p-Block Elements (Part-1)

DISCLAIMER

p-Block Elements (Part-1)

GROUP 13 ELEMENTS

Ionisation Energy

The first ionisation energies (IE_1) of group 13 elements (Boron family) are lower than the corresponding elements of group 2 (AEM). This is due to the electronic configuration of group 13 elements ns2 np1 and the electron thus has to be removed from the p-orbital which is much easier than removing an s-electron of AEM elements, which is more strongly atracted by the nucleus. Boron has higher ionisation energy than its group members because its is considerable smaller. The ionization energy is so high that boron is always covalent.

Concept Ladder

Stability of +3 oxidation state : B > Al > Ga > In > Tl
Stability of +1 oxidation state : Ga < In < Tl
Ionisation energy : B > Al < Ga > In < Tl

Oxidation State

Due to ns^2, np^1 configuration of the valence shell, group 13 elements are expected to be trivalent but there is increase in ability to form univalent compounds on moving down the group. The oxidation state of B and Al is +3 while Ga, In, Tl show oxidation state of both +3 and +1. It is due to **Inert Pair Effect**.

Rack your Brain

Why boron has high melting and boiling point?

Metallic Character/Reducing Power

The order is : B < Al > Ga > In > Tl

The increase in metallic character from Boron to Aluminium due to increase in atomic size but Ga, In, Tl do not follow the trend. They follow immediately after a row of ten transition elements and thus have 10 d-electrons which are less efficient for shielding the nuclear charge than s,p electrons. Thus outer most electrons being more firmly held by the nucleus are more difficult to remove than expected. This leads to decrease in size as well as decreases in metallic character than would be expected. This phenonmenon is know as d-block Contraction.

Previous Year's Questions

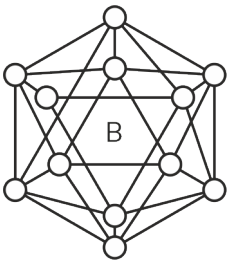
The correct order of atomic radii in group 13 elements is **[NEET 2018]**

(1) B < Al < In < Ga < Tl
(2) B < Al < Ga < In < Tl
(3) B < Ga < Al < Tl < In
(4) B < Ga < Al < In < Tl

Similarly for Tl which is followed immediately after 14-f-block elements, there is much change in the size and metallic character of it. It is due to the Lanthanide Contraction which is due to the f-block elements. Note that in general the size increases down the group but is less than as expected.

Acidic Character

From B to Tl acidic character decreases and basic character increases because ionization energy increases. Thus we find that $B(OH)_3$, and B_2O_3 are acidic ; $Al(OH)_3$ and Al_2O_3 are amphoteric; $Ga(OH)_3$ and Ga_2O_3 are amphoteric; and $In(OH)_3$, $TI(OH)_3$ are basic.



Boron & Its Compound

Physical Properties and Occurrence

Boron occurs in two allotropic form :

(a) Crystalline – It is chemically inert, very hard and black in color.

(b) Amorphous – It is chemically active, a non–conductor, difficiult to fuse and brown in color.

All allotropic forms contain icosahedral unit with atoms at all 12 corners. The important minerals of boron are :

Borax (Tincal)	$Na_2B_4O_2.10H_2O$	Boric acid	H_3BO_3
Kernite (Resorite)	$Na_2B_4O_7.4H_2O$	Boronatro calcite	$CaB_4O_7.NaBO_2.8H_2O$
Colemanite	$Ca_2B_6O_{11}.5H_2O$	Boracite	$2Mg_3B_8O_{15}.MgCl_2$
Pandertie	$Ca_2B_6O_{11}.3H_2O$		

Concept Ladder

The electropositive or metallic character of group 13 elements increases from B to Tl. B being a non metal and thus forms an acidic hydroxide. Al forms amphoteric hydroxide and Tl, the most metallic from basic hydroxides.

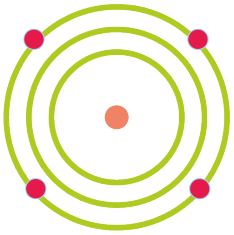
Rack your Brain

Which elements of group 13 will form most ionic and covalent compounds respectively?

BORON FAMILY

B	Al	Ga	In	Tl	Uut
5	13	31	49	81	113
Boron	Aluminium	Gallium	Indium	Thallium	Ununtrium unknown

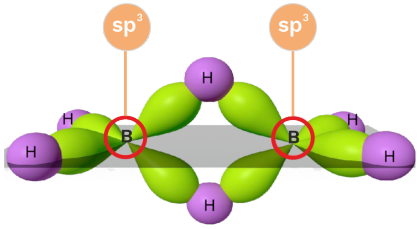
ELECTRONIC CONFIGURATION



ns^2np^1

Valence electrons = 3

Diborone (B_2H_6)



BH_3 is an electron deficient molecule. It has six electrons and a vacant orbital. So, it is used as an electrophile in organic reactions.

Borax ($Na_2B_4O_7$) In used for cleaning and washing purposes.

Aluminium was classified as precious metal during 19th century. Napoleon III gave aluminium cutlery to his most valuable guests, all other guests had to eat with gold cutlery.

PHYSICAL STATE

Boron is a non metal
Aluminium, Indium,
Gallium are metalloids.

Gallium has the second lowest melting point after mercury. it remains in liquid phase even at high temperatures.

31
Ga
Gallium

AMPHOTERIC

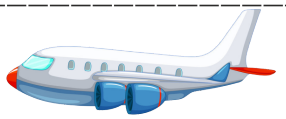
$Al(OH)_3$ is amphoteric

Al—O—H

strength between Al–O and O–H is same

Bond strength Al–O = Bond strength O–H

Aluminium is used in tins, aeroplanes and even in iphone



Indium is used in display screens of television and mobiles

Thallium is used as rat poison.

Extraction of Boron : It includes 2 steps :

1. Preparation of Boric anhydride (B_2O_3) :

[Method–I]

$$\underset{\text{(powdered Borax)}}{Na_2B_4O_7} + \underset{\text{(conc.)}}{2HCl} \longrightarrow 2NaCl + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{(sparingly soluble orthoboric acid)}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O$$

[Method–II]

$$\underset{\text{(powdered colemanite)}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \xrightarrow{\text{fuses}} 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

The fused mass is extracted with. $CaCO_3$ remains filtrate and insoluble containing sodium metaborate. By obtained borax crystals, borax is put to crystallisation. The remaining solution is treated with CO_2.

$$4NaBO_2 + CO_2 \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + Na_2CO_3$$

Then Method I is followed.

[Method III]

Suspension of colemanite mineral in H_2O is formed and SO_2 gas is passed to obtain crystal of boric acid on cooling.

$$Ca_2B_6O_{11} + 4SO_2 + 4H_2O \longrightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11}$$

$$H_4B_6O_{11} + 7H_2O \longrightarrow 6H_3BO_3$$

$$\overline{Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3}$$

Then, $\underset{\text{crystals}}{2H_3BO_3} \xrightarrow{\Delta} B_2O_3 + 3H_2O$

Rack your Brain

If Borax can be formulated as $Na_2[B_4O_5(OH)_4].8H_2O$ then how would you formulate Colemanite?

