

## ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-11) TOPIC- GROUP-14 ELEMENTS (P-BLOCK) PREPARED BY: MR. ARNAB PAUL CHOWDHURY SET NUMBER-12 DATE: 01.02.2021



# What are Group 14 Elements?

The group 14 elements are the second group in the p-block of the periodic table. It is also called the carbon group. The members of this group are:

- Carbon (C)
- Silicon (Si)
- Germanium (Ge)
- Tin (Sn)
- Lead (Pb)
- Electronic Configuration
- Oxidation States
- Anomalous Behaviour of Carbon
- <u>Chemical Properties</u>
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- Compounds of Group 14 Elements

## **Electronic Configuration of Group 14 Elements**

The group 14 elements have a general electronic configuration of ns<sup>2</sup>np<sup>2</sup>. These elements have 2 electrons in the outermost p orbitals. The <u>electronic configuration</u> of these elements is shown below:

Group 14 Elements				
Period	Element	Atomic No.	Electronic Configuration	
2nd	Carbon (C)	6	[He]2s2 2p2	
3rd	Silicon (Si)	14	[Ne]3s2 3p2	

4th	Germanium (Ge)	32	[Ar]3d10 4s2 4p2
5th	Tin (Sn)	50	[Kr]4d10 5s2 5p2
6th	Lead (Pb)	82	[Xe]4f14 5d10 6s2 6p2

As all the elements in group 14 have 4 electrons in the outermost shell, the valency of group 14 elements is 4. They use these electrons in the <u>bond formation</u> in order to obtain octet configuration.

# Oxidation States and Inert pair Effect of Group 14 Elements

The general oxidation states exhibited by the group 14 elements are +4, and +2.

As we go down the group, the tendency to form +2 ion increases. This is due to inert pair effect. This effect is exhibited by p-block elements.

This can be explained using the inert pair effect. It is the non-participation of the s-orbital during bonding due to the poor shielding of the intervening electrons.

For elements like Sn and Pb, d and f orbitals are filled with electrons. Since the shielding ability of d and f orbitals are very poor, the nuclear charge that seeps through attracts the s orbital closer to the nucleus. This makes the s orbital reluctant to bond, thereby only the p electrons involved in bonding.

Therefore, Pb<sup>4+</sup> is a very good oxidizing agent.

## Anomalous Behaviour of Carbon

Carbon exhibits different behaviour from the rest of the group due to,

- Small Size
- High Electronegativity
- High Ionization Enthalpy
- Absence of d-orbital in the Valance Shell

### Chemical Properties of Group 14 Elements

### **Covalent Radii**

The radii of group 14 elements are lesser than that of group 13 elements. This can be explained by the increase in the effective nuclear charge.

The increase in the radii from C to Si is considerable, after which the increase in the radii is less. This can be attributed to the poor shielding of d and f orbitals, which increase the effective nuclear charge, thereby making the radii small.

### **Ionization Enthalpy**

The ionization energy of group 14 elements is greater than that of <u>group 13 elements</u>. This can be attributed to size.

Down the group, the Ionization Enthalpy decreases. There is a sharp decrease from C to Si, after which the decrease is nominal.

The order is as follows, C > Si > Ge > Pb >Sn

Here Pb has a greater Ionization Enthalpy than Sn due to ineffective shielding of d and f orbitals.

## **Physical Properties:**

#### **Metallic Character**

Group 14 elements are less electropositive than group 13 owing to their small size and high ionization enthalpy.

Down the group, the metallic character increases. C and Si are non-metals, Ge a metalloid, and Sn and Pb are soft metals with low melting points.

### **Melting and Boiling Points**

The melting and boiling point of carbon, silicon, and germanium is significantly high because they have a very stable solid structure. Sn and Pb have a lower melting point because only two bonds are formed instead of four, due to inert pair effect.

The <u>melting point of carbon</u> is extremely high. All the elements of group-14 possess diamond-type lattice structure which is highly stable in nature. The process of melting results in the breakage of these highly stable lattice structures.

Down the group, the melting point decreases as the M-M bonds are reduced as the size of the atoms increases. Since, Tin and lead are metals therefore, the melting points of these elements are much lower.

#### Four Covalent Compounds:

Four covalent compounds are compounds in which the four <u>electrons in the valence shell</u> play an active role in bonding. Most of the group 14 element possesses this property.

