

SOME P-BLOCK ELEMENTS

GROUP 13 ELEMENTS

GENERAL INTRODUCTION, ELECTRONIC CONFIGURATION, OCCURRENCE, VARIATION OF PROPERTIES, OXIDATION STATES, TRENDS IN CHEMICAL REACTIVITY:

- * N_2 to form nitrides, which on hydrolysis gives ammonia.
$$2B + N_2 \rightarrow 2BN \xrightarrow{H_2O} NH_3 + H_3BO_3$$
$$2Al + N_2 \rightarrow 2AlN \xrightarrow{H_2O} NH_3 + Al(OH)_3$$
- * Atomic radius increases suddenly from "B" to "Al". due to greater screening effect of electrons of penultimate shell of Al.
- * The atomic radii "Al" and "Ga" is same
Reason: Poor shielding effect of d-electrons in Ga.
- * The decreasing order of electronegativity of IIIA elements is Due to poor shielding effect of 'd' or 'f' orbitals the EN values of Tl, In and Ga are more than Al.
- * The melting and boiling points of Boron are very high. Since "B" exists as giant covalent polymer in liquid and in solid states.
- * "Ga" has low melting point, since it exists as simple molecules.
- * The difference between the melting point and boiling point of Ga is high i.e., liquid range is very wide. Hence Ga is used as thermometric liquid.
- * The decreasing order of melting point of IIIA elements is: B>Al>Tl>In>Ga
- * Order of densities: B<Al<Ga<In<Tl Al has relatively low density due to its large atomic volume.
- * Order of boiling points B>Al>In>Ga>Tl.
- * Ionisation potential order B>Tl>Ga>Al>In.
- * Order of SRP values Al<B<Ga<In<Tl.
- * The common oxidation state of IIIA elements is +III. Boron exhibits oxidation state of -3 (Eg: $Mg_3 B_2$)
- * The inability of ns^2 electrons in the participation of chemical bond is called inert pair effect.
- * Inert pair effect is more prominent in larger atoms in a group of p-block
- * "Tl" exhibits stable +1 oxidation state due to inert pair effect. B and Al do not exhibit +1 oxidation state.
- * The compounds of boron are always covalent. Compounds of Al and Ga are covalent only in anhydrous state.
- * In aqueous solutions, the compounds of "Al" and "Ga" like $AlCl_3$ and $GaCl_3$ are ionic because. The large amounts of hydration energy evolved compensate the effect of their high ionisation energies. They give Al^{3+} , Ga^{3+} ions in solutions.

Anomalous Properties Of First Element Of The Group, Boron, Some Important Compounds: Borax, Boric Acid, Boron Hydrides:

- * **Anomalous properties of B.**
 - i) Boron is a non metal. Al is an amphoteric metal Ga, In and Tl are metals. Al is most metallic in nature.

- ii) B always forms covalent compounds
- iii) Boron shows diagonal relationship with Si.
- iv) Boron does not displace hydrogen from acids
- v) B_2O_3 is an acidic oxide Al_2O_3 is amphoteric; TIOH is strong base.
- vi) $B(OH)_3$ or H_3BO_3 is an acid while the hydroxides of other elements are either amphoteric or basic in nature.
- vii) Simple borates and silicates can polymerize readily
- viii) Boron has covalency maximum of 4 only. But others exhibit a covalency maximum of 6.
- ix) Boron forms covalent hydrides which are stable.
- x) Boron never appears as a cation and does not form B^{+3} ion
- xi) The halides of B except BF_3 hydrolyze readily and vigorously in water whereas the other metal halides undergo either partial hydrolysis or no hydrolysis with water.
- xii) Boron forms borides with metals while others all most do not react.
- xiii) Boron forms an oxide and nitride (B_2O_3+BN) when burnt in air.

* **Similarities of Boron and Aluminium**

- a) Boron and Aluminium show similar chemical properties due to similar valence shell configuration.
- b) The trihalides of "B" and "Al" are covalent. Electron deficient and can act as Lewis acids.

* The important minerals of boron are

- i) Borax (Tincal): $Na_2 [B_4O_5 (OH)_4] \cdot 8H_2O$ (or) $Na_2B_4O_7 \cdot 10H_2O$
- ii) Kernite (Razorite) $Na_2 [B_4O_5 (OH)_4] \cdot 8H_2O$ or $Na_2B_4O_7 \cdot 2H_2O$
- iii) Colemanite: $Ca_2 [B_3O_4 (OH)_3]_2 \cdot 2H_2O$ or $Ca_2B_6O_{11} \cdot 5H_2O$

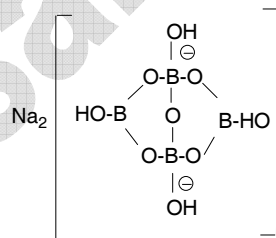
Compounds of Boron

Borax, Boric acid & Boron Hydrides

Borax:

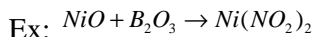
- * Borax is represented by the molecular formula $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2 [B_4O_5 (OH)_4] \cdot 8H_2O$. Impure borax is called tincal
- * Borax is available in nature as kernite or Razorite ($Na_2B_4O_7 \cdot 4H_2O$).
- * Borax exists in three crystalline forms namely (1) prismatic borax $Na_2B_4O_7 \cdot 10H_2O$; (2) Octahedral borax $Na_2B_4O_7 \cdot 5H_2O$, (3) Borax glass ($Na_2B_4O_7$)
- * Borax glass is obtained by heating borax to above its melting point.
- * The aqueous solution borax is alkaline in nature due to hydrolysis.
- * Structure of borax: It contains the tetrahedral Nuclear units $[B_4O_5 (OH)_4]^{-2}$,

It has two tetrahedral and two triangular units joined together as shown in the following figure.

