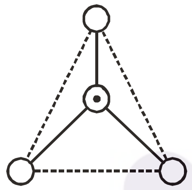
or



Each O – atom carries one unit negative charge. In polymeric silicates $SiO_4$ units share O – atoms(s). It provides a way of classification.

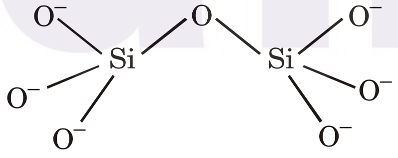
### Orthosilicates (Mononuclear silicates)

These are silicates having discrete $SiO_4^{4-}$ ions. Metal ions are surrounded by O–atoms.



### Pyrosilicates ($Si_2O_7^{-6}$) :

When two $SiO_4$ units share only one O – atom pyrosilicates, $Si_2O_7^{-6}$, are formed. These are also discrete units.



## Glass

Solids are most stable in crystalline form. However, if a solid is formed rapidly (for example, when a liquid is cooled quickly), its atoms or molecules do not have time to align themselves and may become locked in positions other than those of a regular crystal.

If we mix sodium carbonate and calcium carbonate with sand and fuse the mixture at about 1500 C, we get a liquid mixture of sodium and calcium silicates. When this mixture is cooled, it becomes viscous and eventually ceases to flow; it becomes solid –called glass. Glass is thus super-cooled liquid (solid solution). Amorphous solids, such as glass, lack regular three dimensional arrangement of atoms. Glass thus refers to an optically transparent fusion product of inorganic materials that has cooled to a rigid state without crystallising.

$$Na_2CO_3 + SiO_2 \xrightarrow{\Delta} Na_2SiO_3 + CO_2$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

By varying the proportions of the three basic ingredients, and by adding other substances, we can alter the properties of the glass as given :

| | | |
|---|---|---|
| • Calcium-alkali silicate glass | – | normal domestic glass for windows |
| Sodium silicate | – | soda glass used in cheap laboratory glassware |

- Fining agents such as $NaNO_3$ or $As_2O_3$ are added to remove bubbles.
- Decolorising agents may be added to eliminate impurities and to obtain colourless glass. $CaF_2$ is sometimes added to make opal glass.

Glass is attacked by HF and this property is used to make marking on the glass (etching)

$$\underset{\text{(in glass)}}{Na_2SiO_3} + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

$$CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

HF, however does not attack wax. The portion of the glass on which etching is to be done is covered with wax layer. Markings are carved on the wax layer with a pin and HF is poured on the carved parts and left for sometime. After washing with water, wax is removed and permanent marking is obtained.

---

**Example 5**

**The standard free energies of formation of $B_2O_3$ and MgO are – 1194 kJ $mol^{-1}$ and – 569 kJ $mol^{-1}$ respectively. Should it be possible to prepare boron by reacting $B_2O_3$ with magnesium ?**

**Solution :**

$$B_2O_3 + Mg \longrightarrow 2B + 3MgO$$

$$\begin{aligned} \Delta G &= \Delta G_{product} - \Delta G_{reactant} \\ &= 3\Delta G_f\,(MgO) - \Delta G_f\,(B_2O_3) \\ &= 3(-569) - (-1194) \\ &= -513 \text{ kJ mol}^{-1}\ [\Delta G_f\,(\text{element}) = 0] \end{aligned}$$

The negative sign of $\Delta G$ shows that the reaction should be spontaneous. (However, the reaction is initially endothermic when two reactants are heated.)

### Example 6

**(i) What type of bonding holds the layer in graphite ?**

**(ii) Why will graphite conduct electricity well in a direction parallel to the planes of hexagons, but not at all well in a direction perpendicular to the planes ?**

**(iii) What is the name we give to crystal or substances, that show different properties in different directions ?**

**Solution :**

(i) Van der Waals bonding

(ii) The delocalised orbitals in graphite lie parallel to the planes and electrons can move along the planes making use of these orbitals; conduction is good parallel to the planes. There is no overlap of orbitals perpendicular to the planes, so conduction is poor in this direction.

(iii) They are anisotropic.

---

### Example 7

**If you had a mixture of CO and $CO_2$, how would you find out relative proportions of the two gases in the mixture ?**

**Solution :**

**Method I :** Mixture of $CO_2$ is run into $Ca(OH)_2$ solution. $CO_2$ is absorbed by $Ca(OH)_2$ and thus residual volume will be that of CO.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

**Method II :** Mixture of CO and $CO_2$ is passed over heated charcoal :

$$CO_2 + C \longrightarrow 2CO$$

Increase in volume will be due to $CO_2$. By measuring total volume after passing over heated charcoal, composition of mixture of CO and $CO_2$ can be determined.

---

### Example 8

**CO and $CN^-$ ions are highly poisonous. A sign that some one has been poisoned by either of these two chemicals is that the person's blood changes colour. They both have the effect of preventing oxygen being taken up by the blood stream. What might happen to haemoglobin to stop oxygen being taken up ?**

**Solution :**

CO and $CN^-$ ions are able to bond more strongly to the iron atom in haemoglobin than can oxygen. If you were to breathe in CO for any length of time, your haemoglobin would become saturated with CO molecules rather than oxygen. As a result, all the body processes that rely on a supply of oxygen gradually cease. Death is the result.

## Example 9

**What would you expect to happen when :**

**(a) Tin is heated with a concentrated aqueous solution of sodium hydroxide**

**(b) Sulphur dioxide is passed over lead dioxide**

**(c) Carbon disulphide is shaken with aqueous sodium sulphide**

**(d) Dichlorosilane is hydrolysed by water**

**(e) 4 mol of $ClCH_2SiCl_3$ react with 3 mol of $LiAlH_4$ in diethyl ether solution ?**

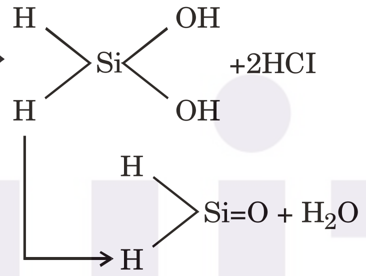
**Solution :**

(a) $Sn + 2OH^- + 4H_2O \longrightarrow [Sn(OH)_6]^{2-} + 2H_2$

(b) $PbO_2 + SO_2 \longrightarrow PbSO_4$

(c) $CS_2 + Na_2S \longrightarrow \underset{\text{sodium thiocarbonate}}{Na_2CS_3}$

(d) $SiH_2Cl_2 + 2H_2O \longrightarrow$



(e) $4ClCH_2SiCl_3 + 3LiAlH_4 \longrightarrow 4ClCH_2SiH_3 + 3LiCl + 3AlCl_3$

---

## Example 10

**Suggest syntheses (starting from deuterium oxide as the only source of deuterium) for:**

**(a) $B_2D_6$ (b) $B(OD)_3$ (c) $B_3N_3D_6$ (d) $B(CH_2CH_2D)_3$.**

**Solution :**

(a) $P_2O_5 + 3D_2O \longrightarrow 2D_3PO_4$

$Mg_3B_2 + 2D_3PO_4 \longrightarrow Mg_3(PO_4)_2 + B_2D_6$

(b) $B_2O_3 + 3D_2O \longrightarrow 2B(OD)_3$

(c) $Mg_3N_2 + D_2O \longrightarrow ND_3 + Mg(OD)_2$

$2ND_3 + B_2D_6 \longrightarrow [D_2B(ND_3)_2)][BD_4] \xrightarrow{\Delta} B_3N_3D_6$

(d) $6CH_2 = CH_2 + B_2D_6 \longrightarrow 2B(CH_2CH_2D)_3$

## Example 11

**Explain the following :**

**(a) Boron does not usually form a cation :**

B has

$(IE)_1 = 801$ kJ mol$^{-1}$, $(IE)_2 = 2427$ kJ mol$^{-1}$,

$(IE)_3 = 3659$ kJ mol$^{-1}$

⇒ Thus, the total energy required to give $B^{3+}$ ions is far more than that which would be compensated by lattice energies of ionic compounds or hydration of such ions in solution. Thus formation of cation (like $B^{3+}$) is not possible.

**(b) The polarity of B–X bonds is in the order : B–F > B–Cl > B–Br but Lewis acidicity shows the sequence : $BF_3 < BCl_3 < BBr_3$.**

⇒ With increase in polarity of B–X bond, acidity also increases and should be thus in the order :

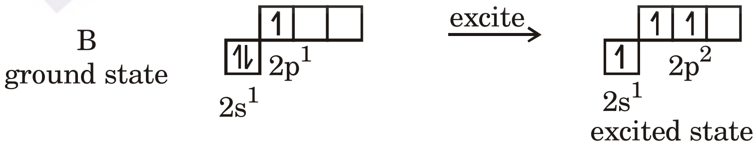
$$BF_3 > BCl_3 > BBr_3$$

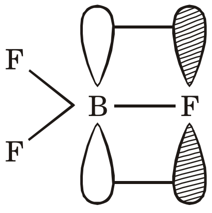
But Lewis acidity is in reverse order :

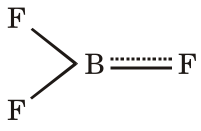
$$BF_3 < BCl_3 < BBr_3$$

There is lateral overlap of the vacant 2p orbital of B with one completely filled orbital of F leading to pπ-pπ bonds between B and F. This B–F bond thus acquires double bond character. This also leads to compensate electron deficiency of boron and thus Lewis acid character of $BF_3$ is reduced. This pπ-pπ bonding decreases going from $BF_3$ to $BBr_3$ and thus Lewis acidic nature increases in the order :

$$BF_3 < BCI_3 < BBr_3$$







**(c) Al and Ga are trivalent in their compounds but in case of Tl, monovalent compounds are the most stable. Why ?**

⇒ It is due to 'inert pair' effect due to which stability of + 3 state decreases and that of + 1 state increases while going down the group (in this case Group 13)

$$Al^{3+} > Ga^{3+} > In^{3+} > TI^{3+}$$

(most stable)

$$Al^{+} < Ga^{+} < In^{+} < TI^{+}$$

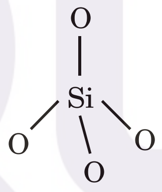
(most stable)

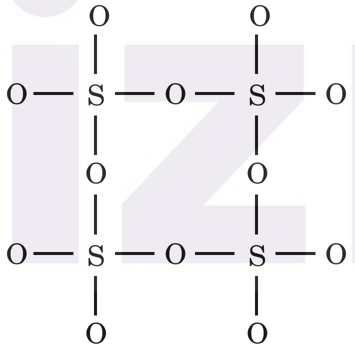
**(d) $CO_2$ is a gas but $SiO_2$ is a solid :**

⇒ Carbon and silicon (Group 14, IVA) have four valence electrons. We might expect carbon and silicon to form oxides with similar properties. In $CO_2$ the ability of C and O atoms to form π bonds through the side-wise overlap of their 2p orbitals is strong. The result is strong C–to–O double bonds and a very stable triatomic molecule.

$$O{=}C{=}O$$

Silicon, being in third period, would have to use 3 p orbitals to form double bonds with oxygen. The side-wise overlap of these orbitals with the 2p orbitals of oxygen is too limited for π bond formation. From an energy stand point, a stronger bonding arrangement results if the Si atoms from four single bonds with O atoms (bond energy : 464 kJ/mol) rather than two double bonds (bond energy : 640 kJ/mol) since each O atom must be simultaneously bonded to two Si atoms, the result in a network of –Si–O–Si–bonds and thus a hard (giant) solid :