Concept Ladder

On a large scale, boron is extracted from its minerals, borax $Na_2B_4O_7$ and colemanite $Ca_2B_6O_{11}$. The latter is first converted to borax by boiling with a solution of sodium carbonate in the requisite proportion and then the same method is followed.

2. Reduction B_2O_3

[Method–I]

$$\underbrace{B_2O_3 + 3M}_{\text{fused}} \xrightarrow[\text{crucible}]{\text{heated in}} 2B + 3MO \qquad (M = Na, K \text{ or } Mg)$$

To oxidise unreacted metal M, the fused mass is stirred with iron rod. The mass is then boiled with dil. HCl to obtain insoluble amorphous boron powder with is 95% pure.

[Method–II] : Modern Method

A fused mixture containing magnesium fluroide, boric anhydride and magnesium oxide at 1100°C is electrolysed in a carbon crucible (anode). Iron rod is used as cathod.

Cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$

$Mg + B_2O_3 \longrightarrow \underset{\text{amorphous}}{B} + MgO$

Anode : $2O^{2-} \longrightarrow O_2 + 4e^-$

[Method–III]

To obtain crystalline boron in small amounts, B_2O_3 is redused with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

Removal of Aluminium is made by heating the fused mass with NaOH solution.

Chemical Properties of Boron

1. B is unaffected by H_2O under ordinary conditions but :

$$\underset{\text{(red hot)}}{2B} + 3\underset{\text{(Steam)}}{H_2O} \longrightarrow B_2O_3 + 3H_2 \uparrow$$

Rack your Brain

What acts as a reducig agent during the reduction of boron?

Concept Ladder

Boron generally forms covalent bonds rather than +3 ions. This is due to the small size of boron which makes the sum of its first three ionization enthalpies very high. Boron is generally unreactive when comes in contact with acids and alkalis at moderate temperatures.

2. Amorphous boron burns in air at 700°C with a reddish flame forming oxide and nitride.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$2B + N_2 \longrightarrow 2BN$$

3. Boron is unaffected by reducing acids. With oxidising acids it gives boric acid.

$$B + \underset{\text{O.A.}}{3HNO_3} \longrightarrow H_3BO_3 + 3NO_2 \uparrow$$

4. Boron dissolves is fused alkalies liberating hydrogen.

$$2B + \underset{\text{fused}}{6NaOH} \longrightarrow 2Na_3BO_3 + H_2 \uparrow$$

5. Generally, boron forms Non-Stoichiometric compounds with metals (not of Group 1)

$$2B + 3Mg \longrightarrow Mg_3B_2$$

6. Action of non-metals :

$$4B + C \xrightarrow[\text{electric furnance}]{\Delta} B_4C$$
$$2B + 3Cl_2 \xrightarrow{\Delta} 2BCl_3$$

Uses : Boron carbide rods are used to control nuclear reactions. Boron has a very high cross-section for capturing the neutorns. Also to make boron of having an even number of neutrons B absorbs neutrons.

$$_5B^{10} + {}_0n^1 \longrightarrow {}_5B^{11}$$

[a] Diborance B_2H_6 :

Structure and Physical Properties :

In diborane the bridge hydrogens form abnormal 3 centre 2 electron 'banana-shaped' bonds with two B atoms.

For having delocalized molecular orbital covering all three nuclei, an sp3 hybrid orbital from each boron atom overlaps with 1s orbital of hydrogen.

Concept Ladder

Boron is added to glass to increase its resistance to heat shock. Most chemistry glassware is made from borosilicate glass.

Previous Year's Questions

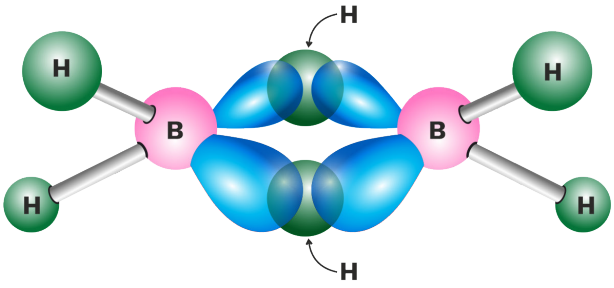
Which one of the following elements is unable to form MF_6^{3-} ion?

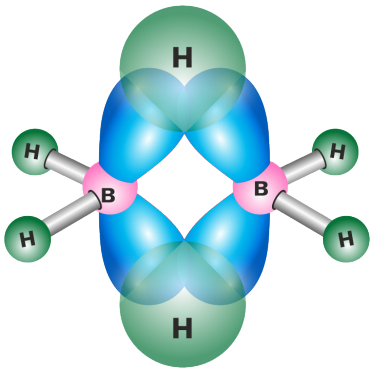
[NEET 2018]

(1) Ga (2) Al
(3) B (4) In

Concept Ladder

Boron forms hydrides of the type B_nH_{n+4} and B_nH_{n+6} which are called Boranes.





Diborane is a highly reactive and colorless gas with disagreeable odour. It is used as a catalyst in polymerization reactions and a reducing agent in organic reactions.

Preparation :

(i) $4BCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiCl + 3AlCl_3$

$4BCl_3 + 3LiAlH_4 + H_2 \xrightarrow{\text{silent electric discharge}} B_2H_6 + HCl$

(ii) $8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$

Chemical Properties :

1. It is instantly hydrolysed by aqueous alkali or water.

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2$

$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$

2. It catches fire spontaneously in air and explodes with dioxygen.

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

Thus in the laboratory, diborane is handled in a vacuum frame.

3. $B_2H_6 \xrightarrow{\text{red heat}} 2B + 3H_2$

4. Other reactions :

$B_2H_6 + 2LiH \xrightarrow{\text{ether}} 2LiB_4$

$B_2H_6 + 3Cl_2 \longrightarrow 2BCl_3 + 6HCl$

$B_2H_6 + \underset{\text{dry}}{HCl} \xrightarrow[AlCl_3]{\text{anhyd}} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + H_2$

Rack your Brain

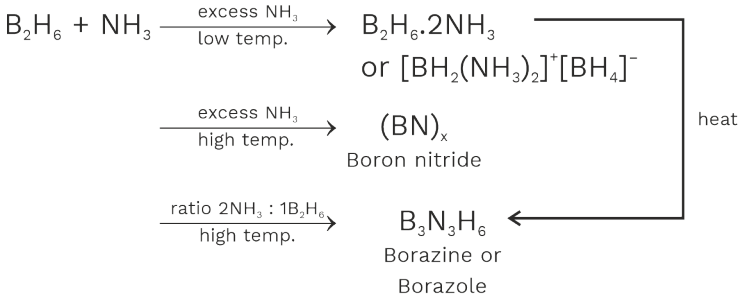
Why boranes are electron deficient compounds?