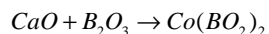


- * **Borax bead Test:** This test is useful in the identification of basic radicals. On heating borax decomposes and swells losing water of crystallisation. On further heating it melts and forms a clear transparent bead of boric oxide and sodium metaborate. Sodium Meta Boric oxide borate. When the glassy bead is touched with some coloured cations such as Ni^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} etc, and

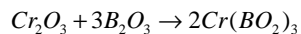
heating again, it gives characteristic coloured beads of metaborates of different Ions. This is known as borax bead test.



Nickel meta borate (violet)



Cobalt meta borate (Blue)



Chromium meta borate (yellow)

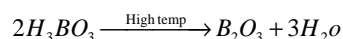
Cu (BO₂)₂ is green coloured,

Fe BO₂)₂ is Greenish colored and

Mn (BO₂)₂ is violet coloured metaborate.

- * Acidic Character: Boric acid is a weak monobasic acid. It does not act as a protonic acid but behaves as a Lewis acid by accepting a pair of electrons from OH⁻ ion.

- * H₃BO₃ loses water on heating



The reaction takes place depending on temperature



Uses:

It is used as an antiseptic and also used in enamel and glass industries.

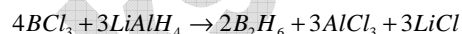
- * **Structure of Boric acid:** Boric acid has a layer structure in which planar units are joined by hydrogen bonds.

Diborane:

- * Hydrides of B are called boranes. They are electron deficient molecules.
- * Boranes can be classified into two types with general formula
a) B_nH_{n+4} and b) B_nH_{n+6}
- * Boranes have different kinds of structures and unusual stoichiometry.
- * Li and Na tetrahydrido borates are called borohydrides. These are used as reducing agents in organic synthesis.

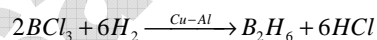
- * **Preparation of Diborane:-**

1) BCl₃ reduction with LiAlH₄ gives B₂H₆ in presence of ether.

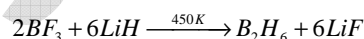


(99.4%)

- * A mixture of BCl₃ and H₂ at low pressure when subjected to silent electric discharge gives B₂H₆



- * Industrial method: - BF₃ on reduction with LiH gives Diborane.



- * Oxidation of NaBH₄ with I₂ gives diborane.

- * **Properties of B₂H₆:-**

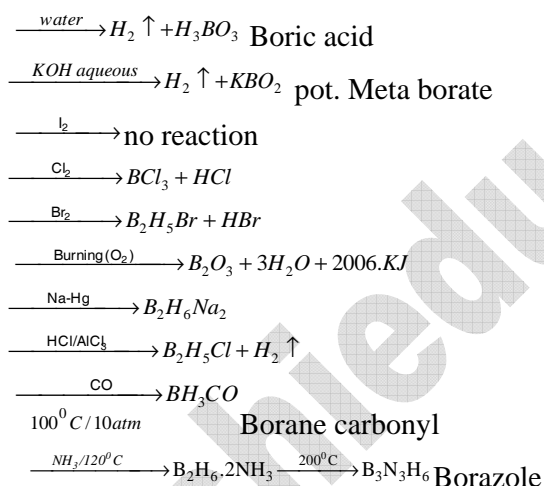
a) B₂H₆ is a colourless toxic gas

b) It is stable in the absence of grease and moisture and at low temperatures.

c) It catches fire on exposing to air.

* **Chemical Properties of B₂H₆**

- * B₂H₆. 2N₃ is formulated as [BH₂(NH₃)₂]⁺ [BH₄]⁻
- * Diborane burns in O₂ to give B₂O₃ with liberation of excess of energy. So it is used as a potential rocket fuel. Boranes are better fuels than hydrocarbons. The heat of combustion of diborane is very much higher than that of C₂H₆.
- * B₃N₃H₆ is called borazole or borazine. It is known as inorganic benzene.
- * Diborane molecule contains only 12 bonding electrons. So it is an electron deficient molecule. It has not B-B bond.
- * It has two coplanar BH₂ groups. There are 4 terminal and 2 bridge H atoms. Methylation of B₂H₆ gives Me₄B₂H₂. Hybridisation of B is sp³.
- * B-H-B bond or Tau (or) banana (or) hydrogen bridge bond is formed by sp³-s-sp³ orbital overlapping. It is a 3 centered -2 electron bond. In diborane there are B-H-B bonds.
- * B-H bond is formed by sp³ - s overlapping.
- * Distance between two boron atoms in diborane is 1.77 Å.
- * B-H_{bridge} length is 1.33 Å, B-H_{term} length is 1.77 Å.
- * H-B-H terminal angle is 121.5°, H-B-H bridged angle is 97°.
- * **Chemical properties of B₂H₆:-**