## Compounds formed by Group 14 Elements

### Hydrides of Group 14:

All the elements of group 14 form hydrides. Carbon forms hydrides extensively due to their ability to catenate. The hydrides of carbon are categorized as below

- Alkanes (paraffin's): General formula: C<sub>n</sub>H<sub>2n+2</sub>
- Alkenes (olefins): General formula: CnH2n
- Alkynes (Acetylenes): General formula: C<sub>n</sub>H<sub>2n-2</sub>
- Aromatic compounds
- Silicon forms hydrides having the general formula Si<sub>n</sub>H<sub>2n+2</sub> and are called silanes.
- Germanium forms hydrides of the form  $Ge_nH_{2n+2}$ , where  $n_{max}=5$  and are called germanes.
- Tin forms SnH<sub>4</sub> and are called stannane. It is much less stable.

#### **Oxides of Group 14:**

Group 14 elements form oxides of the type MO and  $MO_2$ . Lead also form an oxide  $Pb_3O_4$  which is a mixed oxide of PbO and PbO<sub>2</sub>. Among the monoxides, CO is neutral, GeO is basic while SnO and PbO are amphoteric.

In CO<sub>2</sub>, C is <u>sp hybridized</u>. It is different from SiO<sub>2</sub> in which Si is sp<sup>3</sup> hybridized. In SiO<sub>2</sub>, each O atom is bonded to two Si bonds. This gives rise to a three-dimensional structure for SiO<sub>2</sub>. This also attests to the high melting point of SiO<sub>2</sub>.

Among the dioxides, the acidic character decreases down the group.  $CO_2$  is the most acidic and  $PbO_2$  being the most basic among the dioxides.

#### Halides of Group 14:

They form tetrahalides of the form MX4. The central atom is sp<sup>3</sup> hybridized and assumes a tetrahedral shape.

**Note:** Elements below C, have empty d-orbitals, with which they can exhibit back bonding with the halogens ( $p\pi$ -d $\pi$ )

Carbon does not form dihalides. The dihalides are sp<sup>2</sup> hybridized and have a bent shape.

The phenomenon by which an element can exist in more than one physical state is called allotropy. **The allotropes of carbon can be categorized into two:** 

- Amorphous Carbon Allotropes
- Crystalline Carbon Allotropes

### What are Allotropes of Carbon?

Carbon with atomic number 6 and represented by the symbol **'C'** in the periodic table is one of the most influential elements we see around us. Carbon is one of the elements which shows allotropy. The allotropes of carbon can be either amorphous or crystalline (Diamond, Graphite).

#### **Table of Content**

- <u>All Carbon Allotropes</u>
- <u>Graphite</u>
- Diamond
- Other Carbon Allotropes
- <u>Silicates</u>

Carbon due to its capability of having variable oxidation states or <u>coordination number</u> makes carbon one of the few elements to have multiple numbers of allotropic forms. Carbon's ability to catenate is another contributing factor. Thus, it leads to the formation of various allotropes of carbon.

### How many Carbon Allotropes are there?

- Diamond: It is extremely hard, transparent crystal, with the carbon atoms arranged in a tetrahedral lattice. This allotrope of carbon is a poor electrical conductor and an excellent thermal conductor.
- Lonsdaleite: These are also called hexagonal diamond.
- Graphene: It is the basic structural element of other allotropes, nanotubes, charcoal, and fullerenes.
- Q-carbon: These carbon allotropes are <u>ferromagnetic</u>, tough, and brilliant crystal structure that is harder and brighter than diamonds.
- Graphite: It is a soft, black, flaky solid, a moderate electrical conductor. The C atoms are bonded in flat hexagonal lattices (graphene), which are then layered in sheets.
- Linear acetylenic carbon (Carbyne)
- Amorphous carbon
- Fullerenes, including Buckminsterfullerene, also known as "buckyballs", such as C60.
- Carbon nanotubes: Allotropes of carbon with a cylindrical nanostructure.

Let us now take a look into the more widely known allotropes of carbon:

### Graphite

It is also a pure form of carbon. This allotrope of carbon is composed of flat two-dimensional layers of carbon atoms which are arranged hexagonally. It is a soft, black and slippery solid. This property of graphite persists because it cleaves easily between the layers.

