

P-Block Elements

Elements of group 13 to 18 of the periodic table are collectively called p-block elements. The general electronic configuration of these elements is $ns^2 np^{1-6}$.

The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons. The number of possible oxidation states increases towards the right of the periodic table. The first member of each of group 13 to 17 of p-block differ from the remaining members of their corresponding group in two major respects.

1. Small size —
2. Absence of vacant d-orbital in valence shell.

— Characteristics of p-block elements.

1. Atomic and ionic radii — The atomic radii of p-block elements decreases on moving from left to right in a given period and increases from top to bottom in any group.
2. Ionisation enthalpy — The ionisation enthalpy of p-block elements increases from left to right in a period and decreases on descending a group. However the ionisation enthalpy of group 13 elements be smaller than the group 2-elements.
3. Electron gain enthalpy — Electron gain enthalpy increases from left to right along a period and decreases from top to bottom in a particular group.
Elements of group 15 are known to have exceptionally low values of electron gain enthalpy. This is due to their extra stability because of the presence of exactly half filled orbitals in their valence shell. Similarly elements of group 18 have zero electron affinities due to stable configuration.
4. Electronegativity — It is the property of an atom in a molecule.

It refers to the tendency of an atom to pull the shared pair of electrons towards itself. It depends upon (i) Size of atom.
(ii) electron needed to complete the valence shell.

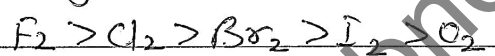
The electronegativity increases from left to right along the period and decreases from top to bottom in a group.

5. Metallic character — The metallic character decreases along a period and increases in a group.

The metallic character is governed by (i) Size of atom (ii) ionisation energy. An element having lower ionization energy and bigger size has a greater metallic character.

6. Oxidising and reducing properties — Amongst the p-block elements some of the elements act as good reducing agents.

The oxidising property of elements decreases on descending down the group and increases from left to right in a period.

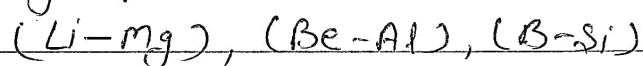


7. Oxidation State — The p-block element shows a variety of oxidation states both positive and negative.

The positive oxidation state increases and the negative oxidation state decreases on moving left to right in a period.

8. Diagonal Relationship — On moving diagonally across the periodic table the elements show certain similarities.

Although these similarities are usually weaker than similarities within a group.



Group-13 elements -

The elements boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl) constitute group 13 of the

Periodic table

Boron is classified as a non metal and all other elements of this group are metals. Non metallic character of boron is due to small atomic size and high ionisation energy.

— General trends in Physical Properties

1. **Electronic Configuration** — The outer electronic configuration of these elements is ns^2np^1 .
2. **Density** — The density of members of this group increases down the group due to increase in mass per unit volume. Al has an exceptionally low density.
3. **Melting and Boiling Point** — The melting point decreases from B to Ga and then increases from Ga to Ti. Ga has a low melting point and therefore exists as a liquid at room temp. However the boiling points show a gradual decrease from B to Ti.
B has a high melting point because it has an icosahedral structure. and Ga exists as discrete diatomic molecule and hence its melting point is low.
4. **Atomic radii and ionic radii** — The atomic radii of members belonging to 3 group are smaller than the corresponding group 2 elements. on moving B to Ti the atomic radii increases.
The atomic radii of Ga is slightly less than Al. It is because in going from Al to Ga the electrons are also filled into d-orbital. Since these intervening electrons do not screen the nuclear charge therefore the electrons in Ga experience more force of attraction than in Al. Causing a decrease in its radii.
The ionic radii follow a regular trend.
5. **Electronegativity** — Down the group electronegativity first.

decreases from B to Al and then increases. This is because of the discrepancies in atomic size of the elements.

6. Ionisation Enthalpy and Electropositive character— Ionisation enthalpy decreases down the group due to increase in size. But Ionisation enthalpy of Ga is more than Al due to its small size.

As we move down the group the electropositive character increases.

7. Oxidation states— The atoms of group 13 elements have three valence electrons, two in s-subshell and one in p-subshell. So +3 should be the most common oxidation state of these elements.

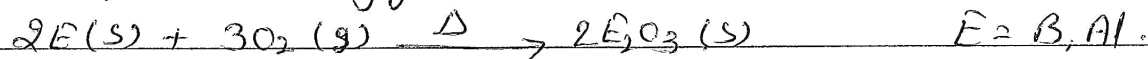
8. Reducing Properties— The order of decreasing reducing power of group 13 elements.



9. Nature of Compounds— Boron the first member of the group forms covalent compounds only. Aluminium the next member forms covalent compounds but also possesses a little tendency to form ionic compounds.

Chemical Property.

1. Reactivity towards air— Boron is unreactive in crystalline form. Al forms a very thin oxide layer on the surface which protects the metal from further attack. Ga, In, Tl do not react with nitrogen to form nitrides. Amorphous boron and Al metal on heating in air form B_2O_3 and Al_2O_3 . With dinitrogen, at high temperature they form nitrides.



2. Hydrides — Group 13 elements form hydrides of the type of MH_3 . None of the group 13 elements reacts directly with hydrogen. The boron hydrides are sometimes called boranes. Boranes can be classified into two series.

(i) B_nH_{n+4} called nido-boranes.

(ii) B_nH_{n+6} called arachno-boranes.

The simplest borane is diborane B_2H_6 (BH_3 being unstable has not been isolated).

The hydrides are weak Lewis acids and readily form adducts with strong Lewis bases to form compounds.

3. Oxides and hydroxides: — Almost all the elements of group 13 form oxides and hydroxides of the composition M_2O_3 and $M(OH)_3$. The nature of these oxides/hydroxides change from weakly acidic to amphoteric and amphoteric to basic in moving down the group from B to Tl.

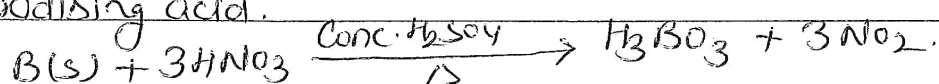
$B(OH)_3$, B_2O_3	$Al(OH)_3$, Al_2O_3	$Ga(OH)_3$, Ga_2O_3	$In(OH)_3$, In_2O_3
Acidic	Amphoteric	Amphoteric	Basic.

4. Aqueous solutions — Al, Ga, In and Tl exhibit a well defined aqueous chemistry in their +3 positive states.

Aluminium Sulphate forms double salt with Sulphates of other metals. These are called alums and represented by general formula $MAl(SO_4)_2 \cdot 12H_2O$. Here M is univalent cation. These alums are used in softening of hard water and as mordant in dyeing and printing of textiles. A mordant helps the dye to get bounded to the fabric.

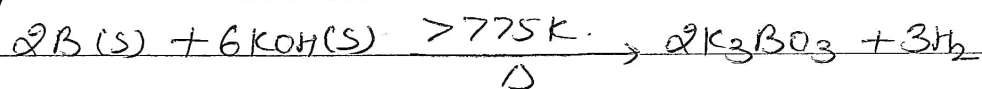
5. Reactivity towards Acids and Alkalies.

a. Action of acids: — B does not react with non-oxidising acids such as HCl. However it is attacked at high temperature by strong oxidising acid.



other elements of the group react with both oxidising and non-oxidising acids.

b. Action of alkalis — B does not react with alkalis upto 775K but above this temperature it forms borates liberating dihydrogen gas.



Al and Ga react with aqueous alkalis to liberate H_2 gas.

