THE CARBON FAMILY

Preface

This booklet is designed not only to reinforce the students formal knowledge about "**The Carbon family** . The main objective behind putting up prudently organised strategic edition of this booklet is to develope their urge to excel & ability for original thinking, to offer them the unique joy that only solving of truly challenging problem can bring, to acquiring them with chemical ingenuity & idea which is new to them.

We have meticulously culled out the latest & the most relevant mechanism aspects of reaction & the latest challenging problems.

This book consists of theoritical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total number of Questions in **The Carbon Family** are :

In Chapter Examples 03

Solved Examples 00

Total no. of questions **03**

CARBON FAMILY

1. ELECTRONIC CONFIGURATION

C	6	
Si	14	
Ge	32	ns^2np^2
Sn	50	
Pb	82	

2. IMPORTANT POINTS

General electronic configuration - $ns^2\ np^2$
Ge, Sn and Pb have 18 e^- in penultimate shell whereas C has $2e^-$ and Si has $8e^-$.

3. GENERAL PROPERTIES OF IV-A GROUP

(i) Nature : C and Si have more non metallic character. Ge has both properties i.e. metalloids and Sn and Pb are metals.
Reason : Due to reduced nuclear charge and increased in the size of the atom.

(ii) Ionisation Energy : T ↓ B — Generallly Decreases.
Exception : Sn to Pb I.P. Increases

(iii) Electron Negativity : T ↓ B — Decreases.

(iv) Melting and Boiling Points : Decreases.

(v) Oxidation State : They can form M^{+4} or M^{-4} ions. But due to high I.E. they do not form M^{+4}. C and Si show + 4 oxidation state while Ge, Sn and Pb shows +4 and +2 oxidation state due to inert pair effect.

(vi) Least variation in size of Sn and Pb due to lanthanide contraction.

(vii) Sn has least I.P. in IV Group because size change by small amount but nuclear charge changes by larger amounts.

(viii) Allotropic Forms : The phenomenon of existance of a substance in various physical forms but same chemical form is known as allotropy.

4. ALLOTROPIC FORMS

Carbon have two types of Allotropic forms
(1) Crystalline
(2) Amorphus

4.1 Crystalline : Diamond and Graphite

(a) Diamond :

(1) Each carbon is linked to another atom and so very closed packing in structure of Diamond.

(2) Density and hardness is very much greater for diamond because of closed packing in diamond due to sp^3 hybrid and are tetrahedrally arranged around it.

(3) Diamond has sharp cutting edges that's why it is employed in cutting of glass.

(4) Diamond crystals are non conductor of electricity because of not presence of mobile electron.

(5) 1 carat of diamond = 200 mgm.

(6) Diamond powder if consumed is fatal and causes death in minutes.

(b) Graphite :

(1) In graphite carbon are sp^2 hybridised and due to this carbon exist as hexagonal layer.

(2) Each carbon is lined with 3 carbons and one carbon will be left and form a two dimensional shed like structure.

(3) Distance between two layers is very large so no regular bond is formed between two layers. The layers are attached with weak vander waal force of attraction.

(4) The carbon have unpaired electron so graphite is a good conductor of current.

(5) C–C bond length in Graphite is shorter (1.42 Å) than that of Diamond (1.54 Å).

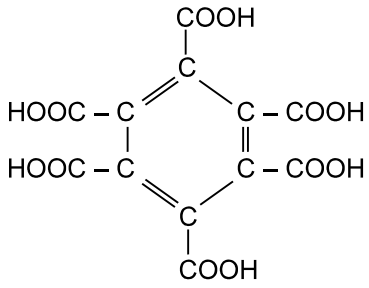
(6) Due to wide separation and weak interlayer bonds, graphite is soft, greasy and has a lubricant character and low density.

(7) Graphite marks the paper black so it is called Black lead or plumbago and so it is used in pencil lead.

(8) Composition of pencil lead is graphite + clay. The percentage of lead in pencil lead = 0%

(9) Graphite has high melting point so it is employed in manufacture of crucible.

(10) Graphite when heated with oxidising agents like alkaline $KMnO_4$ forms metallic acid.



Benzene hexa carboxylic acid

(11) Graphite on oxidation with conc. HNO_3 gives acid i.e. known as Graphite acid ($C_{11}H_4O_5$)

4.2 Amorphous Allotropic Forms of Carbon :

(A) Lamp Black :

(i) Obtained by incompletely combustion of compounds which contains higher % of carbon, benzene, turpentine, acetylene etc. These all on combustion form black carbon called lamp black.

(ii) Black blue ink, printing ink, black paints, varnishes are made from lamp black.

(iii) In Diamond 100% carbon and next to it is lamp black has highest % of carbon.

(iv) Anthracite is the purest form of carbon while lamp black is the softest form of carbon.

