

Group-B : Chemistry of Group-IV or 14 elements [By Dr. Birendra Kumar Maharaja College]

Group-14 of modern periodic table contains C, Si, Ge, Sn, Pb & Uuq. They are called carbon group elements, since carbon is most common and important member of the group. Carbon is the essential constituent of biosphere (plants & animals). Whole earth crust is made up of silicates.

⇒ General Chemistry of Group-14 elements:

1. Electronic Conf. - The general electronic conf. of group-14 elements is  $[noble\ gas] ns^2 np^2$ , (where  $n = 2$  to  $7$ ) e.g.,  $C_6: [He] 2s^2 2p^2$ ,  $Si_{14}: [Ne] 3s^2 3p^2$ ,  $Ge_{32}: [Ar] 3d^{10} 4s^2 4p^2$  etc.

2. Oxidation states: Carbon & Silicon can show oxidation states +4 or -4, but usually form compounds with covalency 4. Ge, Sn & Pb also show oxidation state +2 due to inert pair effect, in addition to +4. In carbon max<sup>23</sup> covalency is 4 but other elements 5 or 6 coordinated species are common. Order of stability of O. states:  $Ge^{2+} < Sn^{2+} < Pb^{2+}$ ;  $Ge^{4+} > Sn^{4+} > Pb^{4+}$ .

3. Catenation property: Catenation (i.e. self linking property to form long chain of covalent bonds) of carbon group (Gr. 14) is high and maximum in C ( $C > Si > Ge > Sn > Pb$ ) due to smaller size and so C-C bond is quite strong (348 kJ/mole).

4. Atomic/covalent & Ionic radii: Atomic/Ionic radii of Gr. 14 are less than that of Gr. 13 due to higher effective nuclear charge and so more nuclear attraction on outermost electron. In the group, atomic/ionic radii increase from C to Pb due to increase of number of orbitals but less increase from Si due to poor shielding by intervening d & f electrons compared to s & p.

5. I.E./E.A. & EN values: Ionization energy (IE) & Electron affinity (EA) values are higher than Gr. 13 elements due to decrease in atomic sizes & increase of effective nuclear charge. I.E. & EA values decrease (with some exceptions) from C to Pb due to increase of size.

\* I.E. of Pb is unexpected more than Sn, due to intervening 4f-electrons with very poor shielding effect in case of Pb, which increase effective nuclear charge and so slight increase in IE value. Electronegativity (EN) decreases from C to Pb. C has highest electronegativity (2.5) so it is non-metal, Si is slightly metallic, Ge is metalloid & Sn, Pb are metals.

6. Formation of hydrides: Gr. 14 elements combine directly or indirectly with  $H_2$  to form hydrides (covalent). Hydrides of C are called hydrocarbons which may be acyclic ( $C_nH_{2n+2}$ ,  $C_nH_{2n}$ ,  $C_nH_{2n-2}$  types), alicyclic ( $C_nH_{2n}$ ) or aromatic. Si forms hydrides, called silanes of type  $Si_nH_{2n+2}$ ,  $n \geq 8$ ; Ge forms Germanes of type  $Ge_nH_{2n+2}$ ,  $n \geq 5$ ; Sn forms two hydrides  $SnH_4$  &  $Sn_2H_6$ . Pb forms only one hydride  $PbH_4$  (Plumbane). Stability of hydrides decrease from C to Pb, while reducing property increases from C to Pb.

7. Formation of Oxides: Gr. 14 elements form oxides of type MO (monoxide, except Si) &  $MO_2$  (dioxide). CO is neutral while other monoxides are basic ( $GeO < SnO < PbO$ ).  $SiO_2$  is acidic, while other are amphoteric.  $CO_2$  is linear (sp),  $SiO_2$  is tetrahedral (sp<sup>3</sup>), thus are solid network (octahedral).  $M + \frac{1}{2}O_2 \rightarrow MO$ ;  $M + O_2 \xrightarrow[\text{air}]{\text{excess}} MO_2$

8. Formation of halides: Gr. 14 elements form halides of type  $MX_2$  (except C & Si) and  $MX_4$  (except  $PbBr_4$ ,  $PbI_4$ ). Order of thermal stability:  $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$ ;  $CF_4 > CCl_4 > CBr_4 > CI_4$ . All tetrahalides (except  $CCl_4$ ) are readily hydrolysed and tendency decreases from Si to Pb.  $SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$ . Tetrahalides are covalent and tetrahedral in shape. Formation of dihalides by higher members is due to inert pair effect. Stability order:  $GeX_2 < SnX_2 < PbX_2$ .  $SnCl_2$  is ionic solid at room temp. while  $SnCl_4$  is covalent volatile liquid.

9. Action of water: All (except Pb) decompose steam ( $H_2O$ ) at red hot temp. to give  $H_2$  gas.  $M + H_2O \rightarrow MO + H_2$  ( $M = C, Si, Ge, Sn$ )

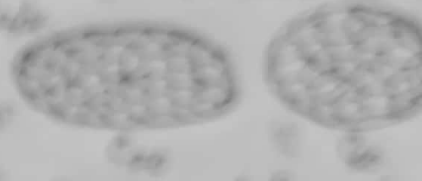
10. Action of Acids: C & Si do not react with HCl & dil.  $H_2SO_4$  but conc.  $H_2SO_4$ ,  $HNO_3$  oxidises C & Si into  $CO_2$  &  $SiO_2$  respectively.  $C + H_2SO_4 \rightarrow CO_2 + SO_2 + 2H_2O$ ;  $Si + H_2SO_4 \rightarrow SiO_2 + SO_2 + 2H_2O$ . Ge reacts with HCl (g) to form germanium chloride ( $GeHCl_3$ ).  $Ge + 3HCl \rightarrow GeHCl_3 + H_2 \uparrow$ . Sn & Pb dissolve in dil. HCl to form salts &  $H_2$ . But Pb reacts with conc. HCl to form  $H_2PbCl_4$ .  $Sn + 2HCl \rightarrow SnCl_2 + H_2 \uparrow$ ;  $Pb + 2HCl (dil) \rightarrow PbCl_2 + H_2 \uparrow$ ;  $Pb + HCl (conc) \rightarrow H_2PbCl_4$ .

12. Amorphous Solids: All by soft & react with aqueous... (not soluble) (not soluble)

Fullerene: It forms a hollow ball or tube... prepared by... (not soluble)

Carbon nanotube: It is prepared by... in the presence of... are separated by...

Graphite: Fullerenes are the only form of carbon... (not soluble)



It is a good conductor of electricity... (not soluble)

Zeolites: Zeolites are crystalline aluminosilicates... (not soluble)



They are used as ion-exchange... (not soluble)

Aluminosilicates are metal derivatives of silica... (not soluble)

1) Orthosilicates: Silicates having simplest... (not soluble)

2) Pyrosilicates: Silicates containing two units... (not soluble)

3) Metasilicates: Silicates containing one unit... (not soluble)

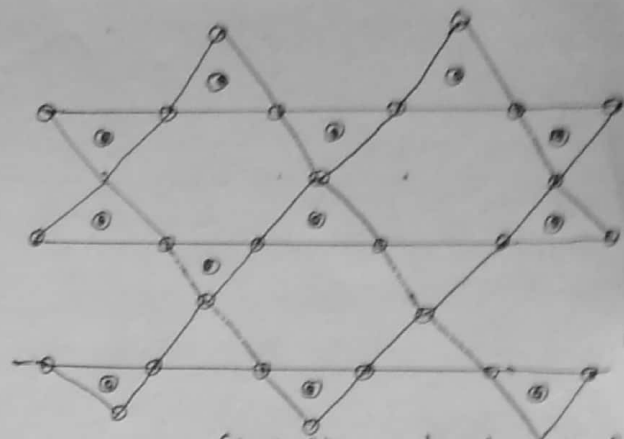
4) Tectosilicates: Silicates having general formula... (not soluble)



(3)

Structure of general formula  $(Si_2O_5)^{2n-}$ .

e.g., Talc,  $Mg(Si_2O_5)_2 \cdot Mg(OH)_2$ ; Kaolin,  $Al_2(OH)_4 Si_2 O_5$  etc.



(b) Three dimensional Silicates: Silicates involve all four O-atoms in sharing with adjacent  $SiO_4^{4-}$  (tetrahedra) units giving three dimensional or spatial network e.g. Feldspar,  $KAlSi_3O_8$ ; Zeolite,  $Na_2Al_2Si_2O_8 \cdot xH_2O$  etc. In the structures of different types, dot (•) indicates Si-atom and circle (○) indicates O-ion.

Q. Write notes on: (i)  $SiF_4$  (ii) Carborundum ( $SiC$ )

(i) Silicon tetrafluoride ( $SiF_4$ ): Preparation - It is prepared by heating sodium silicate with  $CaF_2$  & Conc.  $H_2SO_4$ .  
 $Na_2SiO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SiO_3$   
 $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$ ;  $H_2SiO_3 + 4HF \rightarrow SiF_4 + 3H_2O$

Properties: 1. It is a colourless gas.

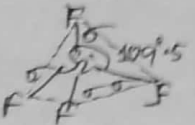
2. It fumes in moist air.

3. It dissolves in water to give gelatinous precipitate of silicic acid.



4. It forms a double salt with  $NH_3$  and so it is Lewis acid.

Structure: It is covalent compound. It has tetrahedral shape/geometry.



(ii) Carborundum ( $SiC$ ): Silicon Carbide ( $SiC$ ) is called 'Carborundum'.

Preparation - It is prepared by heating a mixture of silica ( $SiO_2$ ) and crushed coke (C) with a little salt and sawdust in an electric furnace at about  $2000^\circ C$ . The salt acts as a flux and sawdust provides the necessary porosity to the charge for the escape of CO.  
 $SiO_2 + 3C \xrightarrow{2000^\circ C} SiC + 2CO \uparrow$

The product is crushed and washed successively in  $H_2SO_4$ ,  $NaOH$  and water, and then dried in a kiln.

Properties: 1. It is a colourless transparent crystalline substance when pure but yellow, green or blue coloured when impure.

2. It is very hard though less than diamond.

3. It is extremely inert.

4. It resists the action of almost all reagents, acids even HF acid.

5. When fused with alkali ( $NaOH$ ) in presence of air, it decomposes to form carbonate and silicate.

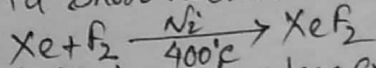
$SiC + 4NaOH + 2O_2 \rightarrow Na_2CO_3 + Na_2SiO_3 + 2H_2O$   
uses: It is used (i) as an abrasive (ii) in furnace linings (iii) in making knives, wheels, grinding etc.

### Noble gas compounds

The noble gases have most stable conf. ( $ns^2 np^6$ ). However, recent researches have shown that they form a few compounds under certain conditions. In 1962, Bartlett discovered first real compound of Xenon ( $XePtF_6$ ) by the action of  $Xe$  &  $PtF_6$ . A number of compounds of  $Xe$  &  $Kr$  with strong electron acceptors/electronegative elements  $F$  &  $O$  have been prepared. The most stable of these compounds are fluorides, oxyfluorides and oxides of  $Xe$  &  $Kr$ .

1. Fluorides of  $Xe$ : The fluorides of Xenon ( $Xe$ ) are amongst the important compounds of  $Xe$ . A series of stable fluorides of  $Xe$  are  $XeF_2$ ,  $XeF_4$ ,  $XeF_6$  &  $XeF_8$ . Of which  $XeF_2$  &  $XeF_4$  are most stable.

Xenon difluoride ( $XeF_2$ ): Preparation: It is prepared by heating 1:3 mixture of  $Xe$  &  $F_2$  in a short nickel tube at  $400^\circ C$ . On cooling quickly, a colourless  $XeF_2$  formed.



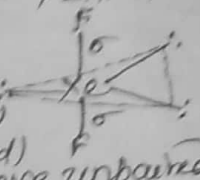
Properties: 1. It is a colourless, crystalline solid, melting point  $140^\circ C$

2. It dissolves in hydrofluoric acid without reacting with it.

3. It reacts with hydrogen to give hydrogen fluoride (HF) and xenon.  $XeF_2 + H_2 \rightarrow 2HF + Xe$

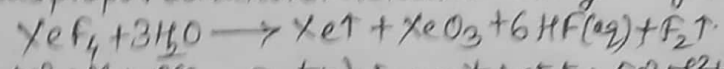
4. It reacts with water to evolve  $O_2$  gas.  $2XeF_2 + 2H_2O \rightarrow O_2 \uparrow + 2Xe \uparrow + 4HF$

Structure:  $Xe_{54}; 5s^2 5p^6 5d^0$  (Ground state); Excited state:  $5s^2 5p^5 5d^1$  (sp<sup>3d</sup> hybridisation).  
 One of the 5p electron in Xe gets unpaired and shifts to the 5d-orbital. For orbitals (5s, 5p, 5d) hybridised to give 5 hybrid orbitals, out of which two have unpaired electron, bonded with 2 2p orbitals of F atoms, remaining three (sp<sup>3d</sup>) hybrid orbitals have lone pair of electrons. The geometry of molecule is trigonal bipyramidal and linear shape (VSEPR Theory).

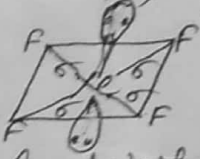


Xenon tetrafluoride ( $XeF_4$ ): Preparation: It is prepared by passing Xe & excess of  $F_2$  in a ratio of about 1:10 (Vol), through a long heated nickel tube.  $Xe + 5F_2 \rightarrow XeF_4$

Properties: 1. It is a colourless, crystalline solid, melting point 100°C  
 2. It sublimes readily. 3. It dissolves in HF without reacting.  
 4. It reacts with hydrogen to form HF.  $XeF_4 + 2H_2 \rightarrow 4HF + Xe$   
 5. It undergoes disproportionation reaction in water giving a highly explosive compd.  $XeO_3$

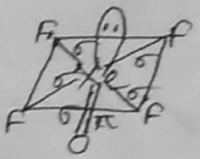


Structure:  $Xe_{54}; 5s^2 5p^6 5d^0$  (Ground state); In excited state:  $5s^2 5p^5 5d^1$  (sp<sup>3d<sup>2</sup></sup> hybridisation).  
 Here Xe atom is sp<sup>3d<sup>2</sup></sup> hybridised, out of 6 sp<sup>3d<sup>2</sup></sup> hybrid orbitals, four has unpaired electron, which bonded with 4 2p orbitals of F atoms, and two have lone pair of electrons. The geometry of molecule is octahedral, and shape is square planar (VSEPR-Theory).



Xenon oxyfluoride ( $XeOF_4$ ): Preparation: It is prepared by the action of xenon hexafluoride with water.  $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Properties: 1. It is a colourless liquid which solidifies at about 35°C.  
 2. It is thermally unstable, decomposes on heating into  $XeF_4$  &  $O_2$ .  
 3. It is decomposed by steam into  $XeO_3$  & HF.  $XeOF_4 + H_2O \xrightarrow{\Delta} XeO_3 + 4HF$



Structure:  $Xe_{54}; 5s^2 5p^6 5d^0$  (Ground state); Excited state:  $5s^2 5p^5 5d^1$  (sp<sup>3d<sup>2</sup></sup> hybridisation).  
 Here Xe atom is sp<sup>3d<sup>2</sup></sup> hybridised, out of which one sp<sup>3d<sup>2</sup></sup> hybrid orbital has lone pair of electron and five sp<sup>3d<sup>2</sup></sup> hybrid orbitals have unpaired electron, four sp<sup>3d<sup>2</sup></sup> hybrid orbitals bonded with 4 2p orbitals of F atoms and fifth sp<sup>3d<sup>2</sup></sup> hybrid orbital with 2p orbitals of O atom to form  $\sigma$ -bond. Remaining one sp<sup>3d<sup>2</sup></sup> hybrid orbital lateral overlap with 2p orbitals of O atom giving  $\pi$ -bond. Thus, geometry of the compound ( $XeOF_4$ ) is octahedral and shape is square pyramidal.

Xenon trioxide ( $XeO_3$ ): Preparation: It is prepared by hydrolysis of  $XeF_4$  in small amounts as a result of disproportionation.  $2XeF_4 + 3H_2O \rightarrow XeO_3 + 6HF + F_2 + Xe$

Properties: 1. It is a white non-volatile solid, soluble in water.  
 2. It is quite stable in aqueous solution. But it explodes violently in dry condition.  
 3. It is a powerful oxidising agent. It oxidises  $Pu^{3+}$  into  $Pu^{4+}$  in the presence of  $H^+$ .  
 $6Pu^{3+} + XeO_3 + 6H^+ \rightarrow 6Pu^{4+} + Xe + 3H_2O$

4. When dissolved in aqueous solution of NaOH, it undergoes disproportionation,  $N_2XeO_6 \cdot 8H_2O$  formed with the evolution of Xe gas.  $2XeO_3 + 4NaOH + 6H_2O \rightarrow Xe \uparrow + N_2XeO_6 \cdot 8H_2O$

Uses: It is used (i) as oxidising agent (ii) as substitute of TNT, an explosive.  
 Compounds of Krypton: Kr also combine with  $F_2$  at suitable conditions to form  $KrF_2$  &  $KrF_4$ .  
 Krypton difluoride ( $KrF_2$ ) is prepared by photochemical combination of Kr &  $F_2$ . While Krypton tetrafluoride ( $KrF_4$ ) by passing an electric discharge through a mixture of Kr &  $F_2$  at liq.  $N_2$  temp.  $Kr + F_2 \xrightarrow{light} KrF_2$ ;  $Kr + 2F_2 \xrightarrow{electric discharge} KrF_4$   
 Krypton fluorides are less stable than corresponding Xenon fluorides. These are easily hydrolysed by water giving Kr,  $O_2$  & HF(aq).  $2KrF_2 + 2H_2O \rightarrow 2Kr + O_2 \uparrow + 4HF(aq)$   
 $KrF_4 + 2H_2O \rightarrow Kr + 4HF + O_2 \uparrow$