6. Halides — Group 13 members react with halogens to produce binary halides having the general formula MX_3 . These halides can be prepared by heating the elements directly with halogens.

(i) The fluorides are ionic and have high melting points.

(ii) The chlorides, bromides and iodides are essentially covalent with low melting points.

a. Boron trihalides — The halides of boron are covalent in nature. This has been indicated by the fact that they are soluble in organic solvents and that they are bad conductors of electricity. Among the trihalides of boron with different halogen atoms, the Lewis acid character:



Q. Why Boron forms electron deficient compounds.

Ans. B has only three electrons in the outermost shell which it can share with other atoms. Hence in the compound, there are only 6 electrons present around B atom. So octet is not complete.

Q. Aluminium chloride exists as a dimer whereas boron does not.

Ans. Aluminium in $AlCl_3$ has got six electrons in its valence shell. To complete its octet it requires two more electrons. To do so it accepts a lone pair of electrons from Cl atom of other neighbouring $AlCl_3$. But boron due to its small size cannot arrange

four large size chlorine atom around it and hence exists as monomer.

Q. Why B-X bond distance in BX_3 is shorter than theoretically expected value.

An. This is due to $P\bar{n} - P\bar{n}$ back bonding of the fully filled p-orbital of halogen (X) into empty p-orbital of boron.

Q. Gold has much higher First ionization energy than boron. yet gold is a metal while boron is a non metal.

An. This is explained on the basis of their crystal structure. Gold has a Co-ordinate number of 12 while boron has 6 or less than 6.

Q. (i) Anhydrous $AlCl_3$ is Covalent but hydrated $AlCl_3$ is electrovalent.

(ii) BBr_3 is a stronger Lewis acid than BF_3 .

An. (i) In the presence of H_2O , Al_2Cl_6 dissociates into hydrated Al^{+3} and Cl^- ions due to high heat of hydration of these ions.

(ii) This is because back donation of electrons into empty 2p orbital of B atom from filled p-orbital of Br atom is much less than that by F atom due to larger size of Br atom than F atom.

Q. Why trihalides of group 13 elements fume in the moist air.

An. They are hydrolysed by water forming hydrogen halides.



Boron.

B is the first member of the elements of group 13 of the periodic table. It is the only non-metal of this group. It has only three electrons in the valence shell. The properties of boron differ from those of other members of the group due to its small size and high ionization enthalpy and low electronegativity. The compounds of boron especially the hydrides are referred to as electron deficient compounds and therefore they behave as Lewis acid. The electron deficiency in boron arises because of the fact that the number.

of valance electrons in boron is one less than the number of valance orbitals.

— Physical Properties —

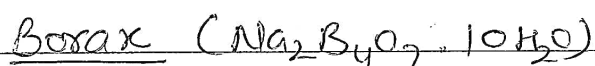
1. Boron is extremely hard solid, only next to diamond. It is because of its three dimensional network structure.
2. Its melting point is $\approx 2450\text{ K}$ and boiling point 2825 K .
3. It is found to exist in four allotropic forms which are obtained under different conditions.
4. It has low electrical conductivity.

— Chemical Property.

Boron has small size and high ionisation enthalpy. It does not form B^{+3} ion. It shares its three valance electrons with other atoms and forms covalent compounds.

— Uses of Boron.

1. Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
2. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and therefore, metal borides are used in nuclear industry as protective shields and control rods.
3. Borax and boric acid is used in the manufacture of heat resistance glasses.
4. An aqueous solution of orthoboric acid is generally used as a mild antiseptic.
5. Boron is used in steel industry for increasing hardness.
6. It is also used as a semiconductor for making electronic devices.

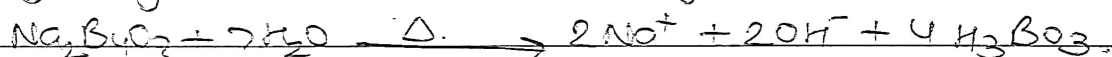


Properties.

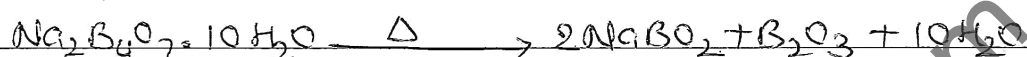
1. It is a white crystalline solid.
2. It is less soluble in cold water but more soluble in hot.

water.

3. It gets hydrated with water to form alkaline solution.



4. Borax bead test — In Qualitative analysis borax bead test is used for the detection of some coloured ions. For performing the test, borax is first heated strongly on a Platinum wire loop. On heating strongly, it loses water molecules and melt into transparent bead.



Boric anhydride (B_2O_3) reacts with certain metal salts to form metaborates having specific colours.

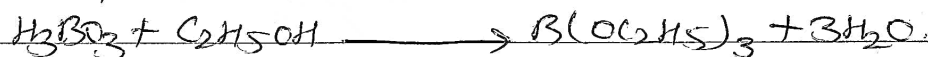
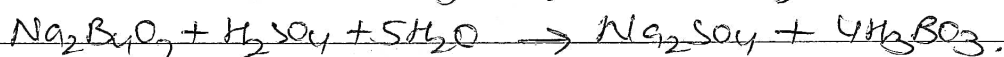
5. Action with NaOH — on adding calculated quantity of NaOH to Borax, sodium metaborate is formed.



6. Action with Sulphuric acid — Hot concentrated solution of borax reacts with Sulphuric acid to form boric acid.



7. Action with ethanol and H_2SO_4 — on heating with ethanol and conc. H_2SO_4 , vapours of triethyl borate are produced, these vapours burn with a green edged flame on ignition.



uses of Borax.

1. As a flux in soldering metals.
2. in making Pyrex glass
3. in Candle industry.
4. as cleaning and stiffening agent in laundry.

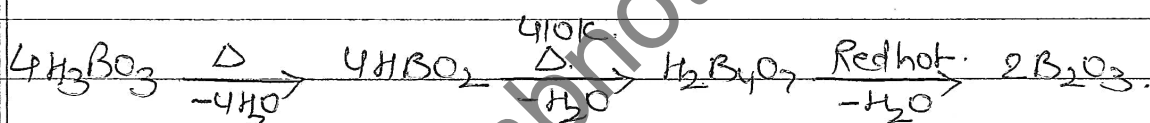
Orthoboric acid (H_3BO_3) or $B(OH)_3$.

Properties:

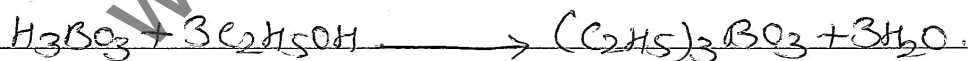
1. It is a white crystalline solid with a soft soapy touch.
2. It is sparingly soluble in cold water but fairly soluble in hot water.
3. Acidic nature — Boric acid is a weak monobasic acid. However it differs from other protonic acids. It does not act as a proton donor but as a Lewis acid by accepting the hydroxylion.



4. Effect of heat — Heating orthoboric acid above 370K leads to partial removal of water to yield metaboric acid HBO_2 . Further heating yield first tetraboric acid $H_2B_4O_7$ and finally boric oxide B_2O_3 which is the principle oxide of boron.



5. Action with ethyl alcohol — Boric acid reacts with ethyl alcohol in the presence of H_2SO_4 to give ethyl borate. The vapour of ethyl borate burns in air with a green flame. This forms the basis of green edged flame test for borates.



