

Choose the correct alternative. Only One Choice is Correct. However, questions marked with '*' may have More than One Correct options.

5. H_3BO_3 is :
 (A) Weak monobasic Lewis acid (B) Weak monobasic Bronsted acid
 (C) Strong monobasic Lewis acid (D) Weak tribasic Bronsted acid
6. Alumina may be converted into anhydrous aluminium chloride by :
 (A) heating it with conc. HCl
 (B) heating in a current of dry chlorine
 (C) heating it with rock salt
 (D) mixing it with carbon and heating the mixture in a current of dry chlorine
- *7. Colemanite on reaction with sodium carbonate gives :
 (A) CaO (B) $CaCO_3$ (C) $NaBO_2$ (D) B_2O_3
- *8. Which of the following compounds have dimers with three center two electron bonds ?
 (A) BH_3 (B) $Al(CH_3)_3$ (C) BCl_3 (D) $AlCl_3$
9. Statement : 1 Boron always forms covalent bonds.
 Statement : 2 The small size of B^{3+} favours formation of covalent bond.
 (A) Statement-1 is True, Statement-2 is True and Statement-2 is a correct explanation for Statement-1
 (B) Statement-1 is True, Statement-2 is True and Statement-2 is NOT a correct explanation for Statement-1
 (C) Statement-1 is True, Statement-2 is False
 (D) Statement-1 is False, Statement-2 is True

GROUP 14 ELEMENTS

Section - 3

Oxidation States :

C and Si show oxidation state of +4 while Ge, Sn, Pb show oxidation states of both +2 and +4 due to the Inert Pair Effect.

Metallic Character :

It decreases down the group. Thus, C and Si are non-metals, Ge is a metalloid and Sn and Pb are metals .

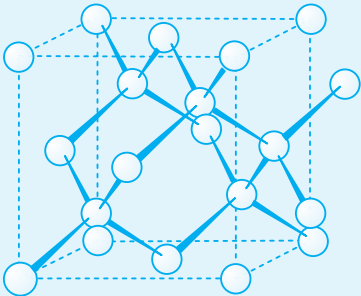
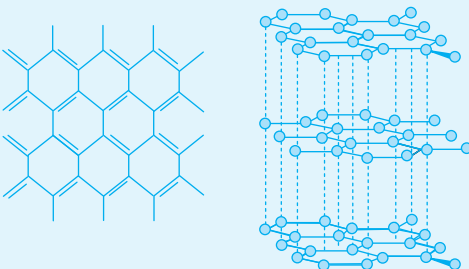
Catenation :

Due to smaller size and higher electron negativity of carbon atom it has the property of linking to other carbon atoms forming long chains. However as we move down, the tendency for catenation decreases in the order :



Carbon and Its Compounds

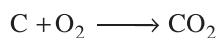
Allotropy : Carbon exists in a large number of allotropic forms. Two main forms are diamond and graphite

Diamond	Graphite
<ul style="list-style-type: none"> Extremely unreactive, colourless, non conductor and shows brilliance due to total internal reflection. The structure comprises of sp^3 hybrid C atoms forming σ-bonds and arranged tetrahedrally.  <p>The crystal structure of diamond.</p>	<ul style="list-style-type: none"> Quite reactive and soft. It has a layer structure with layers held together by weak van der waal's forces. Each sheet consists of sp^2 hybridised carbon atoms which are covalently bonded to three carbon atoms by σ-bonds. The fourth e^- is in unhybridised 'p' orbital and forms a partial 'π' bond  <p>(a) The structure of a graphite sheet. (b) Structure of a-graphite</p> <p>It is used as a lubricant due to slippery layers and electricity is conducted only along sheets.</p>

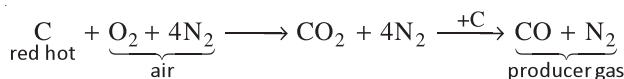
Chemical Properties :

- Water gas is made by blowing air through red or white hot coke : $C + H_2O \xrightarrow{\text{red heat}} \underbrace{H_2 + CO}_{\text{water gas}}$

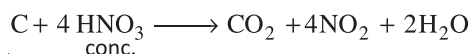
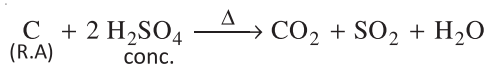
- All allotropes burn in oxygen to form CO_2 .



