GROUP 14 ELEMENTS (IVA Group Elements)

UNIT : 1

1 General introduction, Electronic configuration, Ocurrence

2 Variation of properties, oxidation states trends in chemical reactivity

3 Anomalous behaviour of the first element

4 Carbon – catenation, allotropic forms, Physical and chemical properties and uses

VERY SHORT ANSWER QUESTIONS :

1. Mention the dissimilarity between C and Si.

A. 1) Carbon, in the form of diamond, is harder than Silicon

2) Melting point and boiling point of carbon are higher than those of silicon

3) Carbon allotropes like graphite, gas carbon are good conductors of electricity and heat.

4) Catenation property of carbon is greater than silicon

2. Write the chemical equation for the dehydration of malonic acid in the presence of P_2O_5.

Name the products.

A. By the dehydration of malonic acid in the presence of P_2O_5, carbon sub-oxide (C_3O_2) is obtained.

$$\underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow[\Delta]{P_2O_5} \underset{\text{sub-oxide}}{C_3O_2} + 2H_2O$$

.3. Write the electronic configuration of group IVA elements.

A.

S.No.	Element	Atomic number	Electronic configuration
1	Carbon (C)	6	$[He]2s^2\ 2p^2$
2	Silicon (Si)	14	$[Ne]3s^2\ 3p^2$
3	Germanium (Ge)	32	$[Ar]3d^{10}\,4s^2\,4p^2$
4	Tin (Sn)	50	$[Kr]4d^{10}\,5s^2\,5p^2$
5	Lead (Pb)	82	$[Xe]4f^{14}\,5d^{10}\,6s^2\,6p^2$

4. Express your opinion on the variation of metallic nature in group IV elements.

A. Metallic character increases from carbon to lead.

Carbon, Silicon – non metals

Germanium – Metalloid

Tin, lead – metals

5. What is catenation ? Give one example.

A. The process of self linkage of identical atoms to form long chain or rings is called catenation.

E.g : Due to its high C – C bond energy Carbon has higher catenation ability.

6. Name the crystalline allotropes of carbon and mention any hybridization involved in them.

A. Crystalline forms of carbon :

1) Diamond (sp^3 hybridized)

2) Graphite (sp^2 hybridized)

7. How does graphite function as a lubricant ?

A. Graphite has a series of layers with hexagonal rings. The distance between the layers is $3.35\overset{o}{A}$ and layers are attracted by weak vanderwaals forces.and can slide easily one over the other and thus act as lubricant..

8. Graphite is a good conductor. Explain.

A. In graphite, each carbon has one free electron in pure p – orbital and can freely move in acrystal lattice and thus act as good conducter.

9. Why is diamond hard ?

A. In diamond, each carbon atom is sp^3 hybridized and each carbon forms four strong covalent bonds with other carbons in tetrahedral manner. Thus diamond forms giant molecule and exists as a three dimensional polymer.

10. Mention the hybridization of carbon atom in diamond.

A. In diamond, hybridization of carbon is sp^3

11. Why do you think Carbon in CO is not in + II oxidation state ?

A. The Carbon monoxide is represented by the structure $C \overset{\leftarrow}{=} O$. Due to the coordinate covalent bond presence the oxidation state is not considered as +II.

12. Write the equation for the reaction of Pb with NaOH.

A. $2NaOH + Pb + H_2O \xrightarrow{\Delta} \underset{\text{Sodium Plumbate}}{Na_2PbO_3} + 2H_2 \uparrow$.

13. Which of the following compounds can act as Lewis acids ? Why ?

i) CCl_4 ii) GeF_4 iii) $SiCl_4$

A. GeF_4 and $SiCl_4$ act as lewis acids because Ge and Si have d – orbitals available in their respective valence shells. So they can expand their octet. But CCl_4 is not a lewis acid as carbon does not have d – orbitals

14. Name the element (other than C) in the periodic table that has a high catenation capacity.

A. Silicon of group IVA in the periodic table. Silanes with this formula $Si_n\ H_{2n+2}$ are known where n = up to 8. Germanes $\left(Ge_n H_{2n+2}\right)$ have n = 5 maximum.

15. Which of the group IVA elements differs from other group elements in showing allotropy ?

A. Since Lead is a metal,it can not form allotropy..

16. C reacts with HNO_3 or conc. H_2SO_4 and not with HCl or dil. H_2SO_4. Why ?

A. Because HNO_3 (dil or conc) and conc. H_2SO_4 are oxidizing agents but HCl or dil. H_2SO_4 are non oxidizing agents.

SHORT ANSWER QUESTIONS :

1. Explain the irregularity in the IE of group 14 elements.

A. The ionization energies (IE_1) of the elements of 14 group (IVA) are given below.

Element	C	Si	Ge	Sn	Pb
$IE_1(kJ/mol)$	1084.4	785.7	761.6	706.6	741.3

1) IE_1 decreases from C to Sn and then increases to Pb

2) The IE_1 of lead is slightly higher than expected due to the lanthanide contraction

3) The very high value of carbon is attributed to its small size and high electronegativity value

4) The large decreases in IE from C to Si is due to the increases in the size of the atom from C to Si

5) The decreases in IE from Si to Sn is relatively small due to the less screening effect of d^{10} electrons in Ge and Sn and due to $d^{10}f^{14}$ electrons in Pb

2. Why does EN value remain constant in Si, Ge, Sn and Pb ?

A. The electronegativity of carbon is very high due to its small size. The values for the other elements are almost the same, contrary to the general expected trend of decrease down the group. This is due to the filling of d – orbitals in Sn and Ge and also f – orbitals in Pb.