Uses:

1. In the manufacture of enamels and glazes for pottery.
2. In making heat resisting and shock resisting glass.
3. mild as antiseptic for washing eyes.
4. as a preservative for milk and food stuffs.

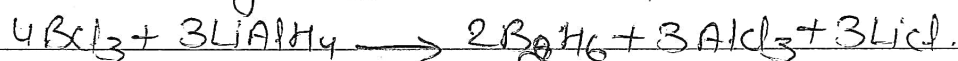
Diborane

- Preparation of Diborane :-

1. By the reaction of Iodine with sodium borohydride in a high boiling solvent.



- (ii) By reduction of BCl_3 with LiAlH_4 .



- (iii) By passing silent electrical discharge through BCl_3 and H_2 .



- Properties of Diborane -

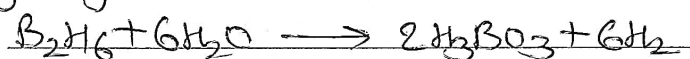
- 1) Stability - It is stable only at low temperatures. When heated at temperature between 373 K and 575 K, it changes into number of higher boranes.



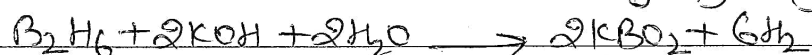
- 2) Combustibility - It undergoes spontaneous combustion in air due to strong affinity of boron with oxygen forming boric anhydride.



3. Hydrolysis - It gets hydrolysis easily by water liberating dihydrogen gas.

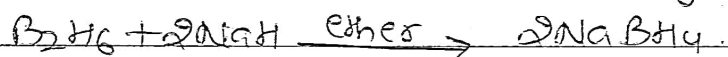


4. Reaction with alkalis - Diborane dissolves in strong alkalis to produce metaborates and dihydrogen gas.



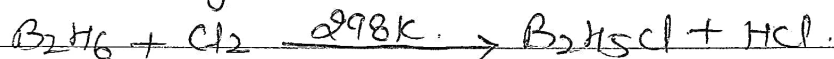
5. Action with alkali metal hydrides - Alkali metal hydrides react with B_2H_6 in ether to form metal tetrahydridoborates.

Which are also called metal borohydrides

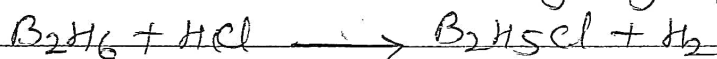


Sodium borohydride

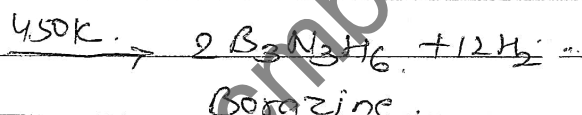
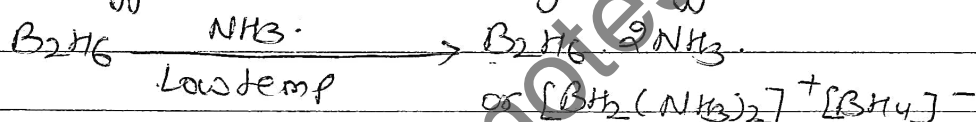
6. Action with halogens — B_2H_6 reacts with halogens under different condition to form halodiboranes.



7. Action with halogen acids — Halogen acids react with diborane to form halodiborane and dihydrogen gas.



8. Action with ammonia — Diborane reacts with ammonia under different condition to give different products.

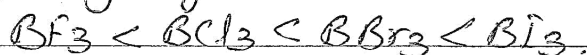


Borazine has cyclic structure similar to benzene and thus it is called inorganic benzene.

Boron Trihalides

The trihalides of boron are electron deficient compound having a planar structure. They act as Lewis acids because of incomplete octet.

The acid strength of trihalides decreases as



Aluminium

Aluminium is one of the elements of group 13 of the periodic table. The other elements are boron (B), gallium (Ga), indium (In) and

and thallium (Tl). These elements have three electrons in the outermost shell, ns^2np^1 .

Aluminium has a high ionisation energy and tends to form more covalent compounds.

Group 14 elements.

Carbon (C), Silicon (Si), Germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. All the elements have four electrons in their valence shell. Their general valence shell electronic configuration is ns^2np^2 .

— Physical Properties —

1. Density — Density increases when we go down the group because of the increase in mass per unit volume.
2. Melting and boiling points — The melting point and boiling points of group 14 are higher than group 13. It is because the atoms of group 14 can form four covalent bonds with each other and therefore there are strong binding forces between their atoms in both solid as well as liquid states. However, the melting and boiling points decrease down the group.
3. Atomic radii — Atomic radius increases as we move down the group due to increase in the number of energy shells.
4. Ionization enthalpy — The ionization energy (enthalpy) decreases down the group due to increase in size and screening effect of inner electrons.
5. Metallic character — The metallic character increases down the group from C to Pb.

6. Oxidation State - The elements of group 14 form Covalent bonds in their Compounds with the highest oxidation state of +4. The elements of this group also exhibit an oxidation state of +2.

As we move down the group the tendency to form ionic Compounds increases.

7. Oxidising and reducing Properties - The group 14 elements show oxidation state of +4 and +2 in their Compounds. The elements in +2 oxidation state can act as reducing agent while those in +4 oxidation state can act as oxidising agents.

8. Electronegativity - The elements belonging to this group are more electronegative than the elements of group 13. It is because these have a small size. The electronegativity value decreases from top to bottom in the group.

9. Catenation - The Property of forming the chains of identical atoms is called Catenation. The Property of Catenation decreases as we move down the group.
 $C \gg Si > Ge = Sn \gg Pb$

10. Chemical Characteristics

1. Hydrides - The elements of group 14 combine with hydrogen to form covalent hydride. Carbon forms a large number of cyclic and acyclic hydrides known as hydrocarbons. Thermal stability of hydrides of this group decreases on moving down the group. The reducing character of these hydrides increases on going down the group.

2. Oxides - The elements of this group form two types of oxides.

a. monoxides - All the elements of this group except Si form monoxides of the general formula MO_2 , Except C which is neutral.

Other monoxides are basic.

Carbon monoxide is a colourless toxic gas and is known to form a number of co-ordination compounds with transition metals ex. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$. Such compounds are called as organometallic compounds because carbon is bonded to metals.

b Di-oxides - All the elements of this group form dioxides of the general formula MO_2 , such as Co_2 , SiO_2 , GeO_2 , SnO_2 and PbO_2 . Some characteristic features

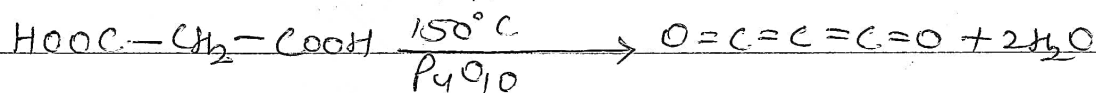
(i) Among these oxides, Co_2 and SiO_2 are acidic, GeO_2 is less acidic and SnO_2 and PbO_2 are amphoteric in nature.

(ii) PbO_2 is a powerful oxidising agent.

(iii) Comparison of properties of Co_2 and SiO_2 .

Co_2	SiO_2
• It exists as gas	• It is a solid.
• It is a linear, monomeric non-polar molecule.	• It is a three dimensional network solid.
• Appreciably soluble in water	• Insoluble in water.
• on reduction with coke given Carbon monoxide	• on reduction with coke give Silicon Carbide.
$\text{Co}_2 + \text{C} \rightarrow 2\text{Co}$	$\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$

c Carbon suboxide (C_3O_2): In addition to Co and Co_2 Carbon also forms Carbon suboxide which is made by dehydration of malonic acid with P_4O_{10}



It is a foul smelling gas with b.p. 6°C . It is linear molecule. It gives back malonic acid on reaction with H_2O or HCl .