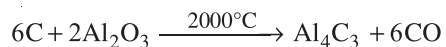
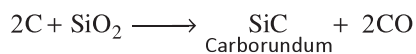
Producer gas is made by blowing air through red hot coke.



- Carbon as reducing agent :



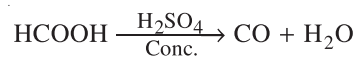
- Carbon as Oxygen acceptor :



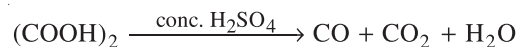
	CO	CO ₂	H ₂ CO ₃
Reaction with	Colourless odourless, poisonous, neutral, quite reactive : $\bar{\text{C}} \equiv \overset{+}{\text{O}}:$	Colourless, ordourless, acidic $\text{O} = \text{C} = \text{O}$	Weak diabasic acid $\left[\begin{array}{c} \text{O} \\ // \\ \text{O}-\text{C}=\text{O} \\ // \\ \text{O} \end{array} \right]^{2-}$ Plane Triangle
H ₂ O	Sparingly Soluble $+ \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	Dissolves and slightly hydrated to H ₂ CO ₃ , HCO ₃ ⁻ , CO ₃ ²⁻	Has never been isolated from aqueous solution.
Air	$+ \text{O}_2 \longrightarrow 2\text{CO}_2$ Burns with a blue flame (test for CO)		
Alkalies	$\text{CO} + \text{NaOH} \longrightarrow \text{HCOONa}$	$\text{Ca(OH)}_2 \xrightarrow{\text{CO}_2} \underset{\text{White}}{\text{CaCO}_3 \downarrow}$ Lime water (test for CO ₂) $\text{CaCO}_3 \xrightarrow[\text{excess}]{\text{CO}_2} \underset{\text{Soluble}}{\text{Ca(HCO}_3)_2}$	
Non Metals	$+ \text{H}_2 \xrightarrow[\text{ZnO, Cu}]{300^\circ} \text{CH}_3\text{OH}$ $+ \text{Cl}_2 \xrightarrow[\text{ZnO, Cu}]{h\nu} \text{COCl}_2$ (phosgene) $\text{HCl} + \text{CO}_2 \xleftarrow{\text{H}_2\text{O}}$ $\quad \quad \quad \downarrow \text{NH}_3$ $\quad \quad \quad \text{NH}_2-\text{C}(=\text{O})-\text{NH}_2$ $\quad \quad \quad \text{Urea}$ $\quad \quad \quad + \text{HCl}$	$+ \text{C} \xrightarrow[\text{Red hot}]{} \text{CO}$	
Metal	$+ \text{Ni} \xrightarrow{28^\circ\text{C}} \text{Ni(CO)}_4$ $+ \text{Fe} \xrightarrow{200^\circ\text{C}} \text{Fe(CO)}_5$	$+ \text{Zn} \longrightarrow \text{CO} + \text{ZnO}$ $+ \text{Mg} \longrightarrow \text{C} + \text{MgO}$	
NH ₃	Soluble in ammonical cuprous chloride and forms [Cu(CO)Cl(H ₂ O) ₂]	$+ \text{NH}_3 \xrightarrow[\text{Pressure}]{180^\circ\text{C}} \text{NH}_4\text{CO}_2\text{NH}_2$ Ammonium carbamate $\text{H}_2\text{O} + \text{CO(NH}_2)_2 \longleftarrow$ Urea	
Uses	<input type="checkbox"/> An important industrial fuel (eg. water gas, producer gas, coal gas) <input type="checkbox"/> Used to prepare phosgene which is toxic and used in warfare.	<input type="checkbox"/> Used as dry ice. <input type="checkbox"/> Has biological importance.	

