10. GROUP 14 ELEMENTS (IV A)

SYNOPSIS:

Symbol	At. No	Valence shell configuration	Penultimate shell configuration
C	6	$2s^2\ 2p^2$	$C \rightarrow 2e^-\ s^2$
Si	14	$3s^2\ 3p^2$	$Si \rightarrow 8e^-\ s^2\ p^6$
Ge	32	$4s^2\ 4p^2$	Ge
Sn	50	$5s^2\ 5p^2$	$Si\ 18e^-$
Pb	82	$6s^2\ 6p^2$	$Pb\ s^2p^6d^{1\circ}$

They belong to p-block.

General valence shell configuration:

Almost all properties will show a normal trend from C to Si, But, beyond Si, the trend or change slows down due to ineffective screening caused by d and f electrons.

General properties:

Abundance: Most abundant is Si. Even C is also more abundant. Least abundant is Ge.

Density: It increases down the group. C has higher density than Si due to its diamond form

Order: Si < C < Ge < Sn < Pb

M.Ps and B.P.s: They will decrease down the group due to decrease in the inter atomic attraction.

- C has highest M.P and B.P in the entire periodic table.
- Order of M.P.'s $\rightarrow$ C > Si >Ge > Sn < Pb
- Order of B.P.'s $\rightarrow$ C > Si < Ge > Sn > Pb

Sn has least M.P.

Pb has least B.P.

Atomic radius: Increases down the group.

- Normal increase from C to Si but slow increase from Si onwards. It is due to poor shielding of d e^- in Ge and d and f electrons in others.
- Thus, the difference in the atomic radii between Si and Ge is much smaller when compared to that of C and Si.
- Even lanthanide contraction accounts for smaller increase in atomic radii.

Ionisation potential: It decrease normally from C to Si.

Thereafter, the decrease is very slow.

Electronegativity: It decreases normally from C to Si but there after, it remains constant.

Metallic nature: It gradually increases from C to Pb.

C, Si are non-metals.

Ge is metalloid

Sn, Pb are metals

- Because of gradual increase in metallic nature, IVA group is best suitable for the study of periodicity in properties.

Oxidation states:

- Common oxidation state is + 4.

- Tin and lead will exhibit + 2 oxidation state also. + 2 is more common and more stable than + 4 for Sn and Pb due to inert pair effect.

Valency :

- Common valency is 4.
- Maximum valency of C is also 4 due to the absence of vacant d-orbitals.
- Si and other elements can exhibit a maximum valency of 6 due to the presence of vacant d–orbitals.

Catenation: The ability to form long chains or rings by the atoms of an element is called catenation.

- Catenation ability decreases due to decrease in the bond energy.
- Thus, C has highest catenation than any other element in the periodic table

Comparison of C and Si

Similarities: Due to similar valence shell configuration they have some similarities.

- Both are non-metals.
- Both are abundant in nature.
- Both exhibit tetravalancy.
- Both exhibit common oxidation state of + 4
- Both will exhibit allotropy.
- Both will form many similar compounds.

	Carbon	**Silicon**
Oxides	CO_2	SiO_2
Halides	CCl_4	$SiCl_4$
Hydrides	CH_4, C_2H_6, C_3H_8, etc.	SiH_4, Si_2H_6, Si_3H_8, etc.
Oxyacids	H_2CO_3 (Carbonic acid)	H_2SiO_3 (Silicic acid)
	$(COOH)_2$ (oxalic acid)	$H_2Si_2O_4$ (Silico oxalic acid)

Differences: C and Si have some differences due to different (n – 1) shell configuration.

$C \rightarrow (n-1)s^2 \quad 2e^-$

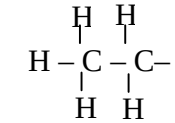
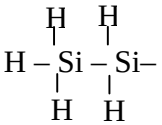
$Si \rightarrow (n-1)s^2p^6\ 8e^-$

Carbon	**Silicon**
It is present in living beings.	It is present in minerals, rocks etc.
It is hard.	It is soft.
It has high m.p.	It has low m.p.
Its catenation ability is maximum.	Its catenation ability is limited.
Its maximum valency is 4.	Its maximum valency is 6.
Some allotropes of C are good conductors.	All its allotropes are bad conductors.