3. Halides - The elements of this group combine with halogen to form tetrahalides of the general formula MX_4 . Except carbon

all other elements of this group also forms dihalides MX_2 , The stability of dihalides increases down the group. The thermal stability of the halides decreases down the group. Carbon halides are not hydrolysed by water because Carbon atom cannot increase its Co-ordination number beyond four. on the other hand all other tetrahalides are easily hydrolysed because of the availability of vacant d-orbital.

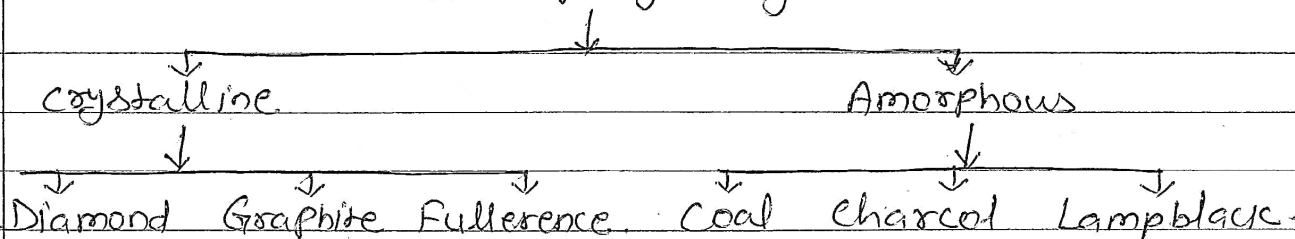
Carbon

Carbon is the first element of group 14 of the periodic table. Its electronic configuration ($1s^2 2s^2 2p^2$) shows that it has four electrons in the outermost shell. It shows maximum tendency of Catenation (Self linking Property)

— Isotopes of Carbon — Naturally occurring Carbon contains two stable isotopes ^{12}C (98.9%) and ^{13}C (1.1%) along with trace of ^{14}C isotope which is radioactive with half life period of 5770 years.

— Allotropic forms of Carbon — It is a Phenomenon of existence of different forms of elements having different Physical Properties. The various forms are called allotropes or allotropic forms.

Allotropic forms of Carbon.



Difference

Diamond

Graphite.

1 Due to its high refractive index. | Although it is black and opaque.

1. It is a transparent substance.	Yet it has metallic lustre.
2. It has high density.	It has relatively low density.
3. It is very hard.	It is soft.
4. It is bad conductor of heat and electricity.	It is good conductor of heat and electricity.
5. It possesses three dimensional network structure.	It possesses a sheet type structure.
6. Chemical reactivity is low.	Chemical reactivity is high.

— Carbon mono oxide: (CO)
Preparation.

1. By heating Carbon in limited supply of oxygen:-

$$C + \frac{1}{2}O_2 \rightarrow CO$$

2. By heating formic acid with H_2SO_4 .

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

— Characteristics of CO.

1. Physical nature — It is a colourless, odourless gas with very small solubility in water. It is neutral in nature.
2. Toxic nature — It is quite poisonous because it combine with the haemoglobin of the red blood cells to form a complex. Carboxy haemoglobin. it destroys the capacity of the blood to carry oxygen.
3. Combustibility — It is highly combustible. Its combustion in air produce Carbon dioxide along with lot of heat.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + \text{heat}$$
4. Reducing nature — It is a very good reducing agent due to its.

ability to get oxidised to CO_2 . It reduces metal oxides to metals. $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$

5. Formation of metal Carbonyls - In Co molecule, there are one sigma and two π bonds between Carbon and oxygen. Because of the presence of a lone pair on Carbon, Co molecule acts as a donor and reacts with certain metals when heated to form metal Carbonyl.



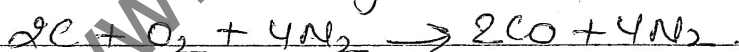
6. Reaction with chlorine - It reacts with chlorine in the presence of sunlight to form another poisonous gas Phosgene



- Water gas - It is obtained by passing steam over red hot coke. It is a mixture of CO and H_2 .



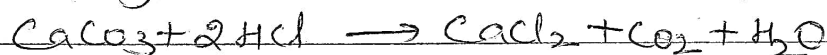
- Producer gas - It is formed by passing air over red hot coke. It is a mixture of CO and N_2 .



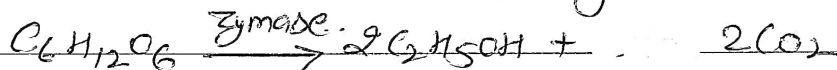
CARBON Di oxide. (CO_2).

Preparation.

1. Combustion of Carbon - $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
2. By decomposing carbonates and bicarbonates -

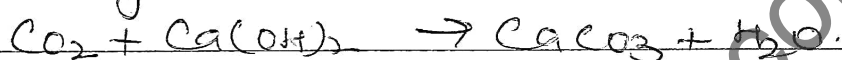


3. By Fermentation process and by calcination of limestone -

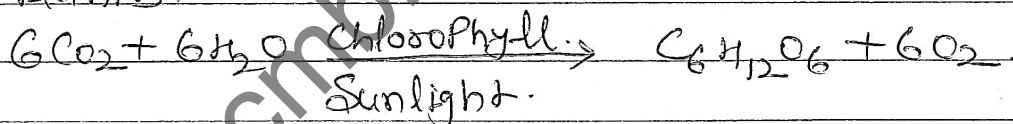


Characteristics of CO_2 .

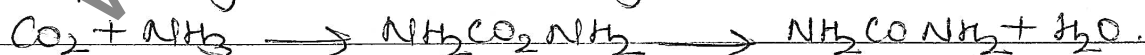
- (1) CO_2 is a colourless, odourless gas.
- (2) It is heavier than air.
- (3) It is not poisonous but it does not support life in animals.
- (4) CO_2 is acidic in nature and is fairly soluble in water.
- (5) Reaction with lime water - CO_2 reacts with lime water ($\text{Ca}(\text{OH})_2$) to form insoluble CaCO_3 which makes it milky. However, if CO_2 is bubbled through lime water for a longer time then milkiness disappears due to the formation of soluble bicarbonate.



6. Photosynthesis - CO_2 is absorbed by plants in presence of chlorophyll and sunlight. The absorbed CO_2 combine with H_2O to form glucose and starch which are used as food by the plants.



7. Action of ammonia - when CO_2 is reacted with liquid ammonia at $273-473\text{K}$ under a pressure of 220 Atmospheres. It first forms ammonium carbamate which subsequently decompose to give urea.



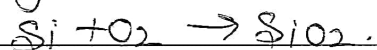
SILICA. (SiO_2).

Forms of Silica.

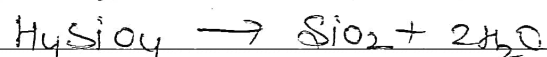
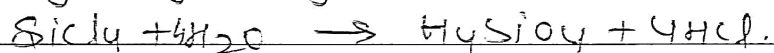
1. Quartz or rock crystal - This is the purest form of silica. It is used in the preparation of costly lenses and prism.
2. Sand - It is crushed form of Quartz which is produced in nature by weathering of rock.

3. Artificial silica — It can be obtained

(i) by burning of silicon.