Preparation of CO :

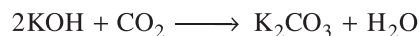
- (i) In laboratory it is prepared by dehydrating formic acid with concentrated H_2SO_4



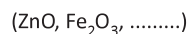
Also,



CO_2 is removed by passing through soda :



- (ii) $\text{C} + \text{oxides of heavy metal} \longrightarrow \text{CO} \uparrow + \text{metal}$

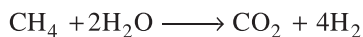
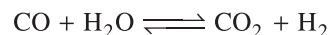


- (iii) $\text{K}_4 [\text{Fe}(\text{CN})_6] + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \xrightarrow{\Delta} 2\text{K}_2\text{SO}_4 + 2\text{FeSO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{CO} \uparrow$
 Potassium conc.
 Ferrocyanide

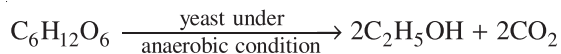
Note: Dil H_2SO_4 is not used, as it gives extremely poisonous HCN.

Preparation of CO_2 :

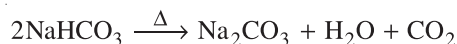
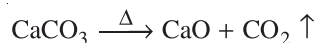
- (i) The main industrial source is as a by product from the manufacture of hydrogen for making ammonia :



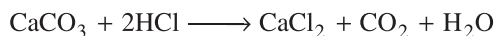
- (ii) It is recovered from alcoholic fermentation :



- (iii) It is obtained by heating carbonates :



- (iv) In laboratory it is prepared by the action of dilute acids on carbonates :