EN of carbon is 2.5 and Si, Ge, Sn and Pb is 1.8.

3. Why does C differ from Si. Mention the main difference between them.

A. **Reasons for the difference between Carbon and Silicon :**

(1) The size of carbon is smaller than silicon

(2) The decrease in the IE and EN values from carbon to silicon is very much

(3) There are vacant d – orbitals in the silicon but there are no vacant d – orbitals in carbon

Differences between C and Si :

1) Carbon present in plant and animal kingdoms. Silicon is present in minerals.

2) Carbon in diamond form is harder than silicon. The MP and BP of carbon are far higher than those of silicon

3) Some allotropes of carbon are good conductors of heat and electricity. But silicon is semiconductor of electricity

4) The catenating capacity of carbon is highest. Silicon has less tendency to catenate

4. Explain why diamonds is very hard.

A. In diamond, each carbon undergoes sp^3 hybridization. A carbon atom is bound to four carbon atoms, arranged in a **tetrahedral symmetry**, with single bonds. **A three dimensional arrangement** of the tetrahedral structures result in giant molecule. The bond energy is very high $\left(348\,kJ\,mol^{-1}\right)$. It is very difficult to break the bonds. So, diamond is hard.

5. Graphite is a conductor of electricity, while diamond is not. Explain.

A. In diamond, each carbon is sp^3 hybridized and each carbon forms four strong covalent bonds with other four carbon atoms tetrahedrally. Thus it forms 3 – dimensional polymer. Hence, diamond has no free electron.

$\therefore$ It is a bad conductor of electricity

In graphite, each carbon is sp^2 hybridized and each carbon forms three covalent bond with other three carbon atoms. Thus graphite has a series of laters with hexagonal rings. Hence, in graphite, one electron is free on each carbon atom.

6. Why does Na_2CO_3 solution turn into a suspension when saturated with CO_2 gas ?

A. When the aqueous solution of Na_2CO_3 is saturated with CO_2 gas, sodium bicarbonate separates out.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

$NaHCO_3$ is relatively less soluble in water

7. Mention a method to synthesize carbon disulphide ? How is it useful ?

A. When white coke is heated with sulphur vapour in an electric furnace, CS_2 is obtained

$$C + 2S \longrightarrow CS_2$$

CS_2 is used in the manufacture of CCl_4, cellophane and artificial silk. It is also useful as a solvent for fat, oil, rubber, etc.

8. What happens when

a) CO_2 is passed through slaked lime

b) CaC_2 is heated in a current of N_2

A. a) CO_2 is passed through slaked lime :

When CO_2 is passed through slaked lime, it turns milky due to the formation of insoluble $CaCO_3$. But on passing some more CO_2 through the solution, the precipitate of $CaCO_3$ dissolves due to the formation of calcium bicarbonate. Now a clear solution is obtained.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(Milky)}}{CaCO_3} \downarrow + H_2O$$

$$CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{(Soluble)}}{Ca(HCO_3)_2}$$

b) CaC_2 is heated in a current of N_2 : When calcium carbide is heated in a current of N_2, calcium cyanamide and graphite are obtained

$$CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2 + C$$

The mixture of calcium cyanamide and graphite is known as nitrolim.

9. Name an allotrope of carbon that has lowest energy.

A. Graphite is thermodynamically more stable allotropic form of carbon as it has relatively less energy.

10. Write the uses of the oxides of carbon.

A. **Uses of CO :**

1) CO is an important component of gaseous fuels like producer gas, water gas and coal gas

2) CO is a good reducing agent for many metal oxides to produce metals

3) CO is a good ligand in the metallurgy of Ni by Mound's process. Many carbonyl compounds are prepared by using CO

Uses of CO_2 :

1) Solid CO_2 is called "dry ice" or "cardice" and it is used as a refrigerant

2) As a coolant in the lab

3) In the manufacture of urea and in creating inert atmosphere and in neutralizing alkalies

4) It is widely used in nitrogeneous fertilizer and in making urea

5) As fire extinguisher

Note : C_3O_2 reacts with water and gives malonic acid $CH_2(COOH)_2$

LONG ANSWER QUESTIONS :