(ii) by hydrolysis of silicon tetrachloride.



4. Amorphous forms of silica — Two amorphous forms are Silica gel and keiselguhr.

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P-Block Elements

Elements of group 13 to 18 of the periodic table are collectively called p-block elements. The general electronic configuration of these elements is $ns^2 np^{1-6}$.

The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons. The number of possible oxidation states increases towards the right of the periodic table. The first member of each of group 13 to 17 of p-block differ from the remaining members of their corresponding group in two major respects.

1. Small size —
2. Absence of vacant d-orbital in valence shell.

— Characteristics of p-block elements.

1. Atomic and ionic radii — The atomic radii of p-block elements decreases on moving from left to right in a given period and increases from top to bottom in any group.
2. Ionisation enthalpy — The ionisation enthalpy of p-block elements increases from left to right in a period and decreases on descending a group. However the ionisation enthalpy of group 13 elements be smaller than the group 2-elements.
3. Electron gain enthalpy — Electron gain enthalpy increases from left to right along a period and decreases from top to bottom in a particular group.
Elements of group 15 are known to have exceptionally low values of electron gain enthalpy. This is due to their extra stability because of the presence of exactly half filled orbitals in their valence shell. Similarly elements of group 18 have zero electron affinities due to stable configuration.
4. Electronegativity — It is the property of an atom in a molecule.

It refers to the tendency of an atom to pull the shared pair of electrons towards itself. It depends upon (i) Size of atom.
(ii) electron needed to complete the valence shell.

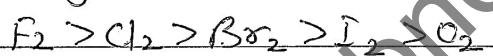
The electronegativity increases from left to right along the period and decreases from top to bottom in a group.

5. Metallic character — The metallic character decreases along a period and increases in a group.

The metallic character is governed by (i) Size of atom (ii) ionisation energy. An element having lower ionization energy and bigger size has a greater metallic character.

6. Oxidising and reducing properties — Amongst the p-block elements some of the elements act as good reducing agents.

The oxidising property of elements decreases on descending down the group and increases from left to right in a period.

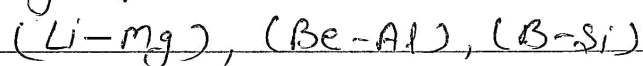


7. Oxidation State — The p-block element shows a variety of oxidation states both positive and negative.

The positive oxidation state increases and the negative oxidation state decreases on moving left to right in a period.

8. Diagonal Relationship — On moving diagonally across the periodic table the elements show certain similarities.

Although these similarities are usually weaker than similarities within a group.



Group-13 elements -

The elements boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl) constitute group 13 of the

Periodic table

Boron is classified as a non metal and all other elements of this group are metals. Non metallic character of boron is due to small atomic size and high ionisation energy.

— General trends in Physical Properties

1. **Electronic Configuration** — The outer electronic configuration of these elements is $ns^2 np^1$.
2. **Density** — The density of members of this group increases down the group due to increase in mass per unit volume. Al has an exceptionally low density.
3. **Melting and Boiling Point** — The melting point decreases from B to Ga and then increases from Ga to Tl. Ga has a low melting point and therefore exists as a liquid at room temp. However the boiling points show a gradual decrease from B to Tl.
B has a high melting point because it has an icosahedral structure. and Ga exists as discrete diatomic molecule and hence its melting point is low.
4. **Atomic radii and ionic radii** — The atomic radii of members belonging to 3 group are smaller than the corresponding group 2 elements. on moving B to Tl the atomic radii increases.
The atomic radii of Ga is slightly less than Al. It is because in going from Al to Ga the electrons are also filled into d-orbital. Since these intervening electrons do not screen the nuclear charge therefore the electrons in Ga experience more force of attraction than in Al. Causing a decrease in its radii.
The ionic radii follow a regular trend.
5. **Electronegativity** — Down the group electronegativity first.

decreases from B to Al and then increases. This is because of the discrepancies in atomic size of the elements.

6. Ionisation Enthalpy and Electropositive character— Ionisation enthalpy decreases down the group due to increase in size. But Ionisation enthalpy of Ga is more than Al due to its small size.

As we move down the group the electropositive character increases.

7. Oxidation states— The atoms of group 13 elements have three valence electrons, two in s-subshell and one in p-subshell. So +3 should be the most common oxidation state of these elements.

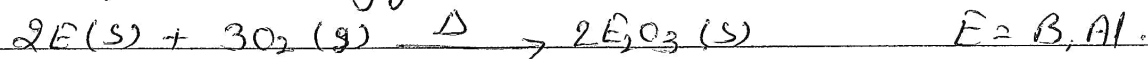
8. Reducing Properties— The order of decreasing reducing power of group 13 elements.



9. Nature of Compounds— Boron the first member of the group forms covalent compounds only. Aluminium the next member forms covalent compounds but also possesses a little tendency to form ionic compounds.

Chemical Property.

1. Reactivity towards air— Boron is unreactive in crystalline form. Al forms a very thin oxide layer on the surface which protects the metal from further attack. Ga, In, Tl do not react with nitrogen to form nitrides. Amorphous boron and Al metal on heating in air form B_2O_3 and Al_2O_3 . With dinitrogen, at high temperature they form nitrides.



2. Hydrides — Group 13 elements form hydrides of the type of MH_3 . None of the group 13 elements reacts directly with hydrogen. The boron hydrides are sometimes called boranes. Boranes can be classified into two series.

(i) B_nH_{n+4} called nido-boranes.

(ii) B_nH_{n+6} called arachno-boranes.

The simplest borane is diborane B_2H_6 (BH_3 being unstable has not been isolated).

The hydrides are weak Lewis acids and readily form adducts with strong Lewis bases to form compounds.

3. Oxides and hydroxides: — Almost all the elements of group 13 form oxides and hydroxides of the composition M_2O_3 and $M(OH)_3$. The nature of these oxides/hydroxides change from weakly acidic to amphoteric and amphoteric to basic in moving down the group from B to Tl.

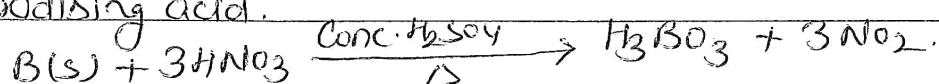
$B(OH)_3$, B_2O_3	$Al(OH)_3$, Al_2O_3	$Ga(OH)_3$, Ga_2O_3	$In(OH)_3$, In_2O_3
Acidic	Amphoteric	Amphoteric	Basic.

4. Aqueous solutions — Al, Ga, In and Tl exhibit a well defined aqueous chemistry in their +3 positive states.

Aluminium Sulphate forms double salt with Sulphates of other metals. These are called alums and represented by general formula $MAl(SO_4)_2 \cdot 12H_2O$. Here M is univalent cation. These alums are used in softening of hard water and as mordant in dyeing and printing of textiles. A mordant helps the dye to get bounded to the fabric.

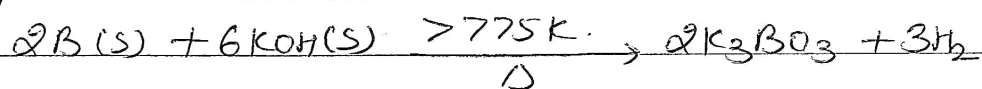
5. Reactivity towards Acids and Alkalies.

a. Action of acids: — B does not react with non-oxidising acids such as HCl. However it is attacked at high temperature by strong oxidising acid.



other elements of the group react with both oxidising and non-oxidising acids.

b. Action of alkalis — B does not react with alkalis upto 775K but above this temperature it forms borates liberating dihydrogen gas.