Previous Year's Questions

The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence **[AIPMT 2010]**

(1) $BCl_3 > BF_3 > BBr_3$
(2) $BBr_3 > BCl_3 > BF_3$
(3) $BBr_3 > BF_3 > BCl_3$
(4) $BF_3 > BCl_3 > BBr_3$

5. Reaction with ammonia and amines :



Borazole is called 'inorganic benzene' due to its similar structure and aromatic character.

Boron nitride is a white slippery solid called **'Inorganic Graphite'** which has a layer structure similar to graphite.

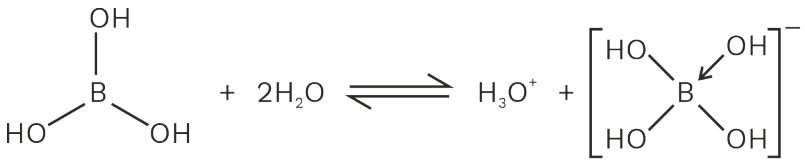
Rack your Brain

What is a dissimilarity between Borazine and Benzene?

[b] Orthoboric Acid H_3BO_3 :

Structure and Physical Properties :

Orthoboric acid is a Lewis acid and better written as $B(OH)_3$. It is a weak monobasic acid, sparigly soluble in water.



Plane Triangle

Tetrahedral Metaborate Ion

$B(OH)_3$ alone is not titrated with sodium hydroxyde as a sharp end point is not obtained. However if a cis-diol is added then $B(OH)_3$ behaves as a strong monobasic acid and can be titrated with NaOH using phenolphthalein as indicator cis-diols form stable complexes with $[B(OH)_4]^-$ thus effectively removing them and carrying the reaction forward.

Concept Ladder

Boric acid is a very weak monobasic acid. It does not act as a proton donor but accepts a hydroxyl ion i.e., it behaves as a lewis acid.

Chemical Properties :

1. Effect of heat

$$\underset{\text{orthoboric acid}}{H_3BO_3} \xrightarrow{100^\circ C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{160^\circ C} H_2B_4O_7 \xrightarrow{\text{red heat}} \underset{\text{boron sesquioxide}}{B_2O_3}$$

Thus, B_2O_3 is also called boric anhydride as it is the anhydride of boric acid.

2.

$$H_3BO_3 + 3CH_3OH \xrightarrow{\Delta} \underset{\text{methyl borate}}{B(OCH_3)_3} + 3H_2O$$

H_2O is removed by conc. H_2SO_4 and the mixture boruns with green flame. This is used as a test for boron compounds.

3. Broic acid dissovles in HF(aq) to give fluoroboric acid HBF_4 which is a strong acid. In dry HF borates give BF_3 which burns with a green colour.

Uses:

Boric acid is used as an antisptic and in glass industry and eyewash under the name 'Boric Lotion'.

Rack your Brain

What is the hybridisation of B in boric acid?

[c] Borax :

Structure :

Borax ($Na_2B_4O_7.10H_2O$) is better written as $Na_2[B_4O_5(OH)_4].8H_2O$ having 8 water molecules and the ion $[B_4O_5(OH)_4]^{2-}$ associated with Na^+ .

Chemical Properties :

1. When borax dissolves in H_2O equal amounts of weak acid and its salt are formed. Thus it is used as a buffer.

$$\left[B_4O_5(OH)_4\right]^{2-} + 5H_2O \rightleftharpoons 2B(OH)_3 + 2\left[B(OH)_4\right]^-$$

Concept Ladder

Boric acid loses water in three different stages ultimately giving boron trioxide.

2. Borax will reacts with 2 moles of acid because only [B(OH)4]– formed will react with H+.

$$2\left[B(OH)_4\right]^- + 2H_3O^+ \longrightarrow 2B(OH)_3 + 4H_2O$$

or $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$

Methyl oranges are used as the indicator, it is unffected by the H_3BO_3 formed.

3. **Borax Bead Test :**
Metaborates $[M(BO_2)]$of many transition elements have characteristic colours and this provides a means of identifying the metal through this test.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} NaBO_2 + \underset{\text{(glassy bead)}}{B_2O_3}$$

Rack your Brain

What property of Borax makes it suitalbe for behaving like water softner and cleaning agent?

Uses :

(i) In analytical chemistry it is used in Borax Bead Test.
(ii) Used as flame retardant for wood and fabric.
(iii) Used in glass industry.
(iv) Used as a flux in silver soldering and brazing/

Concept Ladder

When borax is heated above its melting point until all the water of crystallization is expelled, it forms a colourless glassy substance known as borax glass. It then decomposes to give sodium meta borate and boron (III) oxide. When this mixture is fused with metallic oxide it forms characteristic coloured beads. With the help of the colour, the metal ions can be identified.

Aluminium :

1. Thermodynamically Al should react with H_2O and air, but in fact it is stable in both. As very thin oxide film of Al_2O_3 is formed on surface and protects it. Due to this resistance to high thermal conductivity and corrosion it is used in making domestic utensils.

2. Reduction of some metal oxides like Mn_3O_4 and Cr_2O_3 require temperature high enough for carbon to be used as a reducing agent. Thus Al, a highly electropositive metal which

on oxidation liberates a large amount of energy to Al_2O_3, which is used as the reducing agent. This is know as thermite process. The thermite reaction is :

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s) + \text{energy} \qquad \Delta H^\circ = -1670 \text{ kJ}$$

3. Aluminium metal is moderately soft but lighter and much stronger when alloyed with metals. Some alloys of Aluminium are :

Alloys	Composition	Uses
Magnalium	Al – 95%, Mg – 5%	In construction of airships, balances.
Duralumin	Al – 95%, Cu – 4%, Mg – 0.5%, Mn – 0.5%	In areoplanes and automobile parts
Aluminium bronze	Cu – 90%, Al – 9.5%, Sn – 0.5%	To make utensils, cheap artificial jewellery.
Alnico	Steel – 77%, Al – 20%, Ni – 2%, Co – 1%	To make permanent magnet.

4. Al is amphoteric hence dissolves in both acid and bases.

$$2Al + 6HCl \longrightarrow 2Al^{3+} + 6Cl^- + 3H_2$$

$$2Al + 2NaOH + 6H_2O \longrightarrow \underset{\text{Sodium aluminat}}{2Na\left[Al(OH)_4\right]} \text{ or } 2NaAlO_2.2H_2O + 3H_2$$

However, conc. HNO_3 renders it passive due to the formation of a protective oxide layer.

[a] Aluminium Oxide Al_2O_3 (Alumina) :

Alumina is a white crystalline powder, insoluble in water. It is quite unreactive, stable and amphoteric in nature. The α–from of Al_2O_3 called corundum and found as mineral in nature.

