

# Chapter

# 3

## GROUP IIIA AND GROUP IVA ELEMENTS

### GROUP IIIA ELEMENTS

The elements of group IIIA consist of boron, aluminium, gallium, indium and thallium.

#### Electronic configuration of group IIIA elements

Elements	Symbol	At. Number	Electronic configuration
Boron	B	5	$1s^2, 2s^2, 2p^1$
Aluminium	Al	13	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
Gallium	Ga	31	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1$
Indium	In	49	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^1$
Thallium	Tl	81	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^1$

### PHYSICAL PROPERTIES OF GROUP IIIA ELEMENTS

- (1) **Born is non-metal** while all other members are metals. Boron is non-metal due to its smaller size and high nuclear charge. The abrupt increase in metallic character from B to Al is associated with the increased size of aluminium atom.
- (2) **In a group, size of atom increases** from top to bottom but this increase in size is not regular. Atomic sizes of both Al and Ga are almost similar. It is due to the behaviour of 10 electrons present in d orbital. These electrons have poor shielding as compared to s and p electrons. Increase in atomic size from In to Tl is also very small, due to the presence of f electrons which also have poor shielding.

Some properties of group IIIA are given in the table

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Density g/cm <sup>3</sup>	2.33	2.7	5.93	7.3	11.85
Melting point (°C)	2300	660	30	157	304
Boiling point (°C)	2550	2467	2403	2080	1457
1 <sup>st</sup> ionization potential kJ/mol	801	577	579	558	589
Atomic radius (pm)	80	125	126	144	148
Ionic radius + 3 ion (pm)	20	52	60	81	95
Electron affinity (kJ/mol)	27	45	29	29	30
Electronegativity	2.0	1.5	1.6	1.7	1.8

- (3) Melting points of group IIIA decrease downward in a group due to increase in the size of atoms.
- (4) **First ionization energy decreases** downward the group due to increased size of atom. However first IP value increases from Al to Ga due to the poor shielding of d-electron. First I.E. also shows abnormal behaviour from In to Tl due to the presence of f<sup>14</sup>-electrons. By poor shielding, the force of attraction between nucleus and electronic cloud increases.

### OCCURRENCE OF BORON

Boron is not an abundant element. It occurs in traces in most soils and has been found to be essential in very small amounts for the proper growth of many plants.

Boron is always found in nature combined with oxygen, usually as oxyborate ions. Boron occurs principally as salts of various polyboric acids.

Name of minerals of boron	Chemical formula
Borax or tincal	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
Orthoboric acid	$\text{H}_3\text{BO}_3$

## PECULIAR BEHAVIOUR OF BORON

Boron is the first member of the group IIIA, it shows many dissimilarities with the members of its own group. The difference in the properties of boron and those of the other member of the series is mainly due to the large difference in their sizes and ionization energies.

- (1) Boron is the only element in group IIIA which is non-metallic in behaviour.
- (2) It is the only element with less than four electrons in the outermost shell which is not a metal.
- (3) Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states are +3 and -3.
- (4) One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.
- (5) Boron does not form ionic compound with sulphate, nitrate or other anions because boron does not form a stable cation.
- (6) Boron is black in colour while all other elements are silvery white.
- (7) **Oxide** of boron is **acidic**, while aluminium forms amphoteric oxide and rest of elements form basic oxides.

## COMPOUNDS OF BORON

### Borax or Sodium Tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ :

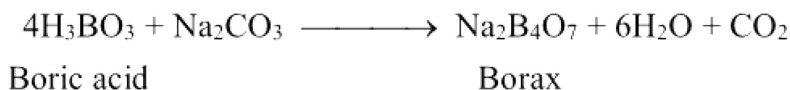
Borax is sodium salt of tetraboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ . It is most important than all other borates. Its chemical name is sodium tetraborate decahydrate.

### Occurrence of Borax:

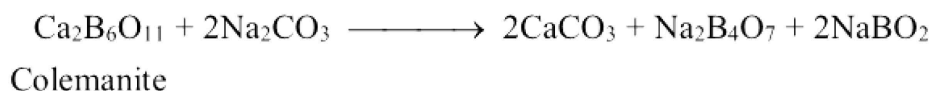
Borax occurs as a natural deposit called **tincal** in the dried up lakes of Tibet and California.

### Manufacture of Borax:

- (1) Formally borax was manufactured by treating a hot solution of boric acid with the proper amount of soda ash.



- (2) Now-a-days borax is almost exclusive obtained from calcium borate. Finely powdered colemanite is boiled with  $\text{Na}_2\text{CO}_3$  solution, when  $\text{CaCO}_3$  precipitates out and a mixture of borax and sodium metaborate is formed.



The clear solution from the top is taken off and is then allowed to crystallize, when crystals of borax separate out. To get more borax,  $\text{CO}_2$  is blown through the mother-liquor, the sodium metaborate is decomposed into borax, which separates out in the form of fine crystals.



Sodium metaborate

- (3) Borax may also be obtained from tincal by treating natural tincal with water and subsequently evaporating the clear solution, when crystals of borax separate out.

### PROPERTIES OF BORAX

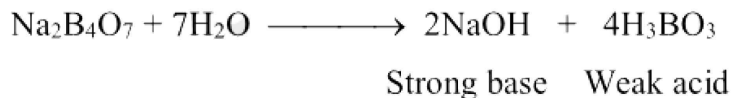
#### Physical Properties:

- (1) Borax is a white crystalline solid.
- (2) It is sparingly soluble (very less soluble) in cold water but more soluble in hot water. In 100 g of water at  $10^\circ\text{C}$  only 3 g of borax is soluble but at  $100^\circ\text{C}$  its solubility is 99.3 grams.
- (3) If a saturated solution of borax is allowed to crystallize above  $62^\circ\text{C}$ , octahedral crystals of penta hydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  separates out, but if temperature is below  $62^\circ\text{C}$  deca hydrate crystals  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  are formed.