(B) Coke :

(i) Obtained by destructive distillation of coal

(ii) Cake is usually employed as weak reducing agent with compared to CO.

(C) Gas Carbon :

(i) Exist in the solid state and when produced it is in gaseous state.

(ii) It is used in the form of electrodes.

(D) Wood Charcoal :

(i) Obtained by incomplete combustion of wood.

(ii) Used to decolourise organic compound.

(E) Animal Charcoal or Bone Charcoal :

(i) Formed by decomposition of animal bone

(ii) Composition of it $Ca_3(PO_4)_2$ and 8-12% of carbon.

(iii) Least percentage of carbon in it.

(iv) Thus is used to decolourise Brown sugar

Example : In sugar Industry. Brown $\rightarrow$ White

(F) Coal :

(i) Which have varying % of carbon from 60 to 95%

(ii) Coal with 60% carbon burns with smoky flame is Peat.

(iii) Lignite has 70% carbon.

(iv) Coal with maximum % of carbon is Anthracite having 95% carbon. It is used in railway engines.

(v) Common variety of coal is Bituminuous (75% carbon).

(G) Buck Minster Fullerene :

(1) It has the formula C_{60} and is made from interlocking hexagonal and pentagonal rings of carbon atoms.

(2) Such molecules are now thought to exist even in chimney root or candle smoke.

(3) The structure of C_{60} is similar to the surface of a football which has also set of interlocking hexagons and pentagons.

(4) Another molecule C_{70} has been recently discovered.

(5) These and similar large carbon molecules are sometimes referred as "bulky balls".

4.3 Allotropic forms of Tin :

(i) It has three allotropic forms

(a) White tin :

(i) Used in containers of oil.

(ii) White tin is more stable and having maximum density.

(b) Grey tin :

(c) Rhombic tin :

(ii) At low temp. (18°C) white tin converts to Grey tin.

(iii) At temp. of 160°C (above) white tin converts to Rhombic tin.

(iv) White tin forms grey tin which is obtained as powdery substance and with formation of this thickness of white tin container decreases. This is called Tin pest or Tin disease or Tin plague.

(v) When tin sheets are folded, they given a peculiar sound which is called as Tin cry.

(vi) Catenation :

(a) It is a tendency to form chain

(b) C >> Si > Ge $\cong$ Sn >>> Pb

(c) Catenation $\propto$ B.E.

(vii) Types of fire Extinguishers -

(a) Dry powder extinguishers contain sand and baking soda ($NaHCO_3$)

(b) Foamite extinguishers contain baking soda and Aluminium sulphate

Examples based on General Properties

Ex.1 Tendency of catenation is strongest in -

(A) C (B) O

(C) N (D) Si

Ans. [A]

Sol. Bond energy for C – C is maximum.

Ex.2 Metalloid among the following is -

(A) Si (B) C

(C) Ge (D) Pb

Ans. [C]

Sol. C and Si are non-metals; Pb is metal.

Ex.3 Graphite is good conductor of current but diamond is non-conductor because -

(A) Diamond is hard and graphite is soft

(B) Graphite and diamond have different atomic configuration

(C) Graphite is composed of positively charged carbon ions

(D) Graphite has hexagonal layer structure with mobile π-electrons while diamond has continuous tetrahedral covalent structure with no free electrons.

Ans. [D]

Sol. It is a reason for the given fact.

5. CHEMICAL PROPERTIES

5.1 Formation of Hydrides :

(i) Carbon form large number of hydrides eq. Alkanes, Alkenes.

(ii) Hydrides of Si are silanes with formula Si_nH_{2n+2}. These are also called as Silicon alkanes.

Eg. SiH_4 Monosilicane Silicon methane

Si_2H_6 Disilicane Silicon ethane

(iii) Silanes with 'n' up to 8 are known.

(iv) Hydrides of Ge are called Germains.

General Formula : $Ge_n H_{2n+2}$

Eg. GeH_4, Ge_2H_6

(v) Tin has only two hydrides i.e.

(a) Stannane – SnH_4

(b) Distannane – Sn_2H_6

(vi) Lead has only one hydride i.e.

Plumbane – PbH_4

(vii) Thermal stability of hydrides $\downarrow$ Decreases, Because (Δ E.N decreases)

5.2 Formation of Oxides :

(i) Two types of oxides

(a) Mono oxide (MO) (b) Dioxides (MO_2)

(ii) CO_2 is a gas at room temp. while other dioxides are crystalline solids, because CO_2 molecules are held together only by weak vander waal's forces.

(iii) Only carbon forms multiple covalent bonds other not because other have large size of p-orbital.

(iv) Silica : SiO_2 has giant molecule having high m.p. In SiO_2 silicon has sp^3 hybridisation.

