Some P-Block Elements

Group - 13 Elements

General Introduction, Electronic Configuration, Occurrence, Variation of Properties, Oxidation States, Trends in Chemical Reactivity

* Boron (B), Aluminium (Al), Gallium (Ga), Indium (In) and Thallium (TI) are IIIA group elements present in the p - block of the periodic table.
* These elements belong to group 13 (IUPAC).
* The valence shell configuration of IIIA elements is.
* Boron differs from "Al", since "B" has 2 electrons and "Al" has 8 electrons in their penultimate shells.
* Boron doesn't occur free in nature but it combined state it occurs as salts of boric acid. (Borax)
* The most abundant element of this group is Al and the least abundant element is Tl
* "Al" is the most abundant metal and 3rd most abundant element in earth crust.
* Al forms nearly 7.28% of the earth's crust.
* Ga, In, Tl occurs in traces along with sulphide ores of Zn and Pb.
* The order of abundance of IIIA group elements is
* Boron is a not metal, all others are reactive metals.
* Boron exist in two isotopic forms (19%) and (81%)
* Boron is extremely hard and black coloured solid.
* Except 'B' all others are good conductors of electricity.
* Gallium is called summer liquid.
* Boron is unreactive in crystalline form
* Boron fibers are used in making bullet - proof vest and light composite material for aircraft.
* 'B' and 'Al' can react with 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" are same.

  Reason: Poor shielding effect of d-electrons in Ga.

* The decreasing order of electro negativity 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 (**E.g.:** $Mg_3 B_2$)

* The inability of ns^2 electrons in the participation of chemical bond in called inert pair effect.

* Inert pair effect is more prominent in larger at oms 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 sillicates can polymerize readily

viii) Boron has covalency maximum of 4 only. But others exhibit a covalency maximum of 6.

ix) Boron form covalent hydrides which are stable.

x) Boron never appears as a cation and do not form B^{+3} ion

xi) The halides of B except BF_3 hydrolyze readily and vigorously in water where as 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): $Na_2\ [B_4O_5\ (OH)_4].\ 8H_2O$ (or) $Na_2B_4O_7\ 10H_2O$

ii) Kernite (Razorite) $Na_2\ [B_4O_5\ (OH)_4].\ 8H_2O$ or $Na_2B_4O_{7+}\ 2H_2O$

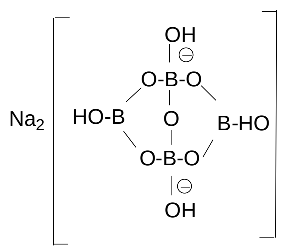
iii) Colemanite: $Ca_2\ [B_3O_4\ (OH)_3]_2\ 2H_2O$ or $Ca_2B_6O_{11}\ 5H_2O$

Compounds of Boron

Borax, Boric acid & Boron Hydrides

Borax

* Borax is represented by the molecular formula $Na_2B_4O_7 10H_2O$ or $Na_2 [B_4O_5 (OH)_4].8H_2O$. Impure borax is called Tincal
* Borax is available in nature as Kernite or Razorite ($Na_2B_4O_7. 4H_2O$).
* Borax exists in three crystalline forms namely (1) prismatic borax $Na_2B_4O_7$ $10H_2O$; (2) Octahedral borax $Na_2B_4O_7$ $5H_2O$, (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.

Ex: $NiO + B_2O_3 \rightarrow Ni(NO_2)_2$

Nickel meta borate (violet)

$CaO + B_2O_3 \rightarrow Co(BO_2)_2$

Cobalt meta borate (Blue)

$Cr_2O_3 + 3B_2O_3 \rightarrow 2Cr(BO_2)_3$

Chromium meta borate (yellow)

$Cu (BO_2) O_2$ is green coloured,

Fe $BO_2)_2$ is Greenish colored and

Mn $(BO_2)_2$ 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.
* H_3BO_3 loses water on heating

$$2H_3BO_3 \xrightarrow{\text{High temp}} B_2O_3 + 3H_2o$$

The reaction takes place depending on temperature

$$H_3BO_3 \xrightarrow{\text{375k}} HBO_2 \xrightarrow{\text{red hot}} B_2O_3$$

$$4H_3BO_3 \xrightarrow{\text{435K}} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

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) BCl_3 reduction with $LiAlH_4$ gives B_2H_6 in presence of ether.

$$4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(99.4%)

* A mixture of BCl_3 and H_2 at low pressure when subjected to silent electric discharge gives B_2H_6

$$2BCl_3 + 6H_2 \xrightarrow{Cu-Al} B_2H_6 + 6HCl$$

* Industrial method: - BF_3 on reduction with LiH gives Diborane.