- * Borazole is known as inorganic benzene.
- * **Halides:**
- * IIIA group elements can form trihalides with halogens. TlI₃ has no existence.
- * Boron can't form due to the absence of vacant 'd' orbitals.
- * Boron forms BX₃, type of halides BF₃, BCl₃, BBr₃, BI₃ (unstable)
- * These are formed by heating boron with halogens.
- * These are covalent; electron deficient and act as Lewis acids.
- * The order of Lewis acidic strength BBr₃ > BCl₃ > BF₃.
- * BF₃ is expected to behave as a stronger Lewis acid than BCl₃ and BBr₃ because of more electronegativity of fluorine. But practically BF₃ is less acidic.
- * BF₃ has delocalized dative bond from fluorine to boron which is called 'back bonding'.
- * Back bonding ability is more with fluorine atoms as B-F bond involves the overlap of almost equal orbitals (2p-2p)

- * Boron halides readily hydrolysed forming H_3BO_3 .
- * BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$.

Aluminium: Uses, Reactions With Acids And Alkalies:

Aluminium:

- * a) Bauxite containing FeO and Fe_2O_3 impurities is known as Red Bauxite.
- * b) Bauxite containing silica (SiO_2) impurity is known as White Bauxite.
- * Properties of Aluminium;-
 - 1) "Al" metal is a good conductor of electricity.
 - 2) "Al" is soft. Malleable, ductile and tenacious
 - 3) "Al" forms amalgams and other alloys also.
 - 4) "Al" is highly electropositive and acts as powerful reducing agent.
- * "Al" metal is passive towards conc.

HNO_3 due to formation of Al_2O_3 layer on the surface Because of this property, cans made of "Al" metal are used for the transportation of conc. HNO_3

* Chemical Properties of Al:

$\xrightarrow{\text{dry air}}$ no action

$\xrightarrow{\text{Pure cold water}}$ no action

$\xrightarrow{\text{boiling water}}$ $Al(OH)_3 + H_2 \uparrow$

$\xrightarrow{\text{moist air}}$ Al_2O_3

(prevents further corrosion)

$\xrightarrow{\text{burning in air}}$ $Al_2O_3 + AlN + 3229KJ$

$\xrightarrow{N_2}$ AlN

$\xrightarrow{Cl_2}$ $AlCl_3$

$\xrightarrow{\text{Conc. } HNO_3}$ no action

$\xrightarrow{\text{dil. } HNO_3}$ $Al(NO_3)_3 + NH_4NO_3 + H_2O$

(with impure Al)

$\xrightarrow{\text{Conc. } H_2SO_4}$ $Al_2(SO_4)_3 + H_2O + SO_2 \uparrow$

$\xrightarrow{\text{dil. } H_2SO_4}$ $Al_2(SO_4)_3 + H_2 \uparrow$

$\xrightarrow{\text{dil./conc. } HCl}$ $AlCl_3 + H_2 \uparrow$

$\xrightarrow{\text{dil. } NaOH}$ $H_2 + NaAlO_2$

(Sod. meta aluminate)

$\xrightarrow{\text{Fused } NaOH}$ $H_2 + Na_3AlO_3$

(Sod. aluminate)

$\xrightarrow{Fe_2O_3}$ Fe

$\xrightarrow{Cr_2O_3}$ Cr (in molten state)

$\xrightarrow{Mn_2O_4}$ Mn

- * a) In aqueous state meta Aluminate ion exists as $[Al(H_2O)_2(OH)_4]^-$.
- * b) In aqueous state Aluminate ion exists as $[Al(OH)_6]^{-3}$

* **Alloys of Aluminium:-**

| Alloy | Composition | Uses |
|---------------------|---------------------------------------|---|
| Magnalium | Mg=2-15% Al=85-98% | in making cheap balances, utensils |
| Aluminium Bronze | Al=10-12% Cu=88-90% | in making utensils, jewellery, photo frames |
| Duralumin | Al=95% Cu=4% Mg=0.5% Mn=0.5% | in making air ships |
| γ -alloy | Al=92.5% Cu=4% Mg=1.5% Ni=2% | making parts of aeroplane. |

Aluminium halides:

- * Aluminium forms AlX_3 type of halides, AlF_3 , $AlCl_3$, $AlBr_3$, AlI_3
- * AlF_3 is ionic and other halides are covalent.
- * Aluminium halides are also electron deficient and act as Lewis acids.
- * $AlCl_3$ exists as dimer in vapour state and represented as Al_2Cl_6 . Anhydrous $AlCl_3$ is a catalyst in Friedal Craft's reaction.
- * **Uses of "Al":** Aluminium is used
 - 1) for making electrical cables
 - 2) as deoxidiser for removing blow holes in metallurgy
 - 3) for making alloys useful in automobiles
 - 4) in the place of Tin and Zinc for painting Iron surface.
 - 5) in preparing cans for the transportation of conc. HNO_3

GROUP 14th ELEMENTS

General Introduction, Electronic Configuration, Occurrence, Variation Of Properties, Oxidation States, Trends In Chemical Reactivity.