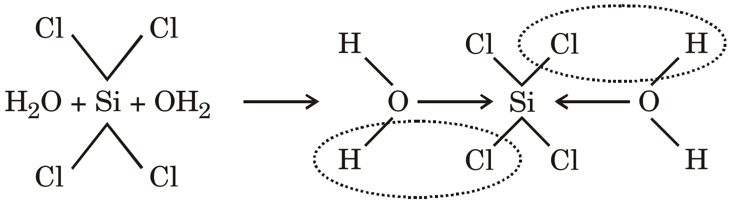




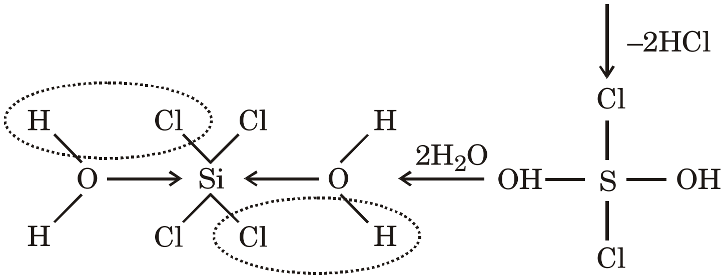
**(e) $SiCl_4$ is hydrolysed but $CCl_4$ is inert to hydrolysis :**

⇒ $SiCl_4$ and $CCl_4$ are covalent compounds. Carbon has maximum covalency of four while silicon has six. Thus $CCl_4$ is inert towards water and is not hydrolysed but $SiCl_4$ can coordinate with 2 mol of $H_2O$ molecules and is thus readily hydrolysed :

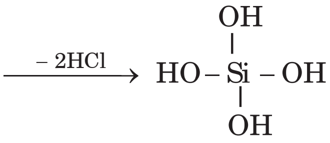
$$SiCl_4 + 2H_2O \longrightarrow Si(OH)_4 + 2HCl$$



Silicon with covalency six



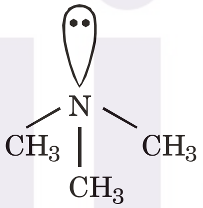
Silicon with covalency six



$$\xrightarrow{-2HCl} HO-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}-OH$$

**(f) $(SiH_3)_3N$ is planar while $(CH_3)_3$ N is pyramidal :**

⇒ In case of $(CH_3)_3N$, lone pair on N and three covalent bonds with $CH_3$ groups results in $sp^3$ hybridisation but lone pair-bond pair repulsion causes distortion hence gives pyramidal structure :



But in case of $(SiH_3)_3N$, lone pair on the nitrogen is transferred to the empty d-orbitals of silicon ($p_\pi - d_\pi$ overlap) thereby causing planarity of unit.

---

### Example 12

**$AlF_3$ is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of $BF_3$, $AlF_3$ is precipitated. Write the balanced chemical equations.**

**Solution :**

$$3KF + AlF_3 \longrightarrow K_3AlF_6$$

$$K_3AlF_6 + 3BF_3 \longrightarrow AlF_3 + 3KBF_4$$

## Example 13

**$(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$. Explain.**

**Solution :**

In $(SiH_3)_3N$, the lone pair of electrons on nitrogen is involved in pπ–dπ back bonding, while such bonding is not possible $(CH_3)_3N$ as d-orbitals are not present in carbon. Hence, the lone pair of electrons on nitrogen in $(CH_3)_3N$ is available for donation to Lewis acids, exactly acting as stronger base.

---

## Example 14

**(i) A white precipitate (B) is formed when a mineral (A) is boiled with $Na_2CO_3$ solution.**

**(ii) The precipitate is filtered and the filtrate contains two compounds (C) and (D). The compound (C) is removed by crystallisation and when $CO_2$ is passed through the mother liquor left, (D) changes to (C).**

**(iii) The compound (C) on strong heating gives two compounds (D) and (E).**

**(iv) (E) on heating with cobalt oxide produces blue coloured substance (F). Identify (A) to (F) and give chemical reactions for the reactions at step (i) to (iv).**

**Solution :**

(i) The mineral (A) is colemanite, $Ca_2B_6O_{11}.\ 5H_2O$

$$Ca_2B_6O_{11} + 2Na_2CO_{3(aq)} \xrightarrow{\text{boiled}} \underset{\text{(B) Insoluble}}{2CaCO_3} + \underbrace{\underset{(C)}{Na_2B_4O_7} + \underset{(D)}{2NaBO_2}}_{\text{Soluble}}$$

(ii) (C), the borax is crystallized. The mother liquor consisting sodium metaborate is treated with $CO_2$.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

(iii) $$Na_2B_4O_7.10H_2O \xrightarrow{\text{heated}} \underset{\text{Anhydrous}}{Na_2B_4O_7} + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow[\text{heated}]{\text{strongly}} 2NaBO_2 + B_2O_3$$

(iv) $$CaO + B_2O_3 \xrightarrow{\text{heat}} \underset{\substack{\text{cobalt meta borate} \\ \text{(blue coloured)}}}{CO(BO_2)_2}$$

### Example 15

**$PbCl_4$ is less stable than $SiCl_4$. Why ?**

**Solution :**

Pb is more stable in + 2 stable due to inert pair effect while Sn is more stable in + 4 state as compared to $Pb^{+4}$.

## GROUP 15 ELEMENTS

Elements : N, P, As, Sb, Bi

Nitrogen and phosphorus are non-metals. The metallic character increases down the group due to lower I.E. and larger size. Hence, bismuth shows metallic character. The group state electronic configuration is $ns^2np^3$.

### Trends in Chemical Reactivity

Most common oxidation states shown by group 15 elements are – 3, + 3 and + 5. The stability of highest oxidation state (+ 5) decreases down the group.

The covalent character goes on decreasing as we move down the group in the sequence, P > As > Sb > Bi. This is due to increasing size of atom which refers to Fajan's rules.

Sb and Bi are the heavier elements of the group and form $M^{3+}$ cations due to decrease in ionization enthalpy.

In contrast to nitrogen, the phosphorus atom forms $p\pi{=}p\pi$ bonding and forms both cyclic and open chain compounds. Hence, it shows catenation.

As we move down the group there is a decrease is covalent character.

$$N > P > As > Sb > Bi$$

Nitrogen is chemically less reactive, due to high stability of its molecule. $N_2$ in which two nitrogen atoms are combined through a triple covalent bond ($N \equiv N$) of which one is sigma ($\sigma$) and two are pie ($\pi$) bonds, thus posses high bond strength (941.4 KJ $mol^{-1}$)

Nitrogen has one special feature that it can form $p\pi$-$p\pi$ multiple bonds with itself, carbon and oxygen due to its small size. In phosphorus rather $p\pi$-$p\pi$, $d\pi$-$p\pi$ is found as in $POX_3$.

### General Trends in Physical Properties

| Sr.No. | Property | Nitrogen | Phosphorus | Arsenic | Antimony | Bismuth |
|---|---|---|---|---|---|---|
| 1. | Configuration | $[He]2s\ 2p^3$ | $[Ne]3s^23p^3$ | $[Ar]4s^24p^3$ | $[Kr]5s^25p^3$ | $[Xe]6s^26p^3$ |
| 2. | Common oxidation state | – 3, + 3, + 5 | – 3, + 5, + 5 | + 3, + 5 | + 3, + 5 | + 3 |
| 3. | Atomic radius (pm) | 70 | 110 | 120 | 140 | 150 |
| 4. | First ionization | 1403 | 1012 | 947 | 834 | 703 |
| 5. | Electronegativity | 3.0 | 2.1 | 2.0 | 1.9 | 1.9 |

Since, it is not easy from energy consideration to gain three electrons to achieve stable noble gas configuration, the formation of the tri-negative ion ($M^{3-}$) is rare. But, nitrogen being the smallest and the most electronegative of all the members of the group, forms trivalent anion with reactive metals which have low ionisation energies. Thus, nitrogen forms ionic nitrides such as $Li_3N$, $Be_3N_2$, $Mg_3N_2$, $Ca_3N_2$. As the electronegativity of the other elements of the group, i.e., P, As, Sb and Bi, is low, most of their compounds are covalent in nature.

Nitrogen is not able to extend its coordination number beyond four, the other elements have coordination numbers of five as well as six. The extension of coordination number is due to the availability of d-orbitals in P, As, Sb and Bi, using which these elements can attain $sp^3d$ and $sp^3d^2$ hybridisation, e.g. in $PCl_5$ and $PCl_6^-$, respectively. Thus, nitrogen does not function as a Lewis acid whereas phosporus, arsenic antimony and bismuth do so. The hybrides of this group and their alkyl derivatives act as Lewis bases, forming a number of addition complexes, e.g., $NH_3 . BF_3$, $CaCl_2 . 4NH_2$, etc.

- Stability of + 3 state increases and that of + 5 state decreases going down the group due to “inert pair effect”, thus

  $Bi^{3+} > Sb^{3+} > As^{3+}$

  $Bi^{5+} < Sb^{5+} < As^{5+}$

  $Bi^{5+}$ salts are very rare and are good oxidising agents :

  $$Bi^{5+} + 2e^- \longrightarrow Bi^{3+}$$

  $As^{3+}$ salts are good reducing agents :

  $$As^{3+} \longrightarrow As^{5+} + 2e^-$$

- They form trihalide and penthalide (except N, which does not form $NCl_5$ etc.) As we go down the group, covalent nature decrease and ionic nature increases; thus $NCl_3$ and $PCl_3$ are covalent while $BiCl_3$ is ionic. This is also in accordance with Fajan’s rule : Smaller the size of cation, larger the size of anion, greater the charge then greater the polarising power and hence greater the covlalent nature. Halides are hydrolysed in water forming oxyacids or oxychlorides :

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$SbCl_3 + H_2O \longrightarrow \underset{\text{(orange ppt)}}{SbOCl \downarrow} + 2HCl$$

$$BiCl_3 + H_2O \longrightarrow \underset{\text{(white ppt)}}{BiOCl} + 2HCl$$

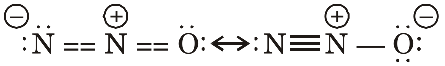
## Compounds of Nitrogen

### Oxides of N

**(i) Dinitrogen oxide (or nitrous oxide) $N_2O$**

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

**Structure :** It is isoelectronic to $CO_2$ and has linear structure. But unlike $CO_2$ it has dipole moment (0.16 D). It shows resonance



$$\overset{\ominus}{:\ddot{N}} = \overset{\oplus}{N} = \ddot{O}: \leftrightarrow :N \equiv \overset{\oplus}{N} - \overset{\ominus}{\underset{..}{\ddot{O}}}:$$

**(2) Nitric oxide (NO)**

⇒ Copper reacts with dil $HNO_3$ (8M) to form NO. It is reduction of $NO_3^-$

$$8HNO_3 + 3Cu \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

⇒ Commercially, NO is obtained by catalytic oxidation of $NH_3$ (ostwald process for $HNO_3$)

$$4NH_3 + 5O_2 \xrightarrow[\Delta]{\text{Pt catalyst}} 4NO + 6H_2O$$

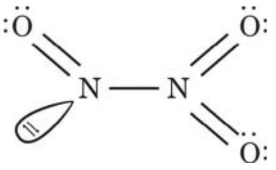
Nitric oxide is a good ligand and form variety of complexes with transition metals which are known as nitrosyls, $Na_2[Fe(CN)_5NO]$

**(3) Dinitrogen trioxide $N_2O_3$**

It can be obtained by mixing NO and $NO_2$ in equimolar quantities at low temperature.

