SYLLABUS

MAHARISHI DAYANAND UNIVERSITY, ROHTAK

B.Sc.–1st Year (Semester–2) : CHEMISTRY

INORGANIC CHEMISTRY
[Paper-I]

Max. Marks: 29

Time: 3 Hrs.

Note: *Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing five short answer type questions, covering the entire syllabus and will be of five marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section will be of six marks each.*

SECTION-A

1. **Hydrogen Bonding & Vander Waals Forces**

Hydrogen Bonding : Definition, Types, effects of hydrogen bonding on properties of substances, application

Brief discussion of various types of Vander Waals Forces

2. **Metallic Bond and Semiconductors**

Metallic Bond- Brief introduction to metallic bond, band theory of metallic bond

Semiconductors- Introduction, types and applications.

SECTION-B

1. **s-Block Elements**

Comparative study of the elements including , diagonal relationships, salient features of hydrides (methods of preparation excluded), solvation and complexation tendencies including their function in biosystems.

Chemistry of Noble Gases : Chemical properties of the noble gases with emphasis on their low chemical reactivity, chemistry of xenon, structure and bonding of fluorides, oxides & oxyfluorides of xenon.

SECTION-C

p-Block Elements

Emphasis on comparative study of properties of p-block elements (including diagonal relationship and excluding methods of preparation).

Boron family (13th gp)

Diborane – properties and structure (as an example of electron – deficient compound and multicentre bonding), Borazene – chemical properties and structure Trihalides of Boron – Trends in fewis acid character structure of aluminium (III) chloride.

Carbon Family (14th group)

Catenation, $p\overline{d} - d\overline{d}$ bonding (an idea), carbides, fluorocarbons, silicates (structural aspects), silicons – general methods of preparations, properties and uses.

SECTION-D

Nitrogen Family (15th group)

Oxides – structures of oxides of N,P. oxyacids – structure and relative acid strengths of oxyacids of Nitrogen and phosphorus. Structure of white, yellow and red phosphorus.

Oxygen Family (16th group)

Oxyacids of sulphur – structures and acidic strength H_2O_2 – structure, properties and uses.

Halogen Family (17th group)

Basic properties of halogen, interhalogens types properties, hydro and oxyacids of chlorine – structure and comparison of acid strength.

1

HYDROGEN BONDING AND VANDER WAAL'S FORCES

Hydrogen Bonding

The idea of 'hydrogen bond' introduced by the Letimer and Rodebush, in 1920. It has been observed that in a compound containing hydrogen atom bonded to highly electronegative atom such as fluorine-(F), oxygen-(O) and nitrogen-(N) by a covalent bond, the electron pair is attracted towards the electronegative atom so that, the electronegative atom aquires slightly negative charge while hydrogen atom aquires slightly positive charge.This positively charged hydrogen atom attracted by the electronegative atom of other molecule and form a weak bond known as hydrogen bond. (fig.-1)

$$H^{+\delta} — X^{-\delta} \ldots\ldots\ldots\ldots\ldots H^{+\delta} — X^{-\delta}$$

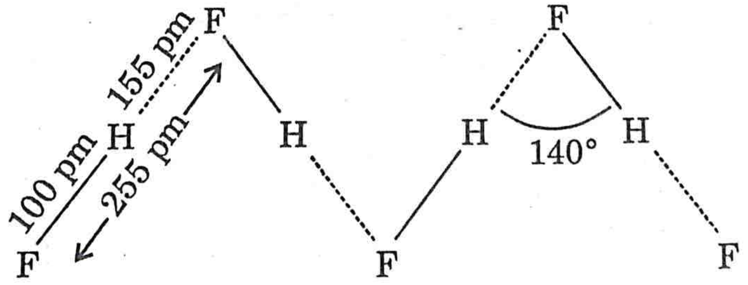
(Fig.1 : Hydrogen bonding between H atom and electronegative atom)

Thus "Hydrogen bond is the electrostatic force of attraction between hydrogen atom of one molecule and electronegative atom (F, O, N) of other molecule of either same substance or different substance."