1. Name the group IVA elements in the order. Write note on the following.

a) Electronic configuration b) Occurrence c) Variation of oxidation states

A. Group IVA of periodic table contains the elements carbon, silicon, Germanium, tin and lead

a) Electronic configuration : The valence shell configuration is $ns^2\ np^2$

Element	Symbol	Atomic number	Electronic configuration	
Carbon	C	6	$1s^2\,2s^2\,2p^2$	$[He]1s^2\,2s^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	$[Ne]3s^2 3p^5$

Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	$[Ar]3d^{10}4s^2 4p^2$ Tin
	Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	$[Kr]4d^{10}5s^2 5p^2$ Lead
	Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	$[Xe]4d^{14}5d^{10}$
			$4d^{10}4f^{14}5s^2 5p^6 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

b) Occurrence : Carbon is very widely distributed in nature as the essential constituent of all living matter. The sources of carbon are graphite, diamond, CO_2, CO, coal, crude oil, carbonates in rocks, etc.

Silicon is the second most abundant element in the earth's crust. It occurs as silica, sand, quartz. Silicate minerals, clays, feldspar, etc

Germanium occurs in traces only. Tin occurs as cassiterite or tinstone (SnO_2) lead occurs as galena (PbS)

The order of abundance in earth crust is Si > C > Sn > Pb > Ge

c) Variation of oxidation states :

Their outermost shell electronic configuration is $ns^2 np^2$. Hence they exhibit +2 and +4 oxidation states. In heavier elements like Sn and Pb exhibit +2 oxidation state because of inert pair effect. (The reluctance of "ns" electrons to participate in the bond formation is called inert pair effect.

2. How does the first element of group 14 differ from other elements of the group ?

A. The first element in this group is carbon. Carbon shows dissimilarities with other elements of its group in the following respects.

i) Carbon is widely distributed in nature where as other elements are almost are available in nature.

ii) In carbon d orbitals not available but in other elements they are available. For carbon coordination number is 4 but for other elements it is 6, due to availability of d – orbitals.

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

iii) The maximum covalency of C is 4 while its 6 for other elements

iv) The catenation ability of carbon is very high due to the high C – C bond dissociation energy $(348\,kJ\,mol^{-1})$

The catenation ability of others is very less (chain of 8 atoms length in silicon)

v) Carbon forms multiple bonds while others can't forms multiple bonds

$$(C = C\ ;\ C \equiv C)(C = O\ ;\ C = S)$$

vi) Hydrocarbons are thermally very stable. The hydrides of other elements are relatively less stable

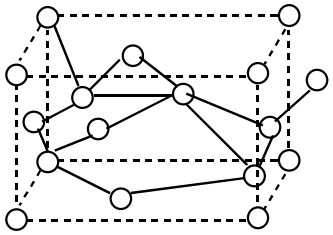
vii) The tetrahalides of other elements readily hydrolyzed while carbon – halogen compounds are not hydrolyzed.

3. What is allotropy ? Name the crystalline allotropes of carbon. What are their uses ?

A. **Allotropy :** The property of an element to exist in two or more physical forms due to difference in the arrangement of atoms is called Allotropy. Allotropes have more or less similar chemical properties but different physical properties.

Diamond and Graphite are the crystalline allotropes of carbon

Structure of Diamond : In diamond, each carbon atom bonded to four carbon atoms situated tetrahedrally around it.



Diamond

In diamond, each carbon atom is in sp^3 hybridization and is linked to four carbon atoms by single covalent bonds.

C – C bond distance in diamond is $1.54\overset{o}{A}$

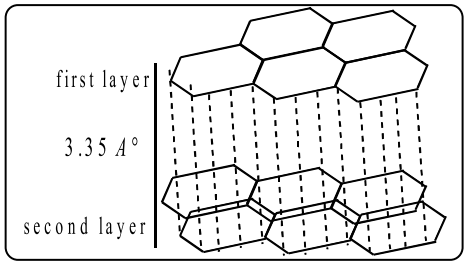
$\overline{|C-\hat{C}-C}$ bond ange in diamond is 109°28"

Uses :

1) Diamonds are used as precious stones for jewellery because of their ability to reflect light

2) Diamonds are used for cutting glass and drilling rocks due to their remarkable hardness

Structure of graphite : Graphite consists of a series of layers in which hexagonal rings made up of carbon atoms.



In Graphite, each carbon atom undergo sp^2 hybridization and forms three covalent bonds with three other carbon atoms

The fourth electron present in the pure ‘p’ orbital which is unhybridised. The electron become free electron.

The C – C bond length in graphite is $1.42\overset{o}{A}$

The distance between the two layers in graphite is $3.4\overset{o}{A}$. These layers are held together by vanderwaal's forces which are weak.