### CHEMICAL PROPERTIES

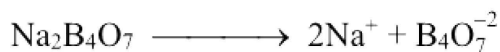
#### (1) Hydrolysis:

Aqueous solution of borax is alkaline in nature due to hydrolysis. Hydrolysis is prevented in the presence of glycerin.



Aqueous solution of borax turns red litmus to blue due to the presence of alkali.

Borax when dissolved in water ionizes as:



Hydrolysis of  $\text{B}_4\text{O}_7^{-2}$  ions occurs as follows:

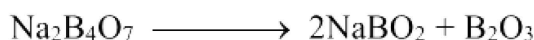


So a strong alkali (NaOH) is formed which is highly ionized. On the other hand boric acid ( $\text{H}_3\text{BO}_3$ ) ionizes to a little extent so it is a weak acid. Hence, solution of borax as a whole is alkaline in nature.



**(2) Effect of Heat:**

When borax is heated, it loses water and swells up into a white porous mass due to the expulsion of water. On further heating it melts into a clear transparent glass, which dissolves many metallic oxides forming coloured beads. This reaction forms the basis of borax bead test.

**(3) Reaction with Acids:**

It reacts with HCl or H<sub>2</sub>SO<sub>4</sub> to form boric acid:

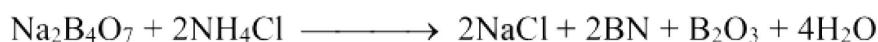


Borax

Boric acid

**(4) Reaction with Ammonium Chloride:**

When borax is heated with ammonium chloride, boron nitride is produced: BN is also called **Borazole or inorganic graphite**.

**Borax Bead Test:**

This test is used for identification of colour ions of the salt, i.e., Cu<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup>. We can perform this test as:

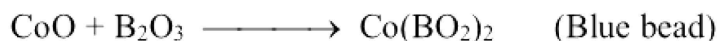
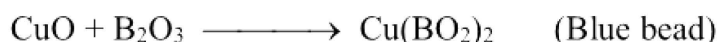
Prepare a loop at the end of a platinum wire. Heat the wire and take a little powdered borax on the hot loop. Heat again, borax first swells up and then melts into colourless, glass-like beads on the loop. Now put a few grains of the substance, under examination, on the beads and re-heat it first in the oxidizing flame and then in the reducing flame. Note the colours of the beads.

**Chemistry of Borax Bead Test:**

Borax, when fused, is decomposed into sodium metaborate and boric anhydride.



The metallic oxide formed from the substance, under examination, combines with B<sub>2</sub>O<sub>3</sub> giving the coloured metallic borates. With cupric oxide, the beads are coloured blue in the oxidizing flame because cupric metal borates are blue in colour.



with CoO, blue bead of cobalt metaborate is formed.

**Uses of Borax:**

- (1) It is used to prepare borate glass, which is heat resistant.
- (2) It is used in softening of water.
- (3) It is employ in borax bead test, for the detection of metallic cations.
- (4) It is used in metallurgical operations.
- (5) It is used as a flux in welding and metallurgy.
- (6) It is employed in making washing powders.
- (7) It is used in leather industry for tanning and dyeing.
- (8) It is used in cosmetics, soaps, textiles, paints, medicine, match industry and as a preservative.

**BORIC ACIDS**

There are three important boric acids. Out of these orthoboric acid is the most important and the stable one. The remaining acids are stable in solid state and change into orthoboric acid in solution:

- |                                    |                                              |
|------------------------------------|----------------------------------------------|
| (1) Metaboric acid, $\text{HBO}_2$ | (2) Orthoboric acid, $\text{H}_3\text{BO}_3$ |
|------------------------------------|----------------------------------------------|

- |                                                       |                                                      |
|-------------------------------------------------------|------------------------------------------------------|
| (3) Tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$ | (4) Pyroboric acid, $\text{H}_6\text{B}_4\text{O}_9$ |
|-------------------------------------------------------|------------------------------------------------------|



Metaboric acid	Orthoboric acid
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Tetraboric acid	Orthoboric acid
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**ORTHOBORIC ACID OR BORIC ACID ( $\text{H}_3\text{BO}_3$ )**

It is well crystalline chemical substance (triclinic), sparingly soluble in cold water (2.6% at  $40^\circ\text{C}$ ) but dissolves readily in hot water (37% at  $107^\circ\text{C}$ ). This temperature variation in solubility forms the basis for its separation and purification.

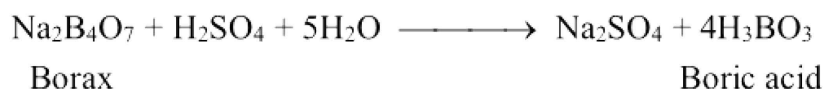
**PREPARATION OF BORIC ACID  
ON COMMERCIAL SCALE**
**(1) Form Colemanite:**

On commercial scale boric acid is prepared from a natural calcium borate called colemanite ( $\text{Ca}_2\text{H}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ) by suspending it in boiling water while sulphur dioxide is passed through it. Boric acid crystallizes out from the solution while the other product  $\text{CaSO}_3$  remains in the solution.

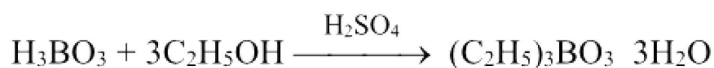


**(2) From Borax:**

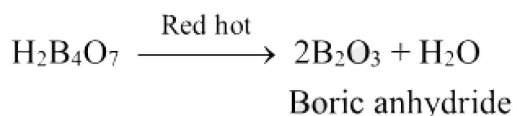
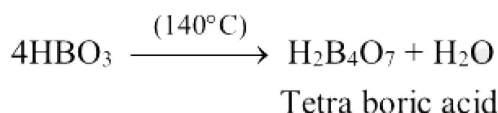
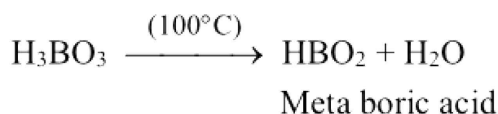
A hot concentrated solution of borax is treated with a calculated quantity of conc.  $\text{H}_2\text{SO}_4$ . On cooling, crystals of boric acid formed separate out.