$$2BF_3 + 6LiH \xrightarrow{450K} B_2H_6 + 6LiF$$

* Oxidation of $NaBH_4$ with I_2 gives diborane.
* **Properties of** B_2H_6

a) B_2H_6 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 B_2H_6

* B_2H_{6},. $2N_3$ is formulated as $[BH_2(NH_3)_2]^+$ [BH_4]
* Diborane burns in O_2 to give B_2O_3 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 C_2H_6.
* $B_3N_3H_6$ 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 BH_2 groups. There are 4 terminal and 2 bridge H atoms methylation of B_2H_6 gives Me_4 B_2H_2 Hybridisation of B is sp^3.
* B-H-B bond or Tau (or) banana (or) hydrogen bridge bond is formed by sp^3-s-sp^3 orbital overlapping. It is 3 centered -2 electron bond. In diborane there are B-H-B bonds.
* B-H bond is formed by sp^3 - s overlapping.
* Distance between two boron atoms in diborane is $1.77A^0$.
* $B\text{-}H_{bridge}$ length is $1.33A^0$, $B\text{-}H_{term}$ length is $1.77A^0$.
* H-B-H terminal angle is 121.5^0, H-B-H bridged angle is 97^0.
* **Chemical properties of B_2H_6**

$\xrightarrow{water} H_2\uparrow + H_3BO_3$ Boric acid

$\xrightarrow{KOH\ aqueous} H_2\uparrow + KBO_2$ POT. Meta borate

$\xrightarrow{I_2}$ No reaction

$\xrightarrow{Cl_2} BCl_3 + HCl$

$\xrightarrow{Br_2} B_2H_5Br + HBr$

$\xrightarrow{Burning\,(O_2)} B_2O_3 + 3H_2O + 2006.KJ$

$\xrightarrow{Na\text{-}Hg} B_2H_6Na_2$

$\xrightarrow{HCl/AlCl_3} B_2H_5Cl + H_2\uparrow$

$\xrightarrow[100^0C/10atm]{CO} BH_3CO$ Borane carbonyl

$\xrightarrow{NH_3/120^0C} B_2H_6.2NH_3 \xrightarrow{200^0C} B_3N_3H_6$ Borazole

* Borazole is known as inorganic benzene.

Halides

* IIIA group elements can form trihalides with halogens. TlI_3 has no existence.
* Boron can't form due to the absence of vacant'd' orbitals.
* Boron form BX_3, type of halides BF_3, BCl_3, BBr_3, BI_3 (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 $BBr_3 > BCl_3 > BF_3$.
* BF_3 is expected to behave as a stronger Lewis acid than BCl_3 and BBr_3 because of more electro negativity of fluorine. But practically BF_3 is less acidic.
* BF_3 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 overlop 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, 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**

  $\xrightarrow{dry\ air}$ No action

  $\xrightarrow{Pure\ coldwater}$ No action

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

$\xrightarrow{moist\,air} Al_2O_3$

(Prevents further corrosion)

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

$\xrightarrow{N_2} AlN$

$\xrightarrow{Cl_2} AlCl_3$

$\xrightarrow{Conc.HNO_3}$ No action

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

(with impure Al)

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

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

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

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

(Sod. meta aluminate)

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

(Sod. aluminate)

$\xrightarrow{Fe_2O_3} Fe$

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

$\xrightarrow{Mn_3O_4} Mn$

* 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 Alluminium**

Alloy	Composition	Uses
Magnalium		Mg=2-15% in making
	Al=85-98%	cheap balances, utensils
Aluminium		Al=10-12% in making
Bronze	Cu=88-90%	utensils, jewellery,
		photo frames
Duralumin	Al=95%	

	Cu=4%	in making
	Mg=0.5%	air ships
	Mn=0.5%	
γ -alloy	Al=92.5%	making
	Cu=4%	parts of aeroplane.
	Mg=1.5%	
	Ni=2%	

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 electronical cables

  2) As deoxidiser for removing blow holes in metallurgy

  3) For making alloys useful in automobiles

  4) In the piece 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 belong 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 exists as oxide and carbonate.
* Silicon exists 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.
* **Electro negativity** of Carbon is 2.5. Electro negativity 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, 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.**

<u>Reactivity</u>

* 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 dissolves readily in dilute HNO_3.

Reactivity with Dilute Base (Alkali)

* C is unaffected by alkalies.
* Si, Sn and Pb also react with alkalies 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

C - C > Si - Si > Ge - Ge > Sn - Sn > Pb - Pb

Order of catenation ability

C > Si > Ge > Sn > Pb

<u>Allotropy</u>

* The phenomenon of an elements 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 block, 6. Gas carbon, 7. Petroleum coke, 8. Sugar charcoal.