Graphite is a layer lattice structure

Uses of Graphite :

1) Graphite is ised as librocant

2) It is used in the manufacturing of lead pencils

3) It is used in the manufacturing of electrodes and refractory crucibles

GROUP 14 ELEMENTS (IVA Group Elements)

UNIT: 2

1 Similarities between carbon and silicon uses of oxides of carbon

2 Important compounds of Silicon, Silicon dioxide and a few uses silicon tetrachloride, silicones, silicates and zeolites (Elementary ideas)

3 Fuel gases – Producer gas and water gas manufacture and uses

VERY SHORT ANSWER QUESTIONS:

1. Name any two three – dimensional silicates.

A. Examples for three – dimensional silicates are quartz, crystobalite, , ultramarine

2. Give the composition of water gas.

A. Water gas is a mixture of CO and H_2. It contains 40 – 50%CO and 45 – 50% H_2

3. How is quartz useful?

A 1) Quartz glass is used for making special glass ware suitable for working with U.V.radiation.

2) Transparent varieties of quartz are used for the manufacture of lenses, optical instruments etc.
3) For the lining of the furnaces in steel industry along with clay and lime
4) As acidic flux in metallurgy

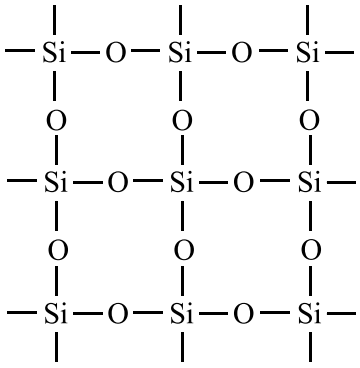
4. What do you understand by the term "Blue gas" ? Why is it so called ?

A. Water gas is called blue gas. The component gases CO and H_2 in water gas burn with blue flame.

Hence, it is called blue gas

5. Draw the structure of silicon dioxide?

A.



6. Which is a better fuel, producer gas or water gas? Give their calorific values.

A. The calorific value of water gas is more than that of producer gas. So water gas is a better fuel than producer gas.

The calorific value of producer gas is $5,439.2\,kJ/m^3$

The calorific value of water gas is $13,000\,kJ/m^3$

7. Can water gas be made to have a different calorific value ? What to do ? Mention such substances.

A. Water gas can be made to have different calorific values by adding certain other gaseous substances.

1) **Carburetted water gas**: The calorific value of water gas is increased by adding gaseous hydrocarbons to it. (They hydrocarbons are obtained by the cracking of petroleum oils). This enriched mixture is called carbureted water gas.

Hydrogen: 30 – 40%

Saturated hydrocarbons: 15 – 20%

Unsaturated hydrocarbons: 10– 15%

Carbon monoxide: 18 – 20%

CO_2 **and** N_2: 2.5 – 5%

The calorific value of carbureted water gas is $15,000\,kJ\,m^{-3}$

2) Semi water gas: In this, due to the presence of N_2, the calorific value is less than that of water gas. The calorific value of semiwater gas is $7520\,kJ\,m^{-3}$

Hydrogen – 10 – 12%

Carbon monoxide – 25 – 28%

Nitrogen: 50 – 55%

Methane – 1 – 12%

8. Give the composition of producer gas.

A. Producer gas is a mixture of CO and N_2. It contains 33% CO and 64% N_2,3% CO_2 and H_2

9. What happens if SiO_2 is heated with HX?

A. Hydrogen halides have no reaction with SiO_2

10. Write an equation for the reaction with SiO_2 with quick lime.

A. $SiO_2 + CaO \longrightarrow CaSiO_3\,(\text{Calcium silicate})$

11. How many kinds of silicones may be possible?

A. Silicones may be long chain linear compounds cyclic and branched chain silicones. .

12. How are organo silicones prepared?

A. Alkyl chloride when passed over silicon at $300°C$ in the presence of Cu catalyst organo silanes are formed

$2R - Cl + Si \xrightarrow{Cu/300°C} R_2SiCl_2$

13. $SiCl_4$ **does not form** $[SiCl_6]^{2-}$ **. Why?**

A. The reasons for $SiCl_4$ not forming $[SiCl_6]^{2-}$ are

i) Si^{+4} is small in size. Six Cl^- ions cannot be accommodated around Si^{+4} ion

ii) The interaction of the lone pairs on Cl^- ion and the Si^{+4} particle is weak

SHORT ANSWER QUESTIONS:

1. Why SiO_2 **does not dissolve in water?**

A. Silicon dioxide (SiO_2) is covalent, three dimensional network solid in which silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. 'Si – O' bond enthalpy is very high. Because of all these reasons it is insoluble in water.