Al and Ga react with aqueous alkalis to liberate H_2 gas.

6. Halides — Group 13 members react with halogens to produce binary halides having the general formula MX_3 . These halides can be prepared by heating the elements directly with halogens.

(i) The fluorides are ionic and have high melting points.

(ii) The chlorides, bromides and iodides are essentially covalent with low melting points.

a. Boron trihalides — The halides of boron are covalent in nature. This has been indicated by the fact that they are soluble in organic solvents and that they are bad conductors of electricity. Among the trihalides of boron with different halogen atoms, the Lewis acid character:



Q. Why Boron forms electron deficient compounds.

Ans. B has only three electrons in the outermost shell which it can share with other atoms. Hence in the compound, there are only 6 electrons present around B atom. So octet is not complete.

Q. Aluminium chloride exists as a dimer whereas boron does not.

Ans. Aluminium in $AlCl_3$ has got six electrons in its valence shell. To complete its octet it requires two more electrons. To do so it accepts a lone pair of electrons from Cl atom of other neighbouring $AlCl_3$. But boron due to its small size cannot arrange

four large size chlorine atom around it and hence exists as monomer.

Q. Why B-X bond distance in BX_3 is shorter than theoretically expected value.

Ans. This is due to $P\bar{n} - P\bar{n}$ back bonding of the fully filled p-orbital of halogen (X) into empty p-orbital of boron.

Q. Gold has much higher first ionization energy than boron. yet gold is a metal while boron is a non metal.

Ans. This is explained on the basis of their crystal structure. Gold has a co-ordinate number of 12 while boron has 6 or less than 6.

Q. (i) Anhydrous $AlCl_3$ is covalent but hydrated $AlCl_3$ is electrovalent.

(ii) BBr_3 is a stronger Lewis acid than BF_3 .

Ans. (i) In the presence of H_2O , Al_2O_6 dissociates into hydrated Al^{+3} and Cl^- ions due to high heat of hydration of these ions.

(ii) This is because back donation of electrons into empty 2p orbital of B atom from filled p-orbital of Br atom is much less than that by F atom due to larger size of Br atom than F atom.

Q. Why trihalides of group 13 elements fume in the moist air.

Ans. They are hydrolysed by water forming hydrogen halides.



Boron.

B is the first member of the elements of group 13 of the periodic table. It is the only non-metal of this group. It has only three electrons in the valence shell. The properties of boron differ from those of other members of the group due to its small size and high ionization enthalpy and low electronegativity. The compounds of boron especially the hydrides are referred to as electron deficient compounds and therefore they behave as Lewis acid. The electron deficiency in boron arises because of the fact that the number.

of valance electrons in boron is one less than the number of valance orbitals.

— Physical Properties —

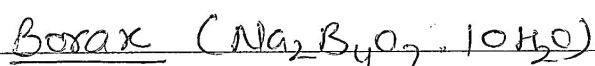
1. Boron is extremely hard solid, only next to diamond. It is because of its three dimensional network structure.
2. Its melting point is $\approx 2450\text{ K}$ and boiling point 2825 K .
3. It is found to exist in four allotropic forms which are obtained under different conditions.
4. It has low electrical conductivity.

— Chemical Property.

Boron has small size and high ionisation enthalpy. It does not form B^{+3} ion. It shares its three valance electrons with other atoms and forms covalent compounds.

— Uses of Boron.

1. Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
2. The boron-10 (^{10}B) isotope has high ability to absorb neutrons and therefore, metal borides are used in nuclear industry as protective shields and control rods.
3. Borax and boric acid is used in the manufacture of heat resistance glasses.
4. As aqueous solution of orthoboric acid is generally used as a mild antiseptic.
5. Boron is used in steel industry for increasing hardness.
6. It is also used as a semiconductor for making electronic devices.

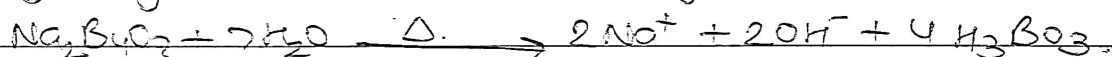


Properties.

1. It is a white crystalline solid.
2. It is less soluble in cold water but more soluble in hot.

water.

3. It gets hydrated with water to form alkaline solution.



4. Borax bead test — In Qualitative analysis borax bead test is used for the detection of some coloured ions. For performing the test, borax is first heated strongly on a Platinum wire loop. On heating strongly, it loses water molecules and melt into transparent bead.



Boric anhydride (B_2O_3) reacts with certain metal salts to form metaborates having specific colours.

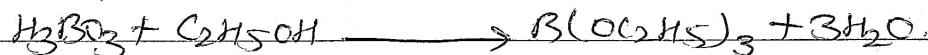
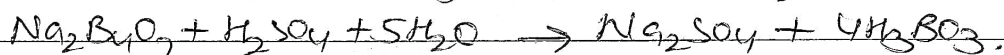
5. Action with NaOH — on adding calculated quantity of NaOH to Borax, sodium metaborate is formed.



6. Action with Sulphuric acid — Hot concentrated solution of borax reacts with Sulphuric acid to form boric acid.



7. Action with ethanol and H_2SO_4 — on heating with ethanol and conc. H_2SO_4 , vapours of triethyl borate are produced, these vapours burn with a green edged flame on ignition.



uses of Borax.

1. As a flux in soldering metals.
2. in making Pyrex glass
3. in Candle industry.
4. as cleaning and stiffening agent in laundry.

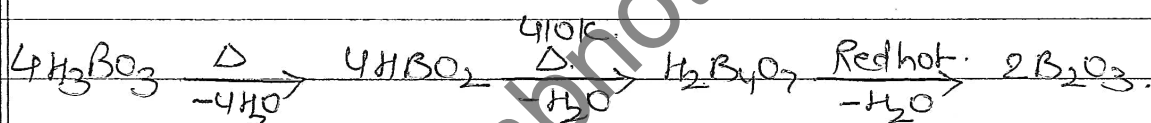
Orthoboric acid (H_3BO_3) or $B(OH)_3$.

Properties:

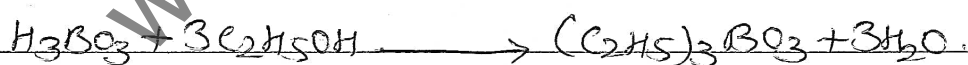
1. It is a white crystalline solid with a soft soapy touch.
2. It is sparingly soluble in cold water but fairly soluble in hot water.
3. Acidic nature — Boric acid is a weak monobasic acid. However it differs from other protonic acids. It does not act as a proton donor but as a Lewis acid by accepting the hydroxylion.



4. Effect of heat — Heating orthoboric acid above $370K$ leads to partial removal of water to yield metaboric acid HBO_2 . Further heating yield first tetraboric acid $H_2B_4O_7$ and finally boric oxide B_2O_3 which is the principle oxide of boron.



5. Action with ethyl alcohol — Boric acid reacts with ethyl alcohol in the presence of H_2SO_4 to give ethyl borate. The vapour of ethyl borate burns in air with a green flame. This forms the basis of green edged flame test for borates.



Uses:

1. In the manufacture of enamels and glazes for pottery.
2. In making heat resisting and shock resisting glass.
3. mild as antiseptic for washing eyes.
4. as a preservative for milk and food stuffs.