* **Introduction - General Properties:**

- * The IV A elements are Carbon (C), Silicon(Si), Germanium (Ge), Tin (Sn) and Lead (Pb).
- * These elements belong to group 14 (IUPAC).
- * The carbon family elements belongs to p-block
- * The general valence shell configuration of IVA group elements is ns^2np^2 .
- * The number of electrons present in the penultimate shell of carbon is 2.
- * The number of electrons present in the penultimate shell of Si is 8 while Ge, Sn, Pb contain 18 electrons each. Due to this difference in their electronic configuration carbon and silicon are different from other elements of this group.
- * Carbon is very widely distributed in nature as essential constituent of all living matter, as proteins, as carbohydrates and fats.
- * Silicon is second most abundant element on earth crust.
- * Germanium is not well known.
- * Tin and Lead are commonly known elements due to their easy extraction methods and their many uses.

Abundance:

- * Except germanium, all the other elements of IV A group are present abundantly in nature.
- * Carbon and silicon are widely distributed compared to Tin and Lead.
- * Abundance of these elements in earth crust is

Occurrence:

- * Except carbon all other elements are found in combined state.
- * Carbon can exist in elemental state and also in combined state.
- * Carbon in combined state mainly exist as oxide and carbonate.
- * Silicon exist as Silica and Silicates.
- * The nature of IVA elements :

| | | |
|------------|-----------|-----------|
| C and Si | Ge | Sn and Pb |
| Non metals | metalloid | metals |

Atomic size:

- * The atomic size increases from C to Pb.
- * The difference in the atomic size of "Si" and "Ge" is less. It is due to ineffective shielding of nuclear charge by the completely filled 3d-shell in "Ge".
- * The difference in the atomic size of "Sn" and "Pb" is also very less. It is due to the presence of completely filled 4f-orbitals in "Pb".

Density:

- * The density decreases from C to Si, and then increases from Si to Pb.
 $Pb > Sn > Ge > C > Si$

- * **Ionisation potential** decrease from C to Pb.

- * **Electronegativity** of Carbon is 2.5. Electronegativity of Si, Ge, Sn and Pb are equal to 1.8.

* **Melting point:**

- * **Boiling point:** In this group, element with the highest boiling point is carbon and element with the lowest boiling point is lead.

Oxidation state:

- * Carbon shows a large no. of oxidation states. The other members of the family exhibit +2 and +4 oxidation states.
- * In carbon monoxide (CO) due to the presence of co-ordinate covalent bond, the oxidation state of carbon is not considered as +2.
- * Sn^{+4} is more stable than Sn^{+2} but Pb^{+2} is more stable than Pb^{+4} due to inert pair effect.
- * The reluctance of ns electrons to participate in bond formation is known as **inert pair effect**.

Reactivity:

- * The elements in this group are relatively less reactive.
- * Reactivity increases down the group.

Reactivity with water:

- * C, Si, Ge are not affected by water.
- * Sn reacts with steam to give SnO_2 and H_2 .
- * Pb is not affected by water due to an oxide layer on the surface.

Reactivity with Dilute acids:

- * C, Si, Ge are not affected by dilute acids.
- * Sn and Pb dissolve readily in dilute HNO_3 .

Reactivity with Dilute Base(Alkali):

- * C is unaffected by alkalis.
- * Si, Sn and Pb also react with alkalis and give silicates, stannates and plumbates respectively.
- * Sodium stannate and sodium plumbate in aqueous solutions exist as

Reactivity with Halogens:

- * For a given element.

Catenation:

- * The linkage of atoms of the same element to form long chains is called catenation.
- * Catenation ability is highest for carbon. This is due to its high bond strength

Order of bond energies:

$\text{C} - \text{C} > \text{Si} - \text{Si} > \text{Ge} - \text{Ge} > \text{Sn} - \text{Sn} > \text{Pb} - \text{Pb}$

Order of catenation ability:

$\text{C} > \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$

Allotropy:

- * The phenomenon of an element existing in two or more physical forms having similar chemical properties but different physical properties is called as allotropy.
- * Allotropy is due to the difference in structure (or) arrangement of atoms.
- * Carbon has two types of allotropes.
(i) Crystalline allotropes (ii) Amorphous allotropes.

Crystalline allotropes:

a) Diamond b) Graphite c) Fullerene

The amorphous allotropes:

1. Coal, 2. Coke, 3. Wood charcoal, 4. Animal charcoal, 5. Lamp black, 6. Gas carbon, 7. Petroleum coke, 8. Sugar charcoal.