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

Diamond	Graphite
a) Each carbon is sp^3 hybridised	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 $1.54A^0$ and bond angle is $109^0\ 28^1$.	d) C_C bond length in hexagonal rings is $1.42A^0$ and bond angle is 120^0.
e) Carbon atoms are firmly held with strong covalent bonds.	e) The distance between two adjacent layers is $3.35A^0$. These layers are held by weak Van der 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 Van der waal'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.

<u>Fullerenes</u>

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 celled **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. Whereas, silicon hydrides are known as silanes.
* Hydro carbons are more in number and more stable than silanes due to less elelctro negativity difference between carbon and hydrogen.
* Hydrides of silicon are less stable because in silanes hydrogen withdraws 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 tetra halides.
* For a given halogen atom thermal stability of tetra halides decreases in the order
  $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
* For carbon atom thermal stability of tetra halides decreases in the order
  $CF_4 > CCl_4 > CBr_4 > CI_4$
* Except CCl_4 tetra halides 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 BEHAVOUR 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 cannot 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 kg / 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	2. Tetrahedral with bonds single bonds
3. More acidic	3. Less Acidic
4. Low M.P due to	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.
* $C_{(d)} + O_2 \xrightarrow{700°C} CO_2$
* $C_{(coke)} + S_2 \xrightarrow{Electric\ furnace} CS_2$
* 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 HNO_3**

  $3C + 4HNO_3 \xrightarrow{\Delta} 3CO_2 + 4NO + 2H_2O$
* **With H_2SO_4**

  $C + 2H_2SO_{4(conc)} \xrightarrow{\Delta} CO_2 + 2SO_2 + H_2O$
* Carbon reacts with dil HNO_3 or Conc HNO_3 or Con H_2SO_4 but not with dil HCl and dil H_2SO_4. Because dil / conc HNO_3, Conc H_2SO_4 are oxidizing agents but dil HCl and dil H_2SO_4 are non-oxidizing agents.

  $C_{(Coke)} + H_2O \xrightarrow{1000°C} CO + H_2$
* Carbon can act as reducing agent.

  $SnO_2 + 2C \rightarrow Sn + 2CO$

  $CO_2 + C \xrightarrow{\Delta} 2CO$

  $Fe_2O_3 + 3C \xrightarrow{250-400°c} 2Fe + 3CO$

* Carbon reduces sodium hydroxide to Na metal.

$$2C + 6NaOH \rightarrow 2Na_2CO_3 + 2Na + 3H_2$$

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

$$3Fe + C \rightarrow Fe_3C$$
$$CaO + 3C \rightarrow CaC_2 + CO$$

* **Uses of carbon**

i. Mainly C is used as a reducing agent.

ii. It is used in manufacture of CS_2.

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

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

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* The elements of IVA group form MX_4 type covalent tetra halides.
* For a given halogen atom thermal stability of tetra halides decreases in the order

  $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
* For carbon atom thermal stability of tetra halides decreases in the order

  $CF_4 > CCl_4 > CBr_4 > CI_4$
* Except CCl_4 tetra halides 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.

<u>Oxides</u>

* Carbon forms three important oxides.

  i) Carbon monoxide (CO)

  ii) Carbon dioxide (CO_2)

  iii) Carbon sub oxide (C_3O_2)

<u>Carbon Monoxide</u>

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

$$C+\frac{1}{2}O_2 \rightarrow CO$$

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

$$HCOOH \xrightarrow{conc H_2SO_4} CO + H_2O$$

* 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.

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{conc\ H_2SO_4} CO_2 + CO + H_2O$$

* Manufacture:

a) $Air \xrightarrow{Red\ hot\ coke} N_2 + CO(producer\ gas)$

b) $Steam \xrightarrow{Red\ hot\ coke} H_2 + CO$
$(water\ gas\ (or)\ blue\ gas\ (or)\ synthesis\ gas)$

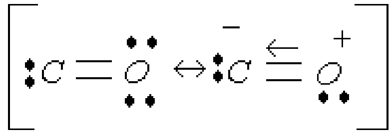
* Other methods: By heating potassium ferrocyanide with conc.

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

* **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.



* Therefore CO acts as a donor in metal carbonyl compounds $M(CO)_n$

$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe$

$ZnO + CO \rightarrow Zn + CO_2$

* It is a non supporter of combustion but combustible.