(v) Quartz : Crystalline form of SiO_2

5.3 Formation of Oxyacids :

(i) Oxyacids are formed by C & Si.

(ii) Main inorganic oxyacid is H_2CO_3

(iii) H_2SiO_3 is silica acid.

5.4 Formation of Halides :

(i) They form tetra halides MX_4 except $PbBr_4$ & PbI_4.

(ii) The non existence of $PbBr_4$ and PbI_4 is due do that Pb^{+4} is a strong oxidising agent while Br^- & I^- are highly reducing agent.

(iii) All MX_4 are covalent except SnF_4. It is Ionic.

(iv) The tetrahalides of carbon cannot undergo hydrolysis due to non availability of vacant 'd' orbitals

$$CCl_4 + H_2O \longrightarrow \underset{\text{phosgene}}{COCl_2} + 2HCl.$$

(v) The tetrahalides of silicon like SiF_4 can form SF_6^{2-}. In this ion silicon undergoes sp^3d^2 hydridisation where carbon cannot form this type of ion.

(vi) Dihalides of these elements are more ionic than their corresponding tetrahalides.

(vii) Thermal stability of tetrahalides

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$.

6. FAMILY MEMBERS OF IV-A GROUP

Carbon (C) :

6.1 Chemical Properties :

(1) Action of HNO_3 : Charcoal dissolves slowly in hot dil. HNO_3 forming a brown substance called "Artificial tannin"

$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

6.1.1 Oxides of Carbon :

(a) Carbon Mono oxide : (CO)

(i) Structure : $:C \overset{\leftarrow}{\equiv} O^{x}_{x}$

(ii) It is extremely poisonous in nature due to the fact that it combines with haemoglobin, oxygen carrier of blood, to form a stable compound carboxy haemoglobin. With the result the oxygen transportation is disturbed and tissues do not get necessary oxygen and ultimately death occurs.

(iii) Used in extraction of Ni -

$$\text{Impure Ni} + 4CO \rightarrow \underset{\text{Highly volatile in the form of vapours}}{[Ni(CO)_4]} + \text{solid}$$

$$\downarrow\ 180°$$

$$\text{Pure Ni} + 4CO$$

This process is Mond's process

(iv) It acts as a reducing agent and reduces metallic oxides to metals.

$$Fe_2O_3 + 3CO \xrightarrow{\text{High temp.}} 2Fe + 3CO_2$$

$$H_2O + CO \xrightarrow{\text{High temp.}} H_2 + CO_2$$

(steam)

(v) It is used in making carbonyls which in turn are used in the extraction of iron and nickel.

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

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

(vi) CO is poisonous gas antidote for CO poisoning is carbogen (Mixture of oxygen & 5 - 10% CO_2)

(b) Carbon Dioxide (CO_2) :

(1) Solid CO_2 is known as dry ice because it evaporates without liquefying.

(2) Solid CO_2 is used as a refrigerant.

(3) CO_2 is used as a fire extinguisher.

(4) CO_2 is absorbed by plants in the presence of sunlight and chlorophyll to from glucose and higher carbohydrates. This

process is known as photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chorophyll}]{\text{Light}} C_6H_{12}O_6 + 6O_2.$$

(5) Carbonic acid : H_2CO_3 is used as a good disinfectant

(6) It is acidic in nature :

$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$

A mixture of solid CO_2 and ether is used to produce very low temperature of order - 80° to - 100°C

(7) It neutralises alkalies to form two series of salts, carbonates and bicarbonates.

$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{(milky)}}{CaCO_3} + H_2O$

$CaCO_3 + H_2O + CO_2 \rightarrow$

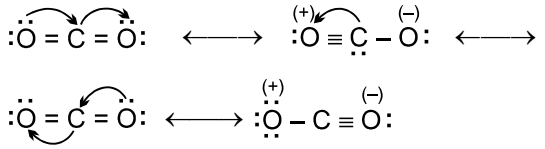
(milky appearance)

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3$$

Cal.bicarbonates (Clear sol.) (Milkiness reappear)

This used as a test of CO_2 and carbonates

(8) Resonance of CO_2 :



6.1.2 Carbides of Carbon :

Compounds of C with less electronegative element are known as carbides.

(a) Ionic or Salt like carbides :

(1) Formed by ionic bonding and exists as crystalline solids.

Ionic carbide = Carbon + Highly Electropositive metal

Eg. Al_4C_3 : Methanide

CaC_2 : Acetylide

Mg_2C_3 : Allylide

(a) Methanides : In these carbon is in - 4 oxidation state. When subjected for hydrolysis form methane.

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

(b) Acetylides : In these carbon is in -1 oxidation state. These on hydrolysis form acetylene

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

(c) Allylides : Carbon is in $-\frac{4}{3}$ oxidation state. They form propyne on hydrolysis

$Mg_2C_3 + 2H_2O \rightarrow 2MgO + C_3H_4$.