Previous Year's Questions

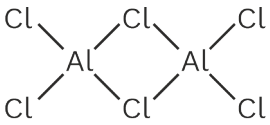
AlF_3 is soluble in HF only in presence of KF. It is due to the formation of

[NEET (II) 2016]

(1) $K_3[AlF_3H_3]$ (2) $K_3[AlF_6]$
(3) AlH_3 (4) $K[AlF_3H]$

[b] Aluminium Trichloride $AlCl_3$:

$AlCl_3$ exists as a dimer, thus attaining an octet of electrons. It is largely covalent when reacts with a non-polar solvent such as C_6H_6.



However, when dissolved in H_2O, the high enthalpy of hydration is sufficient to break the covalent dimer into $[Al.(H_2O)_6]^{3+}$ and $3Cl^-$ ions. At low temperature, $AlCl_3$ exists as a close packed lattice of Cl^- with Al^{3+} occupying octahedral holes.

Crystalline $AlCl_3$ exist as $AlCl_3.6H_2O$. On heating it cannot give anhydrous salt just like $MgCl_2.6H_2O$ (diagnol relationship). Instead it undergoes hydrolysis on heating :

$$2\,AlCl_3.6H_2O \xrightarrow{\Delta} 2\,Al(OH)_3 + 6\,HCl + 6\,H_2O$$
$$2\,Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3\,H_2O$$

The anhydrous compound is prepared by action of dry chlorine gas on aluminium or alumina :

$$Al + Cl_2 \longrightarrow AlCl_3$$
$$Al_2O_3 + C + Cl_2 \longrightarrow AlCl_3 + CO$$

Concept Ladder

Aluminium chloride is mainly produced using an exothermic reaction of two elements namely aluminium and chlorine.

Rack your Brain

$AlCl_3$ — Lewis acid or base?

Concept Ladder

$AlCl_3$ in solid-state features as a cubic close-packed layered structure. In this case, it will be octahedral. When aluminium chloride is in a liquid or molten state it exists as a dimer. Here its coordination geometry will be tetrahedral. At higher temperatures, the dimers dissociate into trigonal planar.

GROUP 14 ELEMENTS

Metallic Character

On moving down the group metallic character decreases. C and Si are non metals, Ge is a metalloid and Sn and Pb are metals.

Oxidation State

Oxidation state of C and Si is +4 while for Ge, Sn, Pb it has value of both +4 and +2 by Inert Pair Effect.

Catenation

C has the property of linking to other carbon atoms forming long chains due to its smaller size and higher electron negativity. However on moving down the group the tendency for catenation decreases in the order :

C >> Si > Ge ~ Sn >> Pb.

Concept Ladder

Reactivity : C < Si < Ge < Sn < Pb

Metallic character : C < Si < Ge < Sn < Pb

Previous Year's Questions

Which of the following does not show electrical conduction?

[AIPMT]

(1) Diamond (2) Graphite

(3) Potassium (4) Sodium

Carbon and its Compounds

Allotropy

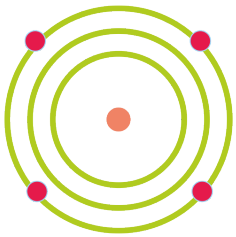
Carbon exists in a large number of allotropic forms. Two main form are diamond and graphite.

Diamond	Graphite
Extremely unreactive, colourless, non conductor and shows brilliant shine due to total internal reflection.	Quite reactive and soft.
The structure comprises of sp^3 hybrid C atoms forming σ-bonds and arranged tetrahedrally.	It has a structure with layers held together by weak van der waal's forces. Each sheet consists of hybridised carbon atoms that are covalently bonded to three carbon atoms by σ-bonds. The fourth e^- is in unhybridised 'p' orbital and forms a partial π-bond.

CARBON FAMILY

C	Si	Ge	Sn	Pb
6	14	32	50	82
12.0107	28.09	72.81	118.71	207.2

Electronic configuration



ns^2np^2

REACTIVITY

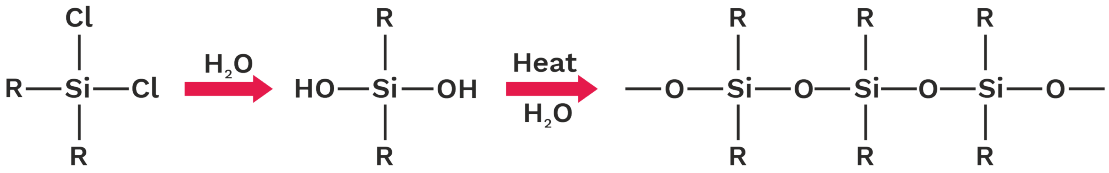
The carbon family elements tend to be fairly unreactive. the elements tend to form covalent compounds, though tin and lead also form ionic compounds.

CARBIDES

Carbon combines with other elements and forms carbides Al_4C_3, Be_2C, SiC and B_4C are considered as the hardest compounds.

SILICONES

Silicones are organo-silicon polymers and are formed by hydrolysis of R_2SiCl_2



Linear silicones

CARBON-GODLY ELEMENT

Every human being and everything around us consists of carbon.

NON STICK PAN

Nonstick pan has a Teflon layer on its surface. Teflon $+CF_2—CF_2+_n$.

LEAD PENCILS

Lead Pencils which we use do not contain Lead. It contains Graphite (an allotrope of carbon).

SILICON

Silicon is used in semiconductor devices, which are used in modern day computers.

TIN-CANS

Initially we used Tin for making cans, later it was replaced by Aluminium.

Chemical Properties :

1. Water gas is made by blow of air through white or red hot coke :

$$C + H_2O \xrightarrow{\text{red heat}} \underbrace{H_2 + CO}_{\text{water gas}}$$

2. All allotropes burn in oxygen to form CO_2.

$$C + O_2 \longrightarrow CO_2$$

Producer gas is made by blow of air through red hot coke.

$$\underset{\text{red hot}}{C} + \underbrace{O_2 + 4N_2}_{\text{air}} \longrightarrow CO_2 + 4N_2 \xrightarrow{+C} \underbrace{CO + N_2}_{\text{producer gas}}$$

3. Carbon as reducing agent :

$$\underset{(R.A)}{C} + 2\underset{\text{conc.}}{H_2SO_4} \xrightarrow{\Delta} CO_2 + SO_2 + H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$C + \underset{\text{dil., hot}}{HNO_3} \longrightarrow \text{Artificial Tannin (brown)}$$

4. Carbon as Oxygen acceptor :

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$2C + SiO_2 \longrightarrow \underset{\text{Carborundum}}{SiC} + 2CO$$

$$6C + 2Al_2O_3 \xrightarrow{2000°C} Al_4C_3 + 6CO$$

Preparation of CO :

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

$$HCOOH \xrightarrow[\text{conc.}]{H_2SO_4} CO + H_2O$$

Also,

$$(COOH)_2 \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2 + H_2O$$

CO_2 is removed by passing through soda

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Concept Ladder

Diamond has a three dimensional polymeric structure involving very strong covalent bonds by which the atoms are held together. Hence diamond possesses high melting point inspite of its covalent nature.