- * Being a metal lead can not exhibit allotropy.
- * Crystalline allotropes of carbon are ... Diamond and Graphite

Diamond

a) Each carbon is sp^3 hybridised

Graphite

a) Each Carbon is sp^2 hybridised

- | | |
|---|--|
| b) Each carbon is bonded to 4 other carbons tetrahedrally | b) Each carbon is bonded to 3 other carbon atoms to form hexagonal rings. It has sheet like structure. |
| c) It is a 3 dimensional polymer. | c) It is a 2 dimensional polymer. |
| d) C - C bond length is 1.54\AA and bond angle is $109^{\circ}28'$. | d) C - C bond length in hexagonal rings is 1.42\AA and bond angle is 120° . |
| e) Carbon atoms are firmly held with strong covalent bonds. | e) The distance between two adjacent layers is 3.35\AA . These layers are held by weak vander waal's forces |
| f) Diamond is very hard | f) Graphite is soft. |
| g) Diamond is an insulator due to the absence of free electrons | g) Graphite is a conductor due to the presence of free electrons |

* **Uses of Diamond:** - Diamonds are used

- a) as precious stones in jewellery
- b) for drawing thin wires.
- c) for cutting glass, drilling rocks and as abrasives.

* Layers of graphite are held together by vanderwaal's forces.

* **Uses of Graphite:-**

- 1) as a lubricant
- 2) for making electrodes in electrical furnaces
- 3) in electroplating and in electrotyping.
- 4) Graphite is used in the manufacture of refractory crucibles.

Fullerenes

- 1) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.
- 2) Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.
- 3) molecule has a shape like soccer ball and called **Buckminsterfullerene**.
- 4) All the carbon atoms are equal and they undergo hybridisation.
- 5) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 139.3 pm respectively.
- 6) Spherical fullerenes are also called bucky balls in short.

Similarities between Carbon and Silicon:

- * "C" and "Si" exhibit tetravalency. "Si" exhibits maximum covalency of 6. For carbon maximum covalence is limited to four.
- * "C" and "Si" are non – metals and can form hydrides, halides and oxides.
- * CO_2 and SiO_2 are acidic oxides.
- * Carbon is the essential element of plant and animal kingdom where as Si is essential element of mineral kingdom.

Hydrides :

- * Hydrides of carbon are known as hydrocarbons. where as silicon hydrides are known as silanes.
- * Hydro carbons are more in number and more stable than silanes due to less electronegativity difference between carbon and hydrogen.

- * Hydrides of silicon are less stable because in silanes hydrogen withdraw electrons from Si-H bond.
- * Silanes are good reducing agents and readily undergo hydrolysis in alkaline medium.

Halides :

- * The elements of IVA group form MX_4 type covalent tetrahalides.
- * For a given halogen atom thermal stability of tetrahalides decreases in the order $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
- * For carbon atom thermal stability of tetrahalides decreases in the order $CF_4 > CCl_4 > CBr_4 > CI_4$
- * Except CCl_4 tetrahalides of IVA group elements acts as Lewis acids. Due to the presence of vacant d-orbitals
- * CCl_4 does not undergo hydrolysis due to absence of d-orbitals in carbon atom.
- * $SiCl_4$ undergoes hydrolysis due to the presence of vacant d-orbitals in silicon atom.

ANOMALOUS BEHAVIOUR OF FIRST ELEMENT, CARBON, ALLOTROPIC FORMS, PHYSICAL AND CHEMICAL PROPERTIES, USES OF SOME IMPORTANT COMPOUNDS: OXIDES

Anomalous Behavior of Carbon :

- * Carbon is widely distributed in nature.
- * Carbon occurs in free state where as other elements found in combined state.
- * Carbon can not expand octet where as the others can due to the availability of empty d-orbitals in them.
- * Carbon shows co-ordination number 4 where as others show 6.
- * Covalency maximum for carbon is 4 and for other elements is 6.
- * Carbon can form covalent compounds because it is a non metal and has small atomic size.
- * Carbon has more capacity to form chains (catenation) it is due to high C-C bond energy [348 kJ / mole].
- * Silicon can form longest chain with eight Si atoms.
- * Carbon can only form multiple bonds.

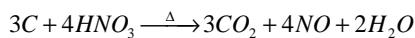
Differences between CO_2 & SiO_2

| CO_2 | SiO_2 |
|--|--|
| 1. It is a gas at RT | 1. It is a solid |
| 2. Linear with double bonds | 2. Tetrahedral with single bonds |
| 3. More acidic | 3. Less Acidic |
| 4. Low M.P due to weak attractive forces | 4. High MP due to weak attractive forces giant polymeric structure |
| 5. Hybridisation of carbon - sp | 5. Hybridisation of Silicon - sp^3 |

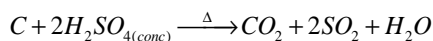
Properties of carbon :

- * The amorphous forms of carbon are more reactive due to their increased surface area.
- * Different allotropes of carbon have nearly same reactivity.
- * $C_{(d)} + O_2 \xrightarrow{700^\circ C} CO_2$
- * $C_{(coke)} + S_2 \xrightarrow{\text{Electric furnace}} CS_2$
- * Carbon reacts with the oxidizing acids like HNO_3 and gives acidic oxides. With hot H_2SO_4 yields CO_2 and H_2SO_4 is reduced to SO_2 .