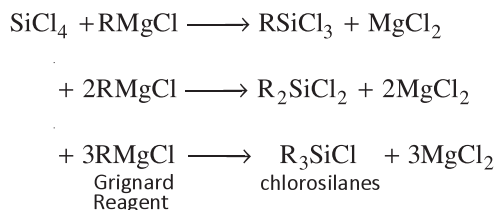
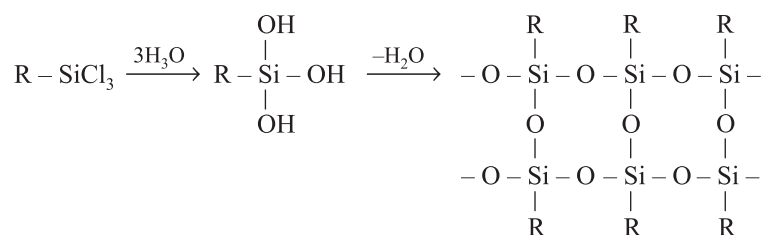
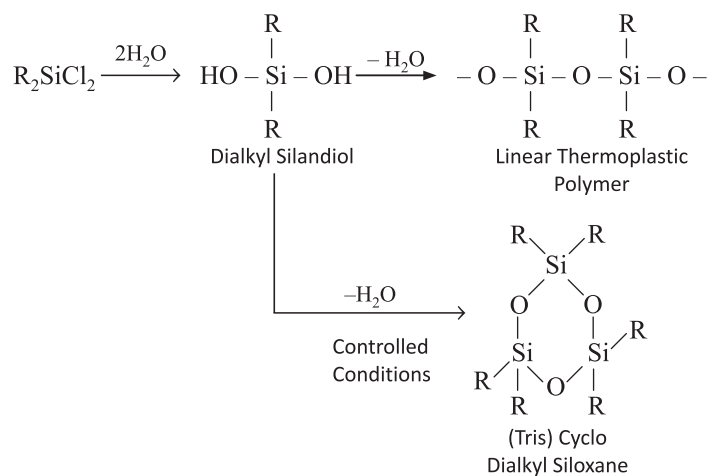
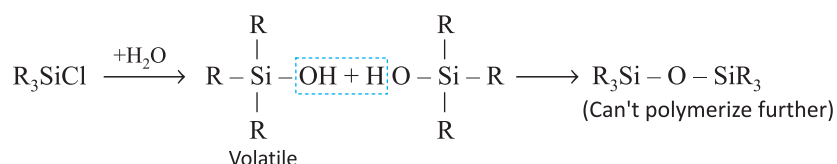
	Si	SiC (Carborundum)	SiO ₂ (Silica)
Reaction with	<ul style="list-style-type: none"> 2nd most abundant element, widely present as SiO₂ Crystalline, very hard, inert Amorphous, brownish, powder, more reactive 	<ul style="list-style-type: none"> Colourless but commercial samples are yellow, green, blue due to traces of Fe, Extremely hard, inert, (structure similar to diamond) and used as abrasive. Amorphous, brownish, powder, more reactive 	<ul style="list-style-type: none"> Widely found as sand, quartz, flint. High melting point Acidic in nature.
Water	<ul style="list-style-type: none"> Unaffected in ordinary conditions +H₂O $\xrightarrow{\text{Red heat}}$ SiO₂ + H₂↑ 	Unaffected	<ul style="list-style-type: none"> SiO₂ + H₂O \rightleftharpoons H₄SiO₄
Air	<ul style="list-style-type: none"> Si + O₂ $\xrightarrow{\Delta}$ SiO₂ Amorphous (Burns brilliantly) Si + O₂ $\xrightarrow{\Delta}$ no effect Crystalline 	Unaffected	Unaffected
Acids	<ul style="list-style-type: none"> Unaffected by dilute acids but amorphous form dissolves in HNO₃ + HCl while crystalline form dissolves in HNO₃ + HF 	Unaffected by acids (except H ₃ PO ₄)	<ul style="list-style-type: none"> Unaffected being acidic oxide (except in HF) HF $\xrightarrow{\text{SiO}_2}$ SiF₄ + H₂O SiF₄ when comes in contact with a drop of water it forms silicic acid seen as floating white solid. [Test for silicates] SiF₄ $\xrightarrow{\text{H}_2\text{O}}$ Si(OH)₄ + HF
Alkalies	+ KOH + H ₂ O \longrightarrow K ₂ SiO ₃ + H ₂ (Slowly if cold and readily if hot)	+ 2NaOH + 2O ₂ \longrightarrow Na ₂ SiO ₃ + CO ₂ + H ₂ O	+ NaOH \longrightarrow Silicates This is the reason why gases stoppers stick in NaOH bottles.
Halogen	<ul style="list-style-type: none"> Si + 2F₂ \longrightarrow SiF₄ Amorphous (spontaneous reaction) 	Unaffected except for : + SiC + 2Cl ₂ $\xrightarrow{100^\circ\text{C}}$ SiCl ₄	Unaffected except for : SiO ₂ + 2F ₂ \longrightarrow SiF ₄ + O ₂
Carbon			+ SiO ₂ + 2C $\xrightarrow{\Delta}$ Si + 2CO
Preparation	<ul style="list-style-type: none"> SiO₂ + 2Mg $\xrightarrow{\Delta}$ 2MgO + Si Powder (Amorphous) SiO₂ + C $\xrightarrow[\text{Fe}]{\text{Electric furnace}}$ Si + CO (Sand powdered) (Crystalline) [Fe is added to prevent formation of SiC] 	<ul style="list-style-type: none"> SiO₂ + C (excess) Sand Coke 2000 – 2500°C electric furnace \downarrow NaCl (flux) + saw dust SiC + CO↑ \downarrow Crushed, washed with H₂SO₄, NaOH and H₂O and then dried 	

[a] Silicones

Silicones are a group of organo - silicon polymers containing Si - O - Si linkages.

Preparation :

Silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes (formed by reaction of Grignard reagents and silicon tetrachloride) and their subsequent polymerisation.