Rack your Brain

Carbon monoxide — A good reducing or oxidising agent?

Previous Year's Questions

It is because of inability of ns^2 electrons of the valence shell to participate in bonding that

[NEET 2017]

(1) Sn^{2+} is oxidising while Pb^{4+} is reducing

(2) Sn^{2+} and Pb^{2+} are both oxidising and reducing

(3) Sn^{4+} is reducing while Pb^{4+} is oxidising

(4) Sn^{2+} is reducing while Pb^{4+} is oxidising

(ii) $C + \text{oxides of heavy metal} \longrightarrow CO \uparrow + \text{metal}$
$(ZnO,\ Fe_2O_3, ...)$

(iii) $\underset{\text{Potassium Ferrocyanide}}{K_4\left[Fe(CN)_6\right]} + 6H_2SO_4 + 6H_2O \xrightarrow{\Delta} 2K_2SO_4 + 2FSO_4 + 3(NH_4)_2SO_4 + 6CO \uparrow$
(conc.)

Preparation of CO_2 :

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

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

(ii) It is recovered from alcoholic fermatation :

$$C_6H_{12}O_6 \xrightarrow[\text{anarobic condition}]{\text{yeast under}} 2C_2H_5OH + 2CO_2$$

(iii) It is obtained by heating crabonates :

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$
$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_3$$

(iv) In laboratory CO_2 is prepared by the action of dilute acids on carbonates :

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

Rack your Brain

How does CO_2 react with lime water?

[a] Silicones :

They are groups of organo - silicon polymers containing Si - O - Si linkages.

Preparation :

They are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes (formed by reaction Grignand regents and silicon tetrachloride) and their subsequent polymerization.

Previous Year's Questions

Carbon and silicon belong to (IV) group. The maximum coordination number of carbon in commonly occurring compounds is 4, whereas that of silicon is 6. This is due to

[AIPMT]

(1) availability of low lying d-orbitals in silicon
(2) large size of silicon
(3) more electropositive nature of silicon
(4) both (2) and (3)

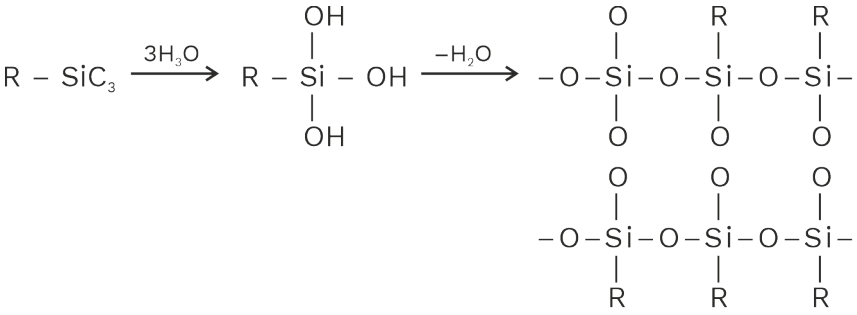
$$SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$$
$$SiCl_4 + 2RMgCl \longrightarrow R_2SiCl_2 + 2MgCl_2$$
$$SiCl_4 + 3RMgCl \longrightarrow \underset{\text{chlorosilanes}}{R_3SiCl} + 3MgCl_2$$

(Grignard Reagent)

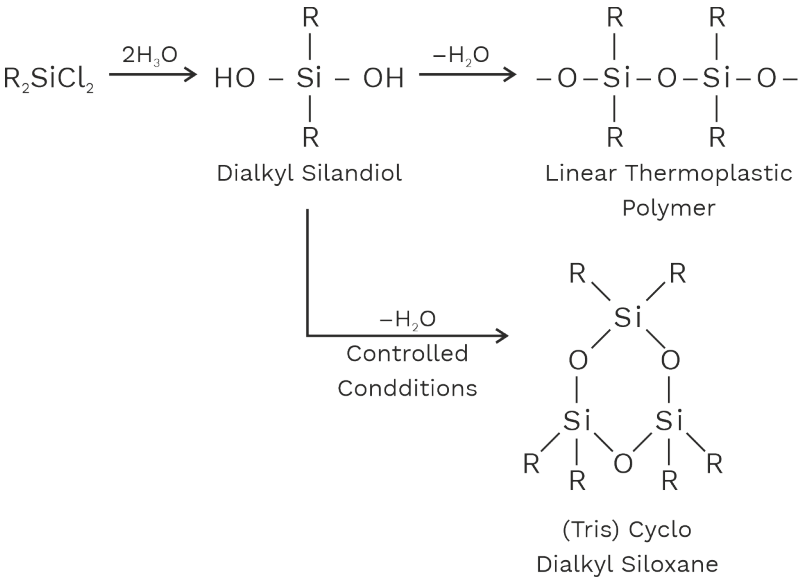
Rack your Brain

Why the name silicone resembles with ketone?

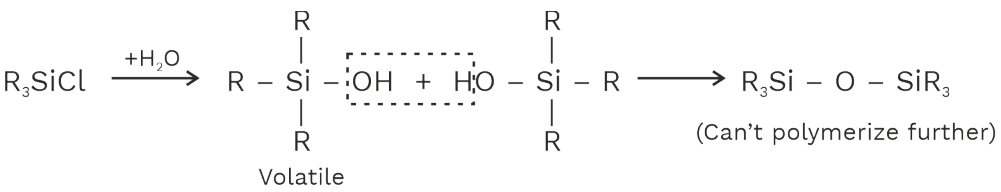
(i) Formation of cross - linked silicones :



(ii) Fomation 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 R_3SiCl is used to produce new cross – links and increase polymerization.
2. Silicones are electrical insulators, water-repellent, strong and inert. Their boiling point and viscosity increases with increase in chain length.
3. Silicones are stable towards heat.
   ph > CH_3 > Et > Pr is the order of stability which varies with attaching R in the order.
4. Being water – repellent silicones are used for treating glass ware and fabrics.
5. They are also used as silicone rubbers and hydraulic fluids.

Rack your Brain

What makes silicones useful for making sealants and electrical insulator?

[b] Silicates :

Silicates are derivaties of silicic and $Si(OH)_4$ or H_2SiO_4. They have basic tetrahedral units SiO_4^{4-} and Si – O bond is considered to be 50% ionic and 50% covalent.

Concept Ladder

The basic structural unit in silicates is the SiO_4 tetrahedron. The SiO_4 tetrahedral can be linked in several different ways. Depending on the number of corners (0, 1, 2, 3 or 4) of the SiO_4 tetrahedral shared, various kinds of silicates, single or double chains, rings, sheet or three-dimensional networks are formed.

Preparation :

Silicates can be prepared in an electric furnance at about 1400°C by fusing an alkali metal carbonate with sand.