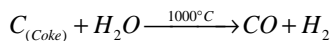
* **With HNO₃:**



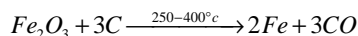
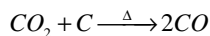
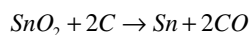
* **With H₂SO₄:**



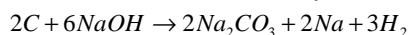
- * Carbon reacts with dil HNO₃ or Conc HNO₃ or Con H₂SO₄ but not with dil HCl and dil H₂SO₄. because dil / conc HNO₃, Conc H₂SO₄ are oxidizing agents but dil HCl and dil H₂SO₄ are non-oxidizing agents.



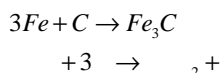
- * Carbon can act as reducing agent.



- * Carbon reduces sodium hydroxide to Na metal.



- * Carbon reacts with metals or metal oxides to form carbides.



* **Uses of carbon:**

i. Mainly C is used as a reducing agent.

ii. It is used in manufacture of CS₂.

iii. In the production of water gas and producer gas.

iv. Activated char coal is used to absorb poisonous gases.

Similarities between Carbon and Silicon:

- * "C" and "Si" exhibit tetravalency. "Si" exhibits maximum covalency of 6. For carbon maximum covalence is limited to four.

- * "C" and "Si" are non – metals and can form hydrides, halides and oxides.

- * CO₂ and SiO₂ are acidic oxides.

- * Carbon is the essential element of plant and animal kingdom where as Si is essential element of mineral kingdom.

Hydrides :

- * Hydrides of carbon are known as hydrocarbons. where as silicon hydrides are known as silanes.

- * Hydro carbons are more in number and more stable than silanes due to less electronegativity difference between carbon and hydrogen.

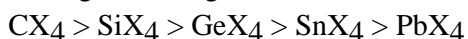
- * Hydrides of silicon are less stable because in silanes hydrogen withdraw electrons from Si-H bond.

- * Silanes are good reducing agents and readily undergo hydrolysis in alkaline medium.

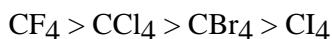
Halides :

- * The elements of IVA group form MX₄ type covalent tetrahalides.

- * For a given halogen atom thermal stability of tetrahalides decreases in the order



- * For carbon atom thermal stability of tetrahalides decreases in the order



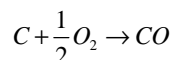
- * Except CCl_4 tetrahalides of IVA group elements acts as Lewis acids. Due to the presence of vacant d-orbitals
- * CCl_4 does not undergo hydrolysis due to absence of d-orbitals in carbon atom.
- * SiCl_4 undergoes hydrolysis due to the presence of vacant d-orbitals in silicon atom.

Oxides :

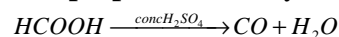
- * Carbon form three important oxides.
 - Carbon monoxide (CO)
 - Carbon dioxide (CO_2)
 - Carbon suboxide (C_3O_2)

Carbon Monoxide:

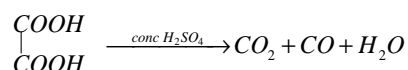
- * Carbon monoxide is formed by the incomplete combustion of carbon or carbonaceous fuels. It is invariably present in automobile exhaust gases.



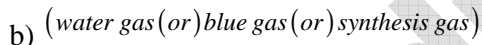
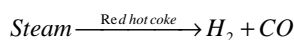
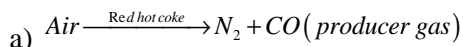
- * **Lab preparation:** dehydration of pure formic acid by conc .



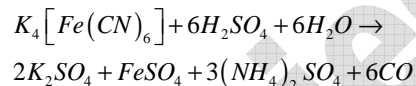
- * Similarly oxalic acid is dehydrated with conc. to produce a mix of CO and CO_2 . When this mixture is passed through caustic potash, CO_2 is absorbed and CO is collected.



- * **Manufacture:**



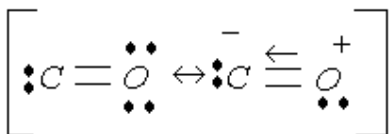
- * Other methods: By heating potassium ferrocyanide with conc



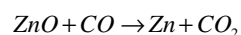
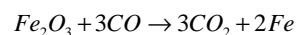
- * **Physical properties:**

CO is a neutral, colorless, odorless, poisonous gas burns with a blue flame. It is almost insoluble in water.

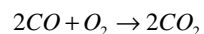
- * It has one and bonds, with 'sp' hybridisation in C and in one of the sp hybrid orbital has one lone pair of electrons.



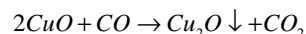
- * There fore CO acts as a donor in metal carbonyl compounds $\text{M}(\text{CO})_n$

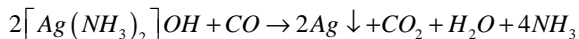


- * It is a non supporter of combustion but combustible.