**(i) Formation of cross - linked silicones :****(ii) Formation of linear polymers :****(iii) Formation of dimers :**

Properties :

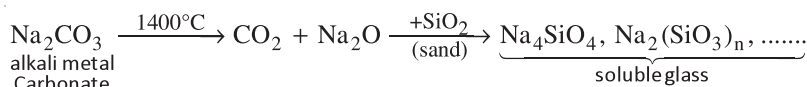
1. R_3SiCl is a chain stopping unit and reduces polymer size as it blocks the end of chain. While $RSiCl_3$ is used to produce new cross - links and increase polymerisation.
2. Silicones are electrical insulators, water-repellent, strong and inert. Their b.p. and viscosity increase with increase in chain length.
3. Silicones are stable towards heat (hence used as electrical insulators). The order of stability varies with R attached in the orders: $ph > CH_3 > Et > Pr$.
4. Being water - repellent they are used for treating glass ware and fabrics.
5. They are also used as hydraulic fluids and silicone rubbers.

[b] Silicates

Silicates are derivatives of silicic acid $Si(OH)_4$ or H_4SiO_4 . They have basic tetrahedral units of SiO_4^{4-} and Si – O bond may be considered 50% covalent and 50% ionic (suggested by a difference of 1.7 in electronegativities).

Preparation :

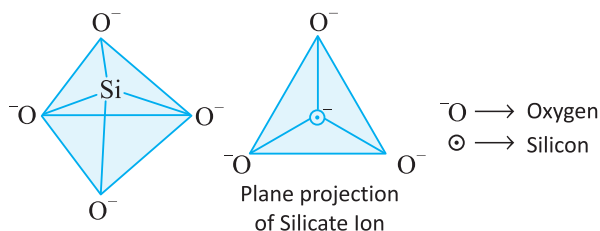
Silicates can be prepared by fusing an alkali metal carbonate with sand in an electric furnace at about $1400^\circ C$.

**Classification of Silicate Minerals :**

(i) **Orthosilicates :** These silicates contain single discrete unit of SiO_4^{4-} tetrahedral.

For example :	Zircon (gemstone)	$ZrSiO_4$
	Forestrite or Olivine	Mg_2SiO_4
	Phenacite	Be_2SiO_4
	Willemite	Zn_2SiO_4

Number of shared oxygen atom = 0



(ii) **Pyrosilicates :** These silicates contain two units of SiO_4^{4-} joined along a corner containing oxygen atom. These are also called as island silicate.

Pyrosilicate ion $\text{Si}_2\text{O}_7^{6-}$,



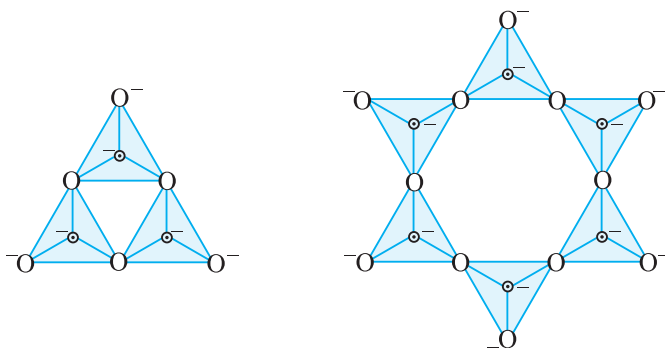
For example :

Thortveitite	$\text{Sc}_2\text{Si}_2\text{O}_7$
Hemimorphite	$\text{Zn}_3(\text{Si}_2\text{O}_7) \cdot \text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$

Number of shared oxygen atoms = 1

(iii) Cyclic Structure : Cyclic or ring silicates have general formula $(\text{SiO}_3)_n^{2n-}$.