The hydrogen bond represented by dotted line (...........). In order words, the hydrogen atom act as bridge between two molecules. It attach with one molecule by a covalent bond while with other molecule by a weak hydrogen bond.

For examples : Hydrogen bonding shown by few compounds (Fig. 2)

(1) Hydrogen bonding between the molecules of same substance.



(a) Hydrogen fluoride

Types of Hydrogen Bonding :

H-bonding are of two types :

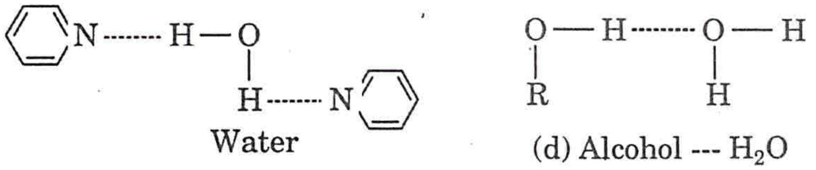
1. Intermolecular H-bonding :– When H-bond is formed between the molecules of same substances *i.e.* $H_2O....H_2O$, $NH_3....NH_3$. and H–F.....HF etc. The types of bond thus formed is called intermolecular hydrogen bond (fig. 7) (Inter-in between two)

(a) Water-water (b) Ammonia-ammonia

Fig. (7) Formation of intermolecular H-bond

(a) $H_2O.....H_2O$ (b) $NH_3............NH_3$

The intermolecular H-bond can be formed between the molecules of different substances (fig. 8).



(c) Pyridine-H_2O (d) Alcohol --- H_2O

Fig. 8 : Intermolecular H-bond between molecules of different substances
(c) Pyridine -H_2O (d) R— OH ----- H_2O

EFFECT OF H-BONDING ON PHYSICAL PROPERTIES OF THE COMPOUNDS

Hydrogen bonding affects the physical properties of the compounds such as :

1. Association :– H-bonding cause association, by which two or more molecules of a compounds exist in associated form.

For example - **carboxylic acid-RCOOH, exists as dimer even in vapour phase** as shown in Fig.-9.

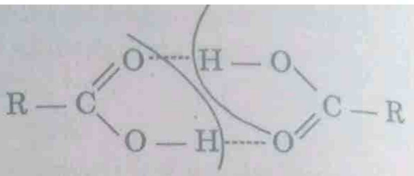


Fig. 9 : Dimeric form of $(RCOOH)_2$

Almost every substance that form intermolecular H-bond always exist in associated form. They generally form cluster.

For example -Cluster formed by the H-bonded water molecules. *i.e.* $(H_2O)_n$ given as :

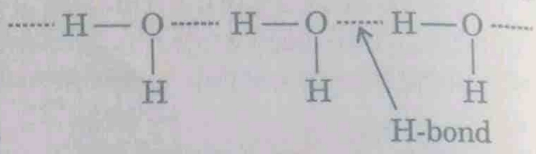


Fig. 10 : Cluster of $(H_2O)_n$

2. Melting point and bonding points : The melting points and boiling points of H-bonded compounds of Group-15, 16 and 17 given as in the table–1

Table : 1 B.Pt. of hydrides of elements of G-15, G-16 and G-17

Hydrides of G-15	B.P*t.*	Hydrides of G-16	B.P*t*	Hydride of G-17	B.P*t*
NH_3	238.5 K	H_2O	313 K	HF	292.4 K
PH_3	185.5 K	H_2S	212K	HC*l*	188 K
AsH_3	210.5 K	H_2Se	231 K	HBr	206 K
SbH_3	254.5 K	H_2Te	271.1K	HI	238 K

From the table it is clear that **B.P*t* of 1st member of hydride of group 15, 16 and 17 generally high as compared to other members of this series.**

Explanation :– The boiling point of NH_3, H_2O and HF is high because due to presence of intermolecular H-bonding, they associates and exist as cluster $(NH_3)n$, $(H_2O)_n$ and $(HF)_n$. So, extra amount of energy is required to dissociates them. Therefore their B.pt is found to be high.