2. Mention a few uses of silicates.

A. **Uses of Silicates:**

i) Clay minerals are used for absorbing chemicals

ii) Micas (i.e, sheet silicates) are used for electrical insulation

iii) Asbestos is used for thermal insulation

iv) Agate and flint are used as hard or sharp surfaces

v) Variety of silicates are used for ornaments and jewellery

vi) Cement, ceramics and glass are all useful materials to the man

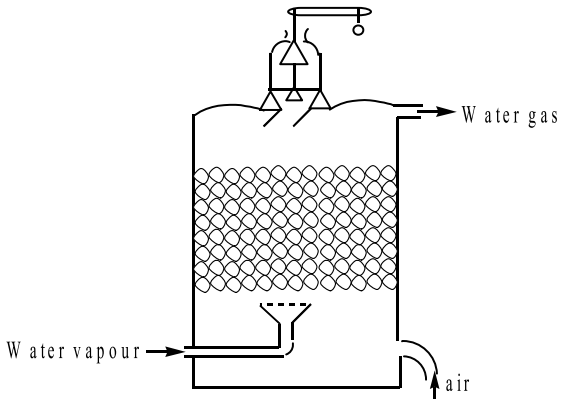
3. How is water gas prepared? Mention its uses.

A. Preparation of water gas:

Principle: In the preparation of water gas super heated steam is passed over white hot coke. A mixture of $(CO + H_2)$ is obtained.

Procedure: The generator is filled with coke. It is provided with coke – inlet at the top and two side tubes in the bottom. One tube is for sending steam and another for sending hot air.

Thus, alternately hot air and steam are blown into the generator.



Water gas generator

When super heated steam is passed over white hot coke, a mixture of CO and H_2 is obtained

$$C + H_2O \longrightarrow CO + H_2 ; \Delta H = +121.22 kJ/mole$$

The above reaction is endothermic. The temperature of the coal comes down. So, alternately hot air is passed over the coke.

$$C + O_2 \longrightarrow CO_2 \ ; \Delta H = -394 kJ/mole$$

CO_2 formed in the reaction is allowed to escape out. The reaction being exothermic, the temperature increases.

When the supply of air is stopped, steam is passed over hot coke and now water gas is produced.

Uses of water gas:

1. The calorific value of water is higher i.e., $13,000 kJ/m^3$. Hence it is extensively used as a fuel in industries.

2. It is used in the manufacturing of ammonia by Haber's process as a source of H_2

3. Semi water gas and carburetted water gas are prepared from water gas to use it in steel industry (or) in internal combustion engines.

4. Describe the structure of silica and mention its uses.

A. 1) Silica exists as a giant molecule

2) In silica, silicon atom undergoes sp^3 hybridization

3) Each silicon atom is bonded to four oxgyen atoms tetrahedrally

4) Silica has three-dimensional structure

5) Due to giant molecular structure, silica exists in the solid state

6) Each oxygen at the vertex of the tetrahedron is shared by two silicon atoms. Hence, the formula of silica is SiO_2

7) Silica is not as hard as diamond, because the Si – O – Si bonds of silica are weaker when compared with the C – C bonds of Diamond. Hence M.P of silica is less than that of diamond

USES OF SILICA:

1) Coloured varieties of Quartz are used as gems. Transparent varieties of Quartz are used for the manufacture of lenses and optical instruments

2) Quartz is transparent. So it is used for making special glass ware for working with U.V. radiation

3) Silica is used as a building material

4) Silica is used as an acid flux in metallurgy

5) Sand, clay and lime are used for making bricks. These are used for lining the furnace used in the manufacture of steel

5. Write three properties of silicon dioxide with equation.

A. **PROPERTIES OF SILICA:**

1) Silica is insoluble in water

2) Silica does not react with the acids HCl, HBr and HI. However silica reacts with HF and gives silicon tetrafluoride

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

3) Silica reacts with alkali to form silicate

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium Silicate}}{Na_2SiO_3} + H_2O$$

4) At high temperatures, silica reacts with metal oxides and metal carbonates and gives silicates

$$Na_2O + SiO_2 \longrightarrow Na_2SiO_3$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

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

5) The reactions of silica with alkali, metal oxides and metal carbonates indicate the acidic nature of silica

6) When silica is heated with carbon in electric furnace. Silica is reduced to carborandum, SiC

$$SiO_2 + 3C \longrightarrow \underset{\text{Silicon carbide (or) Carborandum}}{SiC} + 2CO$$

7) When heated to $1600°C$ silica melts to form quartz glass. This is used for making optical instruments because, when dropped into water it does not break into pieces.

6. What are fuels? Mention the advantages of fuel gases over other fuels.

A. **Fuel:** Any substance which liberates energy when burnt in oxygen is called a fuel

A good fuel forms less ash, have low cost and give more energy

Fuels are of three types

1) Solid fuels e.g : coke, coal, etc

2) Liquid fuels e.g : kerosene, petrol, etc

3) Gaseous fuels e.g : coal gas, producer gas, water gas, etc

Advantages:

1) Gaseous fuels have more heat content and do not form ash on burning

2) They can be stored and transported easily.

$\therefore$ Gaseous fuels have more advantages

7. Zeolites functional as molecular sieves. Is it true? If true, explain.

A. **Zoelites** act as ion exchanges and as molecular sieves. The structures of zeolites permit the formation of cavities of different sizes. Water molecules and a variety of other molecules like NH_3, H_2O and ethanol can be trapped in these cavities. Then zeolites serve as molecular sieves. They trap Ca^{+2} ions from hard water and replace them by Na^{+} ions.