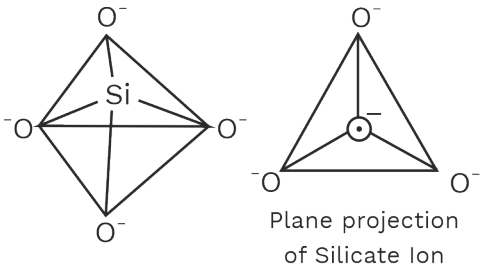
$$Na_2CO_3 \xrightarrow{1400^\circ C} CO_2 + Na_2O \xrightarrow[(sand)]{+SiO_2} \underbrace{Na_4SiO_4, Na_2(SiO_3)_n, ...}_{\text{soluble glass}}$$

Classification of Silicate Minerals :

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

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

Number of shared oxygen atom = 0



Plane projection of Silicate Ion

Concept Ladder

The ortho silicate ion is the strong conjugate base of weak orthosilicic acid as well as it will not persist in aqueous solutions. Hence in nature, ortho silicate minerals are rare and only found with cations which form highly insoluble salts.

(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 $Si_2O_7^{6-}$

Previous Year's Questions

Which of the followign anions is present in the chain structure of silicates?

[AIPMT]

(1) $\left(Si_2O_5^{2-}\right)_n$ (2) $\left(SiO_3^{2-}\right)_n$

(3) SiO_4^{4-} (4) $Si_2O_7^{6-}$

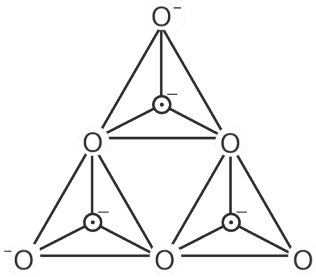
Ex : Thorteveititie $Sc_2Si_2O_7$

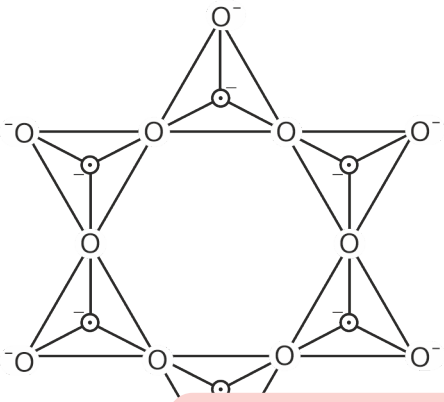
Hemimorphite $Zn_3(Si_2O_7).Zn(OH)_2.H_2O$

Number of shared oxygen atom = 1

(iii) Cyclic structure : They are also known as ring silicates having general formula $(SiO_3)_n^{2n-}$.

Structure and example of cyclic silicates containing $Si_3O_9^{6-}$ ans $Si_6O_{18}^{12-}$ ions are given below :





Ex : Beryl $Be_3Al_2Si_6O_{18}$

Wollastonite $Ca_3Si_3O_9$

Number of shared oxygen atoms = 2

Rack your Brain

Cyclic silicates are oligomer of which unit?

(iv) Chain silicates : These are formed by sharing two O_2 atoms of each tetrahedral units. Anions of chain silicates have 2 general formula.

Ex : Spodumene $LiAl(SiO_3)_2$

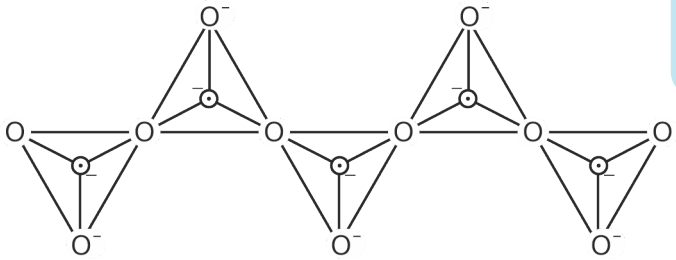
Diposide $CaMg(SiO_3)_2$

Tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

Concept Ladder

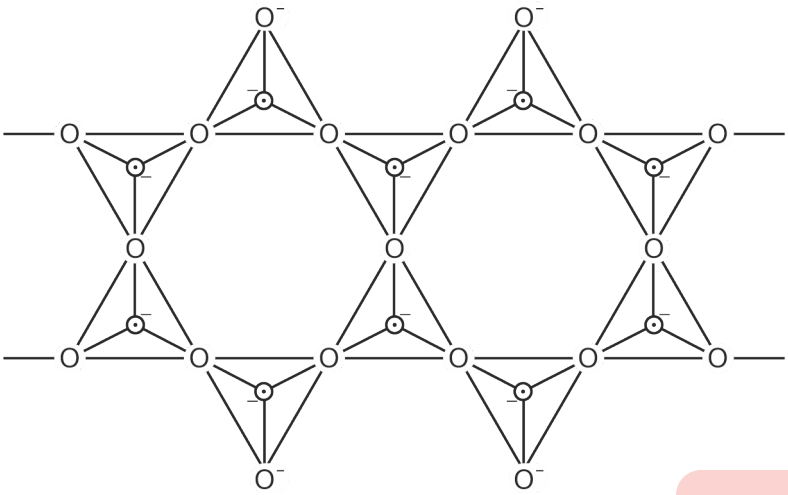
The single and double chain silicates are collectively known as Inosilicates.

(a) $(SiO_3)_n^{2n-}$



Number of shared oxygen atom = 2

(b) $(Si_4O_{11})_n^{6n-}$

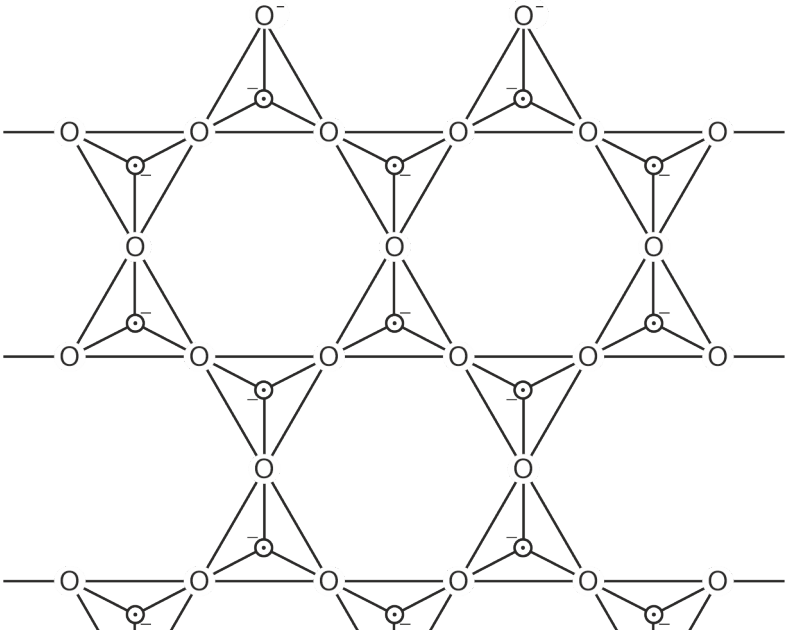


Rack your Brain

If SiO_4^{4-} units are replaced by AlO_4^{5-} units, three structure formed is called?