Differences in their compounds: **Oxides**	
CO_2 is gas.	SiO_2 is solid.
CO_2 exist as monomer and only weak Vanderwaal's forces exists.	SiO_2 is solid. SiO_2 has giant polymeric structure.
In CO_2, C is bonded to two 'O's by double bonds. O = C = O	In SiO_2, Si is bonded to four 'O's by single bonds. -O-Si-
CO_2 is solube in water .	SiO_2 is insoluble in water.

Halides	
It forms CCl_4.	It forms $SiCl_4$.
As C does not contain vacant d orbitals in its valence shell, it cannot extend its valency beyond 4.	As Si contains vacant d-orbitals in its valence shell it can exhibit a valency of 6.

CCl_4 is saturated.	$SiCl_4$ is unsaturated and it can form two more bonds.
CCl_4 is insoluble in H_2O.	It is soluble in H_2O.
CCl_4 is not hydrolysed.	$SiCl_4$ is hydrolysed .
CCl_4 does not form species like $CCl_4.2H_2O$, CCl_6^{2-}.	It forms species like $SiCl_4.2H_2O$, $SiCl_6^{2-}$.
CCl_4 cannot act as Lewis acid.	$SiCl_4$ can act as Lewis acid

Hydrides	
It forms large number of hydrides.	It forms very few hydrides.
Its hydrides are stable because C – H bond is non polar and it doesnot weaken the adjacent C – C bond.	Silanes are unstable because Si – H bond is slightly polar and it weakens the adjacent Si – Si bond.
	
Hydrides of C are not hydrolysed due to non-polar nature .	They are hydrolysed due to polar nature.
These are weak reducing agents.	These are strong reducing agents.

Allotropy:

- The existence of same element in different physical forms is called allotropy.
- Allotrops of an element have similar chemical properties, but different physical properties.
- Allotropic forms may differ in
  1) Crystal structure
  2) Arrangment of atoms
  3) Atomicity
- Carbon has two types of allotropic forms
  1) Crystalline (a) Diamond (b) Graphite
  2) Amorphous (Microcrystalline) coal, coke, charcoal, animal charcoal. Lamp black, carbon black, petroleum coke, gas carbon, sugar charcoal.

Diamond:

Diamonds are measured in carats.

One carat = 0.2 g = 200 mg

- In India, Kohinoor and pitt diamonds are available. Kohinoor is 186 carats and pitt is 136.25 carats.
- Heaviest known diamond in the world is cullinan. It has 3026 carats (S.Africa)

Properites:

- Diamond is the hardest known substance
- It glitters because its refractive index is high i.e., 2.45.
- It has highest m.p. than any other element i.e., 4200 K.
- Diamonds are insulators i.e., bad conductors of electricity.
- It is transparent to light and x-rays.
- It is insoluble in any solvent.
- It is the purest crystalline form of C.
- It is inert form of carbon.
- It is stable upto 1500°C. On heating invaccum above 1500°C, it changes to graphite. [1500 – 800°C]

Structure:

- In diamond, C is sp^3 hybridised. Each C is tetrahedrally bonded to four other carbons by strong sigma bonds.
- C – C bondlength is 1.54 A°.
- C – $\hat{C}$ – C bond angle is 109°.
- It is three dimensional gaint polymeric
- It is the hardest with highest m.p. because of its polymeric structure.
- It is bad conductor as all the four valence electrons are utilised in bonding and number of electrons is left free.

Uses:

- In jewellary as precious stones.
- In cutting tools.
- As abrasives.

Graphite:

- It is also known as black lead or plumbago.

- It is thermo dynamically more stable. It is good conductor of heat and electricity because each C is left with one free electron.
- It's melting point is very high i.e., around 3500°C.

Preparation of artificial graphite:

- Graphite is artificially prepared by Acheson's process. Coke is heated with silica above 3500°C in an electric furnace.
- The SiC is formed and it decomposes to give graphite on further heating

$$SiO_2 + 3C_{(coke)} \rightarrow SiC + 2CO$$

$$SiC(carborundum) \xrightarrow{\Delta} Si + C_{graphite}$$

Structure of graphite:

- C is sp^2 hybridized. Each C is bonded to three other carbons by strong σ bonds. The fourth valence electron of all carbon atoms together will form a delocalised π-electron cloud which is responsible for the conducting nature of graphite.
- Graphite consists of hexagonal rings.
- It has layer lattice structure.
- The layers are bound by Vanderwall forces.
- The distance between the layers is 3.35 A°.
- C – C bondlength is 1.42 A°.
- High meting point of graphite is due to its to two dimensional polymeric sturcture.
- $C-\hat{C}-C$ bond angle is 120°.
- The soft and slippery nature of graphite is due to layer lattice structure.