8. What silicon compound is useful as in inert filler in silicone rubbers ? Give its method of preparation.

A. Silicon is useful as inert fillers in silicon rubbers. The silicon rubbers are long straight chain polymers, mixed with a filter (usually SiO_2). Silicon rubbers retain their elasticity over a wide range of temperature

($-100°C$ to $+250°C$)

Silicon rubbers are prepared by the hydrolysis of dimethyl dichlorosilicones with an alkali (KOH)

9. Why do we need to send air and steam alternately in the manufacture of water gas?

A. Water gas is produced by passing super heated steam over white hot coke

$$C + H_2O \longrightarrow CO + H_2 \; ; \Delta H = +121.22\, kJ\, mol^{-1}$$

This reaction is endothermic and so the temperature of the furnace (coke) comes down, which favours a different reaction.

$$C + 2H_2O \longrightarrow CO_2 + 2H_2$$

To prevent this reaction and to maintain the high temperature enough, alternately hot air and steam are introduced into the furnace. When hot air is passed over coke, a mixture of CO_2 and N_2 is formed. They escape from the furnace (generator).

$$C + O_2 \longrightarrow CO_2 \; ; \Delta H = 394.0\, kJ\, mol^{-1}$$

This reaction is exothermic and so the temperature of the furnace (generator) increases. When the supply of air is stopped after some time and super heated steam is passed over hot coke, water gas is produced.

10. What happens when the following are heated?

a) $CaCO_3$ alone

b) $CaCO_3$ and silica together

c) $CaCO_3$ with excess of coke. Give equations

A. a) When $CaCO_3$ alone is heated, it decomposes and gives lime and CO_2

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

b) When a mixture of $CaCO_3$ and silica is heated, calcium silicate is obtained

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

c) When $CaCO_3$ is heated with excess of coke, calcium carbide is obtained

$$CaCO_3 + 4C \longrightarrow CaC_2 + 3CO$$

11. Why is CCl_4 not effected by H_2O while $SiCl_4$ is rapidly changed.

A. Carbon has no d – orbitals in its valency shell and so it cannot expand its valency shell. Its maximum covalency is only 4. So CCl_4 cannot be coordinated with water molecules. In addition, C – Cl bonds are strong. So CCl_4 is a stable compound and it is not hydrolysed by water.

Silicon has vacant d p orbitals in its valency shell. Its maximum covalency is 6. $SiCl_4$ is relatively less stable and it is hydrolysed by water.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{orthosilicic acid}}{H_4SiO_4} + 5HCl$$

12. How are the silicates present in Al ores removed?

A. Most of the silicates present in a aluminium ores are washed away with a stream of water. Then the aluminium ore associated with silica or silicates is mixed with coke and heated to 2075K in a current of nitrogen gas. Silica is reduced to silicon which escapes out as vapour.

$$Al_2CO_3 + 3C + N_2 \xrightarrow{2075K} 2AlN + 3CO$$

$$SiO_2 + 2C \longrightarrow Si\uparrow + 2CO\uparrow$$

13. Write the uses of the oxides of carbon.

A. **Uses of CO:**

1) CO is an important component of gaseous fuels like producer gas, water gas and coal gas

2) CO is a good reducing agent for many metal oxides to produce metals

3) CO is a good ligand in the metallurgy of Ni by Mound's process. Many carbonyl compounds are prepared by using CO

Uses of CO_2 :

1) Solid CO_2 is called "dry ice" or "cardice" and it is used as a refrigerant

2) As a coolant in the lab

3) In the manufacture of urea and in creating inert atmosphere and in neutralizing alkalies

4) It is widely used in nitrogeneous fertilizer and in making urea

5) As fire extinguisher

Note: C_3O_2 reacts with water and gives malonic acid $CH_2(COOH)_2$

14. Compare CO_2 with SiO_2

A. **Comparison between CO_2 and SiO_2 :**

Carbon dioxide CO_2	**Silicon dioxide SiO_2**
1) It is a gas at ordinary temperature	1) It is a polymeric solid
2) It has a linear structure	2) It has a giant polymeric structure
3) In CO_2 carbon is linked to oxygen by double bond	3) In SiO_2 each silicon is bonded to four oxygen atoms by single bonds
4) Between the molecules carbon dioxide very weak Vander Waals attractive forces are present. So, it exists as a gas	4) Due to giant molecular structure silica exists in solid state
5) Carbon dioxide has low melting point	5) Silica has high melting point
6) Carbon dioxide is an acidic oxide	6) Silica is weekly acidic

LONG ANSWER QUESTIONS:

1. Carbon and Silicon are similar in many of their properties. Discuss? How they differ from each other?

A. **Similarities between Carbon and Silicon:**

The following are some of the important similarities between carbon and silicon:

1) Both have similar outer shell configuration $ns^2\ np^2$

2) Both are non metals

3) Both exhibit valency 4

4) Both exhibit catenation capacity

5) Both exhibit allotropy

6) C and Si form similar type of compounds like dioxides, Acids, Hydrides and Chlorides.