**PROPERTIES OF BORIC ACID**

- (1) Boric acid is a white lustrous crystalline solid having a soft soapy touch, slightly soluble in cold water but fairly soluble in hot.
- (2) It is volatile in steam.
- (3) It reacts with ethyl alcohol, forming ethyl borate.



- (4) When heated strongly, it swells to frothy mass losing water molecules. It is first converted into meta boric acid, then to tetra boric acid and finally to boric anhydride.



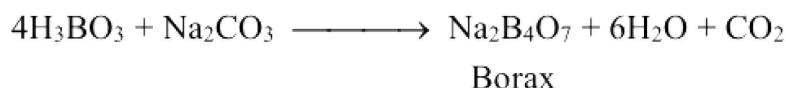
- (5) It is a very weak acid and ionizes to a very limited extent mainly as a mono basic acid.



- (6) Its solution has no effect on methyl orange although it turns blue litmus red.
- (7) It is partially neutralized by caustic soda and gives borax.



- (8) When boric acid is neutralized by soda ash  $\text{Na}_2\text{CO}_3$ , borax is obtained.



- (9) Boric acid being a weak acid, cannot be titrated with alkalis in the usual manner. In the presence of glycerol, however, it can be titrated against a standard alkali using phenolphthalein as an indicator. In the presence of glycerol, it act as much stronger acid as compared to pure  $\text{H}_3\text{BO}_3$ .

**Uses of Boric Acid:**

- (1) Boric acid is used in medicines as an antiseptic, e.g., dusting powder, boric ointment and boric solution is used as an eye-wash.
- (2) It is used in pottery as a glaze because borate glazes are more fusible than silicate glazes and posses a higher coefficient of expansion.
- (3) It is also used in candle industry for stiffening of wicks.

**OCCURRENCE OF ALUMINIUM**

Aluminium is the most abundant element in the Earth's crust (after oxygen and silicon).

It occurs primarily as alumino-silicate minerals found in the rocks of the outer portion of the earth.

Name of minerals of aluminium	Chemical formula
Feldspar	$\text{KAlSi}_3\text{O}_8$ or $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
Mica (Muscovite)	$\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$
Kaolin (Clay)	$\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$ $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Corundum	$\text{Al}_2\text{O}_3$
Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$
Emerald	$\text{Al}_2\text{F}_2\text{SiO}_4$
Cryolite	$\text{Na}_3\text{AlF}_6$

The other elements of group IIIA gallium, indium and thallium are relatively rare and are obtained as by-products during the processing of other metals.

**Physical Properties of Aluminium:**

- (1) It is silvery white metal.
- (2) Its density is  $2.7 \text{ g cm}^{-3}$ . It is light metal.
- (3) It is brittle below its M.P ( $659^\circ\text{C}$ ).
- (4) It is excellent conductor of heat and electricity.
- (5) It is malleable and ductile.

**Anodizing:**

The thin layer of  $\text{Al}_2\text{O}_3$  is very useful. The metal is resistant to corrosion due to this layer. Its thickness is purposely increased in the industry by electrolytic process called "Anodizing".

**REACTIONS OF ALUMINIUM****(a) Reaction with Air:**

Aluminium is a reactive metal. When it is left in air even for a short time, it is coated with a layer of aluminium oxide,  $\text{Al}_2\text{O}_3$ . This oxide protects the aluminium from further attack. This oxide layer is very useful and its thickness is purposely increased in industry by an electrolytic process called anodizing.

- (1) Aluminium burns in air at high temperature. The reaction is accompanied with the evolution of heat and intense white light. This property of aluminium is used in flash flight photography.



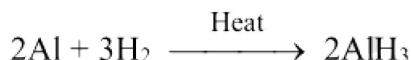
- (2) When aluminium is burnt in air, the product is a mixture of the oxide and equally white aluminium nitride.



Because of its ability to combine with both oxygen and nitrogen, the metal is often used to **remove air bubbles** from molten metals. Salt solutions corrode aluminium badly so aluminium and aluminium alloys are not suitable for marine use.

**(b) Reaction with Non-metals:**

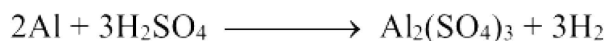
- (1) Aluminium on heating with hydrogen forms aluminium hydride.



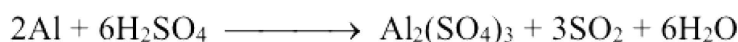
- (2) When halogens are passed over heated aluminium powdered aluminium halides are produced.

**(c) Reaction with Acids:**

Aluminium is attacked rapidly by most acids but remains passive in concentrated nitric acid due to the formation of a protective layer of  $\text{Al}_2\text{O}_3$ . Aluminium dissolves in dilute acids giving out hydrogen:



With hot and concentrated sulphuric acid reacts instead of  $\text{H}_2$ , sulphur dioxide gas is produced.



It is passive with conc.  $\text{HNO}_3$ .

**(d) Reaction with Alkalis:**

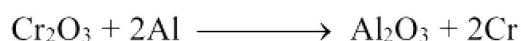
Aluminium when dissolved in aqueous alkalis producing hydrogen gas and soluble aluminate ion.



Aluminium utensils are not washed with alkali solution. Hydrogen gas is also prepared by this method for filling in balloons.

**(e) Thermite Process:**

The process in which Al is used as reducing agent is called Alumino-thermite process (discovered by Goldschmidt in 1905).



The process is highly exothermic and is used for welding purpose (thermite welding) i.e., welding of tramway rails and heavy machinery.