Uses:

Used in lead pencils (consists graphite and clay).

- As dry lubricant.
- In making electrodes.
- As moderator in nuclear reactors.
- In painting stoves.
- In electroplating and electrotyping.

Physical and chemical properties of carbon:-

- **Different allotropes of carbon have nearly same reactivity.**
- **The amorphous forms of C are more reactive due to their increased surface area.**
- **C reacts with air (or) O_2 and forms CO_2.**
- **C (diamond)** $+O_2(excess) \xrightarrow[\Delta]{700^\circ C} CO_2$
- **C (white hot coke) + S(vapour)** $\xrightarrow[furnace]{Electric} CS_2$
- **Carbon reacts with the oxidizing acids like HNO_3 and gives acidic oxides.**
- $3C + 4HNO_3 \xrightarrow{\Delta} 3CO_2 + 4NO + 2H_2O$
- **Hot H_2SO_4 yields CO_2 and H_2SO_4 is reduced to SO_2.**
- $C + 2H_2SO_4(conc) \xrightarrow{\Delta} CO_2 + 2SO_2$ **$+2H_2O$**

- **C 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 (white, hot coke) + H_2O (steam)**

  $\rightarrow \underset{water\ gas}{CO\uparrow} + H_2\uparrow$
- **Carbon can act as reducing agent.**
- $SnO_2 + 2C \rightarrow Sn + 2CO$

  $CO_2 + C \xrightarrow{\Delta} 2CO$
- $Fe_2O_3 + 3C \xrightarrow{250-400^\circ c} 2Fe + 3CO$
- **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.**

  $3Fe + C \rightarrow Fe_3C$

  $CaO + 3C \rightarrow CaC_2 + CO$
- **<u>Uses of carbon:</u>**

  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.

USES OF OXIDES OF CARBON:

Carbon monoxide

- **CO is important component of gaseous fuels like producer gas, water gas and coal gas.**
- **CO is a good reducing agent for many metal oxides to produce metals.**
- **CO is a good ligand in the metallurgy of Ni by Mond's process.**

Carbon dioxide

- **Solid CO_2 is called as dry ice or cardice and used as refrigerant.**
- **As a coolant in the lab.**
- **In the manufacturing of urea and in creating Inert atmosphere and in neutralizing alkalies.**
- **As fire extinguisher.**
- **Used in nitrogenous fertilizer and making urea.**
- C_3O_2 **reacts with water and gives malonic acid** $CH_2(COOH)_2$.

Silica (SiO_2)

- Silica is more abundant in the nature in the form of silicates. Mainly in the form of aluminium silicate.
- SiO_2 exhibits allotropy.

  (1)**Crystalline forms:** Quartz, trydimite, Crystobalite

At low temperature, α form and at high temperature β form of each crystalline exists. Pure quartz is colourless and impure quartz is coloured

(2) **Amorphous Forms:** Agate, Jaspar, Onyx are the amorphous forms of silica.

- Sand stone consists of sand particles and iron oxide.
- Flint silica consists of both Quartz and amorphous forms.
- Kiesulguhr silica consists of minute sea organisms.

Preparation of silica:

(1) By burning of Si in O_2

$$Si + O_2 \rightarrow SiO_2$$

(2) By hydrolysis of $SiCl_4$ or SiF_4.

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

$$3SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6(\text{orthosilicic acid})$$

$$H_4SiO_4 \rightarrow SiO_2 + 2H_2O.$$

- Silica is insoluble in water
- Silica is soluble only in HF among all the acids

Chemical properties:

1) With HF: It reacts with HF to give SiF_4.

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

2) With coke: on heating silica with coke, SiC or carborundum is formed. SiC is very hard substance

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

3) Acidic nature:

- SiO_2 is slightly acidic in nature.

∴ It reacts with bases, basic oxides and basic carbonates to give corresponding silicates.

$$SiO_2 + Na_2O \rightarrow Na_2SiO_3$$

$$SiO_2 + CaO \rightarrow CaSiO_3$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$$

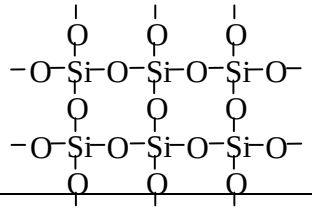
$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$$

Action of Heat :

- On heating, one form changes to another form and above 1700°C all the forms change into liquid state.
- Quartz is the purest form of silica.