In each layer, each C atom is linked to three C atoms via a C-C covalent bond. Each carbon here is sp2 hybridized. The fourth bond is formed as a <u>pi bond</u>. Since the  $\pi$ -electrons are delocalized, they are mobile and can conduct electricity.

#### Graphite is of two forms: $\alpha$ and $\beta$ .

In  $\alpha$  form, the layers are arranged in the sequence of ABAB with the third layer exactly above the first layer.

In the ß form, the layers are arranged as ABCABC.

#### **Properties of Graphite:**

- Since the layers are stacked over each other, this carbon allotrope can act as a lubricant.
- It also has metallic lustre which helps in the conduction of electricity. It is a very good conductor of both heat and electricity
- One of the most important properties of graphite is that it is used as a dry lubricant for machines at high temperature where we cannot use oil.
- Graphite is used to make crucibles which have the property that they are inert to dilute acids as well as to alkalis.

Note: In comparison to diamond, Graphite is thermodynamically more stable.

#### Structure of Carbon Allotrope (Graphite):

Graphite has a unique honeycomb layered structure. Each layer is composed of planar hexagonal rings of carbon atoms in which carbon-carbon <u>bond length</u> within the layer is 141.5 picometers.



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#### **Graphite Structure – Allotropes of Carbon**

#### Diamond

It is the purest crystalline allotrope of carbon. It has a number of carbons, linked together tetrahedrally. Each tetrahedral unit consists of carbon bonded to four carbon atoms which are in turn bonded to other carbons. This gives rise to an allotrope of carbon having a three-dimensional arrangement of C-atoms.

Each carbon is sp3 hybridized and forms covalent bonds with four other carbon atoms at the corners of the tetrahedral structure.

Out of four carbon atoms three forms sigma bonds whereas the fourth carbon forms pi-bond. The layers in graphite are held together by Vander Waal forces.





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Structure of Diamond

#### Do you know why a Diamond is Hard?

It is hard because breaking a diamond crystal involves rupturing many <u>strong covalent bonds</u>. Breaking covalent bonds is no easy task. This property makes this carbon allotrope the hardest element on earth.

#### **Physical Properties of Diamond**

- It is extremely hard
- It has a very high melting point
- It has a high relative density
- It is transparent to X-rays
- It has a high value of the refractive index
- It is a bad conductor of electricity
- It is a good conductor of heat
- It is insoluble in all solvents

## Other Carbon Allotropes

#### **Buckminsterfullerene**

Buckminsterfullerene (C60) is also one of the allotropes of carbon. The structure of fullerene is like in a cage shape due to which it looks like a football.

#### **Fullerenes**

They are spheroidal molecules having the composition, C2n, where  $n \ge 30$ . These carbon allotropes can be prepared by evaporating graphite with a laser.

Unlike diamond, fullerenes dissolve in <u>organic solvents</u>. The fullerene C60 is called 'Buckminster Fullerene'. The carbon atoms are sp2 hybridized.

Note: There are 12 five-membered rings and 20 six-membered rings in C60.

#### **Silicates**

Fusing alkali oxides with SiO2 gives silicates. They contain discrete tetrahedral units. Silicon is <u>sp3</u> <u>hybridized</u>. These allotropes of carbon are classified based on their structures.

1. Orthosilicates: They contain discrete SiO4 units. For example, Willemite (ZrSiO4).

**2. Pyrosilicate:** Two units are linked together via an oxygen atom. The simplest ion of this type is Si2O76-. For example, Thortveite (Sc2[Si2O7]).

**3. Cyclic Silicates:** The units share two oxygen atoms. Only two ions are known as of now, Si3O96and Si6O1812-. For example, Beryl – Be3Al2Si6O18.

**4. Chain Silicates:** The linking of the units linearly results in the formation of chain silicates. They are of two types:

- **Metasilicates:** Each tetrahedral unit shares two oxygen atoms to form a single chain carbon allotrope. For example, Spodumene NaAl(SiO3)2.
- **Amphiboles:** When two linear chains are linked together, it results in amphiboles carbon allotrope. The parallel chains are held by sharing the <u>oxygen atoms</u>. For example, Asbestos: CaMg3O(Si4O11).

**5. Two-dimensional silicates:** Sharing of three oxygen atoms results in the formation of a two-dimensional silicate. For example, mica.

**6. Three-dimensional silicate:** When all the oxygen atoms are shared, it results in a threedimensional network. For example, Zeolites.

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