$$NO + NO_2 \xrightarrow[\substack{\text{Temp.} \\ (-30°F)}]{\text{Low}} \underset{\text{(blue liq.)}}{N_2O_3}$$

In gaseous state it has the structure



The N – N distance is very large, 1.864Å

**(4) Nitrogen dioxide $NO_2$ ($N_2O_4$)**

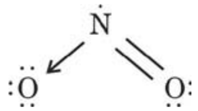
(i) Cu + conc. $HNO_3 \xrightarrow{\Delta} NO_2$

$$Cu + 4HNO_3 \xrightarrow{\Delta} Cu(NO_3)_2 + 2H_2O + 2NO_2$$

(ii) Di or trivalent metal nitrate decomposes on heating to $NO_2$

$$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \tfrac{1}{2}O_2$$

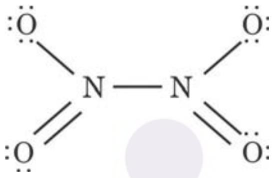
**Structure :** $NO_2$ is an odd electron (17 electrons) molecule and is paramagnetic. It has the structure



The unpaired electron ensures ready dimerisation to a diamagnetic colourless species $N_2O_4$ (dinitrogen tetraoxide).

$$2NO_2 \rightleftharpoons N_2O_4$$

$N_2O_4$ is planar

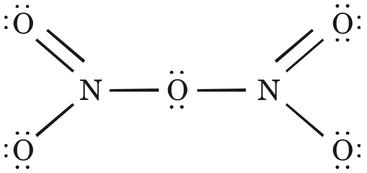


**(5) Nitrogen pentaoxide $N_2O_5$**

It is obtained by dehydration of $HNO_3$ by $P_2O_5$

$$2HNO_3 + P_2O_5 \xrightarrow{\Delta} 2HPO_3 + N_2O_5$$

**Structure :** $N_2O_5$ is solid and in this state it is $NO_2^+.NO_3^-$ i.e. nitronium nitrate. In gaseous state it has the structure



## AMMONIA – $NH_3$

It can be prepared in many ways :

(i) Any ammonium salt on heating with alkali forms ammonia.

$$NH_4Cl + NaOH \xrightarrow{\Delta} NH_3 + NaCl + H_2O$$

$$2NH_4\ OOCCH_3 + Ca(OH)_2 \longrightarrow NH_3 + Ca(CH_3COO)_2 + 2H_2O$$

(ii) Ionic nitrides are hydrolysed by water to produce $NH_3$.

$$Mg_3N_2 + 3H_2O \longrightarrow 2NH_3 + 3MgO$$

(iii) $NH_4^+$ salts which contain non-oxidizing anions, on heating given $NH_3$.

$$NH_4Cl \xrightarrow{\Delta} NH_3 + H_2Cl$$

Non-oxidizing anions are $Cl^-$, $SO_4^{2-}, CO_3^{2-}, CH_3COO^-, PO_4^{3-}$ etc.

However $NH_4^+$ salts which contain oxidizing anions forms $N_2$ or $N_2O$ on heating.

$$NH_4NO_3(l) \longrightarrow N_2O + 2H_2O$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

$$(NH_4)_2\,Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

(iv) $NH_3$ is manufactured by :

(a) Haber's process $N_2 + 3H_2 \underset{\substack{Fe(Fe_2O_3)\text{ catalyst} \\ MO\ (\text{Promoter})}}{\overset{\substack{\text{High pressure} \\ \sim 450°\,C}}{\rightleftharpoons}} 2NH_3(g) + Q$

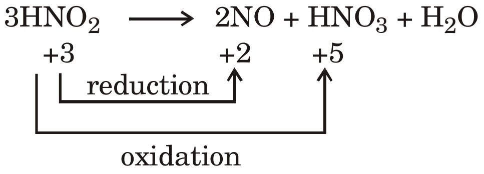
(b) Cyanamide process

$$CaC_2 + N_2 \xrightarrow[\substack{\text{furnace} \\ (\sim 1100°C)}]{\text{Electric}} \underset{(\text{Nitrolum})}{CaCN_2} + C$$

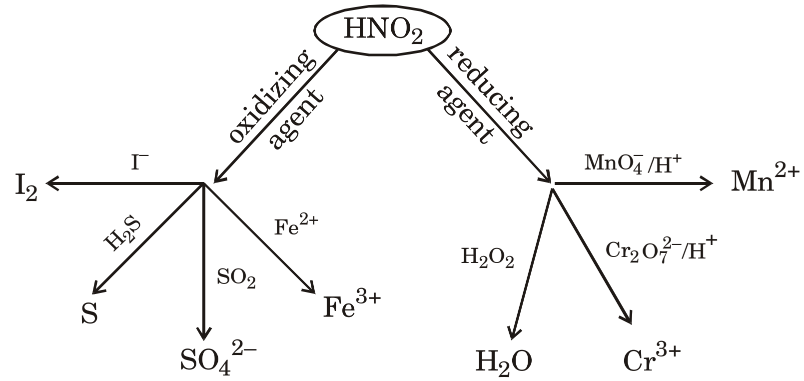
$$CaCN_2 + 3H_2O \xrightarrow{\Delta} CaCO_3 \downarrow + 2NH_3$$

**Nitrous acid ($HNO_2$)**

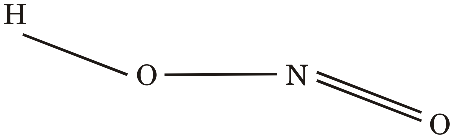
- It disproportionates to $HNO_3$ (oxidation) and NO (reduction)



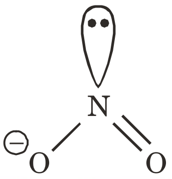
$$\underset{+3}{3HNO_2} \longrightarrow \underset{+2}{2NO} + \underset{+5}{HNO_3} + H_2O$$



**Structure :**

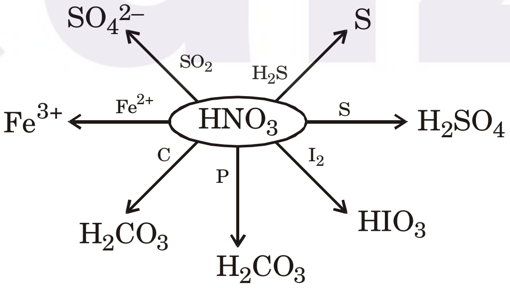


$NO_2^-$ has planar triangular structure



**Nitric acid ($HNO_3$)**

$HNO_3$ can act as an oxidizing agent.



## Aqua regia

A mixture of conc. HCl and $HNO_3$ in the ratio 3 : 1 is called aquaregia. This is a powerful oxidizing agent and dissolves metals like Au and Pt. The two acids on mixing react as

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

The presence of NOCl and Cl makes aquaregia a powerful oxidizing agent.

$$Au + 3Cl \longrightarrow AuCl_3$$

$$AuCl_3 + Cl^- \longrightarrow AuCl_4^- \text{ (or } HAuCl_4\text{, chloroauric acid)}$$

$$Pt + 4Cl^- \longrightarrow PtCl_4$$

$$PtCl_4 + 2Cl^- \longrightarrow PtCl_6^{2-} \text{ (or } H_2PtCl_6\text{, Chloroplatinic acid)}$$

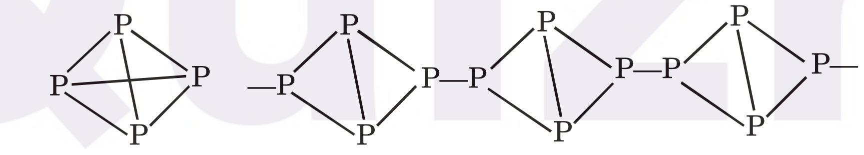
**Note :** Au is not oxidized by $HNO_3$ alone but by aquaregia.

## Red Phosphorus

Red phosporus is prepared by heating white phosphorus in the absence of air at 250 C for a few hours with a trace of iodine as catalyst in a closed iron vessel fitted with a safety valve. At the end of conversion, the product is ground under water and treated with hot caustic soda solution to eliminate any unchanged white phosphorus. It is finally washed with hot water and dried by heating with steam.

Another allotrope of phosphorus is black phosphorus and is obtained by heating white phosphorus at 470 K under high pressure. A series of phases of black phosphorus are formed and one of these phases consists of an extended layer structure in which each phosphorus is bonded to three neighbours by single covalent bonds. Thermodynamically, black phosphorus is the most stable form.

White phosphorus, the form produced in the industrial synthesis, is a toxic, waxy, white solid that contains discrete tetrahedral $P_4$ molecules. Red phosphorus, by contrast, is essentially nontoxic and has a polymeric structure :



White phosphorus Red phosphorus

As expected for a molecular solid that contains small, non-polar molecules, white phosphorus has a low melting point, (44 C) and is soluble in non-polar solvent such as $CS_2$. It is highly reactive, bursting into flames when exposed to air, and is thus **stored under water.**

## Phosphine ($PH_3$)

(i) When a mixture of white P ($P_4$) and NaOH soln. is heated, $PH_3$ is formed.

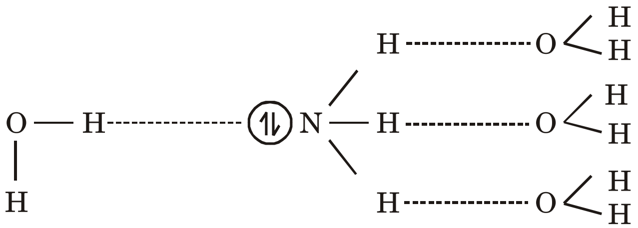
$$P_4 + 2NaOH + 3H_2O \xrightarrow{\Delta} 3NaH_2PO_2 + PH_3$$

In this reaction some $P_2H_4$ is also formed as side product. It is inflammable in air.

(ii) Ionic phosphides react with water to form $PH_3$.

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

$NH_3$ is highly soluble in water by $PH_3$ is insoluble in water. $NH_3$ dissolves due to H-bonding.



$PH_3$ cannot form H-bond, so it is insoluble in water.

## Oxides of Phosphorus

### P – oxides $P_4O_6$ and $P_4O_{10}$

$$(P_4)_X \xrightarrow[600°C]{\text{Stream of air}} P_4O_6$$

$$P_4 \xrightarrow[\Delta]{\text{Excess of air}} P_4O_{10}$$

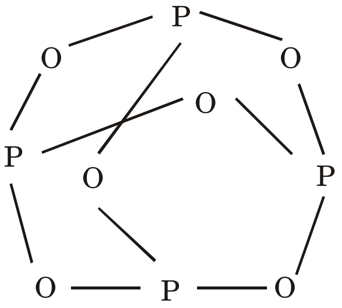
These oxides are solids.

They differ from N oxides in stoichiometry and structure. It is due to inbality of P to form (p – p)π bonds.

$P_4O_6$ and $P_4O_{10}$ both have cage structure. The structures are based upon $P_4$ tetrahedra.

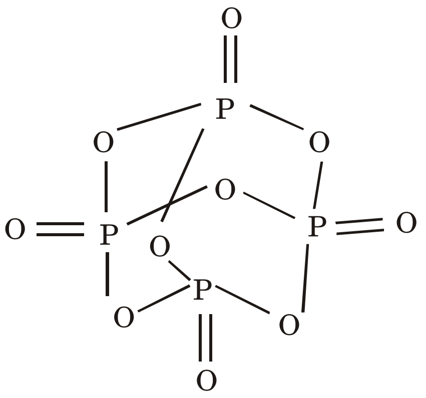
### $P_4O_6$

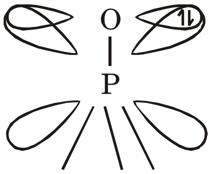
In this oxide P – atoms form a regular tetrahedron and O – atoms are present at six edges of the tetrahedron and bridge P – atoms.