Structure of silica:

- In SiO_2, each Si is tetrahedrally bonded to four oxygen atoms.
- Though Si is bonded to four 'O's, the formula is SiO_2 because those four 'O's are inturn shared by other silicons.
- It is 3-dimensional giant polymer resembling diamond.
- But, SiO_2 is soft with low m.p. when compared to diamond because Si – O – Si bonds are weak.



There is no direct Si – Si Bond

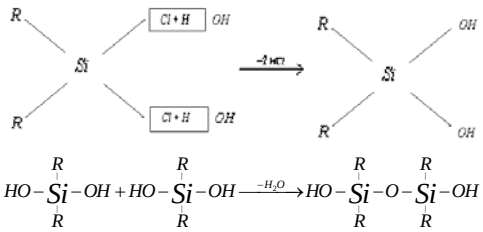
SILICONES

- 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.
- Silicones contain R_2 SiO repeating unit.
- The empirical formula of silicone R_2SiO is analogous to that of ketone (R_2CO) and hence are named silicones.

- Alkyl or aryl substituted chlorosilanes are prepared by the reaction of R – Cl with silicon in the presence of metallic copper as a catalyst

$$2RCl + Si \xrightarrow[370k]{Cu\ power} R_2SiCl_2$$

- Hydrolysis of substituted chlorosilicones yield corresponding silicones which under polymerization.



- Polymerization of dialkyl silane diols yield linear thermoplastic polymers.
- Cyclic or ring silicones are formed when water is eliminated from terminal –OH groups of linear silicones.
- Hydrolysis of $RSiCl_3$ gives crosslinked silicone.
- 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.
- **SILICATES:**
  - 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 nor do they mix with other substances readily.

The silicates can be divided into six types. They are mentioned here.santhoshi

i) Orthosilicates or Nesosilicates : Their general formula may be $M_2^n(SiO_4)$.

Example : Willemite $Zn_2(SiO_4)$

ii) PyroSilicates or SoroSilicates or DiSilicates : These contain SiO_7^{-6} units. PyroSilicates are rare.

Example : Thortveitite $Ln_2[Si_2O_7]$.

iii) Chain Silicates : They have the units $(SiO_3)_n^{2n-}$

Example : Spodumene $LiAl(SiO_3)_2$.

Amphiboles are one type 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 $(SiO_3)_n^{2n-}$. Rings containing three, four, six and eight tetrahedral units are known. But rings with three and six are the most common.

Ex: Beryl $Be_3Al_2[Si_6O_{18}]$

v) Sheet Silicates : When SiO4 units share three corners the structure formed in an infinite two – dimensional sheet. The empirical formula $(Si_2O_5)_n^{2n-}$. These compounds appear in layer structures. They can be cleaved. Ex: Kaolin $Al_2(OH)_4\ Si_2O_5$.

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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_4.

Example : Quartz; Tridymite; Cristobalite; Feldspar and Ultramarine ($Na_8[Al_6Si_6O_{24}]S_2$), Zeolites

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 used for ornaments and jewellary.
vi) Cement, ceramics and glass are all useful material to the man.

- Simple ortho silicates contain discrete SiO_4 units Eg: olivine-, Zircon - $ZrSiO_4$, phenacite - Ba_2SiO_4, willimitc Zn_2SiO_4 - . Mg_2SiO_4
- Pyrosillicates are formed when two SiO_4 tetrahedral share a corner.
- Pyrosilicates contain units $(Si_2O_7)^{6-}$.
- Examples for Pyrosilicates thortveitite $Sc_2Si_2O_7$ - , Hemimophite $Zn_3Si_2O_7\ Zn(OH)_2$ - $2H_2O$,

- When SiO_4 units share two oxygen atoms with each other cyclic and linear single chain silicates having the empirical formula $\left|(SiO_3)\right|_n^{-2n}$.
- Beryl - $Be_3Al_2Si_6O_{18}$ is cyclic silicate.
- 1 linear silicate chain is present in Diopside - $MgCa(SiO_3)_2 \text{ or } MgCaSi_2O_6$
- If two linear chains are cross-linked, the resulting double stranded silicates have the composition $\left|(Si_4O_{11})^{6-}\right|_n$ and are called amphiboles.