Similarly, **the M.P*t.* of first member is generally high than rest of the members** as seen in the table 2.

Table 2-M.P*t.* (K) of Hydrides of G-15, G-16 and G-17.

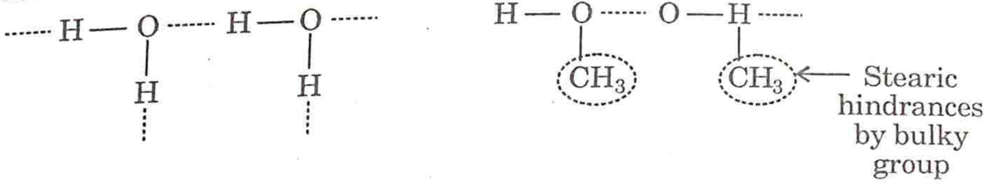
Hydrides of G-15	M.Pt. (K)	Hydride of G-16	M.Pt. (K)	Hydrides of G-17	M.Pt. (K)
NH_3	195.5	H_2O	273	HF	181
PH_3	138	H_2S	190	HC*l*	161
AsH_3	159	H_2Se	209	HB*r*	185
SbH_3	184	H_2Te	222	HI	222

3. Melting Point, Boiling Point, Heat of Fusion, Heat of evaporisation of H-bonded compounds and their alkyl derivatives. given in table-3

Table-3 M.Pt, B.Pt, ΔH_f and ΔH_v of some compounds

Exmple	M.Pt.	B.Pt.	ΔH_f	ΔH_v
H_2O	273 K	373 K	279 K	314 K
CH_3OH	175 K	338 K	275.2 K	309 K
$(CH_3)_2O$	134 K	249 K	278 K	295 K

From the table it is clear that the M.Pt, BPt, ΔH_f and ΔH_v generally decreases as the H-atom is replaced by the alkyl group. This is due to the fact, the alkyl group (bulky size) decrease the magnitude of intermolecular H-bonding. (fig. 11)



Stearic hindrances by bulky group

Fig. 11 : Effect of Bulky group on B.Pt. M.Pt, ΔH_f and ΔH_v via H-bonding

4. **B.Pt of CH_4, NH_3, H_2O and HF**

The order of boiling point given as :

H_2O	>	HF	>	NH_3	>	CH_4
373 K		292 K		238 K		112 K

Explanation :

The order of boiling points of hydrides of elements of different group depends upon the

(I) Magnitude of H-bonding

(II) and strength of H-bonding

The number of H-bond formed by the hydrides of elements of various group given as :

Water (H_2O) : The total number of H-bond is formed by the molecule of water is four in number Two-H-bond is formed through the two H-atoms and other two H-bond, formed via lone pairs on atom of oxygen. (fig 12)

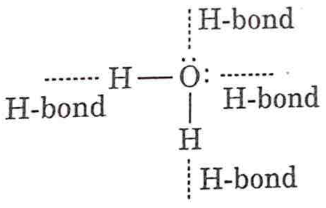


Fig. 12 : Formation of H-bond by oxygen atom of H_2O

Ammonia (NH_3) : Total number of H-bonds formed by the molecule of ammonia is also four in number. Three H-bonds is formed with H-atoms while forth, H-bond is formed by the lone pair of N-atom. (fig. 13)

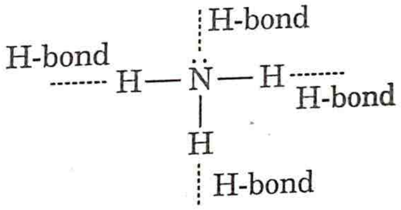


Fig. 13 : Formation of H-bond by ammonia molecule

Hydrogen fluoride (HF) : Total number of H-bonds formed by the molecule of HF is two. One H-bond is formed via H-atom while other H-bond is formed via lone pair of F-atom as shown in Fig. 14.