### $P_4O_{10}$

In this oxide $P_4$ tetrahedron has six edge–bridging O–atoms and four terminal O–atoms. The terminal P – O bonds have (d – p)π bonding. Therefore, there are two types of P – O distances in $P_4O_{10}$ large bridging P – O and small terminal P – O distances.





(d – p)π bonding in $P_4O_{10}$

## Oxy acids of P

The common oxy acids of P are :

| Oxidation State of P | Name | Formula | Proticity | Structure |
|---|---|---|---|---|
| + 1 | Hydrophosphorous acid (phosphinic acid) | $H_3PO_2$ | 1 | Td |
| + 3 | Phosphorous acid | $H_3PO_3$ | 2 | Td. |
| + 5 | Metaphosphoric acid | $(HPO_3)n$ | 1 | Td. Polymeric and contain $PO_4$ Td units |
| + 5 | Orthophosphoric acid | $H_3PO_4$ | 3 | Td<br>Highly hydrogen bonded |
| + 5 | Pyrophosphoric acid | $H_4P_2O_7$ | 4 | Td. (two tetrahedra joined through O – atom) |

$$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \xrightarrow{320°C} (HPO_3)$$

## Phosphorus Halides

$P_4 + 6X_2 \longrightarrow 4PX_3$ (in limited supply of $X_2$)

$P_4 + 10X_2 \longrightarrow 4PX_5$ (in excess amount of $X_2$)

- $SO_3 + PCl_3 \longrightarrow POCl_3 + SO_2$
- $PCl_3 + H_2O \longrightarrow H_3PO_3 + 3H_2O$
- $PCl_3 + HI \longrightarrow PI_3 + 3HCl$
- $3ROH + PCl \longrightarrow 3RCl + H_3PO_3$
- $ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$

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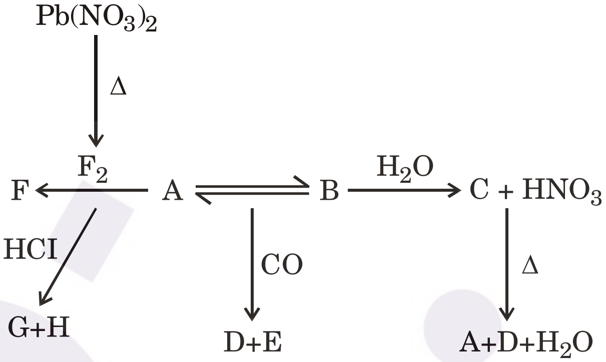
**Example 16**



**Solution :**

A = $NO_2$, $N_2O_4$, C = $HNO_2$, D = NO, E = $CO_2$, F = $NO_2F$, G = NOCl, H = $Cl_2$.

---

**Group 16 (VIA–The Chalcogens)**

- The first four elements are called chalcogens meaning ore forming (oxides, sulphides, selenides, tellurides).
- Similar to the groups discussed earlier, the metallic character in Group 16 increases with increasing atomic number. Oxygen and sulphur are entirely non-metallic in their chemical behaviour. Selenium and tellurium though essentially non-metallic, assume increasing metallic character and are termed as metalloids. Polonium is most metallic in the group.

  Density, melting and boiling points covalent and ionic radii, show a regular increase from oxygen to polonium. The large difference in melting and boiling points between oxygen and sulphur can be explained on the basis of their structure. Oxygen exists mostly as a diatomic molecule held together by weak van der Waals forces while others exist as polyatomic molecules, e.g., $S_8$, $Se_8$, etc., where the atoms are bonded by covalent bonds associated with high dissociation energy. Their existence as diatomic and polyatomic molecules can be explained as follows. The bond energy of the oxygen-oxygen double bond. O=O, is 498 kJ $mol^{-1}$. This makes the O=O bond more than three times as strong as the O–O bond (bond energy for O–O is 142 kJ $mol^{-1}$). By comparison the S=S bond is less than twice as strong as the S–S single bond (bond energy for

S=S, 431 kJ $mol^{-1}$; S–S, 265 kJ $mol^{-1}$). This results in catenated –O–O–O– chains begining unstable relative to O=O, but catenated –S–S–S– chains being stable relative to the molecule S=S.

The elements of Group 16 are characterised by high ionisation energies. Their electronegativities decrease with increasing atomic number. Thus, in view of the fall in electronegativity, metallic character within the group increases with increasing atomic size.

Oxygen, the second most electronegative element, fluorine being the first, has a strong tendency to accept two electrons and give $O^{2-}$ ion. Thus, almost all metal oxides are ionic and contain $O^{2-}$ ions. Usually oxygen exhibits an oxidation state – 2 in its other compounds also. It exhibits positive oxidation states only in a few compounds formed with fluorine, i.e., $OF_2$ and $O_2F_2$. The tendency for the formation of divalent anions decreases from sulphur downwards because of the increasing size and decreasing electronegativity of the elements. Sulphur, selenium an tellurium show a tendency for covalent with formal oxidation states + 2, + 4 and + 6 in compounds in which they are combined with more electronegative elements such as oxygen and halogens. In the higher oxidation states of + 4 and + 6 of these elements electrons are unpaired and promoted to vacant d orbitals.

- Selenium has unique property of photoconductivity and is used in photocopying (xerox) machines and also a decoloriser of glass. Te and Po are highly toxic. Po is higher due to its intense radioactivity. Se and Te are found as selemides and tellurides in sulphide ores ($Cu_2Se$, $Cu_2Te$). The colour of the red glass in the traffic signals is due to CdSe.
- With valence electronic configuration $ns^2$ $np^4$ the group 16 (VI A) elements are just two electrons short of an octet configuration, and – 2 oxidation state is therefore, a common one. The stability of 2 state decreases with increasing metallic character as indicated by E (redox) values. This oxygen is powerful oxidising agent and $H_2Se$ and $H_2Te$ are reducing agent (E values of Se and Te are negative). Because S, Se, and Te are much less electronegative than oxygen, they are commonly found in positive oxidation states as + 4 in $SF_4$, $SO_2$ and $H_2SO_3$, and + 6 in $SF_6$, $SO_3$, $H_2SO_4$.
- $H_2Se$ and $H_2Te$ are unpleasant gaseous hydrides like $H_2S$ but less stable than $H_2S$, order being $H_2O > H_2S > H_2Se\ H_2Te > H_2Po$.
- Oxoacids of S, Se and Te exist and $H_2SO_4$ and $H_2SeO_4$ and considered as strong acids.
- The tendency for catenation decreases markedly as we go 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 compounds such as cysteine, some proteins and enzymes. Stable polyoxides and polysulphides are known. Examples are :

  H–O–O–H, H–S–S–H, H–S–S–S–H,
  H–S–S–S–S–H.
- The metallic character increases as we descend the group. S is non-metal and insulator. Se and Te are metalloids and are semiconductors. Po is a metal.

- Unlike oxygen, the maximum coordination number of sulphur and other elements can exceed four and valency is not limited to two because of available d-orbitals for bonding. Stability of + 6 state decreases and that of + 4 state increases going down the group due to inert-pair effect. It is :

$$Se^{4+} < Te^{4+} < Po^{4+}$$
$$Se^{6+} > Te^{6+} > Po^{6+}$$

- The tendency to form multiple bonds to C, N and O decreases as we descend the group from Se to Te. Thus S=C=S is moderately stable; Se=C=Se decomposes readily whereas Te=C=Te does not exist.
- Thermal stability of the hyrdies decreases as we go down the group :

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

- They form halides of different oxidation number + 1, + 2, + 4 and + 6.

| **Halides** | **X** | **Oxidation number** |
|---|---|---|
| $S_2X_2$ | F, Cl, Br, 1 | + 1 |
| $SX_2$ | F, Cl | + 2 |
| $SX_4$ | F | + 4 |
| $SX_6$ | F | + 6 |
| $Se_2X_2$ | Cl, Br | + 1 |
| $SeX_2$, $TeX_2$ | Cl, Br | + 2 |
| $SeX_4$, $TeX_4$ | F, Cl, Br | + 4 |
| $TeX_4$ | I | + 4 |
| $SeX_6$, $TeX_6$ | F | + 6 |

The stability of the halides decreases in the order F > Cl > Br > I. + 6 oxidation is observed in fluroide, while iodide of Te($TeI_4$) is formed.

$SF_6$ is thermodynamically inert, non-toxic gas. Inertness of $SF_6$ is due to the presence of sterically protected sulplhur atom. $SF_6$ is used as a gaseous insulator in high voltage generators. $SF_4$ and $SeF_4$ are good fluorinating agents and –COOH group can be converted into $CF_3$ and > C=O and –P=O into $CF_2$ and $-PF_2$ groups.

- Oxides of sulphur are more stable than the corresponding oxides of other elements.

## Ozone ($O_3$)

- In the laboratory, $O_3$ can be made by passing oxygen through a strong electric field. An equilibrium is set up :

$$3O_2(s) \rightleftharpoons 2O_3\ (g)$$

- Some 30 km above the earth's surface oxygen molecules can be split apart by UV light from the sun. Some of the atoms join with other oxygen molecules to make ozone :

$$O_2(g) + O(g) \longrightarrow O_3(g)$$

- $O_3$ is an unstable, dark blue diamagnetic gas, b.p. – 112 C. The colour is due to intense absorption of red light.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_3 + h\nu \longrightarrow O_2 + O$$

$$NO_2 + O \longrightarrow NO + O_2$$

Net reaction : $2O_3 + h\nu \longrightarrow 3O_2$

– based on reactive chlorine species from CFC

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$O_3 + h\nu \longrightarrow O + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

Net reaction : $2O_3 + h\nu \longrightarrow 3O_2$

- $O_3$ is thermodynamically unstable, and decomposes to $O_2$ :

$$2O_3 \longrightarrow 3O_2 \qquad \Delta G = -163 \text{ kJ mol}^{-1}$$

- $O_3$ is an extremely powerful oxidising agent :

$$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$$

$$O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-$$

$$3PbS + 4O_3 \longrightarrow 3PbSO_4$$

$$6NO_2 + O_3 \longrightarrow 3N_2O_5$$

$$S + H_2O + O_3 \longrightarrow H_2SO_4$$

$$2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$$

$$O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$$

$$3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$$

$$2[Fe(CN)_6]^{4-} + H_2O + O_3 \longrightarrow 2[Fe(CN)_6]^{3-} + O_2 + 2OH^-$$

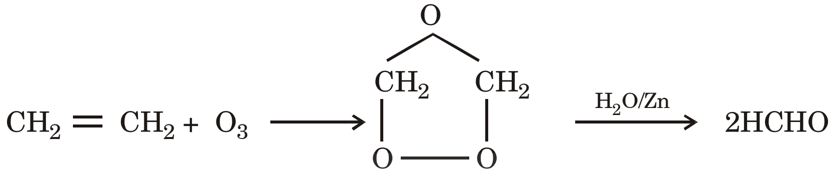
Potassium ozonide $KO_3$ is an orange coloured solid and contains the paramagnetic $O_3^-$ ion.

- The amount of $O_3$ in a gas mixture can be determined by passing the gas into a KI solution (at a constant pH 9.2 using borate buffer). The iodine that is liberated is titrated with sodium thiosulphate solution.