ZEOLITES:

- Aluminium silicates are called Zeolites Eg. $Na_2Al_2Si_2O_8.xH_2O$
- (sodium aluminium orthosilicate)
- If aluminium atoms replace few silicon atoms in 3-D net work of silica (SiO_2) the overall structure know as alulminium is formed and it acquires negative charge.
- Cations such as Na^+, K^+, Ca^{2+} etc. balance the negative charge.
- Eg: Feldspar & zeolites.
- These have honey comb like structure and have the general formula

  $M_{x/n}(AlO_2)_x(SiO_2)_y.H_2O$

  $(M = Na^+, K^+ \text{ or } Ca^{2+})$ (n = charge on metalion)
- These act as ion exchanger and molecularsieves
- Artificial Zeolites can be prepared by heating chain clay silica & Na_2CO_3
- Eg of artificial zeolite is permutite, $Na_2Al_2Si_2O_8.xH_2O$ used in the softening of hard water.

USES OF ZEOLITES:

As catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation eg: (A type of zeolite) used to convert alcohols directly into gasoline hydrated zeolites are used as ion exchangers of hard water.

SILICON TETRACHLORIDE:

1. $SiCl_4$ is know as tetrachlorosilico methane.
2. 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 $SiCl_2$. This $SiCl_2$ is used in epoxy paints and resins.
   (iv) $SiCl_2$ obtained as above is used as an inrert filler in silicons rubber.
3. $SiCl_4$ does not form $[SiCl_6]^{2-}$. Because
   (i) Si^{+4} is small in size. Six Cl^{-1} ions cannot be accommodated around Si^{+4} ion.
   (ii) The interaction of the lone pairs on Cl^{-1} ion and the Si^{+4} particle is weak.

Uses of Silica :

- As building material .
- Quartz glass is used to prepare glass to work with u, v radiation.
- In the preparation of sand bricks used for lining of furnaces.
- Coloured quartz is used in making lenses, optical instruments.
- As acid flux in metallurgy.

Fuel gases:

- Fuels burn in air and produce heat energy.
- Calorific value can be expressed as the heat energy released per gram.
- Calorific value is also expressed as kJ/m^3 for gaseous fuels.
- Out of solid, liquid and gaseous fuels, the gaseous fuels are more advantageous because of
  a) High calorific value
  b) No ash and no smoke.
  c) Easy to transport.

Producer gas:

- It is the mixture of CO(33%) + N_2(64%).

Manufacture:

- It is manufactured in a furnace named as gas producer by the incomplete combustion of coal.
- The furnace is filled with coal and air is sent into it through its bottom.
- Some of the coal is burnt to give CO_2, which rises up through hot beds of coal and gets reduced to CO.

  $C + O_2 \rightarrow CO_2$

  $CO_2 + C \rightarrow 2CO$
- Through the exit at the top, producer gas is collected.
- Its calorific value is very low because N_2 is non-combustible.
- It should be used on the spot to avoid loss of heat.

Uses:

- As fuel in steel and glass industries
- As fuel in gas engines.
- As fuel in the manufacture of ammonia

Water gas:

- It is the mixture of CO and H_2 in 1 : 1 ratio by volume. It is also known as blue gas as both components burn with blue flame.
- It is also called synthesis gas.

Manufacture:

- By passing steam over white hot coke water gas is prepared.

  $C + H_2O \xrightarrow{>1000^0 C} CO + H_2 - \text{heat}$
- The above reaction is endothermic and hence the coke becomes cold after some time. If steam is passed over cold coke, unwanted reaction occurs.

  $C + 2H_2O \rightarrow CO_2 + 2H_2$
- To maintain required temperature air is supplied for sometime. Thus, steam and air are supplied alternately over coke to produce water gas.
- Water gas has high calorific value.

Uses:

- As fuel in various industries.
- In the manufacture of ammonia by Haber's process.

Semiwater Gas: (Thin producer gas)

- It is the mixture CO, H_2 and N_2($CO + H_2 + N_2$)
- The order of their volumes in semiwater gas.
  $N_2 > CO > H_2$
  55%, 25%, 10%
- Semi-water gas is obtained by passing steam and air simultaneously over white hot coke.
- Its calorific value is less than that of water gas.

Uses:

- As fuel in steel industry.
- In internal combustion engines.

Carburetted water gas:

- It is mixture of water gas and hydro carbons.
- The order of volumes of various gases in the carbureted water gas : H_2 > CO > Saturated hydrocarbons > Unsaturated hydrocarbons
- Its calorific value is very high.
- It is also used as industrial fuel.
- For the above fuel gases, the order of calorific values is

Carburetted water gas > water gas > semi water gas > producer gas