**USES OF ALUMINIUM**

- (1) It is very light metal (three times less dense than iron) but possess high tensile strength. Due to these properties, it is used in the transport industries, in the construction of aircrafts, ships and cars.
- (2) It is good conductor of heat and electricity. It is used as heat exchanger in chemical industry, oil industry and many other industries.
- (3) Its smooth surface reflect the radiations. For this reason it is commonly used to insulate buildings, and telescope mirrors. Aluminium foil is also used to jam RADAR.
- (4) It is non-magnetic and used in **navigational equipments**.
- (5) It is a good reducing agent and thus be used in chemical and steel industry.
- (6) It is non-ionic and can be used to make food and brewing equipments and packing materials.
- (7) Aluminium readily form alloys with other metals like copper, magnesium, nickel, cobalt and zinc.
- (8) Aluminium due to its conductivity and luster, is used for making cooking utensils, window frames and kitchen foil.
- (9) Aluminium is used for making petrol and milk storage tanks because it reflects radiations and prevent them of being over-heated in the sun.

## GROUP IVA ELEMENTS

Elements of group IVA consist of carbon, silicon germanium, tin and lead.

The electronic configuration of group IVA elements are given below in the table:

Element	Symbol	At. No.	Electronic configuration
Carbon	C	6	$1s^2, 2s^2, 2p^2$
Silicon	Si	14	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
Germanium	Ge	32	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$
Tin	Sn	50	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^2$
Lead	Pb	82	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^2$

### COMMON PROPERTIES OF THE ELEMENT GROUP IVA

- (1) The elements of group IVA have four electrons in their valence shells and their valency is four or elements show four oxidation states in their compounds, e.g.,  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{PbCl}_4$  etc.
- (2) All the members of group IVA form hydrides of formula  $\text{XH}_4$ , e.g., Methane  $\text{CH}_4$ , Silane  $\text{SiH}_4$ , Germane  $\text{GeH}_4$  etc.
- (3) All the members of group IVA form tetra halides e.g.,  $\text{CCl}_4$ ,  $\text{CF}_4$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_4$ .
- (4) Members of group IVA form dioxides, e.g.,  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$  and  $\text{PbO}_2$ .

### GENERAL TREND OF PROPERTIES IN GROUP IVA

There is a marked change of properties from carbon to lead. Due to this gradation of properties, there are few similarities between extreme members carbon and lead.

#### (1) **Metallic Characters:**

Carbon is non-metal, silicon and germanium are semi-metals and tin and lead are good metals. Metallic characters increase from top to bottom in a group.

Table – Physical properties of group IVA elements

Property	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Density (g/cm <sup>3</sup> )	2.33	2.7	5.93	7.3	11.85
Melting point (°C)	3930	1420	937	232	328
1 <sup>st</sup> ionization energy (kJ/mol)	1086	736	760	707	715
Atomic radius (pm)	77	117	122	140	154
Ionic radius (pm)	20	39	53	71	84

**(2) Atomic Radii:**

Atomic radii increase from top to bottom in a group, but this increase is very small from Si to Ge due to the presence of d-electrons.  $d^{10}$  electrons have poor shielding and hold of nucleus on valence electrons increases.

**(3) Ionization Energy:**

Ionization energy usually decreases in a group from top to bottom. In this group ionization energy increases from Si to Ge due to poor shielding of  $d^{10}$ -electrons. This abnormality is also present in Sn to Pb due to poor shield of  $f^{14}$ -electrons.

**(4) Variable Oxidation State:**

The elements of group IVA have four electrons in their valence shell as  $ns^2, np^2$ . Carbon and silicon use their four electrons for bonding and have four oxidation state. Ge, Sn and lead have **oxidation +2 and +4**. Lower oxidation states ends with -ous. e.g., Germinous, Stannous and Plumbous, Higher oxidation states ends with -ic. e.g., Germinic, Stannic and Plumbic. In  $Ge^{2+}$ ,  $Sn^{2+}$  and  $Pb^{2+}$  only two p-orbitals take part in bond formation. Two s-electron do not involve in bond formation. *“The s-pair of electrons which do not take part in bond formation is called, s-inert pair effect.”*

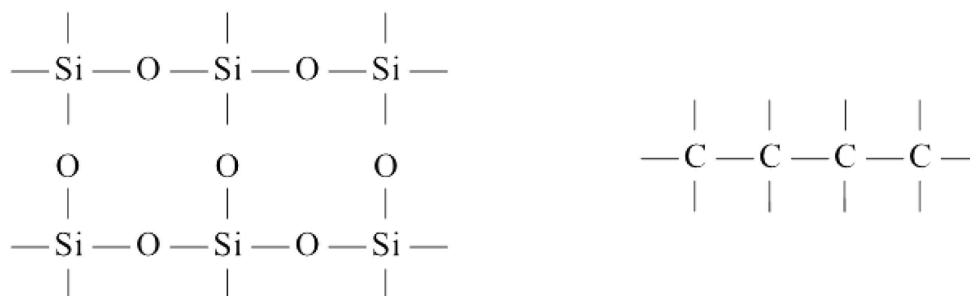
**(5) Electropositive Characters:**

The electropositivity or the tendency to lose electron increases downward in group IVA. This trend is due to the increase in the atomic mass and metallic characters.



## SOME COMMON PROPERTIES OF CARBON AND SILICON

- (1) Carbon and silicon both form covalent bonds.
- (2) Carbon and silicon both form acidic oxides, whereas oxides of Ge, Sn and Pb are amphoteric.
- (3) Carbon and silicon have property of chain formation (catenation). However chain of silicon is alternate with oxygen.



- (4) Both carbon and silicon react with hydrogen and halogen to form their hydride and halides respectively. e.g.,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{CF}_4$ ,  $\text{SiF}_4$ , etc.