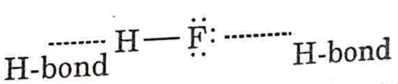


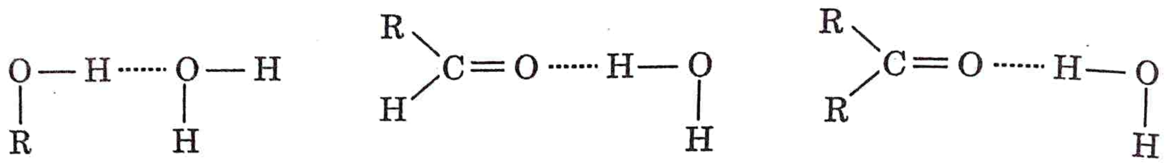
Fig. 14 : Formation of H-bond by HF

But strength of H-bond formed by the molecules of H-F is more, as compared to the molecule of NH_3.

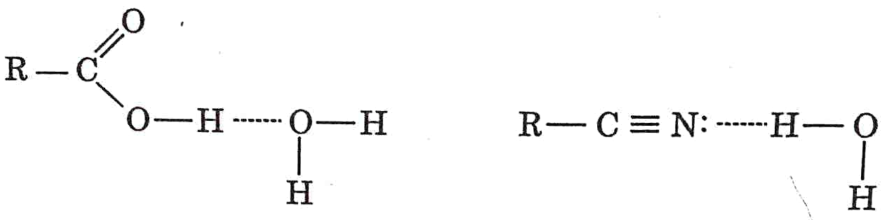
Methane (CH_4). The molecules of CH_4 does not form any H-bond.

∴ The order is as given above,

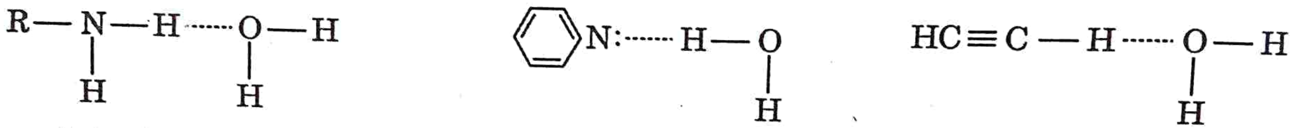
5. Solubility : **The solubility of an organic compounds in water** due to its ability to form intermolecular H-bonding with the molecules of water. Any compound that is capable to form intermolecular H-bonds with the molecules of H_2O generally soluble in it. Solubility of lower alcohol (ROH), aldehydes (RCHO), Ketones (R_2CO), carboxylic acid (RCOOH), cyanide (—CN), amine ($R\text{-}NH_2$), pyridine (C_5H_5N), acetylene ($CH \equiv CH$) in water due to formation of inter molecular H-bonding with it (fig. 15).



(a) Alcohol-water (b) Aldehyde-water (c) Ketone-water



(d) Acid-water (e) Cyanide-water



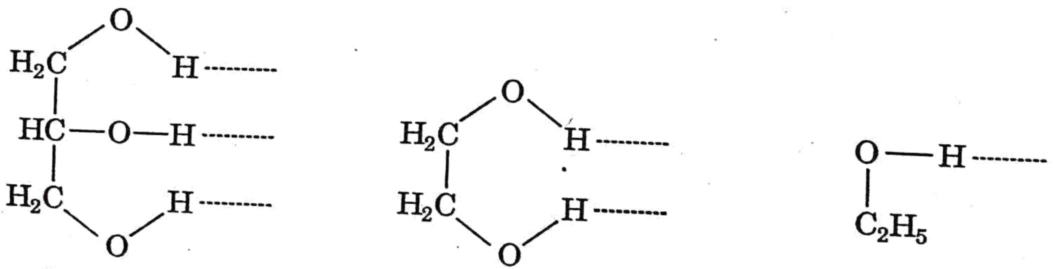
(f) Amine-water (g) pyridine-water (e) Acetylene-water

Fig. 15 : Association of various molecules via-H-bonding with the molecules of water

6. Viscocity : Formation of intermolecular H-bonding between the molecules of liquid, decrease their tendency to flow, so liquid become viscous.