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + 2OH^- + O_2$$

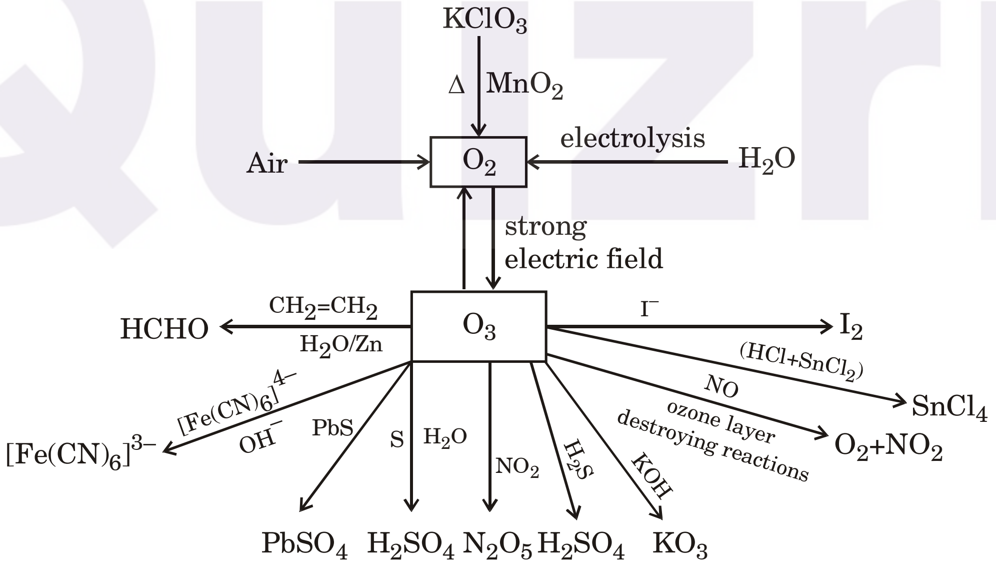
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

- $O_3$ also adds to unsaturated organic compounds at room temperature forming ozonides which can be cleaved to aldehydes and ketones in solution :

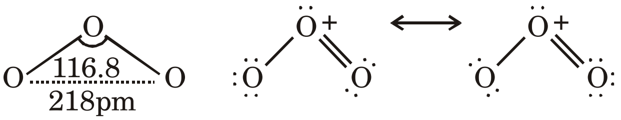


- $O_3$ is used as a disinfectant; it is used to purify drinking water since, it can destroy bacteria and viruses. It is better than $Cl_2$ since, it ($O_3$) avoids the unpleasant smell and taste of $Cl_2$ and any excess $O_3$ soon decomposes to $O_2$.

$$CH — CH = CH — CH_3 + O_3 \xrightarrow{H_2O/Zn} 2CH_3CHO$$



The molecules $O_3$ is bent with an OOO angle 116.8  and equal O–O distance of 128 pm and may be described 90  canonical forms.



## Allotropy and Polymorphism of Sulphur

Many different molecular species are possible for the elemental sulphur, and this accounts for the existence of the large number of physical forms in which the element may appear. Allotropy is more complex for the element sulphur than for any other element of group 16 (VI). Sulplhur may exist as :

- **rhombic sulphur ($S_\alpha$)** which has sixteen $S_8$ rings in a unit cell
- **monoclinic sulphur ($S_\beta$)** which has six $S_8$ rings in its unit cell.
- **liquid sulphur ($S_\lambda$)** comprised of $S_8$ molecules. This is yellow, transparent, mobile liquid. At 160 C, a remarkable transformation occurs. The $S_8$ rings open up and join together into long spiral-chain molecules, resulting in :
- **liquid sulphur ($S_\mu$)** which is dark in colour and very thick and viscous. The chain length and viscosity of the liquid reach a maximum at about 180 C. At higher temperatures the chains break up and viscosity decreases again. At 445 C, this liquid boils, producing :
- **sulphur vapours,** which consists of molecules ranging from $S_2$ to $S_{10}$, but predominantly $S_8$. At higher temperatures, $S_2$ predominates. $S_2$ is paramagnetic.
- Plastic sulphur forms if liquid sulphur (μ) is poured into cold water. It consists of chain-like molecules and has rubber-like properties when first formed. On standing, it becomes brittle and finally converts to rhombic sulphur. Above transformations can be written as :

$$S_\alpha \xrightarrow{95.5^\circ C} S_\beta \xrightarrow{160^\circ C} S_\mu \xrightarrow{445^\circ C} S_8(g)$$

$$S \xleftarrow{2000^\circ C} S_2 \xleftarrow{1000^\circ C} S_4 \longleftarrow S_6$$

- If rhombic sulphur is heated rapidly, it fails to convert into monoclinic sulphur and melts at 113 C.
- In cyclo-$S_6$, the the ring adopts the chair form chain polymers, catena-$S_n$ **are also known.**

## Compound of Sulphur

### Oxide :

Sulphur forms several oxides of which sulphur dioxide ($SO_2$) and sulphur trioxide ($SO_3$) are important.

### Sulphur dioxide

**Preparation :**

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

### Properties :

1. As reducing agent

   (i) Action on halogens :

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

   (ii) Action on $FeCl_3$

   $2FeCl_3 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2FeCl_2 + 2HCl$

2. Reaction with acidified $KMnO_4$

   $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

3. Reaction with acidified $K_2Cr_2O_7$

   $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

4. Oxidising property

   (i) $2H_2S + SO_2 \longrightarrow 2H_2O + S \downarrow$

   (ii) $SO_2 + 2Mg \longrightarrow 2MgO + S \downarrow$

### Sulphur trioxide

**Preparation :**

By dehydration of $H_2SO_4$

$$H_2SO_4 \xrightarrow[\text{heat}]{P_2O_5} SO_3 + H_2O$$

Reaction : $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$

$H_2SO_4$ saturated with $SO_3$ is called oleum.

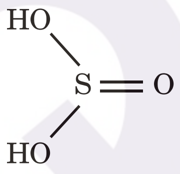
**Oxyacids of sulphur :**

Based on the structural similarities, oxoacids or (oxyacids) of sulphur may be classified as :

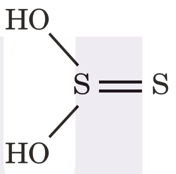
1. **Sulphoxylic acid,** $H_2SO_2$
2. **Sulphurous acid series**
   - (a) Sulphurous acid, $H_2SO_3$
   - (b) Thiosulphurous acid, $H_2S_2O_2$
   - (c) Dithionus acid, $H_2S_2O_4$
   - (d) Di or pyrosulphurous acid $H_2S_2O_5$
3. **Sulphuric acid series**
   - (a) Sulphuric acid, $H_2SO_4$
   - (b) Thiosulphuric acid, $H_2S_2O_3$
   - (c) Di or pyrosulphuric acid, $H_2S_2O_7$
4. **Peroxo-acid series**

   Peroxomonosulphuric acid (also called Caro's acid, $H_2SO_5$)

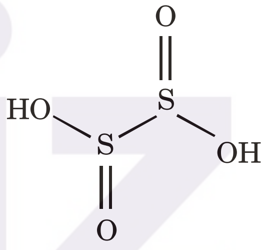
   Perdisulphuric acid (also called Marshall's acid, $H_2S_2O_8$)



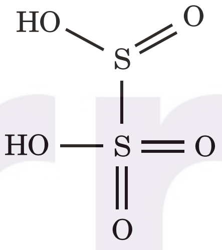
Sulphurous acid



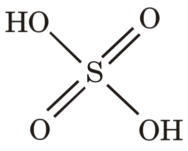
Thiosulphurous acid



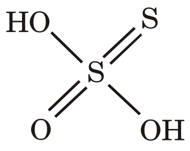
Dithionous acid



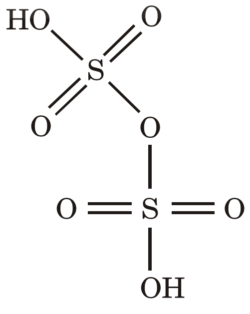
Pyrosulphurous acid



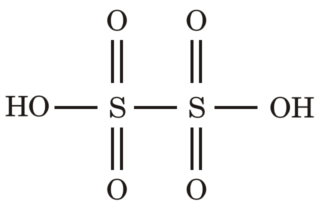
Sulphuric acid



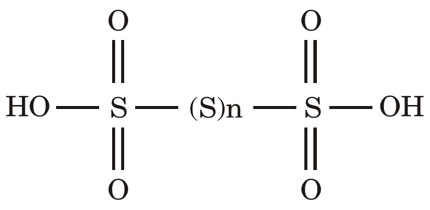
Thiosulphuric acid



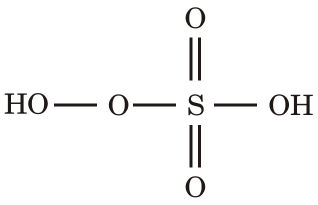
Pyrosulphuric acid



Dithionic acid

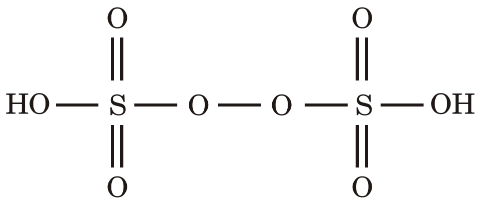


Polythionic acid



$HO-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

Peroxomonosulphuric acid



$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

Peroxodisulphuric acid

(Structure of oxoacids of sulphur)

**Sulphuric Acid ($H_2SO_4$)**

- As an oxidizing agent

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

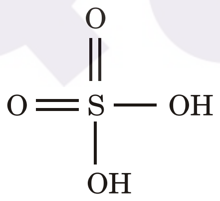
$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

$8HI + H_2SO_4 \longrightarrow H_2S + 4I_2 + 4H_2O$

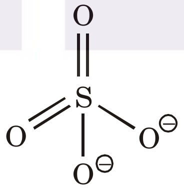
- As a dehydrating agent

$CH_3CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

- $HO - SO_2 - OH + 2PCl_5 \longrightarrow \underset{\text{Sulphuryl Chloride}}{SO_2Cl_2} + 2POCl_3 + 2HCl$



$O=\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{S}}-OH$



S-atom is $sp^3$ hybridised. $SO_4^{2-}$ ion is tetrahedral.

---

**Example 17**

**$H_2SO_4$ cannot be used to obtain HBr from KBr. Why ?**

**Solution :**

$H_2SO_4$ oxidises HBr.

---

**Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) :**

If one of the oxygen atoms in the sulplhate ion is replaced by sulphur, the resulting ion ($S_2O_3^{2-}$) is known as thiosulphate.

## Preparation :

(i) Sodium thiosulphate is prepared by boiling aq. solution of metal sulplhites with elemental sulphur.

$$Na_2SO_3 + \frac{1}{8}S_8 \xrightarrow[H_2O]{373K} Na_2S_2O_3$$

Hydrated sodium thioosulphate $Na_2S_2O_3.5H_2O$ is known as HYPO.

(ii) Spring's reaction may be used for the preparation of sodium thiosulphate. It consists in treating a mixture of sodium sulphide and sodium sulphite with calculate quantity of iodine.

$$Na_2S + Na_2SO_3 + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$$

## Properties :

(i) Reaction with dilute acids : It reacts with dilute acids to liberate sulphur dioxide gas along with precipitate of sulphur.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + S\downarrow + SO_2$$

(ii) Reaction with $BaCl_2$ : It gives white ppt. of barium thiosulphate.

$$S_2O_3^{2-} + Ba^{2+} \longrightarrow \underset{\text{White}}{BaS_2O_3} \downarrow$$

(iii) Reaction with silver nitrate solution : Gives white ppt. which quickly changes to yellow, brown and finally black due to the formation of silver sulphide.

$$S_2O_3^{2-} + 2Ag^{+} \longrightarrow \underset{\text{White ppt.}}{Ag_2S_2O_3} \downarrow$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

With conc. solution of sodium thiosulphate, silver nitrate gives no ppt.