(2) Carbon is varying in oxidation state in these three compounds

Eg. $CaC_2 \equiv Mg_2C_3 \equiv Al_4C_3$

(3) CaC_2 : Calcium carbide

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

nitroline

$CaCN_2 + H_2O \rightarrow 2NH_3 + CaCO_3$

∵ It releases NH_3 on hydrolysis, it is mainly used as fertilizer.

(b) Covalent Carbides :

(a) Small discrete molecules : Eg : CH_4, CCl_4 etc

(b) Carbides consist of giant molecules : Eg SiC etc.

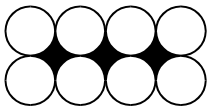
(1) C + Non metals = Covalent carbides

(2) SiC is a polymeric covalent carbide known as carborundum

(3) These are very hard & used for cutting

(4) These are of the two types -

(c) Interstitial carbides or Refractory Carbides :

(1) 

Interstitial sties are occupied by carbon.

(2) Carbon are hold by weak vander waal force in interstitial carbides

Eg. Steel

(3) Iron carbides having atomic radii < 1.37 A° is not a interstitial carbides

∵ Interstices are very less.

(4) Ti, Zr, Hg, W, Mo, V : Forms Interstitial carbides, while Co, Ni, Fe do not forms interstitial carbides. Rest of transition metal forms interstitial carbides

(5) Characteristics of interstitial compounds :

(i) Density is high so very hard & have high m.p. & b.p.

(ii) They are employed in cutting of tools especially tungustun carbide.

(6) Interstitial compounds are non stoichiometric compounds

∵ here ratio is not fixed and is in fraction.

6.1.3 Fuels of Carbon :

Calorific value : It is the total quantity of heat liberated by the complete combustion of a unit mass of the fuel in air

Unit = Kcal / m^3

(a) Water gas :

(a) It is a mixture of CO + H_2 with a small amount of CO_2 & also known as synthesis gas.

(b) A mixture of water gas and producer gas is used for manufacture of NH_3 by Haber's process

(c) Water gas is also known as blue gas because it burns with blue flame.

(d) Contains maximum percentage of CO.

(b) Producer gas :

(a) It is a mixture of CO + N_2

(b) Cheapest gaseous fuel

(c) Coal gas :

(a) It is a mixture of H_2 + CH_4 + CO and other gases like N_2, C_2H_4, O_2 etc.

(d) Oil gas :

(a) It is a mixture of H_2 + CH_4 + C_2H_4 + CO and other gases like CO_2.

(e) Gobar gas : or Bio gas

(a) $CH_4 + CO + H_2$

(f) Natural gas :

(a) $CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}$

(g) L.P.G. (liquid Petroleum Gas) :

(a) Butane + Isobutane

6.2 Silicon (Si) :

6.2.1 Silicones :

(a) These are organosilicon polymers containing Si – O – Si linkage.

(b) Water proof papers, clothes & machines can be prepare by spraying silicons as they acts as water proof substances.

(c) Silicone is used as a lubricant in aeroplane parts where temp is low and all other machines which work at low temp.

∵ It does not solidify even at low temp.

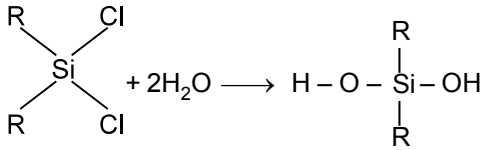
(d) C.Q. Which of the following compounds does not form a silicone on hydrolysis followed by heating.

(i) R_2SiCl_2 (ii) $RSiCl_3$

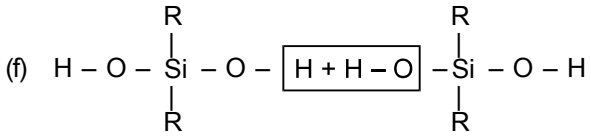
(iii) R_3SiCl (iv) None of these

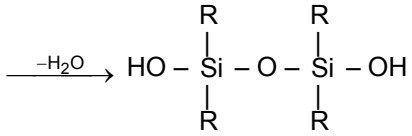
↓

Only form dimers.

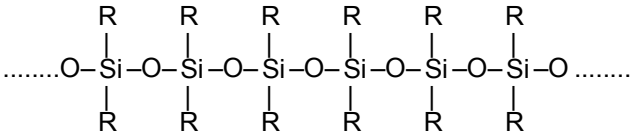
(e) 

Dialdichloro Silane Silicon (dialkyl silandiol)

(f) 



The terminal 'OH' groups which are active, allows the polymerisation reaction to continue and the length of the chain continues to incre



a straight chain silicane is formed.

(g) A complex cross linked polymer is obtained on the hydrolysis of alkyl trichloro silane.