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B. Sc. Chemistry Semester-1
C-101 Chapter 2

Chemistry Of s And p Block elements

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Semester-1 – Chapter 2

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❖ **Contents**

Sr. No.	Topic	Page No.
1	Introduction	1
2	s-block elements	2
3	Ionization Enthalpy and Hydration Enthalpy of alkali metals	5
4	P-block elements	7
5	Diagonal Relationship	10
6	Anomalous Behavior	15
7	Formation of complex	17
8	Catenation (Self Linkage)	20
9	Allotropes of carbon	21



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B. Sc. Chemistry (CBCS) C-101

Semester-1 – Chapter 2

Chemistry Of s And p Block elements

CHEMISTRY OF s AND p BLOCK ELEMENTS

❖ Introduction:

The periodic table is an arrangement of all the elements known to man in accordance with their increasing atomic number and recurring chemical properties. They are assorted in a tabular arrangement wherein a row is a period and a column is a group. Elements are arranged from left to right and top to bottom in the order of their increasing atomic numbers. Thus,

- Elements in the same group will have the same valence electron configuration and hence, similar chemical properties.
- Whereas, elements in the same period will have an increasing order of valence electrons. Therefore, as the energy level of the atom increases, the number of energy sub-levels per energy level increases.

The first 94 elements of the periodic table are naturally occurring, while the rest from 95 to 118 have only been synthesized in laboratories or nuclear reactors. The modern periodic table, the one we use now, is a new and improved version of certain models put forth by scientists in the 19th and 20th century. Dimitri Mendeleev put forward his periodic table based on the findings of some scientists before him like John Newlands and Antoine-Laurent de Lavoisier. However, Mendeleev is given sole credit for his development of the periodic table.

Chemistry is basically related with the study of elements. These elements are classified in some categories and the two most important categories of the elements are known as representative elements.

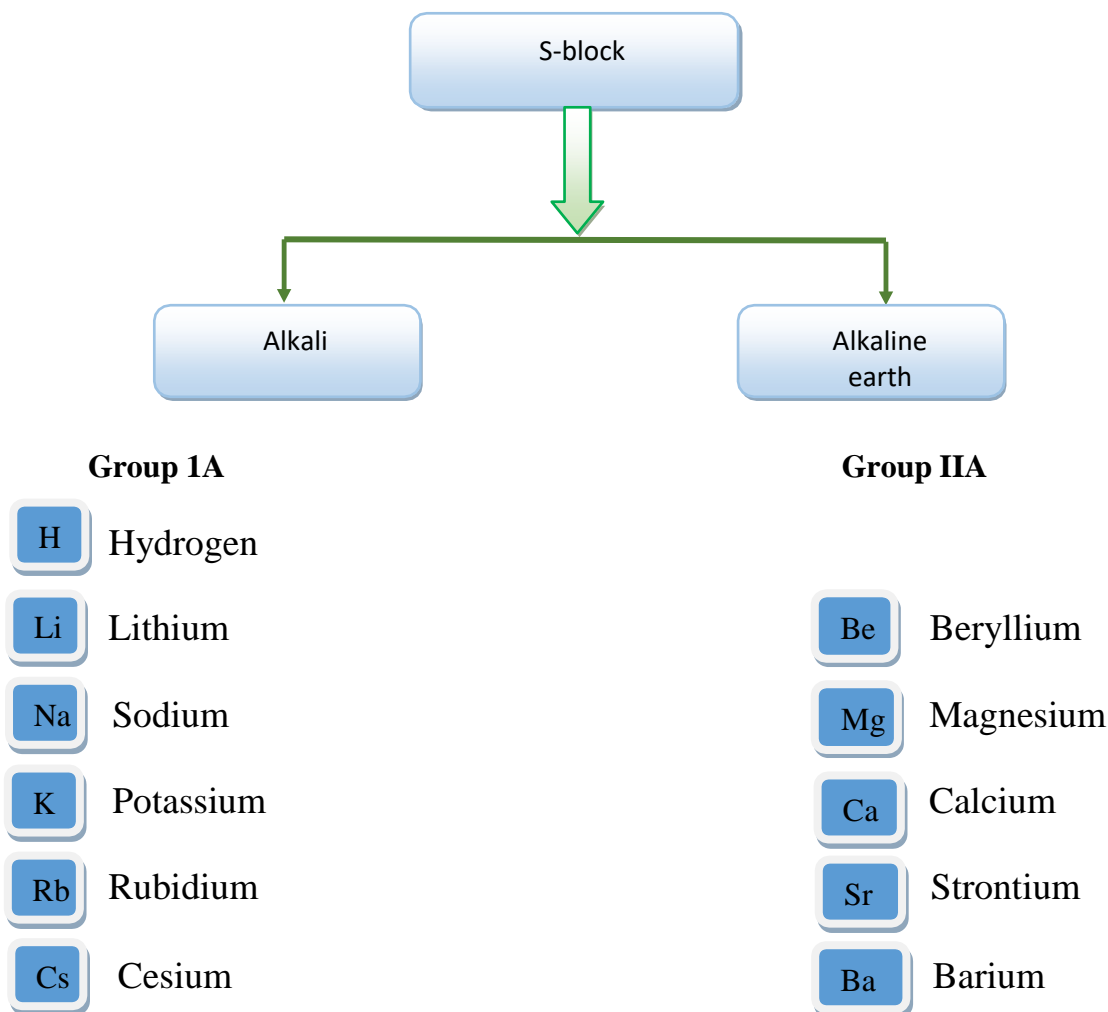
Representative elements of the periodic table include s and p block elements. s-block elements include the elements of group 1 and group 2 of the periodic table while p – block elements include the elements of group 13, 14, 15, 16, 17 and 18.

s- block elements are all metals on the other hand p- block elements are mainly non-metals but they include some metalloids and metals also.