(iv) It reacts with silver salts to form sodium argento thiosulphate complex

$$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\substack{\text{Sodium argento}\\\text{thiosulphate complex}}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

(v) Thiosulphate $\left(S_2O_3^{2-}\right)$ ion is oxidized by iodine $I_2$ to tetrathionate $S_4O_6^{2-}$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

## Example 18

**Why sodium thiosulphate is used in photography ?**

**Solution :**

It can remove the undecomposed AgBr as soluble thiosulphate complex.

$$2Na_2S_2O_3 + AgBr \longrightarrow Na_3\,[Ag(S_2O_3)_2] + NaBr$$

---

## Hydrogen sulphide

**Preparation :**

Prepared by the action of dil. HCl or $H_2SO_4$ on iron sulphide

$$FeS + 2HCl\ (dil) \longrightarrow FeCl_2 + H_2S \uparrow$$

**Properties :**

It is a colourless, poisonous gas having the smell of rotten eggs.

1. **As reducing agent**

   (i) **Action on halogens**

   $$H_2S + Cl_2 \longrightarrow 2HCl + S \downarrow$$

   (ii) **Action on $FeCl_3$**

   $$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S \downarrow$$

2. **Reaction with acidified $KMnO_4$**

   $$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + S \downarrow$$

3. **Reaction with acidified $K_2Cr_2O_7$**

   $$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + S \downarrow$$

---

## Example 19

**The two atoms of sulphur in $Na_2S_2O_3$ have**

**(A)** **+ 2 and + 4 oxidation state** **(B)** **– 2 and + 6 oxidation state**

**(C)** **+ 4 and + 6 oxidation state** **(D)** **same oxidation states**

**Solution :** (B)

---

## Example 20

**Bleaching action of $SO_2$ is due to**

**(A)** **reduction** **(B)** **oxidation**

**(C)** **hydrolysis** **(D)** **its acidic nature**

**Solution :** (A)

Example 21

**When sulphur is boiled with $Na_2SO_3$ solution, the compound formed is**

**(A) sodium sulphide** **(B) sodium sulphate**

**(C) sodium persulphate** **(D) sodium thiosulphate**

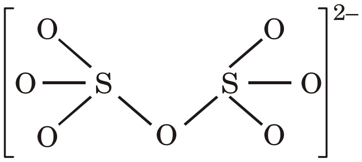
**Solution :** (D)

---

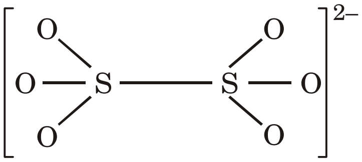
Example 22

**The structure of dithionate ion is**

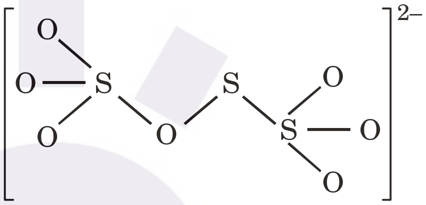
**(A)**



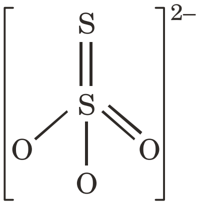
**(B)**



**(C)**



**(D)**



**Solution :** (B)

---

Example 23

**When $SO_2$ gas is passed into an acidified solution of $K_2Cr_2O_7$, the oxidation state of chromium changes**

**(A) from + 12 to + 6** **(B) from + 3 to + 6**

**(C) from + 6 to + 3** **(D) from + 6 to + 4**

**Solution :** (C)

---

Example 24

**The stability of the hydrides of oxygen, sulphur, selenium and tellurium decreases in the order**

**(A) $H_2Te > H_2Se > H_2S > H_2O$** **(B) $H_2O > H_2S > H_2Se > H_2Te$**

**(C) $H_2O > H_2S > H_2Se > H_2Te$** **(D) $H_2O \approx H_2S > H_2Te > H_2Se$**

**Solution :** (B)

### Example 25

Which of the following reaction does produce $SO_2$ ?

(A) $Ag + H_2SO_4 \text{ (conc.)} \xrightarrow{\Delta}$ (B) $CaSO_4 + C \xrightarrow{\Delta}$

(C) $FeS_2 + O_2 \xrightarrow{\Delta}$ (D) $Zn + H_2SO_4 \xrightarrow{\Delta}$

**Solution :** (D)

---

### Example 26

In preparing a standard aqueous solution of Mohr' salt, $[FeSO_4.(NH_4)_2SO_4.\ 6H_2O]$ a few millitres of $H_2SO_4$ is added to the solution. The added $H_2SO_4$

(A) prevents reduction of the salt

(B) prevents oxidation of the salt

(C) makes the solution homogeneous by converting insoluble $Fe(OH)_2$, which is formed by hydrolysis, into soluble $FeSO_4$

(D) neutralizes the ammonia formed by hydrolysis

**Solution :** (C)

---

## Group 17 (Halogens)

### Halogens ($X_2$)

- $F_2$ is extremely reactive, and this causes great difficulties in the preparation and handling of the element.
  - Moissan (1886) prepared it from $CaF_2$ :

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$KF + HF \longrightarrow KHF_2$$

$$KHF_2 \xrightarrow{\text{electrolysis}} \underset{\text{at cathode}}{H_2} + \underset{\text{at anode}}{F_2}$$

  - Modern method uses graphite anode and steel cathode in a steam heated steel tank.
  - If $F_2$ were formed by the electrolysis of aqueous fluoride solution, it would immediately oxidise water to $O_2$

$$F_2 + 2H_2O \longrightarrow 4HF + O_2$$

- The commercial production of $Cl_2$ is by electrolysis, either of concentrated aqueous NaCl or of molten salt such as NaCl(l) or $MgCl_2$(l) :

$$2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{2NaOH + H_2}_{\text{at cathode}} + \underbrace{Cl_2}_{\text{at anode}}$$

- $Br_2$ is obtained from sea water and brine lakes. Sea water contains about 65 ppm Br. $Br_2$ is isolated in following which oxidises $Br^-$ to $Br_2$.

$$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$$

– $Br_2$ is quite volatile hence is removed by a stream of air.

– $Br_2$ is absorbed into aq $Na_2CO_3$ solution when NaBr and $NaBO_3$ are formed :

$$3Na_2CO_3 + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$

or $$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$$

- $I_2$ is obtainable in small quantities from dried seaweed, since certain marine plants absorb and concentrate $I^-$ selectively in presence of $Cl^-$ and $Br^-$. Low concentration of $I^-$ are also found in some natural brines (salt solutions) associated with oil fields.

Chile saltpetre is mainly $NaNO_3$ but it contains traces of sodium iodate $NaIO_3$ and sodium periodate $NaIO_4$.$I_2$ is recovered by reducing $IO_3^-$ to $I^-$ by $NaHSO_3$ and then oxidation of $I^-$ to $I_2$ by $IO_3^-$ itself :

$$IO_3^- + 3HSO_3^- \longrightarrow I^- + 3SO_4^{2-} + 3H^+$$

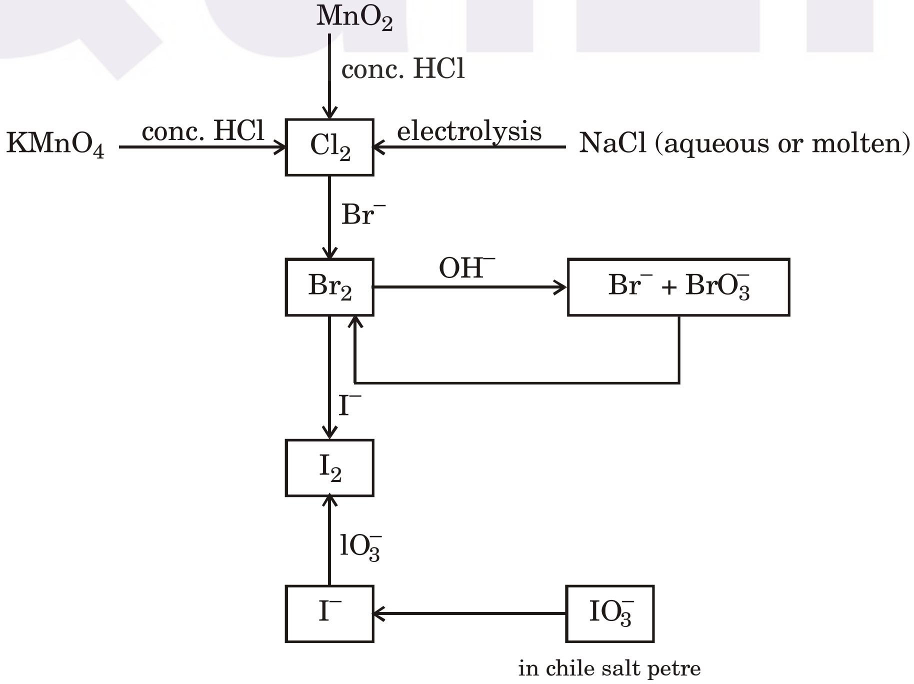
$$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Natural brine is treated with $Cl_2$ water to oxidise $I^-$ to $I_2$ and the solution is passed through an ion-exchange resin which absorbs $I_2$ as $I_3^-.I_3^-$ is removed from the resin by treatment with alkali.

– Reactivity of halogens is based on bond-energy (BE) value.

$$F_2 > Cl_2 > Br_2 > I_2$$

Greater the BE, smaller the reactivity



- Oxidising power is in order :

$$F_2 > Cl_2 > Br_2 > I_2 .$$

$$\frac{1}{2}X_2\ (\text{solid, liquid, gas}) \longrightarrow X^-\ (\text{hydrated})$$

$F_2$ has the most negative $\Delta G$ value, hence is strongest oxidising agent and can oxidise $Cl^-$, $Br^-$ and $I^-$ to respectively $Cl_2$, $Br_2$ and $I_2$. $F_2$ can also oxidise $H_2O$ to $O_2$.

$$F_2 + H_2O \longrightarrow 2HF + \frac{1}{2}\ O_2$$

Similarly $Cl_2$ will oxidise $Br^-$ and $I^-$, and $Br_2$ will oxidise $I^-$. In general any halogen ($X_2$) of lower atomic number will oxidise halide ions ($X^-$) of higher atomic number.