Structure and example of cyclic silicates containing $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$ ions are given below:



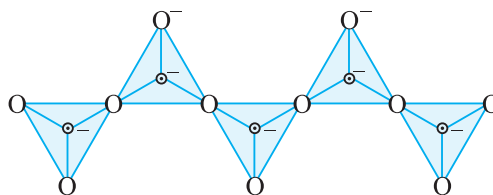
For example :

Beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
Wollastonite	$\text{Ca}_3\text{Si}_3\text{O}_9$

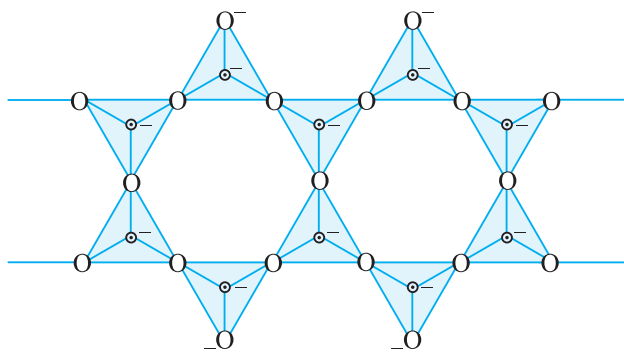
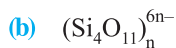
Number of shared oxygen atoms = 2

(iv) Chain silicates : Chain silicates are formed by sharing two oxygen atoms by each tetrahedral. Anions of chain silicates have two general formula.

(a) $(\text{SiO}_3)_n^{2n-}$



Number of shared oxygen atoms = 2

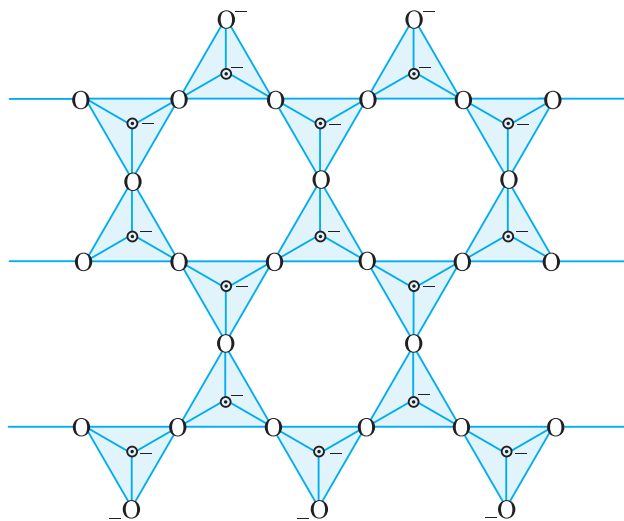


Number of shared oxygen atoms = 2.5

For example :

Spodumene	$\text{LiAl}(\text{SiO}_3)_2$
Diopside	$\text{CaMg}(\text{SiO}_3)_2$
Tremolite	$\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

(v) Two Dimensional Sheet Silicates : In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedral, such sharing forms two dimensional sheet structure with general formula $(\text{Si}_2\text{O}_5)_n^{2n-}$.



For example :

Talc	$\text{Mg}(\text{Si}_2\text{O}_5)_2\text{Mg}(\text{OH})_2$
Kaolin	$\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$

Number of shared oxygen atoms = 3

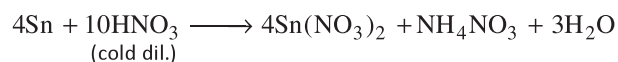
(vi) Three Dimensional Sheet Silicates: These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral. For example, Quartz, Feldspars, Zeolites and Ultramarines. Here all 4 oxygen atoms are shared.

Tin and its Compounds :

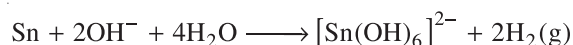
Tin is a white lustrous, soft, malleable metal. It produces a cracking sound called *tincry* whenever it is bent.

Properties :

1. Tin reacts with steam to give SnO_2 and H_2 .
2. It dissolves in dilute HNO_3 forming $\text{Sn}(\text{NO}_3)_2$



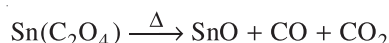
3. It is slowly attacked by cold alkalies and rapidly by hot alkalies. Thus it is amphoteric.