The viscous nature of liquid depend upon the magnitude of intermolecular H-bonding. Greater the magnitude of H-bonding, greater will be its viscocity. For example, glycerol is more viscous than glycol and glycol is more viscous than monohydric alcohol.

Explanation : In glycerol the number of —OH groups are three. Therefore, form three H-bond bond as compared to glycol (form two H-bond) and monohydric alcohol (form one H-bond only) [(fig.16) (i), (ii), (iii)]



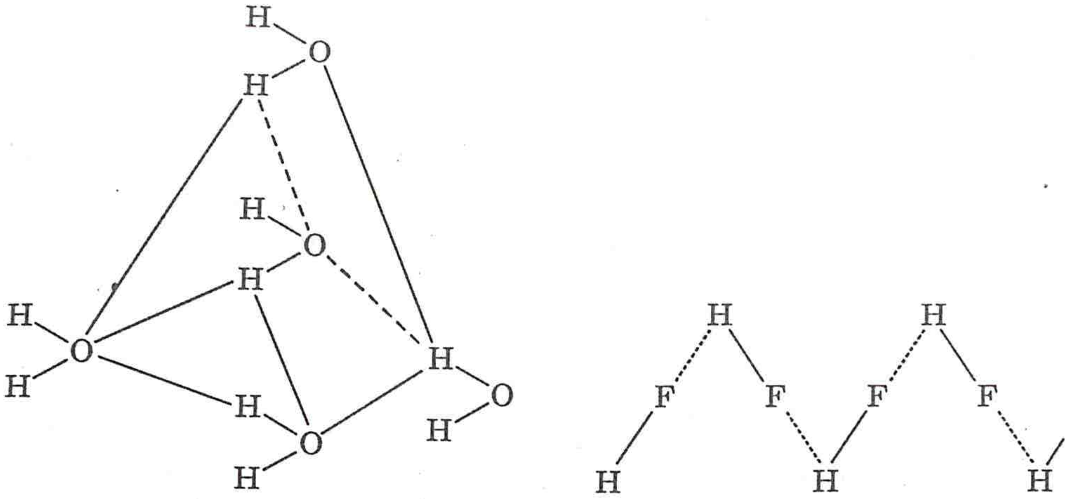
(i) Glycerol (ii) Glycol (iii) Monohydric alcohol

Fig. 16

Therefore association in glycerol is more than glycol and alcohol

7. Physical state of hydride :– Hydride of Group 15, 16 and Group-17 (Specially first member) are generally liquid while the rest of the hydrides are gases.

Explanation : Because the first number of Group-15, 16 and 17 are small in size form strong H-bonding with each other and exist as cluster (fig. 17). So generally exist in the form of liquid at ordinary temperture. For example :– **HF and H_2O exists as liquid.**



(a) H_2O (b) HF

Fig. 17 : Structure of H-bonded (a) water (b) HF

8. Existence of HF_2^- : HF_2^- ion exist, due to the presence of highly electronegative fluorine atom. First, its size is very small. Secondly, it is highly electronegative elements of the periodic table. Therefore, form strong intermolecular H-bonding with H-F molecules and exist as in associated form. (fig.-18).

$$H—F + F^- \rightarrow HF_2^-$$

But HCl_2^-, HBr_2^- and HI_2^- not formed due to large size and less electronegativities of Cl, Br, and I.