- * It reduces Fehlings solution and ammonical silver nitrate solution

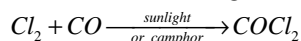




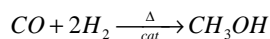
* **Unsaturated nature:**

Being unsaturated compound CO gives addition products.

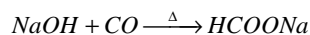
1) Formation of Phosgene



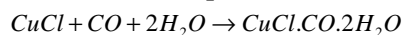
2) Formation of Methyl alcohol



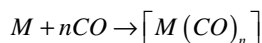
3) Formation of Sodium formate



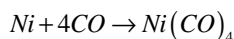
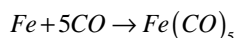
4) In ammonical cuprous chloride or acidic medium



* It acts as a Lewis base and electron pair donor to form dative bonds.

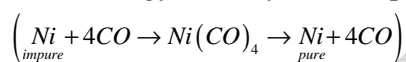


(M = Ni, Cr, Fe, Co)



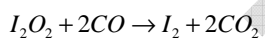
* **Uses:**

1. as a component of many fuel gases.
2. as a reducing agent in metallurgy
3. manufacture of methanol, phosgene, synthetic petrol, acetic acid etc.
4. Metallurgy of Ni by Mond's process.



* **Tests:**

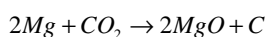
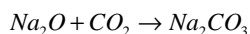
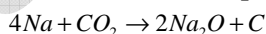
1. Burns with blue flame
2. Reduces iodine pentoxide to I₂ which imparts colour to solvent.



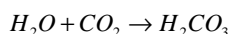
(CHCl₃ or CCl₄ layer turns violet)

Carbonyl:

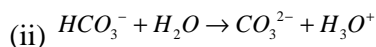
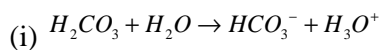
- * It is naturally available in air (0.03% by volume).
- * It is prepared by complete combustion of carbon or carbon containing fuels in excess of air.
- * In the lab, it is prepared by treating calcium carbonate with dilute HCl.
- * Large scale preparation by heating limestone in the absence of air. (calcination).
- * It is a colourless, odourless and non-poisonous gas which is 1.5 times heavier than air and can be poured downwards like a liquid.
- * It is neither combustible nor a supporter of combustion. But highly reactive metals such as Na, Mg continue to burn in the presence of CO₂.



- * It is less soluble in water but more than that of carbon monoxide. Its aqueous solution is acidic due to formation of carbonic acid, H₂CO₃.



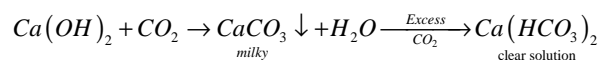
* Carbonic acid is a weak dibasic acid and dissolves in water in two steps :



It can form two series of salts i.e., bicarbonates and carbonates.

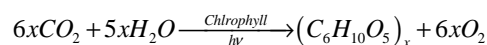
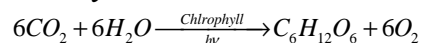
* H_2CO_3 / HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

* CO_2 is an acidic oxide and reacts with metaloxides, hydroxides, bicarbonates to form salts.



* It is reduced by red hot coke to carbon monoxide.

* **Photosynthesis:**



Uses:

* It is used in the manufacture of urea.

* Carbogen (A mixture of 95% O_2 + 5% CO_2) is used for artificial respiration for victims of CO poisoning.

* Dryice or Drikold or solid CO_2 is used as a refrigerent for ice-cream and frozen foods

* Gaseous CO_2 is extensively used for carbonation of soft drinks

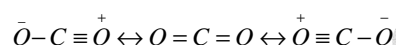
* Being heavy and non-supporter of combustion it is used in fire extinguishers.

Dry powder fire extinguisher contains

($NaHCO_3$ + Sand) which is decomposed by heat.

Foamite extinguisher, containing baking soda and aluminium sulphate, is used for putting off oil fires.

Structure: It is a linear molecule with sp hybridization and with equal bond lengths (115pm)



* As a lab cooling agent to perform reactions below 273K ($0^\circ C$).

* Supercritical CO_2 is used as a solvent to extract organic compounds from their natural sources (Caffeine from Coffee, perfumes from flowers).

* The acidic nature of oxides decreases in the order



Carbon suboxide: C_3O_2

* It is an anhydride of malonic acid.

* It reacts with water and gives malonic $CH_2(COOH)_2$ acid

IMPORTANT COMPOUNDS OF SILICON AND A FEW USES, SILICON TETRA CHLORIDE, SILICONES, SILICATES AND ZEOLITES, THEIR USES:

Silicones:

* Silicones are organo silicon polymers containing Si – O – Si bonds.

* Silicones are formed by the hydrolysis of alkyl or aryl substituted chloro silicates and their subsequent polymerization.