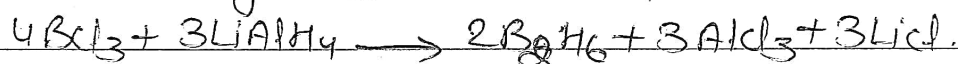
Diborane

- Preparation of Diborane :-

1. By the reaction of iodine with sodium borohydride in a high boiling solvent.



- (ii) By reduction of BCl_3 with LiAlH_4 .



- (iii) By passing silent electrical discharge through BCl_3 and H_2 .



- Properties of Diborane -

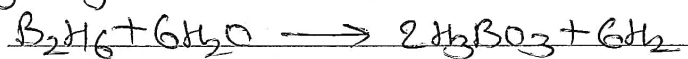
- 1) Stability - It is stable only at low temperatures. When heated at temperature between 373 K and 575 K, it changes into number of higher boranes.



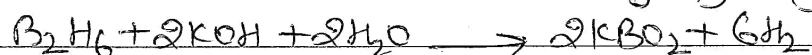
- 2) Combustibility - It undergoes spontaneous combustion in air due to strong affinity of boron with oxygen forming boric anhydride.



3. Hydrolysis - It gets hydrolysis easily by water liberating dihydrogen gas.

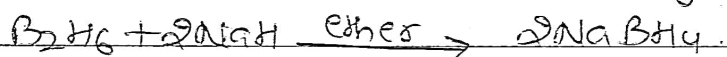


4. Reaction with alkalis - Diborane dissolves in strong alkalis to produce metaborates and dihydrogen gas.



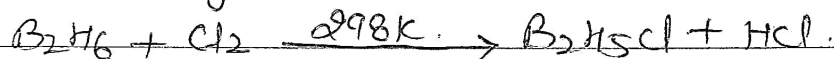
5. Action with alkali metal hydrides - Alkali metal hydrides react with B_2H_6 in ether to form metal tetrahydridoborates.

Which are also called metal borohydrides

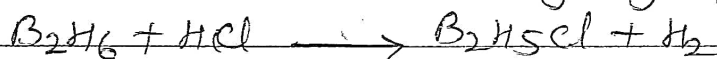


Sodium borohydride

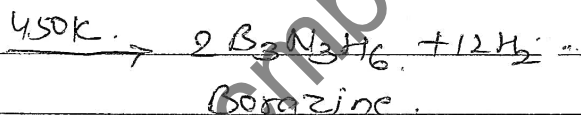
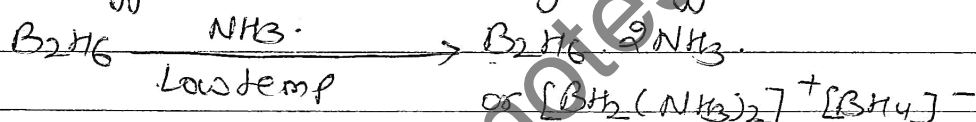
6. Action with halogens — B_2H_6 reacts with halogens under different condition to form halodiboranes.



7. Action with halogen acids — Halogen acids react with diborane to form halodiborane and dihydrogen gas.



8. Action with ammonia — Diborane reacts with ammonia under different condition to give different products.

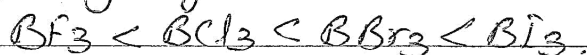


Borazine has cyclic structure similar to benzene and thus it is called inorganic benzene.

Boron Trihalides

The trihalides of boron are electron deficient compound having a planar structure. They act as Lewis acids because of incomplete octet.

The acid strength of trihalides decreases as



Aluminium

Aluminium is one of the elements of group 13 of the periodic table. The other elements are boron (B), gallium (Ga), indium (In) and

and thallium (Tl). These elements have three electrons in the outermost shell, ns^2np^1 .

Aluminium has a high ionisation energy and tends to form more covalent compounds.

Group 14 elements.

Carbon (C), Silicon (Si), Germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. All the elements have four electrons in their valence shell. Their general valence shell electronic configuration is ns^2np^2 .

— Physical Properties —

1. Density — Density increases when we go down the group because of the increase in mass per unit volume.
2. Melting and boiling points — The melting point and boiling points of group 14 are higher than group 13. It is because the atoms of group 14 can form four covalent bonds with each other and therefore there are strong binding forces between their atoms in both solid as well as liquid states. However, the melting and boiling points decrease down the group.
3. Atomic radii — Atomic radius increases as we move down the group due to increase in the number of energy shells.
4. Ionization enthalpy — The ionization energy (enthalpy) decreases down the group due to increase in size and screening effect of inner electrons.
5. Metallic character — The metallic character increases down the group from C to Pb.

6. Oxidation State - The elements of group 14 form Covalent bonds in their Compounds with the highest oxidation state of +4. The elements of this group also exhibit an oxidation state of +2.

As we move down the group the tendency to form ionic Compounds increases.

7. Oxidising and reducing Properties - The group 14 elements show oxidation state of +4 and +2 in their Compounds. The elements in +2 oxidation state can act as reducing agent while those in +4 oxidation state can act as oxidising agents.

8. Electronegativity - The elements belonging to this group are more electronegative than the elements of group 13. It is because these have a small size. The electronegativity value decreases from top to bottom in the group.

9. Catenation - The Property of forming the chains of identical atoms is called Catenation.

The Property of Catenation decreases as we move down the group.



10. Chemical Characteristics.

1. Hydrides - The elements of group 14 combine with hydrogen to form covalent hydride. Carbon forms a large number of cyclic and acyclic hydrides known as hydrocarbons. Thermal stability of hydrides of this group decreases on moving down the group. The reducing character of these hydrides increases on going down the group.

2. Oxides - The elements of this group form two types of oxides.

a. monoxides - All the elements of this group except Si form monoxides of the general formula MO_2 , Except Co which is neutral.

Other monoxides are basic.

Carbon monoxide is a colourless toxic gas and is known to form a number of co-ordination compounds with transition metals ex. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$. Such compounds are called as organometallic compounds because carbon is bonded to metals.

b Di-oxides - All the elements of this group form dioxides of the general formula MO_2 , such as Co_2 , SiO_2 , GeO_2 , SnO_2 and PbO_2 . Some characteristic features

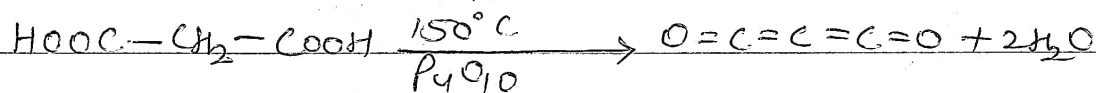
(i) Among these oxides, Co_2 and SiO_2 are acidic, GeO_2 is less acidic and SnO_2 and PbO_2 are amphoteric in nature.

(ii) PbO_2 is a powerful oxidising agent.

(iii) Comparison of properties of Co_2 and SiO_2 .

Co_2	SiO_2
• It exists as gas	• It is a solid.
• It is a linear, monomeric non-polar molecule.	• It is a three dimensional network solid.
• Appreciably soluble in water	• Insoluble in water.
• on reduction with coke given Carbon monoxide	• on reduction with coke give Silicon Carbide.
$\text{Co}_2 + \text{C} \rightarrow 2\text{Co}$	$\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{Co}$

c Carbon suboxide (C_3O_2): In addition to Co and Co_2 Carbon also forms Carbon suboxide which is made by dehydration of malonic acid with P_4O_{10}



It is a foul smelling gas with b.p. 6°C . It is linear molecule. It gives back malonic acid on reaction with H_2O or HCl .