The s and p block elements have a great role in chemistry and also our life. As we will study the properties of all these one by one in this chapter will be able to know about the great importance and applications of these elements.

s-block		p-block					
1	2	13	14	15	16	17	18
3 Li 2s ¹	4 Be 2s ²	5 B 2s ² 2p ¹	6 C 2s ² 2p ²	7 N 2s ² 2p ³	8 O 2s ² 2p ⁴	9 F 2s ² 2p ⁵	10 Ne 2s ² 2p ⁶
11 Na 3s ¹	12 Mg 3s ²	13 Al 3s ² 3p ¹	14 Si 3s ² 3p ²	15 P 3s ² 3p ³	16 S 3s ² 3p ⁴	17 Cl 3s ² 3p ⁵	18 Ar 3s ² 3p ⁶
19 K 4s ¹	20 Ca 4s ²	31 Ga 4s ² 4p ¹	32 Ge 4s ² 4p ²	33 As 4s ² 4p ³	34 Se 4s ² 4p ⁴	35 Br 4s ² 4p ⁵	36 Kr 4s ² 4p ⁶
37 Rb 5s ¹	38 Sr 5s ²	49 In 5s ² 5p ¹	50 Sn 5s ² 5p ²	51 Sb 5s ² 5p ³	52 Te 5s ² 5p ⁴	53 I 5s ² 5p ⁵	54 Xe 5s ² 5p ⁶
55 Cs 6s ¹	56 Ba 6s ²	81 Tl 6s ² 6p ¹	82 Pb 6s ² 6p ²	83 Bi 6s ² 6p ³	84 Po 6s ² 6p ⁴	85 At 6s ² 6p ⁵	86 Rn 6s ² 6p ⁶
87 Fr 7s ¹	88 Ra 7s ²						

Representative Elements



❖ s-block elements:

- ✓ The elements in which the last electrons enter into the outer most orbitals 's' are known as s-block elements.
- ✓ The elements of group-1 and 2 in periodic table are known as s-block elements respectively.
- ✓ Because the outermost electrons occupies the s-orbital.
- ✓ General electronic configuration of s-block elements is ns^{1-2} .
- ✓ Group-1 elements are known as alkali metals.
- ✓ Group-2 elements are known as alkaline earth metals.
- ✓ They all are good conductors of electricity, typically soft, highly reactive, ionic characteristics and colourless compounds.
- ✓ Reactivity increases down the group.
- ✓ They all have lower ionization enthalpies.
- ✓ They all are electro-positive elements.
- ✓ They have lower oxidizing power and highly reducing elements. Note: Na, K like elements is kept in the kerosene.
- ✓ Oxides and hydroxides of alkali metals and alkaline earth metals are strong bases. Salts of group-1 & 2 are very stable.



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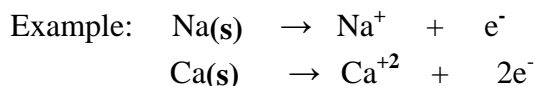
Semester-1 – Chapter 2

Chemistry Of s And p Block elements

❖ Special characteristics of s-block elements:

Metallic character:

- Due to electro-positive nature of group-1 & 2 elements show their metallic character.
- They have tendency to lose one or two electrons from their outermost shell and form their cations.



- Metallic character increases from Lithium to Francium in alkali metals while it also increases from beryllium to Radium.
- Metallic characteristics of alkali metals are greater than the alkaline earth metals. So, in the alkaline earth metals have greater tendency to attract electrons more powerfully by nucleus, thus it is difficult to remove an electron from the valence.

Polarising power:

- In alkali and alkaline earth metals, smaller atomic size \rightarrow more polarizing power \rightarrow have tendency to form more covalent compound.
- The charge on cation is same for s-block elements and anion is common, then polarizing power is decreasing down the group.

Example: $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$

Larger the anion feel greater polarisability down the group
Example: $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$

Polarizing power:

- In the formation of ionic molecule, when two opposite charged ions come closer to each other, the cation attracts the electron charge cloud of the outer most shell of the anion towards itself. Hence the symmetrical shape of the anion gets distorted (polarized or deformed).
- The phenomenon in which the symmetrical shape of the anion gets deformed by the approach of the cations closer to it is called polarization or deformation of the anion.
- The ability of a cation to polarize an anion is called its polarizing power or polarizing ability.
- It may be noted that it is not only the anion gets distorted (or polarized), cation also polarized by anion. But due to smaller size of the cation, it's attracted much toward the anion. Therefore, generally don't consider the polarization of cation.

“The tendency of an anion to get distorted by a cation is known as polarisability of anion and polarizing power of cation.”

Factors affects on polarizing power:

1. Size of anion:

Larger the size of anion \rightarrow more strongly polarized by cation \rightarrow increase in covalent character

2. Size of cation :

Smaller the size of cation \rightarrow Greater its polarization power \rightarrow greater covalent character produced in ionic molecule.

3. Charge of ions :

Higher positive charge on the cation \rightarrow higher polarization power \rightarrow greater covalent character produce in ionic molecule

Higher charges on anion \rightarrow more strongly polarized by cation \rightarrow produce greater covalent character

4. Electronic configuration:

If two cations having same charge and same size \rightarrow cation having $ns^2p^6d^{1-10}$



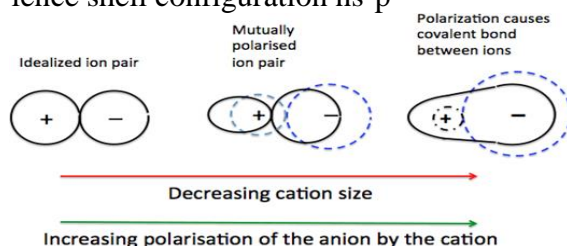
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Semester-1 – Chapter 2

Chemistry Of s And p Block elements

as its valence shell configuration will greater polarize the anion than cation having valence shell configuration ns^2p^{1-6}



❖ Questions (1 Marks) :

1. What are s- block elements?

S-block elements are those in which the last electron enters the outermost s-orbital.

2. Name the elements present in the 1st Group of the Periodic Table

lithium, sodium, potassium, rubidium, cesium and francium. They are collectively known as the alkali metals.

3. Why I group elements are called alkali metals?

Because they form hydroxides on reaction with water which are strongly alkaline in nature.

4. Name the elements present in the 2nd Group of the Periodic Table:

beryllium, magnesium, calcium, strontium, barium and radium

5. Why II group elements are called alkaline earth metals?

Because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust.

6. Which is smaller in size between a metal ion and its parent atom?

The monovalent ions (M^+) are smaller than the parent atom.

7. Which group elements show very low ionization enthalpy in the periodic table?

First group elements (alkali metals)

8. How the ionization enthalpy varies in alkali metals

Ionization enthalpy decrease down the group from Li to Cs.

9. why Li salts are hydrated?

Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated, e.g., $LiCl \cdot 2H_2O$

10. Write the chemical composition of washing soda.

$Na_2CO_3 \cdot 10H_2O$

11. Why do alkali show low density?

Due to weak metallic bond and larger atomic size

12. Why is the first ionization enthalpy of alkali metals lower than those of alkaline earth metals?

Due to large in atomic size in alkali metals.

13. Alkali metals are generally strong reducing agents. Why?

Because they have large atomic size and hence tendency to lose valence electron easily.

14. Give reason for the higher melting point and boiling point of alkali earth metals than alkali metals.

The melting and boiling points of these metals are higher than the corresponding alkali metals due to smaller sizes.

15. Give reason .the compounds of alkaline earth metals are less ionic than alkali metals

This is due to increased nuclear charge and smaller size.



❖ Ionization Enthalpy and Hydration Enthalpy of alkali metals

- Ionization energy is the quantity of energy required to remove loosely bound electron from an atom.
- Down the group ionization enthalpies of alkali metals decreases.
- Increase in atomic number increases the size of the element which in turn outweighs increasing nuclear charge. Therefore the outermost electron experiences strong screening effect from the nuclear charge.
- The energy released as a result of the formation of new bonds between ions and water molecules is called **hydration enthalpy**.
- In alkali metals the **hydration enthalpies decreases with the increase in ionic sizes**.
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$

❖ Ionization Enthalpy of alkaline earth metal

- Ionization energy is the quantity of energy required to remove loosely bound electron from an atom.
- They have low ionization enthalpies due to fairly large size of the atoms.
- Ionization enthalpy decreases with the increase in atomic size down the group.
- The first ionization enthalpy of these metals is higher than corresponding alkali metals due to the small size of these elements compared to the corresponding alkali metals.
- The second ionization enthalpy of these metals is lower than corresponding alkali metals.

❖ Hydration Energy:

- When a gaseous cations or anion reacts with a solvent (liquid state), solvent molecule always surround a metal ion in solution. This phenomenon is referred as solvation process. In this reaction energy is liberated, it is known as solvation energy. Due to liberation of energy, solvation process is exothermic reaction.
- If solvent is water, then the solvation process is called Hydration. In hydration, hydrated cations or anion is produced.
- In hydration, energy is released, it is known as hydration energy. It is an exothermic process.

❖ Hydration energy value of s-block elements

Group – 1	Hydration energy	Group - 2	Hydration energy
Li+	-531	Be++	-2494
Na+	-422	Mg++	-1954
K+	-339	Ca++	-1577
Rb+	-319	Sr++	-1443
Cs+	-280	Ba++	-1352

❖ Oxidation state of s-block elements:

1. Oxidation state of group-1 elements:

- Elements of group-1 shows an oxidation state of +1, in all their ionic compounds. This oxidation state is equal to their group number or equal to the electrons in s orbital of their valence shell.

2. Oxidation state of group-2 elements:



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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

- All the elements of their groups show +2 oxidation state, in all their ionic compounds. This is equal to their group number and outer shell ns-electrons.
- Electronic configuration of this M⁺² ion is same as Noble group configuration so that they are very stable.

I(A)	II(A)
H ⁺	
Li ⁺	Be ⁺⁺
Na ⁺	Mg ⁺⁺
K ⁺	Ca ⁺⁺
Rb ⁺	Sr ⁺⁺
Cs ⁺	Ba ⁺⁺

❖ **Inert pair effect and relative stability of different oxidation state:**

Group 13 ns ² np ¹	Group 14 ns ² np ²	Group 15 ns ² np ³
B = +3	C = +4	N = +3
Al = +3	Si = +4	P = +3,+5
Ga = +3,+1	Ge = +4,+2	As = +3,+5
In = +3,+1	Sn = +4,+2	Sb = +3,+5
Tl = +3,+1	Pb = +4,+2	Bi = +3,+5

❖ **Oxidation state of group 13,14 and 15m p block elements**

- From the above data, we can get the conclusion that in every groups, elements with higher atomic number show two types of oxidation states, which are given below.

1. **Higher oxidation states (Group oxidation states):**

These are equal to the group number and electron present in valence shell electrons, represents as 'G'. These oxidation number obtained when all the elements in valence shell are involved in bond formation.

2. **Lower oxidation states:**

These are equal to group oxidation states minus two (G-2). These may be obtained only when the valence shell's electrons of p-orbitals are involved in bond formation and electron pair of s-orbitals of valence shell don't participate in bond formation.

“In heavy elements, the un-willingness to participate in bond formation of ns² electron pair of valence shell is called inert pair effect”



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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2

Chemistry Of s And p Block elements

❖ P-block elements:

- The *general electronic configuration of p-block elements is $ns^2 np^{1-6}$ (except He)*. Whereas the inner core electronic configuration may differ. Just because of this difference the inner core, there are changes in both physical and chemical properties of the elements.
- The oxidation state of elements in p – block is maximum when it is equal to a total number of valence electrons i.e. the sum of S and P electrons. One of the most interesting facts about the p-block elements is that it contains both non-metals and metalloids.
- P block elements are shiny.
- They usually good conductor of electricity and heat as they have a tendency to lose an electron.
- We can find some amazing properties of elements in a P-block element like gallium (Ga). It's a metal that can melt in the palm of your hand.
- Silicon (Si) is also one of the most important metalloids of the p-block group as it is an important component of glass.
- There are six groups of p-block elements in the periodic table numbering from **13 to 18**.

P - BLOCK ELEMENTS						
Groups →	13	14	15	16	17	18
	5 B	6 C	7 N	8 O	9 F	10 Ne
	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

Metallic character:

p- block elements contain of both metals and non-metals.

Group 13: Boron family: Except Boron (B), all the elements are metals.

B, Al, Ga, In, Tl

Group 14: carbon family : Carbon is a non-metal. Si and Ge are metalloids. While Sn and Pb are metals.

C, Si, Ge, Sn, Pb

Group 15: Nitrogen family: N and P are non-metals. As and Sb are metalloids. While Bi is a metal.

N, P, As, Sb, Bi

Group 16: Oxygen family: O and S are non-metals. Se and Te are metalloids. While Po is a metal.

O, S, Se, Te, Po

Note: Generally, the p-block elements in the upper right side of the periodic table, having strong non-metallic character. While those in the lower left side of the periodic table having strong metallic characters to be found.



❖ **Polarizing power:**

- In group 13, halides of B and Al are more covalent than the halides of other elements of the group.
- In group 17, bromides and iodides are more covalent than fluoride and chlorides because bromide and iodides may form positive radical and Cl and F forms only negative radicals.