### Occurrence of Carbon:

Minerals of carbon	Chemical formula
Limestone (Calcite)	$\text{CaCO}_3$
Dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3$
Magnesite	$\text{MgCO}_3$

### Occurrence of Silicon:

Minerals of silicon	Chemical formula
Analcite (a zeolite)	$\text{NaAl}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$
Asbestos	$\text{CaMg}_3(\text{SiO}_3)_4$
Kaolin (pottery clay)	$\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$
Talc (or soapstone)	$\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$
Zircon	$\text{ZrSiO}_4$

Silicon is very abundant, about 25% of the mass of the earth's crust being due to this element.

Silicon, unlike carbon, is not found in free state. Silicon is found as a major constituent of rocks either in the form of silica or silicates. Most minerals other than sulphides, sulphates, phosphates and carbonates contain a high proportion of silicon.

As oxide, it is found as quartz in the following forms:

Rock crystal, amethyst, quartz, smoky quartz, rose quartz and milky quartz.

Sand is largely silicon dioxide (silica). Opal is a hydrated variety of quartz.

### PECULIAR BEHAVIOUR OF CARBON

Carbon differs from the remaining members group IV-A in the following respects:

**(1) Metallic Character:**

Carbon is non-metal while the other members of the family are metalloids or metals.

**(2) Catenation or Self-linkage:**

Carbon has a tendency to form long chains of identical atoms. The type of linkage of identical atoms with each other is called catenation or self-linkage. The property of catenation decreases on moving down the group from carbon to lead. The maximum tendency of catenation associated with carbon forms the basis of the carbon compounds, which constitute organic chemistry.

**(3) Multiple Bonds:**

Carbon can form multiple (double or triple) bond with other carbon, atom or with nitrogen oxygen, etc.

For example:  $\text{HC} \equiv \text{CH}$ ,  $\text{CH}_2 = \text{CH}_2$ ,  $\text{O} = \text{C} = \text{O}$

### COMPOUNDS OF CARBON AND SILICON

**Structure of Oxides of Carbon:**

Three oxides of carbon are known:

$\text{CO}$       Carbon monoxide

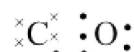
$\text{CO}_2$       Carbon dioxide

$\text{C}_3\text{O}_2$       Carbon sub-oxide ( $\text{O} = \text{C} = \text{C} = \text{C} = \text{O}$ )

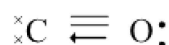
Out of these, the last one is of little importance.

**Structure of Carbon Monoxide:**

Carbon monoxide is diatomic molecule having triple bond between the two atoms. It is slightly polar. The electronic structure of carbon monoxide can be represented as:



It is usually written as:



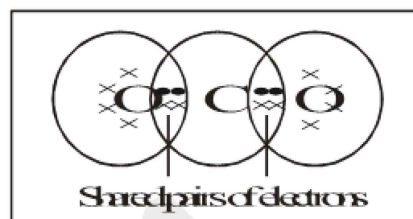
It might appear from the above structure that the molecule should have a large dipole moment, but in fact the molecule has a small dipole moment (0.112 D).



### Structure of Carbon Dioxide:

Carbon dioxide exists in the gaseous state as linear molecules. The observed C–O bond distance is 115 pm and is in agreement with the following structure.

Solid CO<sub>2</sub> (dry ice) has a face-centered cubic structure. Being linear, its dipole moment is zero.



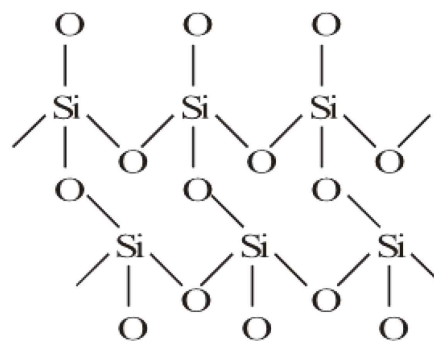
## OXIDES OF SILICON

### Silicon Dioxide (SiO<sub>2</sub>):

Silicon dioxide, SiO<sub>2</sub> called silica, is probably the most common and the most important compound of silicon. In silica every silicon atom is attached tetrahedrally to four oxygen atoms and each oxygen atom has two close silicon neighbours.

The common crystalline form of silicon dioxide, is a hard, brittle, refractor, colourless solid which vary markedly from carbon dioxide.

In SiO<sub>2</sub>, each silicon atom is linked with four oxygen atoms in tetrahedral arrangement. Each oxygen atom is covalently bonded with two silicon atoms. It is a three dimensional network covalent bond.



Due to this continuous arrangement, a giant silicon oxygen network extends out to give a massive silicon dioxide crystal. Because each Si is attached with four oxygen and each oxygen is attached with two silicon it has no molecular formula. We can only write the simplest ratio of atoms of silicon and oxygen, which is 1 : 2 or SiO<sub>2</sub>.

Silicon-oxygen bond is very strong bond and atoms are firmly placed at their places. SiO<sub>2</sub> does not exist in the form of single molecules like CO<sub>2</sub>. It is a macromolecule. Atoms of silicon and oxygen have their complete valence shells and are satisfied but those atoms of Si and O which are present at the surface are not satisfied. Due to this reason silica has high surface activity.

In each of the various crystalline forms of silica, there is a special pattern which is repeated throughout the crystal in a regular definite crystal lattice. The regular tetrahedral arrangement of four oxygen atoms around each silicon persists in each crystalline form but the Si–O–Si bond angles and the rotation about each Si–O bond are different in the different polymorphic species.

### Preparation of Vitreous Silica or Silica Glass:

At 1600°C, silica or quartz melts to give a viscous liquid with a random internal structure. On the average still many molecules of silicon are attached with four oxygen and one oxygen is attached with two silicon atoms. When this liquid silica is cooled, it does not crystallize readily, but usually it under-cools tremendously and eventually becomes rigid without having undergone orientation into a regular crystal pattern. This rigid, highly under-cooled liquid is called vitreous silica or silica glass (frequently incorrectly referred to as fused quartz).