So we can say **KHF_2 exist but $KHCl_2$, $KHBr_2$ and KHI_2 do not exist.**

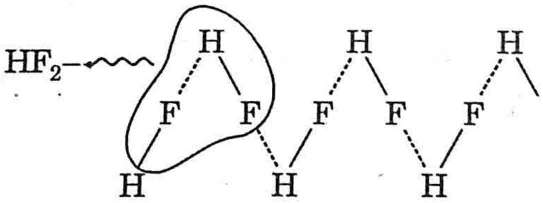


Fig. 18 : H-bonding in HF.

9. Molecular Structure : Due to effect of intermolecular H-bonding the various molecules exist in crystalline form.

(i) Linear chain is formed by HCN (fig. 19).

............H– C $\equiv$ N : ....H— C $\equiv$ N : ....

Fig. 19 : Linear structure of HCN

(ii) Zig-Zag chain formed by molecules HF and CH_3OH etc. (fig. 20)

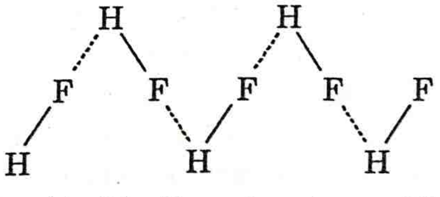


Fig. 20 : Zig Zag structure of HF

(iii) Sheet like structure formed by the molecules of oxalic acid (fig. 21)

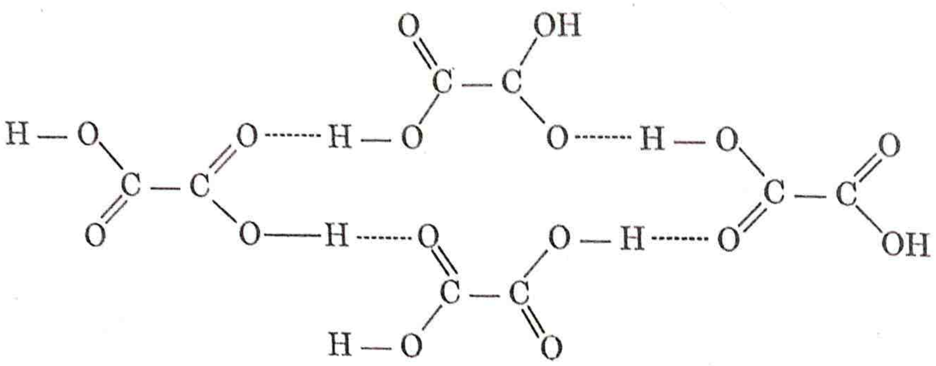


Fig. 21 : Sheet like structure of oxalic acid

10. Polymeric nature of compounds : At low temperature and high pressure, the H-containing compounds unite via-formation of intermolecular H-bond and exist in polymeric form.

Polymeric form of H-containing compounds is given as (fig.-22).

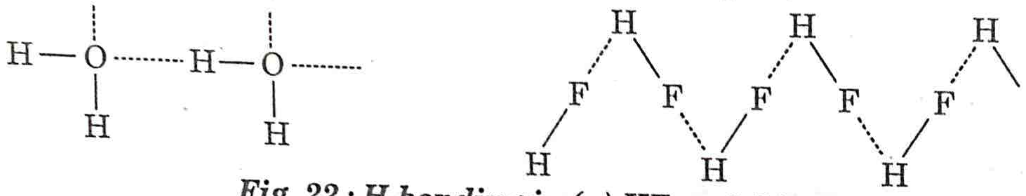


Fig. 22 : H-bonding in (a) HF and (b) H_2O

11. Volatility of organic compounds : Certain organic compounds when associates through intermoleculer H-bonding becomes less volatile in nature (fig. 23). The low volatility of organic species due to development of force of attraction. To over come this force of attraction extra amount of energy is required. Therefore, **organic compound become less volatile in nature.**

For example : O-Nitro phenol is more volatile than m and P-nitrophenol.

Explanation : *m* and *p*-nitrophenol form intermolecular H-bond, that cause association as shown in fig. 23. So *m* and *p*-isomer becomes less volatile in nature.