❖ **Hydration energy:**

- In periodic table, along the period, size of elements decrease with increase in atomic number. Therefore, from moving left to right (Li to F), group number is increased and the value of hydration energy is increased in electropositive group, then value of hydration energy is decreased in electronegative group.
- Therefore, the value of hydration energy of halogen group elements is low, comparatively to s-block elements.

Group 17	Hydration energy
F	515
Cl	381
Br	347
I	305

❖ **Relative stability of different oxidation state:**

Group 13 IIIA	Group 14 IVA	Group 15 VA	Group 16 VIA	Group 17 VIIA
B +3	C +4	N -3,-2,-,0,1,2,3	O -1,-2,+2	F -1
Al +3	Si +4	P -3,+3,+4,+5	S - 2,+2,+4,+6	Cl - 1,+1,+3,+4,+5, +6,+7
Ga +1,+3	Ge +2,+4	As -3,+3,+5	Se - 2,+2,+4,+6	Br - 1,+1,+3,+4,+5, +6,+7
In +1,+3	Sn +2,+4	Sb -3,+3,+5	Te - 2,+2,+4,+6	I - 1,+1,+2,+3,+4, +5,+6,+7
Tl +1,+3	Pb +2,+4	Sb +3,+5	Po +2,+4	

3. Oxidation state of group IIIA (13):

B and Al shows +3 oxidation state. While Ga, In and Tl shows +3 and +1 oxidation state because of inert pair effect they prefer lower oxidation state as +1 in down to order in the group.



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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

4. Oxidation state of group IVA (14):

C and Si shows +4 oxidation state. While Ge, Sn and Pb shows +4 and +2 oxidation state because of inert pair effect.

5. Oxidation state of group VA (15):

In this group, N shows -1 to +5 oxidation state.

P shows -3,+3,+5

As and Sb shows -3,+3,+5

Bi shows +3,+5

6. Oxidation state of group VIA (16):

Oxidation state of O -1,-2

Oxidation state of S, Se and

Te -2,+2,+4,+6

Oxidation state of Po +2,+4

7. Oxidation state of group VIIA (17):

General oxidation state of this group is -1 because the elements of these group have tendency to gain one electron to form noble gas like electronic configuration.

Although except F, the other elements show +1,+3,+4,+5,+6,+7 oxidation state in some compounds.

❖ Questions :(1 marks)

1. Bond angle in NH_4 is greater than that in NH_3 .

NH_3 has lone pair of electron, so, bond angle is 107° , whereas NH_4 does not, therefore, bond angle is 109.5°

2. NH_3 has a higher boiling point than PH_3 .

NH_3 has a higher boiling point than PH_3 .

3. Fluorine is a stronger oxidising agent than chlorine Why?

It is due to low bond dissociation enthalpy, higher hydration energy of F^- and high electron gain enthalpy.

4. N_2 is less reactive at room temperature.

It is due to presence of triple bond which has high bond dissociation enthalpy.

5. TiCl_3 is highly stable than BCl_3 why?

On moving down the group the stability from B to Tl of lower oxidation state increases

6. BF_3 is weaker Lewis acid than BCl_3 why?

Due to more effective back bonding in case of F due to smaller size than Cl

7. Halogens are coloured why?

It is because they absorb light from visible region and radiate complementary colour.

8. F_2 is a stronger oxidising agent than Cl_2 .

It is because F_2 has highest standard reduction potential, higher than Cl_2 .

9. The tendency of BF_3 , BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence

$\text{Br}_3 > \text{BCl}_3 > \text{BF}_3$

10. What is the maximum covalence shown by N?

+4

11. Bi (v) is a stronger oxidizing agent than Bi(III) Why?

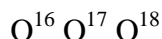
Due to inert pair effect therefore Bi (v) has a strong tendency to act as oxidizing agent.



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Semester-1 – Chapter 2
Chemistry Of s And p Block elements

12. Write different isotopes of oxygen.



13. How does metallic character vary down the 15 group & why?

Due to decrease in ionization enthalpy and increase in size of atom.

14. The only possible oxidation state of fluorine -1 Why?

It is most electronegative element and it has short of only one electron for completing octet.

15. Two uses of chlorine

Bleaching wood pulp, cotton and textiles sterilizing drinking water

Questions: (3 marks)

1. Write a note on metallic character of s-block elements.
2. Write a note on polarizing power of s and p block elements. block elements

Long Questions :(5 Marks)

1. Write a note on polarization power
2. Write a note on Hydration energy
3. Write a note on inert pair effect
4. Explain in brief: factors effect on polarizing power

❖ Diagonal Relationship:

- A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table.
- Diagonal relationships occur because of the directions in the trends of various properties as you move across or down the periodic table. Many of the chemical properties of an element are related to the size of the atom.
- These pairs (lithium (Li) and magnesium (Mg), beryllium (Be) and aluminum (Al), boron (B) and silicon (Si) etc.) exhibit similar properties; for example, boron and silicon are both semiconductors, forming halides that are hydrolyzed in water and have acidic oxides.
- The relationship arises due to the effect of size and charge. In a group, from top to bottom size of atom and ions increase, while in a period, from left to right it is decrease but diagonally remains same.

❖ Diagonal relationship between Li and Mg:

main group

	1	2	13	14	15
period 2	Li	Be	B	C	N
period 3	Na	Mg	Al	Si	P

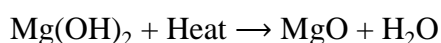
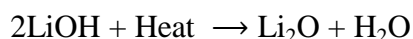
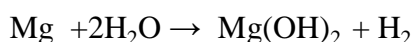
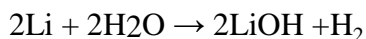


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Semester-1 – Chapter 2
Chemistry Of s And p Block elements

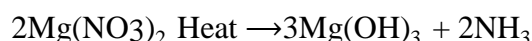
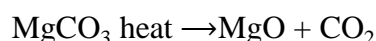
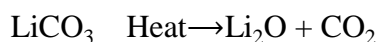
❖ **Following points justify the similarities between Li and Mg:**

1. Li and Mg both are hard metals and having less metallic character.
2. They have nearly same polarizing power.
3. Both the metals can be melted in dry air without losing their brittleness.
4. **Reaction with water:** Both the metals slowly react with water to form metallic hydroxide and hydrogen gas. On decomposing the weak metallic hydroxide on heating to give metal oxide and water.