Differences between C and Si:

1) Carbon is the important element in plant and animal kingdoms. Silicon is important element in minerals.

2) Carbon (Diamond) is harder than silicon

3) M.P and B.P of carbon is very high when compared to Si

4) Carbon allotropes (graphite, gas carbon) are good conductors of electricity. Si is a semiconductor of electricity.

2. **SiO_2 is a solid while CO_2 is a gas at ordinary temperature. Explain?**

A. The reason can be explained, considering the structures of CO_2 and SiO_2 molecules. Carbon has a tendency to form multiple covalent bonds. This is due to small size of carbon, due to which its 2p-orbitals effectively overlap with the p-orbitals of other elements having small radius.

CO_2 molecules is a resonance hybrid of the following three resonating structures.

$$O\text{—}C\equiv O^{+}\longleftrightarrow O=C=O\longleftrightarrow {}^{+}O\equiv C\text{—}O^{-}$$

Since CO_2 molecule is linear, the dipole moment of one carbon – oxygen bond is neutralized by the other carbon – oxygen bond. So there is no net dipole moment in the CO_2 molecule. Consequently carbondioxide molecules are held together only by weak vanderwaal forces and hence it exists as a gas at ordinary temperature.

Silicon does not form multiple bonds because the Si atom is large. The larger size of the p – orbital (3P in Si) cannot effectively overlap 2p orbital of oxygen atom. Therefore Si – O bonds do not exist. Moreover Si – O bonds have some ionic nature, due to large E.N. difference between Si and O than between C and O. As a result, silicon has a three – dimensional infinite structure, in which silicon atom is tetrahedrally bonded to two silicon atoms by covalent bonds. The whole crystal of silica thus exists as a giant molecule and hence silica is a high melting solid.

3. **Give an account of the following:**

i) Silicones ii) Zeolites iii) $SiCl_4$

A. **i) Silicones:** Silicones are organo – silicon compounds. These compounds are second to organo metal compounds. Silicones have silicon strongly linked to oxygen and carbon. They are polymers formed by the hydrolysis of chlorosilanes.

Silicones may be used in

i) Silicon rubbers preparation

ii) To prepare water proof clothes and papers

iii) To prepare grease, lubricants in aeroplanes

iv) In electrical motors and tools silicones are used as insulators

v) They can stand high temperatures and due to their chemical inertness they are used in paints and enamels

ii) Zeolites: Zeolites have three-dimensional structures, with no metal ions. If some of the Si^{+4} in them is replaced Al^{+3} and an additional metal ion an infinite three dimensional lattice is formed. Replacements of one or two silicon atoms in $\left[Si_2O_8\right]^{-2n}$ form zeolites. Zeolites act as ion exchangers and as molecular sieves. The structure of zeolites permits the formation of cavities of different sizes.

Water molecules and a variety of other molecules like NH_3, CO_2 and ethanol can be trapped in these cavities. Then zeolites serve as molecular sieves. They trap Ca^{+2} ions from hard water and replace them by Na^+ ions.

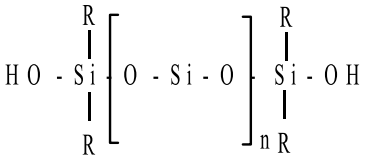
iii) Silicon tetrachloride $\left(SiCl_4\right)$: This is known as tetrachlorosilico methane. $SiCl_4$ is commercially important. It is used

i) To make ultra pure Si for transistors

ii) $SiCl_4$ mixed with ammonia is used in warfare for the production of smoke screens

iii) $SiCl_4$ is hydrolysed at high temperature to give fine SiO_2. This SiO_2 is used in epoxy paints and resins

iv) SiO_2 obtained as above is used as an inert filler in silicon rubber



Some application of Silicones

4. Silicates are always associated with the minerals. Mention any six types of silicates.

A. Silicates are regarded as the metal derivatives of silicic acid $\left(H_4SiO_4\right)$. Many building materials are silicates

Ex : Granites, slates, bricks and cement. Ceramics and glass are also silicates. The Si – O bonds in silicates are very strong. They do not dissolve in any of the common solvents and they do not mix with other substances readily

The silicates can be divided into six types :

i) Orthosilicates or Nesosilicates : Their general formula : $M_2^{II}\left(SiO_4\right)$

Ex : Willemite $Zn_2\left(SiO_4\right)$

ii) Pyrosilicates or Sorosilicates or Disilicates : These contain $Si_2O_7^{-6}$ units. Pyrosilicates are rare.