The ionic character of the M–X bond decreases in the order M–F > M – Cl > M – Br > M – I.

| Reaction | Comment |
|---|---|
| • **With $H_2O$** | |
| $2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$ | Vigorous reaction with $F_2$; atmospheric $O_2$ can oxidise $I^-$ to $I_2$ hence reverse reaction |
| $2X_2 + 2H_2O \longrightarrow 4H^+ + 4X^- + O_2$ | $Cl_2 > Br_2 > I_2$ ($F_2$ does not disproportionate). |
| $X_2 + H_2O \xrightarrow{\text{disproportionate}} X^- + HOX + H^+$ | |
| • **With $H_2$** | |
| $H_2 + X_2 \longrightarrow 2HX$ | All the halogoens with $Br_2$ photochemical reaction, with $I_2$ very slow even at high temperature |
| • **With metals** | |
| $2M + nX_2 \longrightarrow 2MN_n$ | Most metals form halides. |
| • **With CO** | |
| $CO + X_2 \longrightarrow COX_2$ | Only $Cl_2$, $Br_2$ from carbonyl halide |
| • **With P** | |
| $2P + 3X_2 \longrightarrow 2PX_3$ | For F, Cl, Br, I |
| $2P + 5X_2 \longrightarrow 2PX_5$ | For F, Cl, Br |
| • **With S** | |
| $2S + X_2 \longrightarrow S_2X_2$ | Cl, Br |
| $S + 2Cl_2 \longrightarrow SCl_4$ | |
| $S + 3F_2 \longrightarrow SF_6$ | |

| | |
|---|---|
| • **With $H_2S$** | |
| $H_2S + X_2 \longrightarrow 2HX + S$ | All the halogens oxidise $H_2S$ ($S^{2-}$) to S |
| • **With $SO_2$** | |
| $SO_2 + X_2 \longrightarrow SO_2X_2$ | F and Cl |
| • **With $NH_3$** | |
| $8NH_3 + 3X_2 \longrightarrow N_2 + 6NH_4X$ | F, Cl, Br |
| • **With halogens** | |
| $X_2 + X'_2 \longrightarrow 2XX'$ | Interhalogen compounds |
| • **With cold NaOH** | |
| $2NaOH + 2F_2 \longrightarrow 2NaF + OF_2 + H_2O$ | |
| $2NaOH + X_2 \longrightarrow NaX + NaOX + H_2O$<br>$Cl_2$ reacts with dry slaked lime forming bleaching powder | (X = Cl, Br) $I_2$ does not react under the same condition |
| $Ca(OH)_2 + Cl_2 \longrightarrow CaCl(OCl) + H_2O$ | |
| • **With hot NaOH** | |
| $6NaOH + 3X_2 \longrightarrow 5NaX + NaXO_3 + 3H_2O$ | (X = Cl, Br, I) |

$Cl_2$ is used as a bleach or as a disinfectant (as in public water supplies). It reacts slowly with $H_2O$ to form HCl and HOCl. The hypochlorous acid then decomposes into HCl and O radicals, which kill bacteria.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

$$HOCl \longrightarrow HCl + O$$

These oxygen radicals are very strong oxidising as well as effective bleaching and disinfecting agent in aqueous solution of $Cl_2$ or hypochlorite salts.

- The halogens react with each other to form interhalogen compounds of the type AX, $AX_3$, $AX_5$ and $AX_7$ of which A is of higher atomic number as shown :

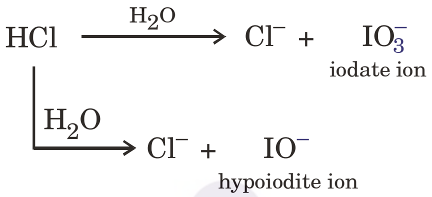
| **AX** | **$AX_3$** | **$AX_5$** | **$AX_7$** |
|---|---|---|---|
| CIF | $CIF_3$ | $CIF_5$ | |
| BrF | $BrF_3$ | $BrF_5$ | |
| ICl | $ICl_3$ ($I_2Cl_6$) | $IF_5$ | $IF_7$ |
| IBr | | | |
| BrCl | | | |

- There are never more than two different halogens in a molecule. The bonds are covalent because of the small electronegativity difference. Ternary combinations occur in polyhalide ions (e.g., $IBrCl^-$)
  - – The electrical conductance of molten $I_2$ is ascribed to self-ionisation

$$3I_2 \rightleftharpoons I_3^+ + I_3^-$$

  - – The interhalogens are generally more reactive than the halogens (except $F_2$). This is because the A–X bond in interhalogens is weaker than the X–X bond in the halogens.
  - – Hydrolysis of interhalogens gives halide and oxohalide Oxohalide is always formed from larger halogens present.

$$BrF_5 \xrightarrow{H_2O} 5F^- + \underset{\text{bromate ion}}{BrO_3^-}$$



$$HCl \xrightarrow{H_2O} Cl^- + \underset{\text{iodate ion}}{IO_3^-}$$

$$HCl \xrightarrow{H_2O} Cl^- + \underset{\text{hypoiodite ion}}{IO^-}$$

## Anomalous Behaviour of Fluorine

Fluorine differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine–fluorine bond dissociation energy. The result of these differences is that fluorine is the most electronegative element in the periodic table and is a powerful oxidant. Some differences between flourine and other halogens are :

- It is more reactive than other halogens because of low F–F bond energy, also due to its high electronegativity the bond between fluorine and other elements is very strong so its compounds are more stable. Some of them are inert. e.g. $SF_6$.
- Fluorine is almost invariably monocoordinate (coordination number = 1) and is never more than mono covalent.
- Fluorides are more ionic.
- Fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous.
- Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, for example in $IF_7$, iodine has oxidation number seven.
- The reactions of fluorine are also different from other halogens. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$X_2 + H_2O \rightleftharpoons HOX + HX$$

Fluorine reacts with alkalies to yield the oxide, $F_2O$ :

$$2F_2 + 2NaOH \longrightarrow OF_2 + 2NaF + H_2O$$

The other halogens react with alkalies to yield a solution of hypohalite ions, which may disproportionate. The oxoacid of fluorine, HOF, prepared recently is very unstable. The oxides of fluorine are not acidic.

$$Cl_2 + 2NaOH \longrightarrow NaClO + NaCl + H_2O$$

## Halogen Acids

- All the halogens acids (HF, HCl, HBr, HI) are known. In aqueous solution, they are typical mineral acids whose acid strengths decrease in the direction of increasing bond energy, that is

$$\underbrace{HI > HBr > HCl}_{\text{strong acids}} > \underset{\text{weak acid}}{HF}$$

- HX can be prepared by direct combination of $H_2$ and $X_2$

$H_2\ (g) + X_2(g) \longrightarrow 2HX\ (g)$

– reaction between $H_2$ and $F_2$ is very fast,

– reaction between $H_2$ and $Cl_2$ is also rapid,

– but reaction between $H_2$ and $Br_2$ or $I_2$ is very slow.

$\Delta G_f^\circ$ of HF, HCl and HBr are large and negative suggesting that for them reaction

$$H_2 + X_2 \longrightarrow 2HX$$

goes to completion. For HI(g), $\Delta G_f^\circ$ is small and positive suggesting that HI should dissociate

$$2HI(g) \longrightarrow H_2(g) + I_2\ (g)$$

to some extent. However, because of the high activation energy the dissociation occurs only very slowly in the absence of a catalyst. As a result, HI(g) is quite stable at room temperature. Thus, at room temperature decomposition of HI(g) is kinetically controlled (rather than thermodynamically controlled).

- $CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + 2HF$

- $CaF_2$ has also $SiO_2$ as impurity otherwise. HF formed would react with $SiO_2$ forming $SiF_4$ and $H_2SiF_6$.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$$

- $NaCl + \underset{\text{conc.}}{H_2SO_4} \xrightarrow{150°C} HCl + \underset{\text{salt cake}}{NaHSO_4}$

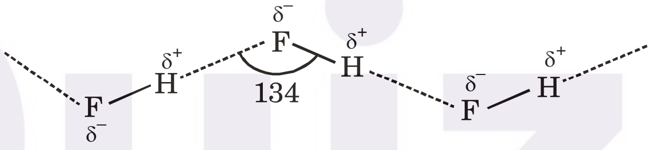
$$NaHSO_4 + NaCl \xrightarrow{550°C} HCl + Na_2SO_4$$

This method is called 'salt-cake' method involves formation of $NaHSO_4$ (salt cake)

- HF is only just liquid at room temperature and HCl, HBr and HI are gases. HF has abnormally high boiling point due to intermolecular H-bonding which is not possible in other halogen acids due to their smaller electronegativity values.

$$HCl < HBr < HI < HF$$

Some H-bonding also occurs in the gas, which consists of a mixture of cyclic $(HF)_6$ polymers, dimeric $(HF)_2$ and the monomeric HF.



Because of the tendency to form hydrogen bond, metal fluorides are solvated by HF giving species of the type $HF_2^-$ etc. $KHF_2$ (KF. HF), $KH_2F_3$ (KF.2HF) and $KH_3F_4$ (KF.3HF) are known examples.

- HF attacks glass, other halogen acids do not. Glass is silicates of sodium and calcium and are converted into complex fluorides :

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

$$CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

Hence HF can't be stored in a glass vessel. Instead, it is stored in a wax-vessel which does not react with HF. This unique property of HF of attacking glass is used for making permanent marking eg. glass-wares.

- In the gaseous state, HX are essentially covalent. In aqueous solution, they ionise to form $H_2O^+$ and $X^-$ but not $H^+$ and $X^-$.

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HX} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{X^-}$$

HF has more ionic character (due to greater electronegativity difference) than HCl, HBr and HI but acid strength varies as : $\underset{\text{weak}}{\text{HF}} < \underbrace{\text{HCl} < \text{HBr} < \text{HI}}_{\text{strong}}$

Acid strength is dependent not on the electronegativity difference of H and X but on the tendency of the hydrated molecule to form hydrogen ions :

$$\text{HX (hydrated)} \longrightarrow \text{H}^+ \text{ (hydrated)} + \text{X}^- \text{ (hydrated)}$$

- Dipole moment of HF is maximum and is in order

$$\underset{1.19\text{D}}{\text{HF}} > \underset{1.05\text{D}}{\text{HCl}} > \underset{0.80\text{D}}{\text{HBr}} > \underset{0.420\text{D}}{\text{HI}}$$

## Preparations of oxo acids

Most of the oxo acids and acid anions of halogens are known only in solution. They can be obtained by reaction of the free halogens with (i) water or (ii) aq. bases :

$$X_2 + H_2O \longrightarrow H^+ + X^- + HOX$$

$$X_2 + \underset{\text{(cold dil.)}}{2NaOH} \longrightarrow NaX + NaOX + H_2O$$

$$3X_2 + \underset{\text{(conc. hot)}}{6NaOH} \longrightarrow 5NaX + NaOXO_2 + 3H_2O$$

$$(X = Cl, Br, I)$$

All the above reactions are rapid disproportionation of halogens.

**Note :**

(i) Reaction of $X_2$ and water can produce HOX only.

(ii) There is appreciable concentration of HOCl.

(iii) The HOI is negligible in a saturated solution of iodine.

## Halic acids $HOXO_2$ (X = Cl, Br, I)

All the three halic acids are known. The acids $HOClO_2$ and $HOBrO_2$ are known only in solution and as salts. Only iodic acid ($HOIO_2$) is stable out of aq. solution. It is a white solid. It can be prepared by oxidizing $I_2$ with conc. $HNO_3$ or $O_3$.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

## $HOClO_2$ and $HOBrO_2$

They can be made by treating barium halates with $H_2SO_4$

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow 2HClO_3 + BaSO_4 \downarrow$$

$Ba(ClO_3)_2$ can be prepared by passing $Cl_2$ in $Ba(OH)_2$ solution

$$6Ba(OH)_2 + 6Cl_2 \longrightarrow Ba(ClO_3)_2 + 5BaCl_2 + 6H_2O$$

They can also be produced by reactions of $X_2$ with hot aq. base (NaOH)

$$3X_2 + 6HO^- \longrightarrow XO_3^- + 5X^- + 3H_2O$$

$KClO_3$ decomposes on heating, the product depends on temperature

(i)
$$\begin{tikzcd} 2KClO_3 \arrow[r, "400-500\text{ C}", "{[MnO_2]}"'] \arrow[r, bend right, "150\text{ C}"'] & 2KCl + 3O_2 \end{tikzcd}$$

(ii) $$4KClO_3 \xrightarrow[\text{Temp.}]{\text{Lower}} 3KClO_4 + KCl$$

$$Zn(ClO_3)_2 \xrightarrow{\Delta} 2ZnO + 2Cl_2 + 5O_2$$

Chlorates are used in matches and fireworks. Sodium chlorate is used as a powerful weed killer.