5. **Oxides:** Li and Mg both form normal oxides on heating with oxygen or air. They both the oxides are sparingly soluble in water.

6. **Carbonates and Nitrates:**



7. **Nitrides:**

Both the metals can combine with nitrogen on heating and form Metal Nitrides. These nitrides are readily hydrolysed to form metal hydroxide and ammonia.

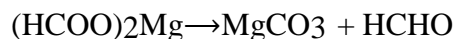
8. **Chloride:**

Li and Mg react with dry Cl_2 and forms metal chlorides. These chlorides are soluble in organic solvent.



9. **Formates:**

Li and Mg formates on heating give carbonates and formaldehydes.



10. Fluorides, carbonates, oxalates and phosphates of both the metals are sparingly soluble in water, while the bicarbonates are freely soluble in water.

❖ **Questions: (1 Marks)**

1. **Reason for diagonal relationship between Li and Mg**

Almost similar atomic size and similar electro negativity

2. **Li metal reacts with water to form....**

LiOH and H_2 gas

3. **Polarization power of Li is similar with which element?**

Mg

4. **On heating, LiOH is converted into**

Li_2O

5. **On decomposition of Li_2CO_3 it gives....**

Li_2O and CO_2

6. **Complete the reaction $\text{Li} + \text{N}_2 \rightarrow$**



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B. Sc. Chemistry (CBCS) C-101

Semester-1 – Chapter 2

Chemistry Of s And p Block elements

Li_3N (Lithium Nitride)

7. Complete the reaction $\text{Mg} + \text{N}_2$

Mg_3N_2 (Magnesium Nitride)

8. Complete the reaction $\text{LiNO}_3 + \text{Heat} \rightarrow$

$\text{Li}_2\text{O} + \text{NO}_2 + \text{H}_2\text{O}$

9. On heating Lithium formate, it give.....

Lithium carbonate and Formaldehyde $\text{HCOOLi} + \text{Heat} \rightarrow \text{Li}_2\text{CO}_3 + \text{HCHO}$

10. Magnesium Nitride reacts with water to form

Magnesium Hydroxide and ammonia $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{NH}_3$

❖ Diagonal relationship between Li and Mg:

Diagonal relationship Be and Al

↓

Due to same atomic and ionic radii $\text{Be} = 125\text{pm}$ $\text{Al} = 130$

pm

$\text{Be}^{+2} = 59\text{pm}$ $\text{Al}^{+3} = 67.5\text{pm}$

↓

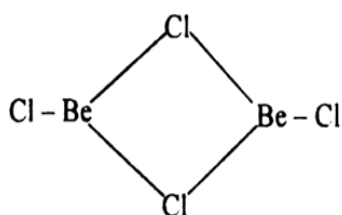
Similar value of electronegativity $\text{Be} = 1.5$ $\text{Al} = 1.5$

❖ Following points justify the similarities between Be and Al:

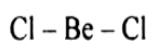
- Both the metals have similar metallic characteristics. Be and Al are hard metals and both having less metallic characteristics.
- Both have strong tendency to form covalent bond.
- In nature Be and Al are found as Beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
- Both the metals can be extracted by electrolytic reduction of oxides.
- The polarizing power of the Be and Al is nearly similar.
- Both the metals react with boiling alkalis to form soluble Beryllate and Aluminate and hydrogen is evolved.
- Both the metals react with nitric acid and form a protective layer of oxide on their surface. This layer makes the metals passive for further action of an acid.
- Both the metal ions have a tendency to combine with ligands and form chelate complexes.
- Both metals combine with halogen and give halide. These anhydrous halides are covalent in nature and dissolves in organic solvent.

$\text{Be} + \text{Cl}_2 \rightarrow \text{BeCl}_2$ (These metallic halides behave as Lewis acid) $\text{Al} + \text{Cl}_2 \rightarrow \text{AlCl}_3$

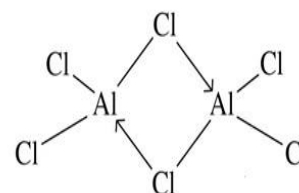
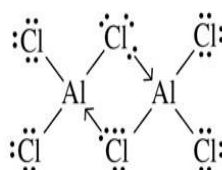
10. Beryllium chloride and aluminum chloride have dimeric structure.



Dimer



Monomer

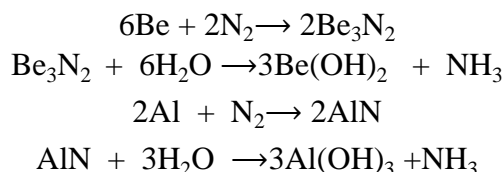




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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

11. Both metals combine with N_2 and form their nitrides. These nitrides are decomposed by water and forms metallic hydroxide and ammonia gas is evolved.



12. Be and Al forms carbides with carbon and these carbides decomposed by water to form methane.



❖ **Diagonal Relationship between B and Si:**

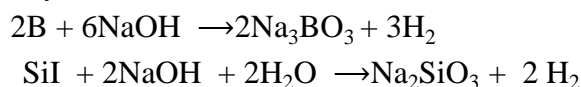
Diagonal relationship B and Si

↓
Due to same ionic potential $B^{+3} = 0.073$ $Si^{+4} = 0.074$

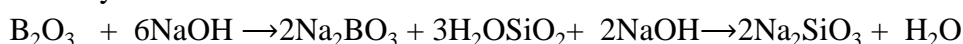
↓
Same ionic radii $B^{+3} = 41\text{pm}$ $Si^{+4} = 54\text{pm}$

↓
Similar value of electronegativity $B = 2.0$ $Si = 1.8$

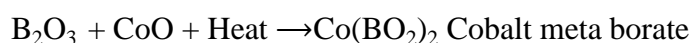
1. Both the metals are attacked by fused alkali to form Borate and meta silicate.



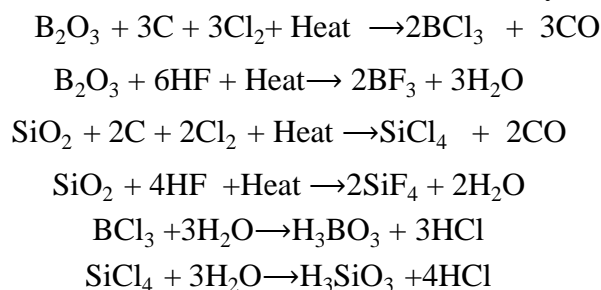
2. Both the metals heat strongly with air and forms oxides. These oxides are acidic in nature and they react with alkali to form the salt.