Ex : Thortveitite $Ln_2\left[SiO_2O_7\right]$

iii) Chain silicates: They have the units $\left(SiO_3\right)_2$

Ex : Spodumene $LiAl\left(SiO_3\right)_2$

Amphiboles are one type of chain silicates. Generally double chains are formed in them.

iv) Cyclic silicates: They are silicates having ring structures. They may be formed of general formula $\left(SiO_3\right)_n^{2n-}$. Rings containing three, four, six and eight tetrahedral units are known. But rings with three and six are the most common

Ex : Beryl $Be_3Al_2\left[Si_6O_{18}\right]$

v) Sheet Silicates: When SiO_4 units share three corners the structure formed in an infinite two – dimensional sheet. The empirical formula $\left(Si_2O_5\right)_n^{2n-}$. These compounds appear in layer structures. They can be cleaved.

Ex : Kaolin $Al_2\left(OH\right)_4 Si_2O_5$

vi) Frame work silicates or three-dimensional silicates: Sharing all the four corners of a SiO_4 tetrahedron results in three-dimensional lattice of formula SiO_2

Ex : Quartz, Tridymite, Cristobalite, Feldspar and ultramarine $\left(Na_8\left[Al_6Si_6O_{24}\right]S_2\right)$, zeolites

5. Describe two methods of preparation of SiO_2 and give its chemical properties.

A. **PREPARATION OF SILICA:**

1) Silica can be prepared by burning of silicon in air or oxygen

$$Si + O_2 \longrightarrow SiO_2$$

2) Silica is formed by the hydrolysis of silicon tetra fluoride $\left(SiF_4\right)$ or silicon tetra chloride $\left(SiCl_4\right)$

$$3SiF_4 + 4H_2O \longrightarrow \underset{\text{Ortho-Silicic acid}}{H_4SiO_4} + \underset{\text{Hydro fluoro-Silicic acid}}{2H_2SiF_6}$$

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Ortho Silicic acid}}{H_4SiO_4} + 4HCl$$

Ortho silicic acid obtained is heated strongly at $1000°C$ to give silica

$$H_4SiO_4 \longrightarrow \underset{\text{Silica}}{SiO_2} + 2H_2O$$

PROPERTIES OF SILICA:

1) Silica is insoluble in water

2) Silica does not react with the acids HCl, HBr and HI. However silica reacts with HF and gives silicon tetrafluoride

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

3) Silica reacts with alkali to form silicate

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium Silicate}}{Na_2SiO_3} + H_2O$$

4) At high temperatures, silica reacts with metal oxides and metal carbonates and gives silicates

$$Na_2O + SiO_2 \longrightarrow Na_2SiO_3$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

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

5) When silica is heated with carbon in electric furnace. Silica is reduced to carborandum, SiC

$$SiO_2 + 3C \longrightarrow \underset{\text{Silicon carbide (or) Carborandum}}{SiC} + 2CO$$

6) When heated to $1600°C$ silica melts to form quartz glass. This is used for making optical instruments because, when dropped into water it does not break into pieces.

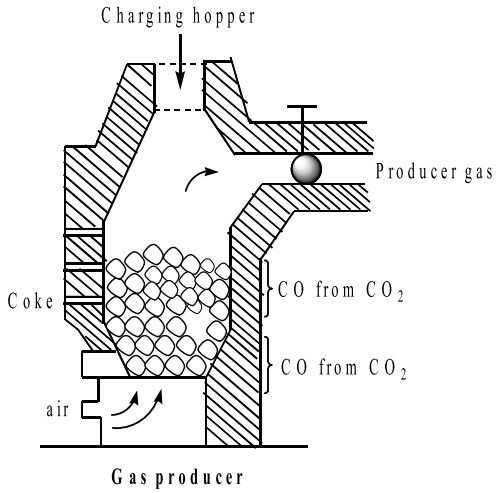
6. What is a fuel? Mention the names of fuel gases – formed by carbon. Describe the preparation of producer gas.

A. Any substance which liberates heat energy when burnt in oxygen can be called a fuel.

Fuel gases formed by carbon: (1) Coal gas (2) Water gas (3) Carburetted water gas (4) Producer gas

Preparation of Producer gas:

A mixture of CO and N_2 is known as producer gas. Its composition is CO = 33%, $N_2 = 64\%$ and $CO_2 + H_2 = 3\%$



The furnace used for the preparation of producer gas is known as Gas producer. It is a tall cylindrical furnace line inside with fire bricks. Coke is fed into the furnace through hopper at the top and a blast of air is blown with the help of pipe from the bottom of the producer. The ash formed during the formation of producer gas is removed from time to time.

Reactions:

$$C + O_2 \longrightarrow CO_2,\ \Delta H = -394\,kJ/mol^{-1}$$
$$CO_2 + C \longrightarrow 2CO,\ \Delta H = +693\,kJ/mol^{-1}$$
$$2C + O_2 \longrightarrow 2CO,\ \Delta H = -231\,kJ/mol^{-1}$$

The producer gas is collected from the exit at the top. The calorific value of producer gas is $5439\,kJ/m^{-3}$