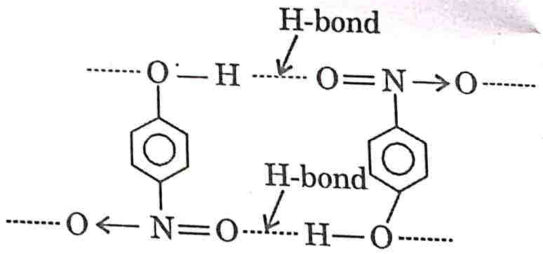


Fig. 23 : Intermolecular H-bonding

While O-nitro phenol form intramolecular H-bond that not cause association therefore become more volatile. (fig. 24).

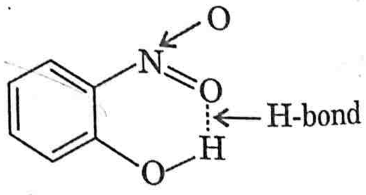


Fig. 24 : Intramolecular H-bonding

12. H-bonding in water and ice :– It is known **that density of water is maximum at 4°C or 277 K.** This interesting behaviour can be explained due to presence of intermolecular H-bonding, between the molecule of water. Let's explain the following phenomenon associated with intermolecular H-bonding.

1. Ice is generally lighter than water.

Explanation : From the X-rays studied (fig-25) it is clear that in ice each oxygen atom tetrahedrally surrounded by four H-atoms. Out of four H-atoms, two H-atoms linked to oxygen atom by covalent bond with a O-H bond length is about 100 pm.

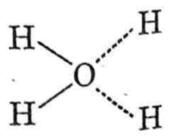


Fig. 25 : Bond formed by water

The other two H-atom linked to oxygen atom by hydrogen bond, with a O—H bond length 176 pm. The H-bond between O----H is longer than O-H covalent bond (fig. 26). Therefore the molecule of water not packed closely. There is sufficient vacant space between the molecules of water (Fig. 27). So structure of ice become cage like and possess large volume. Consequently, density of ice becomes less than water. Hence, **ice float on the surface of water due to there less density.**

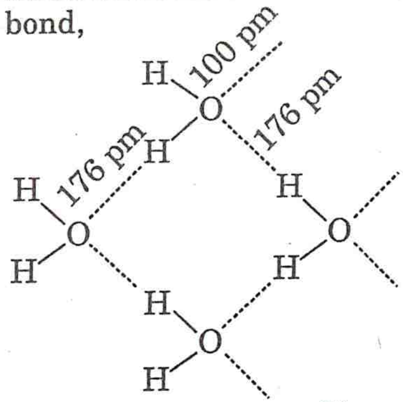


Fig. 26 : Structure of ice

2. Water has maximum density at 4°C or 277 K

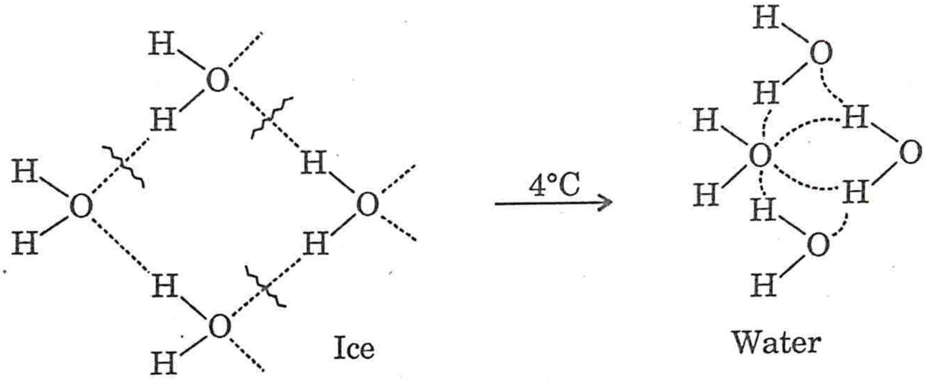


Fig. 27 : Cleavage of H-bond of ice

When ice melts by increasing temperature the hydrogen bond of cage structure start to breaks. So that the molecules of water come close to each other. As a result its volume start decreasing and density of water start increasing and become maximum at 277 K of 4°C.