3. Oxide of both the metals combines with metallic oxides with heating forms meta-borate and Meta silicates.

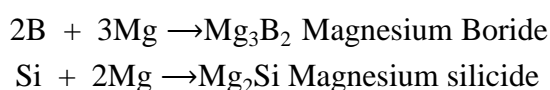


4. Halides of both the elements form similar method. Halides are hydrolysed by water.



Silicic acid

5. Both the elements combine with metals and forms Borides and Silicides.





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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

6. Formation of boranes and silanes:

Both the elements B and Si form hydrides which are known as Boranes and Silanes.

B_2H_6 Boro-ethane, Si_2H_6 Silico-ethane, B_4H_{10} Boro-butane, Si_4H_{10} Silico-butane

7. B and Si, both give carbides, when heated with carbon. Carbides are very hard substances.



Boron carbide



Silicon Carbide

❖ **Question (Answer)**

1. Which element has similarity in property with B?

Si

2. Give the chemical formula of Boric acid

H_3BO_3

3. Give the chemical formula of Silicic acid

H_3SiO_3

4. When SiO_2 is heated with carbon and it forms

SiC (Silicon Carbide)

5. When B_2O_3 is heated with Carbon, it forms

B_4C (Boron Carbide)

6. Complete the reaction : $2B + 3Mg \rightarrow$

Mg_3B_2 (Magnesium Boride)

7. Complete the reaction : $Si + Mg \rightarrow$

Mg_2Si (Magnesium Silicide)



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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

❖ **Anomalous Behavior:**

In the p-block elements, the first element in each group differs from the rest of the elements in same groups. This property of the first element with other group element is called *Anomalous behaviour*.

Following factors are responsible for anomalous behaviour of p-block elements.

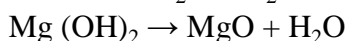
- Small size of the atom and its ion
- The polarizing power of its cation is greatest
- High value of electro-negativity and first ionization energy
- Lack of d-orbitals

a) Anomalous behavior of Lithium:

1. Lithium is much harder and lighter than the other alkali metals. The hardness of lithium is comparable to that of magnesium.
2. Its melting and boiling points are higher than those of the other alkali metals. It can be melted in dry air without its brilliance. The boiling point of lithium (1603 K) is comparable to that of magnesium (1373 K).
3. Due to its high ionization energy, it is the least reactive of all alkali metals towards the various reagents, except nitrogen. Thus
 - (i) Lithium, unlike other alkali metals, is not affected by dry air. Magnesium is also stable in dry air.
 - (ii) Unlike other alkali metals, lithium (like magnesium) decomposes water slowly liberating hydrogen.
 - (iii) It reacts slowly with liquid bromine while other react violently. Magnesium also reacts slowly with liquid bromine.
 - (iv) It forms a stable hydride at 973 — 1073 K while others form less stable hydrides at 673 K. Like lithium hydride, magnesium hydride, MgH_2 is fairly stable.
 - (v) When burnt in oxygen, it forms only monoxide (Li_2O) while other alkali metals form higher oxides (peroxides and superoxide). Magnesium ribbon when burnt in oxygen also forms only the monoxide, MgO
 - (vi) Lithium, like magnesium, does not react with acetylene gas while others react to form metal acetylides.
4. Lithium is the only alkali metal which reacts with nitrogen and silicone to give lithium nitride. Li_3N and lithium silicide respectively. Magnesium also combines readily with nitrogen forming magnesium nitride. Mg_3N_2 .
5. Lithium when heated with ammonia forms imide, Li_2NH , while other alkali metals form amides, MNH_2 .
6. Li^+ and Mg^{2+} ions are strongly hydrated.
7. Lithium and magnesium ions show a tendency to form complexes with ammonia and water (to form hydrates) and also form a large number of organometallic compounds.
8. Lithium and magnesium oxides dissolve in water quietly while the oxides of other alkali metals dissolve in water more energetically.

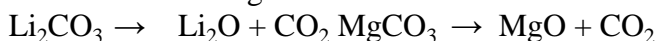


1. Lithium hydroxide is much less soluble and is a much weaker base than the hydroxides of other alkali metal. Lithium hydroxide decomposes at red hot temperatures to Li_2O , while the hydroxides of other sublime, unchanged.

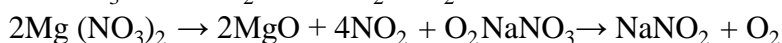
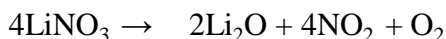


Magnesium hydroxide is also sparingly soluble, less basic and decomposes on heating to form MgO .

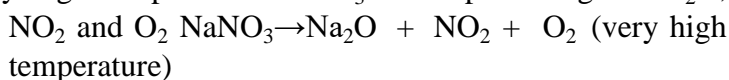
2. Lithium carbonate is not stable to heat while other alkali metal carbonates are very stable towards heat. Magnesium carbonates behave like lithium carbonate.



3. Lithium nitrate, like magnesium nitrate, decomposes on heating giving lithium oxide and nitrogen dioxide; other alkali metal nitrates on heating give nitrites and evolve oxygen.



At very high temperature NaNO_3 decompose to give Na_2O ,



4. Carbonate, phosphate, fluoride and oxalate of lithium (and also magnesium) are sparingly soluble in water while the corresponding sodium and potassium salts are highly soluble in water.

Li_2CO_3 is less soluble than Na_2CO_3 and is used as “**Lithic water**” for treatment of gout.

b) Anomalous behavior of Beryllium:

Beryllium, differs from the rest of the members of its group due to the following reasons

1. Beryllium has a small atomic and ionic size.
2. It has no vacant d-orbitals.
3. It has a high charge density. The points of difference are:

(i) **Hardness** Beryllium is denser and harder than other members of the family.

(ii) **Melting point** Beryllium has high melting point i.e., 1551 K while that of magnesium is 924 K

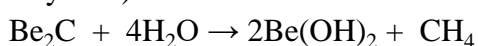
(iii) **Ionization potential** It has higher ionization potential as compared to the rest of the members of this group.

(iv) **Reaction with acids** Due to lower oxidation potential of Be, it does not liberate hydrogen from acids readily.

(v) **Reaction with water** Beryllium does not react with water even at higher temperature while other members of the family liberate hydrogen by reacting with water at room temperature.