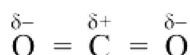
Vitreous silica possesses the following interesting and useful properties:

- (1) High transparency to light.
- (2) Very refractory (heat resistant), does not soften below 1500 to 1600°C.
- (3) Very low thermal expansion (not easily fractured by changing temperature).
- (4) Excellent insulator.
- (5) Hard, brittle and elastic.
- (6) Insoluble in water and inert toward many reagents.
- (7) It is resistant towards all acids except HF.

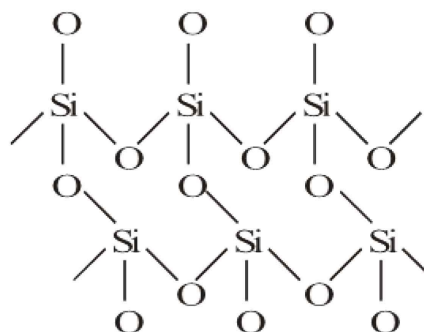


### CO<sub>2</sub> is Gas while SiO<sub>2</sub> is Solid at Room Temperature:

Both carbon and silicon are the members of group IVA and have four electrons in their valence shell. Size of carbon atom is smaller than the size of silicon atom. In CO<sub>2</sub>, each carbon atom forms two double bonds with two oxygen atoms, CO<sub>2</sub> is an independent molecule.



In case of SiO<sub>2</sub>, each silicon atom is covalently bonded with four oxygen atoms and each oxygen atom is attached with two silicon atoms. This networking of bonds is due to bigger size of silicon than carbon. SiO<sub>2</sub> has three dimensional regular arrangement of silicon and oxygen. Due to this network of strong covalent bond atoms of Si and oxygen are present at their fixed position and it exists as solid at room temperature.

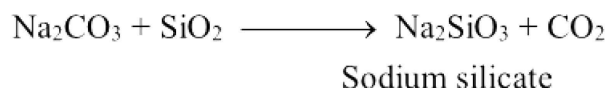


## SILICATES AND THEIR USES

The compounds derived from silicic acid  $\text{H}_2\text{SiO}_3$  are known as silicates.

### (a) Sodium Silicate $\text{Na}_2\text{SiO}_3$ (Water Glass or Soluble Glass):

This is sodium salt of metasilicic acid  $\text{H}_2\text{SiO}_3$ . It is known water glass or soluble glass. It is prepared by fusing sodium carbonate with pure sand. The process is carried out in a furnace called **reverberatory** furnace.



#### Properties:

Sodium silicate is soluble in water and its solution is strongly alkaline due to hydrolysis.



#### Uses of Sodium Silicate:

- (1) It is used as a filler for soap in soap industry.
- (2) It is used in textile as fire proof.
- (3) It is used as furniture polish.
- (4) It is also used in calico printing.
- (5) Preservative for eggs.

#### Chemical Garden:

When crystals of soluble coloured salts like nickel chloride, ferrous sulphate, copper sulphate or cobalt nitrate, etc. are placed in a solution of sodium silicate, they produce a very beautiful growth, like plant, which is called chemical garden.

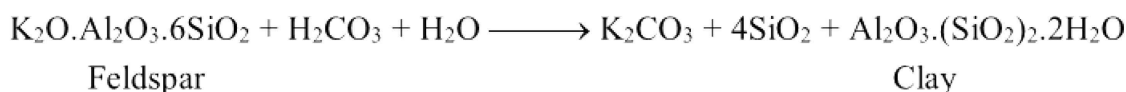
#### How to Grow Chemical Garden?

Prepare concentrated solution of  $\text{Na}_2\text{SiO}_3$  in water and place it in a beaker. Sprinkle some crystals of coloured salt ( $\text{NiCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{CuSO}_4$ ) on the surface of the liquid. Coloured shoots rise up and grow like plant on standing for some time.

### (b) Aluminium Silicates:

Aluminium silicates are formed by the chemical **weathering of the rocks**. Clay is an example of aluminium silicate. Clay is formed by disintegration and weathering of rocks.

The melting and freezing of water in the rocks, and the chemical action of water and carbon dioxide, convert these compounds into potassium carbonate, sand and clay. The following reaction explains the weathering of potassium feldspar:



## PROPERTIES OF KAOLIN OR PURE CLAY

Pure, clay which has the formula shown above, is white and is called kaolin. It is used to make porcelain and china wares. Ordinary clay contains compounds of iron and other metals and it has a yellow or reddish yellow colour.

**Impure clays** can be more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily fusible silicates with sand. Such clays are used to make **bricks, tiles, and stoneware's**. Due to the presence of ferric oxide, the articles of this clay turn reddish when heated in a kiln.

Stoneware is usually glazed to give it a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate  $\text{NaAlO}_2$  and sodium aluminium silicate, which melts readily and covers the entire surface. When the article cools, the covering solidifies, producing a compact, smooth waterproof surface. **China wares** are made from a mixture of **kaolin, bone ash, and feldspar**; the mixture fuses when heated and fills the pores between the grains of kaolin.

The use of clay in making pottery and other ceramic articles depends upon the **plasticity** of the paste. When soaked in water, the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated, the water of hydration is lost, and a hard rock like mass is formed.

### Talc or Soap Stone:

Magnesium silicate  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$  is commonly known as talc or soapstone. Due to weak force in these layers, they can slide over one another and have slippery touch. Talc is used as bath powder or talcum powder. It is used to make cosmetics.