Types of silicones:

1) Linear silicones

2) Cyclic silicones

3) Branched chain silicones

- * Silicones contain R_2SiO repeating unit.
- * Polymerization of dialkyl silane diols yield linear thermoplastic polymers.
- * Cyclic or ring silicones are formed when water is eliminated from terminal $-OH$ groups of linear silicones.
- * Hydrolysis of $RSiCl_3$ gives crosslinked silicone
- * Alkyl or aryl substituted chlorosilanes are prepared by the reaction of $R-Cl$ with silicon in the presence of metallic copper as a catalyst
- * Hydrolysis of substituted chlorosilicones yield corresponding silicones which under polymerization.
- * The empirical formula of silicone R_2SiO is analogous to that of ketone (R_2CO) and hence are named silicones.
- * Commercial silicone polymers are usually methyl derivatives and to a lesser extent phenyl derivatives.
- * Silicones have chemical inertness, water repelling nature, heat resistance and good electrical insulating properties.
- * Silicones are used as sealants, greases, electrical insulators in making water – proof cloth & papers and in silicon rubber preparation.
- * Silicones are used in paints and enamels.

Silicates :

- * Silicon exists mostly in the form of silicate minerals in earth's crust.
- * eg: Feldspar, Zeolites, mica and asbestos.
- * The basic structural unit of silicates is SiO_4 in which Si is tetrahedrally bound to four 'O' atoms.
- * In silicates, either discrete unit is present (or) a number of such units are joined together through corners by sharing 1,2,3 or all the 4 'O' atoms per silicate (SiO_4) unit.
- * When silicate units are linked together in different ways, they form chain, ring, sheet or three-dimensional structures.
- * Negative charge on silicate structure is neutralised by positively charged metal ions.
- * A three -dimensional network is formed when all the four corners of tetrahedron are shared with other tetrahedral units.
- * Two important man-made silicates are cement and glass.
- * In silicates, the central Si atoms undergoes hybridization.
- * Silicates are metal derivatives of silicic acid and can be obtained by fusing metal oxides or metal carbonates with sand e.g.
- * Based on the no.of. 'O' atoms shared between silicate SiO_4 units and the fashion of linkage, silicates can be classified as :

- (i) orthosilicates (ii) Pyrosilicates (iii) chain silicates (iv) Sheet chains (v) cyclic silicate
(vi) 3-dimension silicates.

(i) **Orthosilicates** - They contain discrete SiO_4 tetrahedra, e.g., phenacite Be_2SiO_4 .

(ii) **Pyrosilicates** - Here two SiO_4 tetrahedra units are joined by one oxygen atom forming a large discrete .e.g., hemimorphide $Zn_3(Si_2O_7)Zn(OH)_2H_2O$

(iii) **Chain silicates** - Here two oxygen atoms per SiO_4 tetrahedra are shared giving polymeric anion chains. Discrete unit is $(SiO_3^{2-})_n$. e.g., synthetic sodium silicate Na_2SiO_3 .

(iv) **Double chains** - Here two simple chains are held together by shared oxygen atoms. The discrete unit is $(Si_4O_{11}^{6-})_n$ e.g., mineral tremolde

(v) **Cyclic silicates** - Here two oxygen atoms per SiO_4 tetrahedra are shared giving discrete unit $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$. e.g., Beryl $Be_3Al_2Si_6O_{18}$.

(vi) **Sheet-silicates** - Here three oxygen atoms per tetrahedra are shared giving two dimensional sheet having discrete unit. e.g., .

(vi) **Frame work silicates** - Here all four oxygen atoms of each SiO_4 tetrahedra are shared. $(Si_2O_5^{2-})_n$

Eg., Talc $Mg(Si_2O_5)_2Mg(OH)_2$, Kaolin $Al_2(OH)_4(Si_2O_5)$ Quartz, tridymite, cristobalite and Zeolites.

Zeolites:

- * Alumino silicates are called Zeolites. eg: $Na_2 Al_2 Si_2 O_8 \cdot xH_2O$ (Sodium aluminium orthosilicate)
- * If aluminium atoms replace few silicon atoms in 3-D network of silica (SiO_2), the overall structure known as aluminosilicate is formed and it acquires negative charge.
- * Cations such as Na^+, K^+, Ca^{2+} etc balance the negative charge.
- * Eg: Feldspar & Zeolites
- * These have honey comb like structure and have the general formula

$$\frac{M_x}{n}(AlO_2)_x \cdot (SiO_2)_y \cdot zH_2O$$
 $(M = Na^+, K^+ \text{ or } Ca^{2+})$
- (n = charge on metal ion)
- * These act as ion exchanger and molecular sieves.
- * Artificial zeolites can be prepared by heating china clay, silica & Na_2CO_3 .
- * Eg., of artificial zeolite is permutit, $Na_2 Al_2 Si_2 O_8 \cdot xH_2O$ used in the softening of hard water.

Uses of Zeolites:

(i) As catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation.

Eg : ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of hard water.

- * It is highly poisonous because of its ability to form a complex with hemoglobin (called carboxy hemoglobin). This complex is 300 times more stable than the oxyhemoglobin and hence prevents hemoglobin in RBC from carrying oxygen round the body and ultimately, results in death.
- * It is a powerful reducing agent and has affinity for oxygen. It reduces almost all metal oxides (except those of alkali, alkaline earth metals, Al, and few transition metals) to respective metals. This property is used in metallurgy for the extraction of metals from their oxides.