(vi) **Amphoteric in character** Oxide (BeO) and hydroxide [$\text{Be}(\text{OH})_2$] of beryllium are amphoteric in character and dissolve in acids to form salt and Beryllate in alkali.

(vii) **Formation of carbides** Beryllium when heated with carbon form Be_2C which on reaction with water gives methane. While other members of the group form ionic carbide MC_2 (acetylides) which on reaction with water evolve acetylene.



(viii) It is less reactive metal of all the alkaline earth metals.

(ix) Beryllium salts are extensively hydrolyzed.



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B. Sc. Chemistry (CBCS) C-101

Semester-1 – Chapter 2

Chemistry Of s And p Block elements

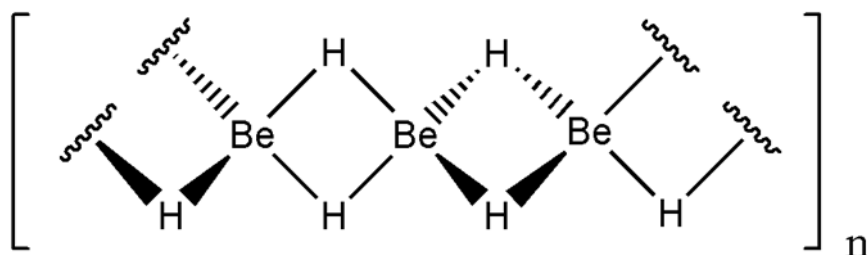
(x) Beryllium does not react directly with hydrogen but other alkaline earth metals react directly with hydrogen to form hydrides.

(xi) Be reacts with HNO_3 and form layer of protective oxide on their surface. This layer makes the metals passive for further action of acid.

(xii) Their oxide and hydroxide are also amphoteric in nature.

Beryllium hydride (BeH_2) is electron deficient and dimeric with multicenter bonding like AlH_3 .

(xiii)



(xiv) Be^+ has greatest polarizing power, so that it has strong tendency to covalence.

Therefore their salts are more soluble in organic solvent. Yet some other salts of alkaline earth metals are insoluble in organic solvents.

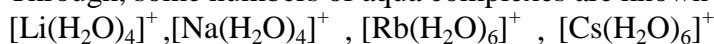
❖ Formation of complex:

The following factors favour the complex formation.

- Small size of metal ion
- High charge
- Empty orbitals of valence shell with low energy for the bond formation with ligand.

s-block elements:

Group-1 alkali metals have less tendency to form complex compound because alkali metals are very large and have a lower charge (+1) and no empty orbitals in valence shell. Through, some numbers of aqua complexes are known such as....



Group-2 All the alkaline earth metals are divalent ions and these are smaller than the group-1 elements.

Be is smaller than the other elements. So, Be can form many complexes. Example: $[\text{BeF}_4]^{-2}$, $[\text{Be}(\text{H}_2\text{O})_4]^{+2}$ and $[\text{Be}(\text{C}_2\text{O}_4)]^{+2}$

- Mg and Ca show much tendency to form complexes in solution and they are generally with oxygen donor ligands.

Example: Ca and Mg ions with EDTA salt and chlorophyll as Mg-complex.

P-block elements:

Group-III A elements form complexes much more readily the s-block elements because smaller in size and higher charge.

Example: LiAlH_4 and $\text{H}[\text{BF}_4]$
Tetrahedral halide and hydride $[\text{GaCl}_6]^{-3}$.



[InCl₆]⁻³ and [TiCl₆]⁻³ octahedral complexes

- Group-IV A elements can form complexes due to smaller atomic size, higher charge and availability of empty d-orbitals. Therefore, except carbon all these group elements form complexes and they generally increase their coordination number from 4 to 6.
Example: [SiF₆]⁻², [SnCl₆]⁻²

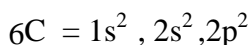
❖ Catenation (Self Linkage):

Catenation can be defined as *the self-linking of atoms of an element to form chains and rings*. This definition can be extended to include the formation of layers like two-dimensional catenation and space lattices like three-dimensional catenation.

Examples: C, Si, S, B

- Catenation, which forms the basis of multiplicity of carbon compounds in organic chemistry.
Reason: The property of catenation in carbon is due to the fact that in carbon atom, the number of valence electrons (4) is equal to the number of valence orbitals.

One 2s and Three 2p orbitals.



- Hence, carbon in the tetravalent state is fully saturated. It has neither any vacant orbital nor any lone pair of electrons on its atom due to which C-C bond is extremely stable.
- The stability or strength of C-C bond and other such bonds (M-M) in other metals is evidenced by the values of their **bond energy**.

Bond	Bond Energy (kJ/mol)	Catenation tendency
C-C	348	Very strong
Si-Si	180	Little
Ge-Ge	167	Very little
Sn-Sn	155	Very little
Pb-Pb	-	Nil

Note:

In group-14, down the group → catenation property decrease
C-C >>> Si-Si >>> Ge-Ge ≅ Sn >>> Pb-Pb

- The reason for greater tendency of carbon for catenation than other elements in the group may further be explained by the fact that *the C-C bond energy is approximately of the same magnitude as the energies of the bond between C and other elements*.
- The Si-Si bond is weaker than the bonds between Si and other elements.

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
C-C	348	Si-Si	180
C-O	351	Si-O	372
C-H	414	Si-H	339



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B. Sc. Chemistry (CBCS) C-101

Semester-1 – Chapter 2

Chemistry Of s And p Block elements

C-Cl	326	Si-Cl	360
C-F	439	Si-F	536

- Carbon can form chains containing 20 or more carbon atoms.
- Si and Ge cannot extend the chain beyond 6 units.
- Sn and Pb do not form chains containing more than one or two atoms. Group-15: (Nitrogen family) :
- In this group, the lighter elements (N, P and As) exhibits the properties of catenation but this properties is much less than in group-14 elements.
- Thus, N forms a chain of two atoms as $N \equiv N$, hydrazine H_2N-NH_2 , and of three atoms as inazide ion N^{-3} .

Note: catenation property of N is less due to weakness of the N-N single bond which in turn may be due to repulsion between lone pair of electrons on the two adjacent nitrogen atoms.

Group-16: Oxygen and Sulphur shows the property of catenation with two or three consecutive atoms in many compounds.