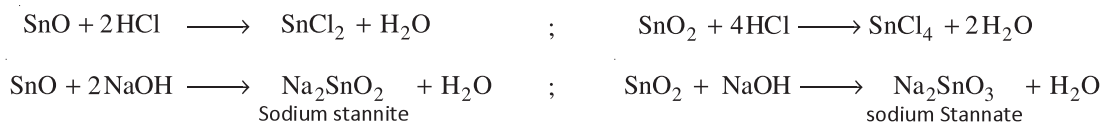
4. Sn is used in tin plating (coating iron or steel sheets with tin) and making alloys like bronze (75% Cu + 25% Sn), and solder (67% + 33% Pb).

Sn^{2+} and Sn^{4+}

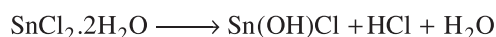
Tin ion exists in two states +II and +IV with the +IV state being more stable. SnO_2 is known as cassiterite and found as a mineral in nature. The other oxide SnO is less stable and is obtained by heating stannous oxalate.



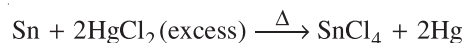
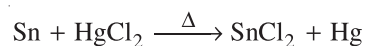
Both SnO and SnO_2 are amphoteric but SnO is slightly more basic than SnO_2 and a good reducing agent too.



Among halides, stannous chloride (SnCl_2) and stannic chloride (SnCl_4) are the most important. SnCl_2 exists as a di-hydrate which undergoes hydrolysis on heating.



The anhydrous salt SnCl_2 is obtained by reaction of Sn with a calculated quantity of HgCl_2 . Excess of HgCl_2 results in the formation of stannic chloride.



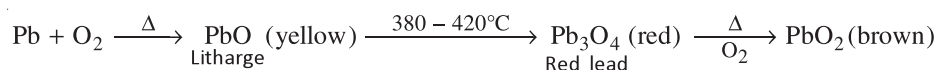
Most of the reactions of SnCl_2 are due to its reducing character. It reduces MnO_4^- to Mn^{2+} , $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} and itself gets oxidised to Sn^{4+} .

Lead and its Compounds

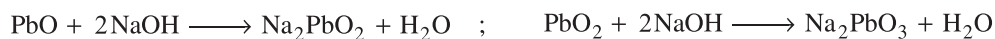
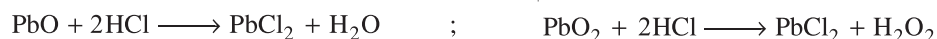
- (i) Lead is a bluish grey soft metal which can be cut with a knife and extremely poisonous.
- (ii) Pb often appears more unreactive than expected from its standard electrode potential. The unreactiveness is due to the surface coating of basic carbonate $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ which forms over lead when exposed to air and moisture. Thus lead is unaffected by water.
- (iii) Pb is amphoteric and dissolves in both acids and hot alkalies similar to Sn. In alkali it forms plumbates like $\text{Na}_2[\text{Pb}(\text{OH})_6]$ or Na_2PbO_3 . However, lead does not dissolve in concentrated HCl because a surface coating of PbCl_2 is formed.
- (iv) Lead is used in making lead chamber for H_2SO_4 plant and certain alloys like solder (Sn – Pb)

[a] Oxides

Pb exists as Pb^{+2} and Pb^{+4} with Pb^{+2} being more stable. This is due to the inert pair effect which increases the stability of +II state while going down the group. Oxide formation is shown as :



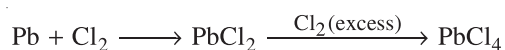
- (i) PbO and PbO_2 are both amphoteric and dissolve in both acids and bases.



- (ii) Pb_3O_4 or Red Lead may be represented as $2\text{PbO} \cdot \text{PbO}_2$ and is used in paint to prevent the rusting of iron and steel.
- (iii) PbO (Litharge) is commercially important and is used in large amounts to make lead glass. PbO_2 is used as a strong oxidising agent and produced in lead storage batteries.

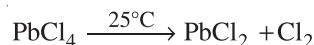
[b] Chlorides

Chlorides are prepared by passing lead through a current of chlorine gas.