## Perbromic acid $HOBrO_3$

It is best prepared by oxidation of $BrO_3^-$ by $F_2$ in 5M NaOH solution.

$$BrO_3^- + F_2 + 2HO^- \longrightarrow BrO_4^- + 2F^- + H_2O$$

Solution of $HBrO_4$ can be concentrated upto 55% (6 M), without decomposition. The hydrate $HBrO_4.2H_2O$ can be crystallized.

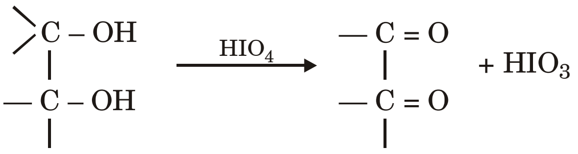
## Periodic acid HO $IO_3$

The common form in aq. solution of this acid is $HIO_4$ and also $H_5IO_6$. $H_5IO_6$ is called paraperiodic acid (or orthoperiodic acid). It is a white crystal. It is decomposes on heating as

$$2H_5IO_6 \xrightarrow[(-\,4H_2O)]{100°C} 2HIO_4 \xrightarrow{\sim 200°C} I_2O_5 + O_2 + H_2O$$

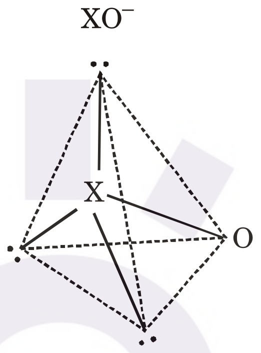
The $IO_4^-$ ion is tetrahedral while $(OH)_5IO$ is octahedral. Periodates can be made by oxiding iodate with $Cl_2$ in alkaline solution.

$$IO_3^- + Cl_2 + 6HO^- \rightarrow IO_6^{5-} + 2Cl^- + 3H_2O$$

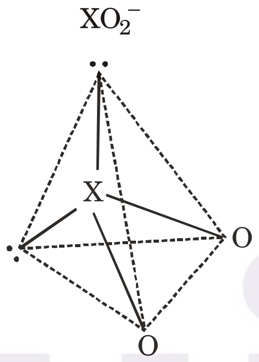


### Structure of oxo anions

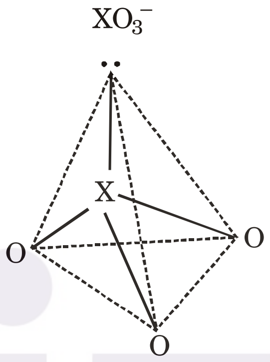
| Anions | $XO^-$ | $XO_2^-$ | $XO_3^-$ | $XO_4^-$ |
|---|---|---|---|---|
| Total valence electrons | 14 | 20 | 26 | 32 |
| No. of bonds (= no. of bps) | 1 | 2 | 3 | 4 |
| Electrons for bonds | 8 | 16 | 24 | 32 |
| Lone pairs | (14 – 8)/2 = 3 | (20 – 16)/2 = 2 | (26 – 24)/2 = 1 | 0 |
| Total electrons pairs | 1 + 3 = 4 | 2 + 2 = 4 | 3 + 1 = 4 | 4 – 0 = 4 |
| Structure | Td | Td | Td | Td |
| Shape | Linear | Angular | Δ pyramidal | Td |



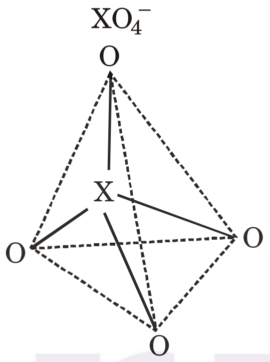
(Linear)



(Angular)

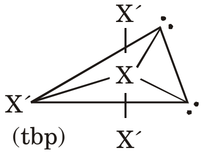
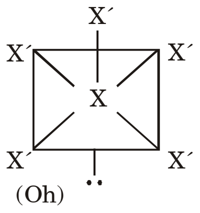
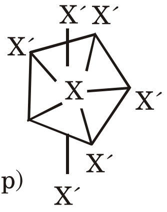


(Δ Pyramid)



(Tetrahedral)

### Structure and shape

| Molecules | Bond pairs | Lone pairs | Total electron pairs | Structure | Shape |
|---|---|---|---|---|---|
| $XX'_3$ | 3 | 2 | 5 |  (tbp) | T – shaped |
| $XX'_5$ | 5 | 1 | 6 |  (Oh) | Square pyramid |
| $XX'_7$ | 7 | 0 | 7 |  (pbp) | Pentagonal bipyramid |

## Pseudohalogens and Pseudohalides

Many substances have properties either like $X_2$ or $X^-$ (X = halogen). They are called pseudohalogens and pseudohalides. They contain two or more atoms in which one at least is N – atom, such as $(CN)_2$, $CN^-$, $SCN^-$ etc.

Some pseudohalogens and pseudohalides

| Pseudohalogens | Pseudohalides |
|---|---|
| | Cyanide ion $CN^-$ |
| | Cyanamide ion $CN_2^{2-}$ |
| Cyanogen gas $(CN)_2$ | Azid ion $N_3^-$ |
| Thiocyanogen $(SCN)_2$ | Thiocyanate ion $SCN^-$ |
| | Cyanate ion $OCN^-$ |
| | Fulminate ion $ONC^-$ |

The cyanogen gas and $CN^-$ ion are best-known pseudohalogen and pseudohalide. They behave like $X_2$ and $X^-$, e.g.,

(a) $(CN)_2$ disproportionate in water like $X_2$

$(CN)_2 + H_2O \rightarrow HCN + HOCN$

$Cl_2 + H_2O \rightarrow HCl + HOCl$

(b) $CN^-$ behaves similar to $I^-$

$$2Cu^{2+}_{(aq)} + 4CN^-_{(aq)} \rightarrow 2CuCN + (CN)_2$$

$$2Cu^{2+}_{(aq)} + 4I^- \rightarrow 2CuI + I_2$$

Both the above reactions are reduction of $Cu^{2+}$ to $Cu^+$ by $CN^-$ and $I^-$ ions.

(c) The solubility of metal halides and metal cyanides are very similar,

NaX and NaCN → Water-soluble

AgX and AgCN → Water-insoluble

(X = Cl, Br, I)

$PbCl_2$ and $Pb(CN)_2$ → Water insoluble

(d) Like halides pseudohalides ($CN^-$, $SCN^-$ etc.) are good ligands $CuCl_4^{2-}$, $ZnCl_4^{2-}$, $Cu(CN)_4^{2-}$.

{Please note, the word ligands will be dealt in chapter co-ordination complexes}

(i) $CN^-$ complexes with transition metals and Zn, Cd and Hg.

(ii) Most of the $CN^-$ complexes are ionic $[Fe(CN)_6]^{4-}$, $[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{4-}$ etc.

(iii) $CN^-$ can stabilize low oxidation states also, e.g $[Ni(CN)_4]^{4-}$.

## Bleaching Powder

The exact chemical composition of bleaching powder is not yet known but it behaves as if it contains calcium hypochlorite $Ca(OCl)_2$ and basic calcium chloride, $Cl_2.Ca(OH)_2.H_2O$

### Preparation

It is prepared by passing chlorine over slaked lime

$$3Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + H_2O}_{\text{Bleaching Powder}}$$

### Properties :

1. **Reaction with dilute acids :** With dilute acids, it gives chlorine which is known as available chlorine.

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2 \uparrow$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2 \uparrow$$

2. When treated with water it decomposes into calcium chloride and calcium hypochlorite.

$$2CaOCl_2 + H_2O \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$$

3. Bleaching powder reacts with $CO_2$ (atmospheric) and gives chlorine which accounts for its oxidising and bleaching actions.

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2 \uparrow$$

4. **Action of heat :** On heating bleaching powder gives a mixture of chlorate and chloride.

$$6CaOCl_2 \xrightarrow{\Delta} Ca(ClO_3)_2 + 5CaCl_2$$

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## Group 18 (The Noble Gases)

- Because of highest ionisation energy of group 18 elements in their respective periods, they were given the name ‘noble gases’ and thus inert. However, at least in the case of xenon, it is not so; it forms series of compounds.
- The noble gases are colourless, tasteless and odourless. In the liquid and solid states the only forces of attraction among the atoms are very weak London or van der Waals forces. Polarisability and interatomic interactions increase with increasing atomic number. The attractive forces among the atoms are so small that they remain liquid at 1 atmospheric pressure even at a temperature of 0.001 K.

- Helium has the lowest boiling point of any element, and its behaviour as a liquid is most unusual. It will creep up the walls of the container in which it is placed and thus it exists in two phases in liquid helium, one of which has an extremely low viscosity.

## Xeon fluorides

Xenon reacts directly with fluorine (only). The products depend on respective amounts of Xe and $F_2$ and temperature also. The reactions are generally carried out in seal tubes.

$$Xe + F_2 \begin{cases} \xrightarrow[\Delta/P]{2:1} XeF_2 \\ \xrightarrow[\Delta/P]{1:5} XeF_4 \\ \xrightarrow[\Delta/P]{1:20} XeF_6 \end{cases}$$

Δ → heart

P → Pressure

These three fluorides are crystalline volatile substances which sublime at room temperature but can be kept in nickel containers.

The fluorides are strong oxidising agents.

$$XeF_2 + 2HCl \longrightarrow Xe + Cl_2 + 2HF$$

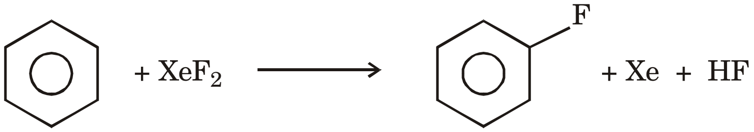
$$XeF_4 + 4KI \longrightarrow Xe + 2I_2 + 4KF$$

$$XeF_2 + Ce_2(SO_4)_3 + SO_4^{2-} \longrightarrow Xe + 2Ce\,(SO_4)_2 + F_2$$

They are good fluorinating agents also.

$$2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$$

$$Pt + XeF_4 \longrightarrow Pt\,F_4 + Xe$$



Their reaction with water is different

(a) $XeF_2$ is water soluble and undergoes slow oxidative hydrolysis.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + O_2 + 4HF$$

(b) $XeF_4$ reacts with water violently to give $XeO_3$

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + \frac{3}{2}O_2 + 12HF$$

In this reaction $XeF_4$ disproportionates and $H_2O$ is parthy oxidized.

(c) $XeF_6$ also reacts violently to give $XeO_3$

$$XeF_6 + 6H_2O \longrightarrow XeO_4 + 12HF$$

With small amount of water

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

---

**Example**

**Xe cannot form $XeF_3$, $XeF_5$ type of compound.**

**Solution :**

The electronic configuration of Xe is $5S^2\ 5p^6$. So, all the electrons are paired up and when it is excited, then either 2 or 4 or 6 etc. electrons will be unpaired. There is no scope to get odd number of unpaired electrons in its outer most shell. For this reason it cannot form $XeF_3$ or $XeF_5$ type of compound.