❖ Questions: (1 marks)

1. The tendency to link with each other is called....

Catenation

2. How is metal metal bond energy affecting the catenation property?

Greater Metal-metal bond energy than greater the catenation property

3. Catenation property of N is weak. Why?

N is less due to weakness of the N-N single bond which in turn may be due to repulsion between lone pair of electrons on the two adjacent nitrogen atoms.

4. Which element has been shown maximum catenation property?

Carbon

❖ Allotropes of carbon:

- The phenomenon by which an element exists in two or more different crystalline or amorphous forms, is called *allotropy* and different forms are known as allotropes of given elements.
- It is important to note that different allotropic forms differ in their physical and chemical properties because of difference in the arrangement and bonding of atoms.
- The phenomenon of allotropy is due to the difference in...
 - i) The arrangement of the atoms in the crystal lattice
 - ii) The number of the atoms in molecule
 - iii) The method of crystallization
 - iv) The amount of available energy

- Carbon exists in three allotropic forms.

1. Diamond 2. Graphite 3. Amorphous carbon

❖ Diamond:

- It is a hard, beautiful crystalline substance found in nature.
- X-ray analysis shows that the crystal of diamond is made of a number of carbons with



tetrahedral units.

- Each tetrahedral unit contains C-atoms in center and this carbon atom is attached with four C-atoms at four corners of tetrahedron.
- Carbon atoms of each tetrahedron are also linked each other by strong C-C covalent bonds. This results in a very big three dimensional polymeric structure in which C-C distance is 1.54 Å and bond angle 109.5°
- Diamond consists of a number of tetrahedral units, it is a giant molecule. Each carbon forms four covalent bonds, it produces a repetitive and rigid three dimensional structure, using only covalent bond.

Properties:

- Insoluble in all solvents
- Hardest and purest structure of carbon due to giant molecular structure.
- Bad conductor of electricity and heat because all four valence shell electrons of each C-atom are linked to other C-atom by four covalent bonds. So, no free electron left in diamond crystal to carry electricity or heat.
- High melting point (about 3000°C)
- Chemically inert
- Transparent to X-ray
- Relative density 3.52
- Refractive index is very high as 2.45

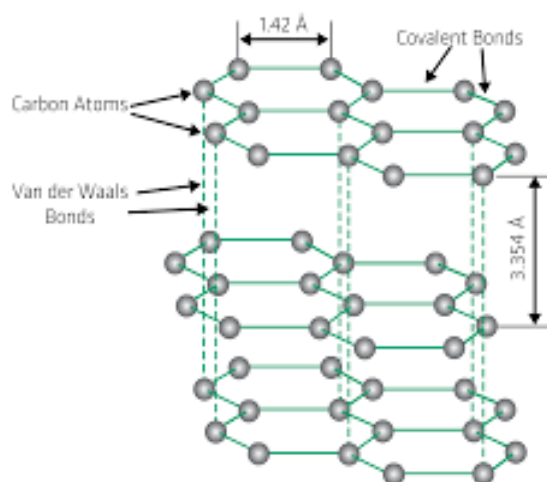
Uses:

- Due to its great hardness, it is used for making glass cutters and rock borers.
- Use as an abrasive for sharpening hard tools
- In manufacturing of tungsten filaments in electric bulbs.
- It is a precious stone so it is used in jewelries, because of their ability to refract and reflect light. It is measured in carat. (1 carat = 200mg)

❖ **Graphite:**

➤ Structure of graphite:

- The structure of graphite consists of a large number of flat parallel layers.
- Each layer is composed of flat hexagonal rings of C-atoms.
- Each C-atom is in sp^2 -hybridisation and joined to three other C-atoms by covalent bonds.
- The fourth electron of C-atom is involved in formation of π -bonding and these π -bonding electrons are delocalized over the whole sheet.
- Electrons are mobile so it conducts electricity along the sheet.
- The C-C distance in each hexagonal ring is 142 pm and the distance between two adjacent layers of C-atoms is 340 pm.
- Large distance between two adjacent layers are joined by weak Van der Waals forces.





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B. Sc. Chemistry (CBCS) C-101
Semester-1 – Chapter 2
Chemistry Of s And p Block elements

➤ **Properties:**

- Graphite is soft, greasy, has a lubricating character because hexagonal layer of graphite are held together by comparatively weak Van der Waal's force. Due to wide separation and weak interlayer bonds, two adjacent layers can easily slide over each other.
- It has a high melting point since C-atoms within a layer is firmly held by strong covalent bond. (m.p. $\approx 3500^{\circ}\text{C}$)
- Graphite is more reactive than diamond due to the presence of mobile electron on each C-atom.
- Heat of combustion of graphite is -94.052kcal/g at room temperature and ordinary pressure
- It can be converted into diamond at 1600°C by a pressure of 5000 to 6000 atm.
- At $700-800^{\circ}\text{C}$, it burns in air to form CO_2
- It is inert with dilute acid and alkali but react with nitric acid HNO_3 or H_2SO_4 below 100°C forms graphitic acid. ($\text{C}_{11}\text{H}_4\text{O}_5$)
- It oxidizes by heating with $\text{H}_2\text{Cr}_2\text{O}_7$ which gives CO_2 .

➤ **Uses:**

- Graphite powder is utilized as a lubricant in the form of dispersion material or powder.
- Graphite is widely used in lead pencils.
- It is used in the manufacture of electrodes of carbon employed in the electrolytic cells, as it is an excellent conductor of electricity.
- It is utilized in the making of graphite crucibles since it possesses high melting points.
- It is widely used in the nuclear reactors and moderators.

❖ **Questions: (1 Marks)**

1. The element exists in two or more different crystalline structure is called.....

Allotropy

2. Enlist factors which arise allotropy...

No. of atoms in molecule, Method of crystallization Amount of energy available

3. Who discovered Fullerene?

H. W. Kroto, E. Smalley, R. F. Curl

4. Give the name of the two well-known crystalline allotrope of C-atoms.

Diamond, Fullerene, Graphite

5. Which substance has been shown amorphous form of C?

Coal, charcoal, animal charcoal, wood charcoal

6. What is the C-C bond length in diamond?

154 \AA

7. Structural geometry of diamond is.....

Tetrahedral

8. Give the reason: Melting point of diamond is high.

Due to high C-C bond energy (348 KJ/mol)

9. Which type of hybridization has been observed in diamond?

Sp^3 hybridization

10. Which type of hybridization has been observed in Graphite?

Sp^2 hybridization



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:: THANK YOU ::