3. Halides - The elements of this group combine with halogen to form tetrahalides of the general formula MX_4 . Except carbon

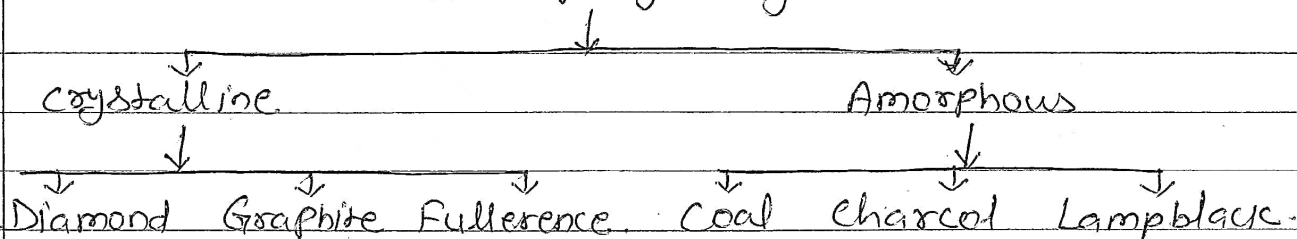
all other elements of this group also forms dihalides MX_2 , The stability of dihalides increases down the group. The thermal stability of the halides decreases down the group. Carbon halides are not hydrolysed by water because Carbon atom cannot increase its co-ordination number beyond four. on the other hand all other tetrahalides are easily hydrolysed because of the availability of vacant d-orbital.

Carbon

Carbon is the first element of group 14 of the periodic table. Its electronic configuration ($1s^2 2s^2 2p^2$) shows that it has four electrons in the outermost shell. It shows maximum tendency of Catenation (Self linking Property)

- Isotopes of Carbon - Naturally occurring Carbon contains two stable isotopes ^{12}C (98.9%) and ^{13}C (1.1%) along with trace of ^{14}C isotope which is radioactive with half life period of 5770 years.
- Allotropic forms of Carbon - It is a Phenomenon of existence of different forms of elements having different Physical Properties. The various forms are called allotropes or allotropic forms.

Allotropic forms of Carbon.



Difference

Diamond

Graphite

- | | | |
|---|----------------------------------|----------------------------------|
| 1 | Due to its high refractive index | Although it is black and opaque. |
|---|----------------------------------|----------------------------------|

1. It is a transparent substance.	Yet it has metallic lustre.
2. It has high density.	It has relatively low density.
3. It is very hard.	It is soft.
4. It is bad conductor of heat and electricity.	It is good conductor of heat and electricity.
5. It possesses three dimensional network structure.	It possesses a sheet type structure.
6. Chemical reactivity is low.	Chemical reactivity is high.

— Carbon mono oxide: (CO)
Preparation.

1. By heating Carbon in limited supply of oxygen:-

$$C + \frac{1}{2}O_2 \rightarrow CO$$

2. By heating formic acid with H_2SO_4 .

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

— Characteristics of CO.

1. Physical nature — It is a colourless, odourless gas with very small solubility in water. It is neutral in nature.
2. Toxic nature — It is quite poisonous because it combine with the haemoglobin of the red blood cells to form a complex. Carboxy haemoglobin. it destroys the capacity of the blood to carry oxygen.
3. Combustibility — It is highly combustible. Its combustion in air produce Carbon dioxide along with lot of heat.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + \text{heat}$$
4. Reducing nature — It is a very good reducing agent due to its.

Ability to get oxidised to CO_2 . It reduces metal oxides to metals. $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$

5. Formation of metal Carbonyls - In Co molecule, there are one sigma and two π bonds between Carbon and oxygen. Because of the presence of a lone pair on Carbon, Co molecule acts as a donor and reacts with certain metals when heated to form metal Carbonyl.



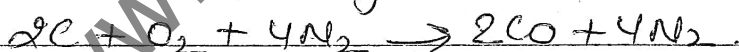
6. Reaction with chlorine - It reacts with chlorine in the presence of sunlight to form another poisonous gas Phosgene



- Water gas - It is obtained by passing steam over Red hot coke. It is a mixture of CO and H_2 .



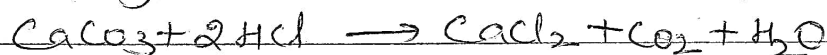
- Producer gas - It is formed by passing air over Red hot coke. It is a mixture of CO and N_2 .



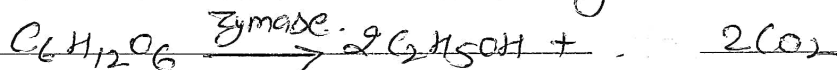
CARBON Di oxide. (CO_2).

Preparation.

1. Combustion of Carbon - $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
2. By decomposing Carbonates and bicarbonates -

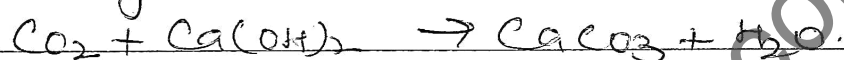


3. By Fermentation process and by calcination of limestone -

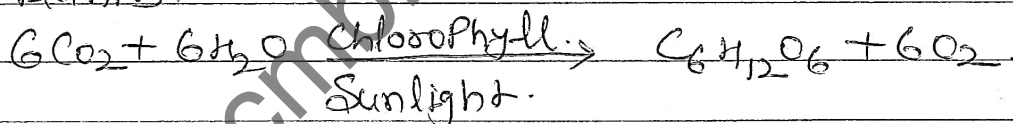


Characteristics of CO_2 .

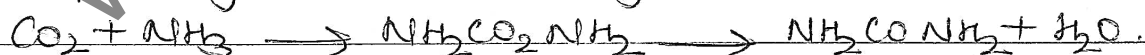
- (1) CO_2 is a colourless, odourless gas.
- (2) It is heavier than air.
- (3) It is not poisonous but it does not support life in animals.
- (4) CO_2 is acidic in nature and is fairly soluble in water.
- (5) Reaction with lime water - CO_2 reacts with lime water ($\text{Ca}(\text{OH})_2$) to form insoluble CaCO_3 which makes it milky. However, if CO_2 is bubbled through lime water for a longer time then milkiness disappears due to the formation of soluble bicarbonate.



6. Photosynthesis - CO_2 is absorbed by plants in presence of chlorophyll and sunlight. The absorbed CO_2 combine with H_2O to form glucose and starch which are used as food by the plants.



7. Action of ammonia - when CO_2 is reacted with liquid ammonia at $273-473\text{K}$ under a pressure of 220 Atmospheres. It first forms ammonium carbamate which subsequently decompose to give urea.



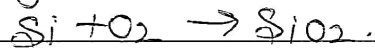
SILICA. (SiO_2).

Forms of Silica.

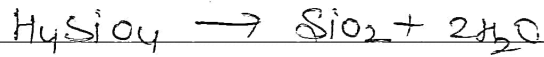
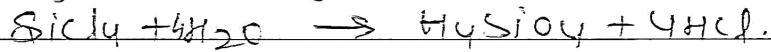
1. Quartz or rock crystal - This is the purest form of silica. It is used in the preparation of costly lenses and prism.
2. Sand - It is crushed form of Quartz which is produced in nature by weathering of rock.

2. Artificial silica — It can be obtained

(i) by burning of silicon.



(ii) by hydrolysis of silicon tetrachloride.



4. Amorphous forms of silica — Two amorphous forms are Silica gel and Keiselguhr.

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