### Asbestos:

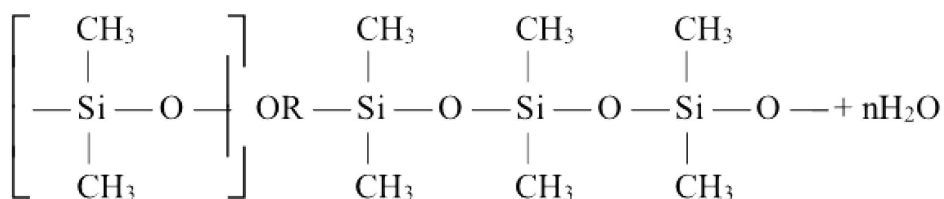
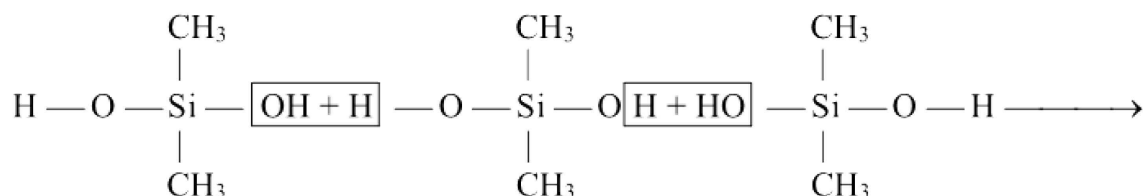
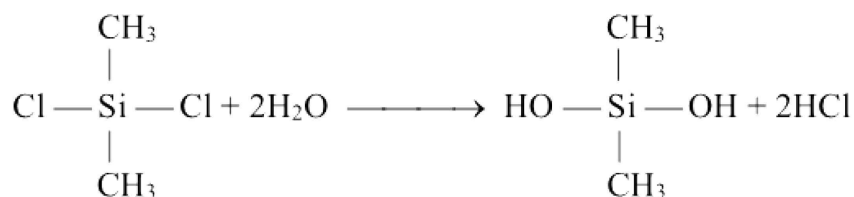
Asbestos is hydrated calcium magnesium silicate  $\text{CaMg}_3(\text{SiO}_3)_4$ . It has fibrous nature. Due to its fibrous nature, it is used to make reinforcing fuller in brakes and clutch linings. Because it is fireproof, it is spun and woven into fabrics used in covers. It is used in insulation and sealers in cars, trucks and planes.

## SILICONES

*“These are polymeric chain compounds consisting of a backbone of alternatively linked silicon and oxygen atoms alkyl or aryl groups are attached to the silicon atoms.”*

Silicones are formed by the hydrolysis of compounds like  $(\text{CH}_3)_2\text{SiCl}_2$ . During the formation of silicon polymer, a hydroxyl intermediate is formed which on elimination of water, produces silicones.

## PREPARATION



Other alkyl group may also be substituted instead of  $-\text{CH}_3$  group. Chain of  $\text{Si}-\text{O}-\text{Si}$  bond can be made of various length. Due to different chain length and alkyl group, silicones are present as oils, greases or rubber like solids.

## PROPERTIES AND USES OF SILICONES

### (1) As Lubricants:

Some methyl silicones are only liquids and become more viscous on increasing chain length, are used as lubricant. They are also used in hydraulic brakes and other hydraulic systems. Very small change in viscosity takes place by changing the temperature of silicones. In this respect, silicones are better lubricant than oils.

If the temperature is dropped from  $100^\circ\text{C}$  to  $0^\circ\text{C}$ , the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicones oil will increase less than four folds. In the presence of **air or oxygen at temperature as high as  $300^\circ\text{C}$** , silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

### (2) As Rubber:

Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.



**(3) Electrical Insulator:**

Silicone molecules can be made in such a way that bridges, or cross linkages bind one long molecule to another, at several points along the chain. These compounds have resinous properties and are extensively used in electrical insulator.

**(4) Water Repellent:**

Another interesting and important application of silicones is their use in the treatment of various surfaces to make them water repellent. A silicones film covers the surface, and repels water like a grease film. Much of the leakage of electricity through moisture film on ceramic electrical insulators can be prevented by a silicone film; cloth, plastics, asbestos, glass, leather and paper, even filter paper and blotting paper become strongly water repellent when covered with silicone film.

**SEMICONDUCTORS**

*“A semiconductor is a solid, crystalline material with an electrical conductivity intermediate between that of metals and that of insulators.”*

The conductivity of metal decreases by increasing temperature while conductivity of semimetals increases by increasing temperature. Semiconductors have different resistance to passage of electric current in different conditions. Some common semiconductor materials are given below in the table:

Elements	III-V compounds	II-VI compounds
Si	AIP – Aluminium phosphide	CdS – Cadmium sulphide
Ge	GaP – Gallium phosphide	ZnS – Zinc sulphide
Se	GaAs – gallium arsenide	CdTe – Cadmium Telluride
	InAs – Indium arsenide	
	In Sb – Indium antimonide	

Semiconductors are of two types:

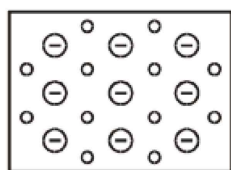
**N-type Semiconductor:**

Semiconductor in which mobile phase is electrons and stationary phase is positive ions.

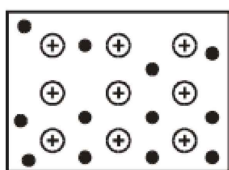
**P-type Semiconductor:**

The semiconductor in which mobile phase are holes and stationary phase is negative ions.