$2CO + O_2 \rightarrow 2CO_2$

* It reduces Fehling's solution and ammonical silver nitrate solution

$2CuO + CO \rightarrow Cu_2O \downarrow + CO_2$

$2\left[Ag(NH_3)_2\right]OH + CO \rightarrow 2Ag \downarrow + CO_2 + H_2O + 4NH_3$

* **Unsaturated nature**

Being unsaturated compound CO gives addition products.

1) Formation of Phosgene

$Cl_2 + CO \xrightarrow[\text{or camphor}]{\text{sunlight}} COCl_2$

2) Formation of Methyl alcohol

$CO + 2H_2 \xrightarrow[cat]{\Delta} CH_3OH$

3) Formation of Sodium formate

$NaOH + CO \xrightarrow{\Delta} HCOONa$

4) In ammonical cuprous chloride or acidic medium

$CuCl + CO + 2H_2O \rightarrow CuCl.CO.2H_2O$

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

$M + nCO \rightarrow \left[M(CO)_n\right]$

$(M = Ni, Cr, Fe, Co)$

$Fe + 5CO \rightarrow Fe(CO)_5$

$Ni + 4CO \rightarrow Ni(CO)_4$

* **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.

$\left(\underset{impure}{Ni} + 4CO \rightarrow Ni(CO)_4 \rightarrow \underset{pure}{Ni} + 4CO\right)$

* **Tests**

1. Burns with blue flame

2. Reduces iodine pentoxide to I_2 which imparts colour to solvent.

$I_2O_2 + 2CO \rightarrow I_2 + 2CO_2$
($CHCl_3$ or CCl_4 layer turns violet)

Carbon dioxide

* 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 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 presence of CO_2.

$4Na + CO_2 \rightarrow 2Na_2O + C$

$Na_2O + CO_2 \rightarrow Na_2CO_3$

$2Mg + CO_2 \rightarrow 2MgO + C$

* It is less soluble in water but more than that of carbon monoxide. Its aqueous solution is acidic due to formation of carbonic acid, H_2CO_3

$H_2O + CO_2 \rightarrow H_2CO_3$

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

(i) $H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$

(ii) $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

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 metal oxides, hydroxides, bicarbonates to form salts.

$Ca(OH)_2 + CO_2 \rightarrow \underset{milky}{CaCO_3} \downarrow + H_2O \xrightarrow[CO_2]{Excess} \underset{\text{clear solution}}{Ca(HCO_3)_2}$

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

$$6xCO_2 + 5xH_2O \xrightarrow[h\nu]{Chlrophyll} (C_6H_{10}O_5)_x + 6xO_2$$

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 refrigerant 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)

$$\overset{-}{O}-C\equiv\overset{+}{O} \leftrightarrow O=C=O \leftrightarrow \overset{+}{O}\equiv C-\overset{-}{O}$$

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

  $CO_2 > SiO_2 > GeO_2 > SnO_2 > PbO_2$

Carbon sub oxide: 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_2 SiO 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 cross linked 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 is 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 scalants, greases, electrical insulators in making water – proof cloth & papers and in silicon rubber preparation.
* Silicones are used in paints and enamels.

<u>Silicates</u>

* Silicon exists mostly in the form of silicate minerals in earth's crust.
* **E.g.:** Feldspar, Zeolites, mica and asbestos.
* The basic structural unit of silicates is 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 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 atom undergoes hybridzation.

* 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 $Zn_3(Si_2O_7)Zn(OH)_2 H_2O$

  (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 .

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

  E.g., $Talc\ Mg(Si_2O_5)_2Mg(OH)_2$, $Kaolin\ Al_2(OH)_4(Si_2O_5)$ Quartz, tridymite, crystobalite and Zeolites.

<u>**Zeolites**</u>

* Aluminosilicates are called Zeolites. eg: $Na_2\ Al_2\ Si_2\ O_8.xH_2O$ (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.
* **E.g.:** Feldspar & Zeolites
* These have honey comb like structure and have the general formula

  $\frac{M_x}{n}(AlO_2)_x \cdot (SiO_2)_y .zH_2O$

  $(M = Na^+, K^+\ or\ Ca^{2+})$

  (n = charge on metal ion)

* These act as ion exchange and molecular sieves.

* Artificial zeolites can be prepared by heating china clay, silica & Na_2CO_3.

  E.g., artificial zeolite is permutit, $Na_2 Al_2 Si_2 O_8.xH_2O$ used in the softening of hard water.

* **Uses of Zeolites**

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

  E.g.: 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 carboxyhemoglobin). This complex is 300 times more stable than the ox hemoglobin 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 in used in metallurgy for the extraction of metals from their oxides.