Number of shared oxygen atom = 2.5

(v) Two dimensional sheet sillicates : 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 $(Si_2O_5)_n^{2n-}$.



Ex : Tale $Mg(Si_2O_5)_2Mg(OH)_2$

Kaolin $Al_2(OH)_4(Si_2O_5)$

Number of shared oxygen atom = 3

(vi) 3D Sheet Silicates : These silicates involve all four oxygen atoms in sharing with adjacent SiO_4^{4-} tetrahedral. For example, Quartz, Zeolites, Ultramarines and Feldspars. Here all four oxygen atoms are shared.

Concept Ladder

The two common forms (allotropes) of tin white tin and gray tin. The sudden degradation of white tin into gray tin is called tin pest.

Tin and its compounds :

Tin is a soft, white lustrous, malleable metal. It produces a cracking sound called tin cry 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 $Sn(NO_3)_2$.

$$4\,Sn + \underset{\text{(cold dil.)}}{10\,HNO_3} \longrightarrow 4\,Sn\left(NO_3\right)_2 + NH_4NO_3 + 3\,H_2O$$

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

$$Sn + 2\,OH^- + 4\,H_2O \longrightarrow \left[Sn\left(OH\right)_6\right]^{2-} + 2\,H_2(g)$$

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

Rack your Brain

Why tin is used in electroplating?

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

Tin ion exists in two states +2 and +4 with the +6 state being more stable. SnO_2 is called as cassiterite and found as a mineral in nature. The other oxide SnO is obtained by heating stannous oxalate and is less stable in nature.

$$Sn\left(C_2O_4\right) \xrightarrow{\Delta} SnO + CO + CO_2$$

CARBON FAMILY do you know

C	Si	Ge	Sn	Pb
6	14	32	50	82
12.0107	28.09	72.81	118.71	207.2

Carbon has three main solid state allotropes:
Graphite, Diamond and **Fullerenes**
(the most commonly known of which,
buckminster fullerene, is also known as a "bucky-ball").

- Carbon is a non-metal
- silicon and germanium are metalloids
- Lead and tin are metal

Germanium

Camera

Germanium is a rare element used in the manufacturing of semi-conductor devices. The physical and chemical properties of germanium are very similar to those of silicon. Germanium is grey-white in color and forms crystal structures.

Silicon

Silicon is the second most common element in the earth's crust (after oxygen) and it is the backbone of the mineral world. Silicon is used extensively as a semiconductor in solid-state devices in the computer and microelectronics industries

Tablet

Tin

Tin is malleable, ductile, and crystalline. It is a superconductor at low temperatures. Tin reacts with bases, acid salts and strong acids. Tin chlorides are good reducing agents and often used to reduce iron ores. Tin fluoride is often the anticavity "fluoride" additive in toothpastes.

Lead

It is a soft, malleable metal with a low melting point. Lead is toxic to humans, especially children. Even low levels of exposure can cause nervous system damage and can prevent proper production of haemoglobin. Its oxides have many industrial uses as oxidizing agents, such as cathodes in lead-acid storage cells.

Point to Remember

Carbon has the highest melting/sublimation point of the elements. The melting point of diamond is 3550°C, with the sublimation point of carbon is around 3800°C.

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

$$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$$

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + H_2O$$

$$SnO_2 + NaOH \longrightarrow \underset{\text{Sodium stannate}}{Na_2SnO_3} + H_2O$$

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.

$$SnCl_2.2H_2O \longrightarrow Sn(OH)Cl + HCl + H_2O$$

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

$$Sn + HgCl_2 \xrightarrow{\Delta} SnCl_2 + Hg$$

$$Sn + 2HgCl_2\,(\text{excess}) \xrightarrow{\Delta} SnCl_4 + 2Hg$$

Most of the reactions of $SnCl_2$ are due to its reducing character. It reduces MnO_4^- to Mn^{2+}, $Cr_2O_7^{2-}$ to Cr^{3+} and itself get oxidized to Sn^{4+}.

Lead and its compounds

(i) Pb is a bluish grey soft metal which is extremely poisonous and can be cut with a knife.

(ii) Lead often appears more unreactive than expected from its standard electrode potential. The unreactiveness of Pb is due to the surface coating of basic carbonate $2PbCO_3.Pb(OH)_2$ which forms over lead when exposed to air and moisture. Thus lead is unaffected by water.

(iii) Pb is amphoteric hence dissolves in both acids and hot alkalies similar to Sn. In

Concept Ladder

Stannic sulphide exists in yellow glistening scales which is used for decorative purposes under and the name mosaic gold.

Rack your Brain

What is the Latin word for tin?

Previous Year's Questions

Which of the following oxidation states are the most charactristic for lead and tin respectively?

[AIPMT]

(1) +2, +4 (2) +4, +4
(3) +2, +2 (4) +4, +2

alkali it forms plumbates like $Na_2[Pb(OH)_6]$ or Na_2PbO_3. However, due to formation of surface coating of $PbCl_2$, lead does not dissolve in concentrated HCl.

(iv) Pb is used in making lead chamber for H_2SO_4 plant and certain alloys like solider (Sn Pb).

Rack your Brain

What is the formula of sindhur?

[a] Oxides :

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

$$Pb + O_2 \xrightarrow{\Delta} \underset{\text{Litharge}}{PbO}\ (\text{yellow}) \xrightarrow{380-420^\circ C} \underset{\text{Red lead}}{Pb_3O_4}\ (\text{red}) \xrightarrow[O_2]{\Delta} PbO_2\ (\text{brown})$$

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

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$
$$PbO_2 + 2HCl \longrightarrow PbCl_2 + H_2O_2$$
$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2P$$
$$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$$

(ii) Pb_3O_4 or Red Lead may be represented as $2PbO.PbO_2$ and is used in paint to prevent the rusting of iron and steel.

(iii) Lead oxide (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.

Concept Ladder

White lead is a white crystalline solid, which turns black when exposed to H_2S due to PbS formation. it is highly poisonous.

[b] Chlorides :

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

$$Pb + Cl_2 \longrightarrow PbCl_2 \xrightarrow{Cl_2(\text{excess})} PbCl_4$$

Dissolving Pb^{2+} salt (PbO, $PbCO_3$, $Pb(NO_3)_2$) in HCl produces $PbCl_2$. $PbCl_4$ is less stable and decomposes on heating at room temperature and liberates Cl_2.

$$PbCl_4 \xrightarrow{25^\circ C} PbCl_2 + Cl_2$$

[c] Tetraethyl Lead $(CH_2CH_2)_4Pb$:

Tetraethyl lead is produced in large amount. It is used as an 'anti-knock' additive for increment in the octane number of petrol. Its commercial preparation is used as a sodium/lead alloy.

$$Na \mid Pb + 4\,EtCl \longrightarrow PbEt_4 + 4\,NaCl$$

For the new cars to run lead-free petrol, $(CH_2CH_2)_4$ is declined rapidly once was produced in very larger tonnages than any other organometallic compound.