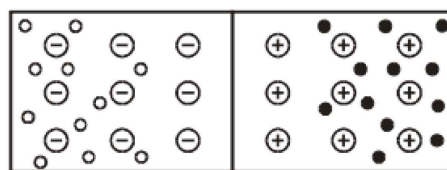




p-type semiconductor  
with mobile holes and  
stationary negative ions



n-type semiconductor  
with mobile electrons and  
stationary positive ions



p-n junction

### Formation of a p-n junction

## PROPERTIES OF SEMICONDUCTORS

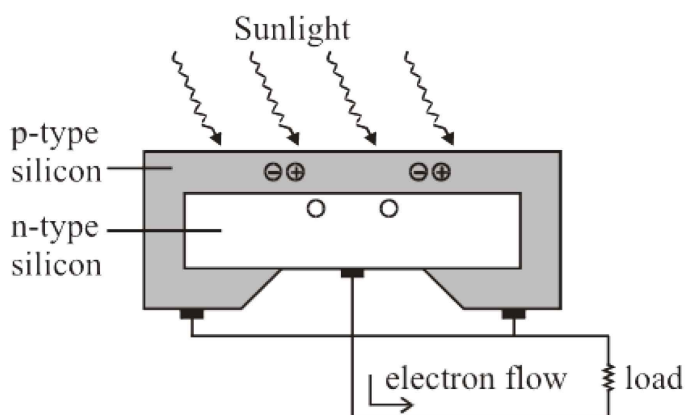
### (1) Electrical Conductivity:

Semiconductors conduct electricity better than insulators, but not as well as good conductors like metals. This gives them their name, which means “Half conductors”. How well they conduct electricity depends upon their temperature. When a metal is heated, its resistance increases, when a semiconductor is heated its resistance decreases.

### (2) Light Sensitivity:

Semiconductors are also sensitive to light. The greater the intensity of the light that shines on them, the better they conduct electricity. The effects that light and heat energy have on semiconductors make them extremely useful. They are used in **photoelectric cells** and in a **solar batteries**.

The electrons of semiconductors do not carry electric current as readily as the electrons of good electric conductors like metals. However, when the atoms of the material absorb heat or light, the electrons become less tightly bound to their atoms. They can now conduct electricity.



A photovoltaic (solar) cell using silicon-based semiconductors

**(3) Use in Transistors:**

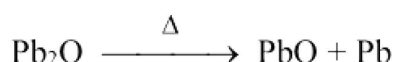
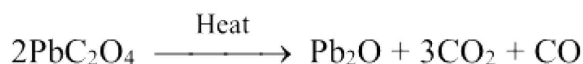
Another special property of semiconductors is the way they behave when they are joined to another material, which may be a metal or a different semiconductor. The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors. Transistors are much smaller and less complicated than old fashioned electronic tubes. They are used in radio, television, computers and calculators.

**USES OF LEAD COMPOUNDS IN PAINTS**

Different oxides of lead, basic lead carbonate and lead chromate are used in paints.

**(1) Lead Suboxide  $\text{Pb}_2\text{O}$ :**

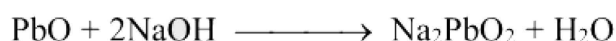
It is black powder, obtained on heating plumbous oxalate in the absence of air.



$\text{Pb}_2\text{O}$  is decomposed by heat into Pb and PbO. Oxidation state of lead is +1. Other than pigment, it is also used in the manufacture of lead storage batteries.

**(2) Lead Monoxide (Litharge, Massicot),  $\text{PbO}$ :**

- (i) Litharge varies in colour from pale yellow to reddish yellow, possibly due to the existence of two forms, a rhombic (yellow) and a tetragonal (red).
- (ii) It is slightly soluble in water.
- (iii) It is amphoteric oxide.
- (iv) It combines with acids and bases to form salt and water.

**Uses of Lead Monoxide:**

- (1) It is usually used in preparing flint glass and paints.
- (2) If litharge is boiled with water and olive oil, lead oleate is formed which is a sticky adhesive mass.
- (3) A paste of litharge and glycerine harden on standing and yield a cement that is stable towards water and is often employed to seal drain pipes of sinks.
- (4) It is also used as glaze for decorating ceramic objects.

**(3) Red Lead,  $\text{Pb}_3\text{O}_4$  or Minimum (Sindhur):**

It is a combination of plumbous and plumbic oxide.

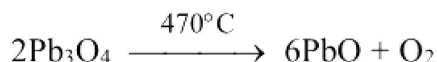


**Preparation:**

When lead is heated in air at about 340°C, it absorbs oxygen and forms a bright scarlet crystalline powder of red lead or **minimum**.



It decomposes at 470°C:

**Uses:**

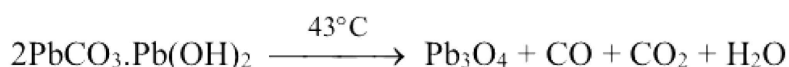
- (1) It is used for manufacture of lead storage batteries.
- (2) It is used as red pigment in paints.
- (3) Mixture of linseed oil and red lead is applied to steel and iron to prevent corrosion.
- (4) It is an important ingredient for the manufacture of flint glass, matches and ceramic glazes.

**(4) Lead Oxide, Plumbic Oxide, PbO<sub>2</sub>:**

When red lead is treated with concentrated nitric acid, it is decomposed into lead nitrate and lead dioxide:



Lead dioxide is a reddish brown powder. It is slightly soluble in water, but it does dissolve in alkaline water to yield soluble plumbates. It is not affected by dilute acids. It is poisonous in nature. It decomposes on heating at 43°C to form red lead.

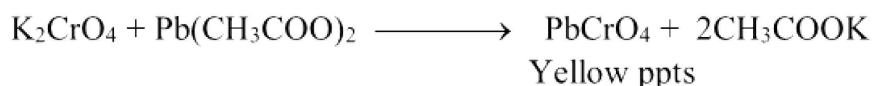
**(5) White Lead 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>:**

Basic lead carbonate 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> is an amorphous white pigment. It mixes readily with linseed oil and has a good covering power. If improperly prepared, it becomes crystalline and its covering power is reduced.

White lead is not suitable for use as a good pigment since it is darkened by the hydrogen sulphide, which is frequently present in the atmosphere.

**(6) Lead Chromate, Chrome Yellow PbCrO<sub>4</sub>:**

It is prepared by reacting K<sub>2</sub>CrO<sub>4</sub> with Pb(CH<sub>3</sub>COO)<sub>2</sub>.



It is used as a pigment under the name of **chrome yellow**. Orange or red basic lead chromates are formed when lead chromate is boiled with dilute alkali hydroxide and are used as pigments. The stable yellow modification of lead chromate is monoclinic. Mixture of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments.