#### THE *p*-BLOCK ELEMENTS

by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.

Hydrolysis can be understood by taking the example of  $SiCl_4$ . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si, finally leading to the formation of Si(OH)<sub>4</sub> as shown below :



### Problem 11. 6

 $[SiF_6]^{2-}$  is known whereas  $[SiCl_6]^{2-}$  not Give possible reasons.

## Solution

The main reasons  $\mathbf{N}$ (i) Strike chloride i modult be be accommodated arount  $\mathbf{S}_{1}^{d}$  due to limitation of its size.

(ii) interaction between lone pair of chloride ion and  $Si^{4+}$  is not very strong.

# 11.6 IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of *d* orbitals.

In carbon, only s and p orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals. Carbon also has unique ability to form  $p\pi$ – $p\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: C=C, C = C, C = O, C = S, and C = N. Heavier elements do not form  $p\pi$ – $p\pi$  bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because C—C bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C >> Si > Ge  $\approx$  Sn. Lead does not show catenation.

Bond	Bond ettalpy / kJ mol <sup>-1</sup>
C-2-2	348
	297
GeG2	260
SI-Sn	240

Due to property of catenation and  $p\pi$ –  $p\pi$  bond formation, carbon is able to show allotropic forms.

## **11.7 ALLOTROPES OF CARBON**

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W.Kroto, E.Smalley and R.F.Curl. For this discovery they were awarded the Nobel Prize in 1996.

## 11.7.1 Diamond

It has a crystalline lattice. In diamond each carbon atom undergoes  $sp^3$  hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this

- 11.9 What are electron deficient compounds ? Are  $BCl_3$  and  $SiCl_4$  electron deficient species ? Explain.
- 11.10 Write the resonance structures of  $CO_3^{2-}$  and  $HCO_3^{-}$ .
- 11.11 What is the state of hybridisation of carbon in (a)  $CO_3^{2-}$  (b) diamond (c) graphite?
- 11.12 Explain the difference in properties of diamond and graphite on the basis of their structures.
- 11.13 Rationalise the given statements and give chemical reactions :
  - Lead(II) chloride reacts with Cl<sub>2</sub> to give PbCl<sub>4</sub>.
  - Lead(IV) chloride is highly unstable towards heat.
  - Lead is known not to form an iodide, PbI<sub>4</sub>.
- 11.14 Suggest reasons why the B–F bond lengths in  $BF_3$  (130 pm) and  $BF_4$  (143 pm) differ.
- 11.15 If B–Cl bond has a dipole moment, explain why  ${\rm BCl}_{_3}$  molecule has zero dipole moment.
- 11.16 Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF. Aluminium trifluoride precipitates out of the resulting solution when gaseous  $BF_3$  is bubbled through. Give reasons.
- 11.17 Suggest a reason as to why CO is poisonous.
- 11.18 How is excessive content of  $CO_2$  responsible for global water  $\mathcal{P}$
- 11.19 Explain structures of diborane and boric acid.
- 11.20 What happens when
  - (a) Borax is heated strong,
  - (b) Boric acid is allow to water,
  - (c) Aluminum is treated with a luce NaOH.
  - $\mathbf{Cd}, \mathbf{Br}_{3}$  is reacted with a number  $\mathbf{R}$
- 1.21 Explain the foll wing reactions
  - (a) Silicon is heated with methyl chloride at high temperature in the presence of copper;
  - (b) Silicon dioxide is treated with hydrogen fluoride;
  - (c) CO is heated with ZnO;
  - (d) Hydrated alumina is treated with aqueous NaOH solution.
- 11.22 Give reasons :
  - (i) Conc. HNO<sub>3</sub> can be transported in aluminium container.
  - (ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.
  - (iii) Graphite is used as lubricant.
  - (iv) Diamond is used as an abrasive.
  - (v) Aluminium alloys are used to make aircraft body.
  - (vi) Aluminium utensils should not be kept in water overnight.
  - (vii) Aluminium wire is used to make transmission cables.
- 11.23 Explain why is there a phenomenal decrease in ionization enthalpy from carbon to silicon ?
- 11.24 How would you explain the lower atomic radius of Ga as compared to Al ?
- 11.25 What are allotropes? Sketch the structure of two allotropes of carbon namely diamond and graphite. What is the impact of structure on physical properties of two allotropes?

#### THE p-BLOCK ELEMENTS

- 11.26 (a) Classify following oxides as neutral, acidic, basic or amphoteric:
  - CO, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, PbO<sub>2</sub>, Tl<sub>2</sub>O<sub>3</sub>
  - (b) Write suitable chemical equations to show their nature.
- In some of the reactions thallium resembles aluminium, whereas in others 11.27 it resembles with group I metals. Support this statement by giving some evidences.
- 11.28 When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl to form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Identify (X), (A), (B), (C) and (D). Write suitable equations to support their identities.
- What do you understand by (a) inert pair effect (b) allotropy and 11.29 (c) catenation?
- 11.30 A certain salt X, gives the following results.
  - (i) Its aqueous solution is alkaline to litmus.
  - (ii) It swells up to a glassy material Y on strong heating.
  - (iii) When conc.  $H_2SO_4$  is added to a hot solution of X, white crystal of an acid Z separates out.

Write equations for all the above reactions and identify X, Y and

- 11.31 Write balanced equations for:
  - (i)  $BF_3 + LiH \rightarrow$
  - (ii)  $B_2H_6 + H_2O \rightarrow$
  - (iii) NaH +  $B_{a}H_{c} \rightarrow$
  - (iv)  $H_{a}BO_{a} \xrightarrow{A} \mathbf{\Gamma}$

om Notesale.co. 19 of 19 Give one met .d 🙆 dustrial preparation and one for laboratory preparation of CO and  $CO_2$  each.

- 11.33 An aqueous solution of borax is
  - (a) neutral (b) amphoteric
    - (d) acidic (c) basic
- 11.34 Boric acid is polymeric due to
  - (a) its acidic nature (b) the presence of hydrogen bonds
  - (c) its monobasic nature (d) its geometry
- 11.35 The type of hybridisation of boron in diborane is
  - (b)  $sp^2$ (c)  $sp^{3}$ (d)  $dsp^2$ (a) *sp*
- 11.36 Thermodynamically the most stable form of carbon is
  - (a) diamond (b) graphite
  - (c) fullerenes (d) coal
- 11.37 Elements of group 14
  - (a) exhibit oxidation state of +4 only
  - (b) exhibit oxidation state of +2 and +4
  - (c) form  $M^{2-}$  and  $M^{4+}$  ions
  - (d) form  $M^{2+}$  and  $M^{4+}$  ions
- If the starting material for the manufacture of silicones is  $\mathrm{RSiCl}_3$ , write the 11.38 structure of the product formed.