Concept Ladder

Covalent character follows the order :
$PbI_2 > PbBr_2 > PbCl_2 > PbF_2$

Q.1 Standard electrode potential values, E^- for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Sol. Standard electrode potential values for 2 half cell reactions suggest that Al has high tendency to make $Al^{3+}(aq)$ ions, while Tl^{3+} is a powerful oxidising agent but unstable in solution also. Thus Tl+ is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

Q.2 Whtie fumes apear around the bottle of anhydrous aluminium chloride. Give reason.

Sol. Anhyd. $AlCl_3$ is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears whtie in colour.

Q.3 Boron is unable to form BF_6^{3-} ion. Explain.

Sol. Due to non-availability of d-orbitals, B is unable to expand its octet. Therefore, the maximum covalence of boron cnanot exceed 4.

Q.4 Why is boric acid considered as a weak acid?

Sol. As it is not able to release H^+ ions on its own. From H_2O molecules it receives OH^- ions to complete its octet and in turn releases H^+ ions.

Q.5 Diamond is covalent, yet it has high melting point. Why?

Sol. Diamond has a 3D network involving strong C—C bonds, which are difficult to break & in turn has high melting point.

Q.6 What are silicones?

Sol. Simple silicones consist of $\left(-\underset{|}{\overset{|}{Si}}-O-\right)_n$ chains in which alkyl or phenyl groups occupy the remaining bonding positions on each Si atom. They are hydrophobic (water repellant) in nature.

Q.7 Explain the following :
(i) CO_2 is a gas whereas SiO_2 is solid.
(ii) Silicon forms SiF_6^{2-} ion whereas the corresponding fluoro compound of carbon is not known.

Sol. (i) Si has a large size compared to C. It does not form good pi overlapping. It forms 4 single covalent bonds with O_2 atoms. Each O_2 atom is linked with two Si atoms. Thus, a large giant molecule of a 3D structure is formed whereas C form a double bond with O_2 atom due to pi overlapping.
(ii) Si has lower energy 3D orbital so it can expand its octet giving sp^3d^2 hybridization while d orbitals are not present in the valence shell of C. It can undergo sp^3 hybridisation only. The size of the C atom is very small to accommodate six F-anions.

Q.8 The +1 oxidation state in group 13 and +2 oxidation state in group 14 becomes more and more stable with increasing atomic number. Explain.

Sol. Because of poor shielding of s-orbital electrons by d and f orbitals, the tendency of s-orbital to form the bond and it will decreases down the group in group 13 and 14.
This property is known as inner pair effect. Thus, the +1 O.S. in group 13 and +2 oxidation state in group 14 becomes more stable with increasing atomic number.

Q.9 Identify the compounds A, X and Z in the following reactions :
(i) $A + 2HCL + 5H_2O \longrightarrow 2NaCI + X$

$X \rightarrow HBO_2 \longrightarrow Z$

Sol. A is Borax which reacts with hydrochloric acid in presence of water to give Orthoboric acid (X).
On heating orthoboric acid it gives metaboric acid and further on heating gives the compound Z i.e. Boron trioxide.

Q.10 Explain the following :
(i) Gallium has a higher ionisation enthalpy than aluminium.
(ii) Boron does not exist as B^{3+} ion.

Sol. (i) The effective nuclear charge on gallium is slightly higher than that on aluminium because of ineffective shielding of valence e^-s by the intervening 3d e^-.
(ii) Boron has 3 electrons in the valence shell. Because of its small size and a high sum of the first three IE, it does not form B^{3+} ion.

Q.11 Carbon and silicon both belong to the group 14, but despite the stoichiometric similarity, the dioxides, (i.e., carbon dioxide and silicon dioxide), differ in their structures. Comment.

Sol. C can form stable pπ-pπ bonding with itself and other small atoms like O_2 and N_2 due to its small size. In CO_2 each O_2 atom is double-bonded with the C atom with pπ-pπ overlapping. Si cannot form this bonding because of its large size.

Q.12 Explain the nature of boric acid as a Lewis acid in water.

Sol. H_3BO_3 is a weak monobasic acid and accepts electons from a hydroxyl ion therefore acts as a Lewis acid.

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

H_3BO_3 accepts OH- and the formation of hydroxyl ion takes place. Thus, H_2BO_3 act as a Lewis acid in H_2O.

Q.12 Explain the following :
(i) Carbon shows catenation property but lead does not.
(ii) BF_3 does not hydrolyse.

Sol. (i) The catenation property depends on the size of atom and the M—M bond energy. Atomic radii is inversly proportational to the M-M bond energy, the greater is the tendency to show catenation. On decending down the group the size of atom increases and the M-M bond energy also reduces.
(ii) BF3 does not hydrolyze completely. Instead, it hydrolyzes incompletely to form H_3BO_3 and HBF_4. As HF first formed reacts with H_3BO_3.

Chapter Summary

1. Al atom is larger in size than Ga atom.
2. B_4C_3 (Boron Carbide) is one of the hardest known artificial substance and is called Norbide.
3. Jewellers borax is $Na_2B_4O_7.5H_2O$.
4. Al is most abundant element on earth crust.
5. Conc. HNO_3 renders Al passive.
6. H_3BO_3 renders Al passive.
7. $AlCl_3$ exists as Al_2Cl_6 in solid state. When dissolved in water it dissociates as $[Al(H_2O)_6]^{3+} + 3Cl^-$.
8. Tin disease or tin plague or tin pest - When white tin changes to grey tin its volume increase, it becomes brittle and crumbles in form of powder. It is called tin disease.
9. Tin cry - When bent, tin metal produces cracking sound (due to rubbin g of crystals) which is called tin cry.
10. PbO_3O_4 (Red lead or minimum) is mixed oxide of $PbO_2.2PbO$.
11. CO_2 is anhydride of H_2CO_3.
12. CCl_4 can't be hydrolysed and $SiCl_4$ is easily hydrolysed.
13. Solid CO_2 is called dry ice because it cools surface without wetting it. Trade name of dry ice is **drikold.**
14. Plumbo solvency is dissolution of lead in H_2O containing air and CO_2 forming soluble $Pb(OH)_2$ which gives highly poisonous Pb^{2+} ions. So lead pipes are not used for carrying water.
15. Thermodynamically graphite is more stable than diamond.
16. Carbogen is (95% O_2 and 5% CO_2) and is used in artificial respiration.
17. Pyrene is trade name of CCl_4 and uis used as fire exitinguishes.
18. U.V. rays are checked by Crooke's glass.
19. Lead marks paper just like graphite, thereofre graphite pencils are called lead pencils.
20. BN and graphite have similar structure.
21. Lead is used in making radiation shields because it stops harmful radiations.