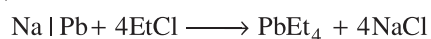
Dissolving Pb^{2+} salts (PbO , PbCO_3 , $\text{Pb}(\text{NO}_3)_2$) in HCl produces PbCl_2 .

PbCl_4 is less stable and decomposes on heating at room temperature and liberates Cl_2 .



[C] Tetraethyl Lead $(\text{CH}_3\text{CH}_2)_4\text{Pb}$:

It is produced in large amounts and used as an 'anti-knock' additive to increase the octane number of petrol. The commercial preparation uses a sodium/lead alloy.



Once it was produced in larger tonnages than any other organometallic compound but the production is declining rapidly as a result of legislation requiring that new cars must run on lead-free petrol.

IN-CHAPTER EXERCISE-B

- Identify the group 14 element that best fits each of the following description :
 - Prefers the +2 oxidation state
 - Forms the strongest π bonds.
 - Is the second most abundant element in the earth's crust.
 - Forms the most acidic oxide.
- Give reasons for the following observations/applications :
 - Solid CO_2 is known as dry ice.
 - Carbon acts as an abrasive and also as a lubricant.
 - Glass stoppers stick in NaOH bottles.
 - Thermodynamically, graphite is more stable than diamond but still diamond (the less stable form) exists.
 - CCl_4 is unaffected by water whilst SiCl_4 is rapidly hydrolysed.
 - SnCl_4 fumes in moist air.
- Identify A, B, C,
 - $$\text{CO} + \text{Cl}_2 \longrightarrow \text{A} \xrightarrow{+\text{NH}_3} \text{B} \xleftarrow{+E(\text{basic})} \text{D}$$

$$\quad \quad \quad \downarrow \text{H}_2\text{O} \quad \quad \quad \text{C} + \text{D}$$
 - $$\text{Si} \xrightarrow[\text{(conc.)}]{\text{HNO}_3/\text{HF}} \text{A} \xrightarrow{\text{HF}} \text{B} ; \quad \text{A} \xrightarrow{\text{H}_2\text{O}} \text{B} + \text{C}$$
 - $$\text{Na}_2\text{CO}_3 + \text{Si (fused)} \longrightarrow \text{A}$$
 - $$\text{Sn}(\text{C}_2\text{O}_4) \xrightarrow{\Delta} \text{A} + \text{B(g)} + \text{C(g)} ; \quad \text{A} \xrightarrow{\text{dil HCl}} \text{D}$$

B is measured quantitatively using I_2O_5 solution.
- CO_2 goes to the atmosphere (greenhouse effect) and thus gets dissolved in H_2O . pH of the water increases or decreases and what is the effect on the fertility of the soil ?
- Starting from SiCl_4 prepare the following in steps not exceeding the number given in parenthesis :
 - Silicon (1)
 - linear silicon containing methyl group only (4)
 - Na_2SiO_3 (3)
- How are the following compounds detected qualitatively ?
 - CO
 - CO_2
 - silicates
 - PbCl_2

Choose the correct alternative. Only One Choice is Correct. However, questions marked with '*' may have More than One Correct options.

- Moderate electrical conductivity is shown by :
 - Silica
 - Graphite
 - Diamond
 - None of these
- Name the structure of silicates in which three oxygen atoms of $[\text{SiO}_4]^{4-}$ are shared.
 - Pyrosilicate
 - Sheet silicate
 - Linear chain silicate
 - 3-D silicate
- Which of the following halides is least stable and has doubtful existence ?
 - CCl_4
 - GeI_4
 - SnI_4
 - PbI_4
- Me_2SiCl_2 on hydrolysis will produce :
 - $\text{Me}_2\text{Si}(\text{OH})_2$
 - $\text{Me}_2\text{Si} = \text{O}$
 - $[-\text{O}-\text{Me}_2\text{Si}-\text{O}-]_n$
 - $\text{Me}_2\text{SiCl}(\text{OH})$
- Lead nitrate on heating gives :
 - NO_2
 - O_2
 - PbO
 - Pb