But on further increase in temp. the molecules of water aquires K.E. and start to move away from each other. Therefore volume start increasing. Consequently, density start decreasing. Therefore, we can say water has maximum density at 4°C.

2. Intramolecular H-bonding : In Intramolecular H–bonding, the H-bond is formed between the atoms of same molecule. In this H-bonding a 5 to 6 membered chelate ring is formed.

Conditions :

1. A molecule that form intramolecular H-bond must contain two groups.
   (a) In one group, H-atom must be attached with a highly electronegative atom (such as F, O, or N)
   (b) In other group, a highly electronegative atom (F, O, N) must be attached with a less electronegative atom (any atom)
2. The group, that associates via intramolecular H-bond must be adjacent to each other *i.e.*, in benezene ring the two groups placed at ortho (1, 2) position to each other (fig.-28).

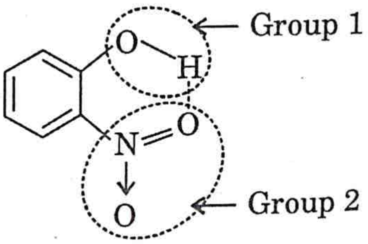
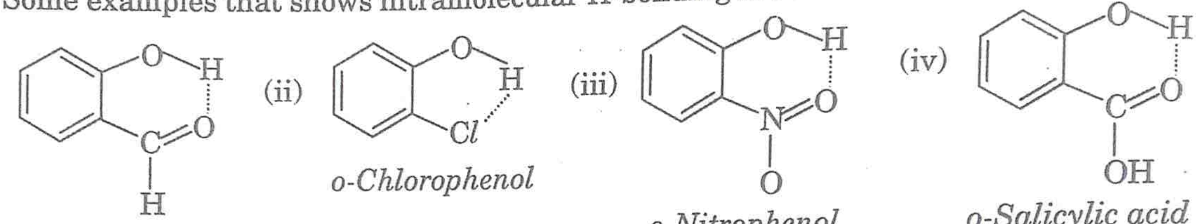


Fig. 28 : Condition for Intramolecular H-bond

Some examples that shows intramolecular H-bonding are :

(i) (ii) (iii) (iv)



o-Benzaldehyde

o-Chlorophenol

o-Nitrophenol

o-Salicylic acid

Fig. 29 : Intramolecular H-bonding (i) – (iv)

Consequences of intramolecular H-bonding. The intramolecular H-bonding prevent the association of the molecules so that physical properties like melting point, boiling point, viscosity, surface tension and solubility decreases and substances aquires volatile character.

VANDER WAAL FORCES

Dutch scientist J.D. Vander Waals noticed that the existence of weak attractive forces among the molecules of non-polar species (H_2, O_2, Cl_2, Br_2, CH_4, I_2) in their solid and liquid state. These weak forces called as Vander Waal forces.

Noble gases have stable noble gas configuration. But these noble gases can be liquified via, Vander Waal forces. The Vander Waal forces is very-very weak forces can be indicated by the low values of melting and boiling points of the noble gases. Its bond strength is 2-20 KJ mol^{-1} respectively.

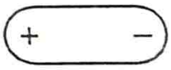


Fig. 30 : Polar molecule

Vander Waal forces is of three types :–

1. Dipole-dipole interaction (Keesom forces) .
2. Dipole-induced dipole interaction
3. Instantaneous dipole-induced dipole interaction (London forces)

1. Dipole-dipole interaction (Keesom forces)

:– The dipole-2 interaction studied by Keesom in 1912. The dipole-dipole interaction occur between polar molecular solid. The polar molecule has centre of positive and negative charges (fig.30)

The positive end of a polar molecule attract the negative end of other polar molecule and vice versa (fig. 31).

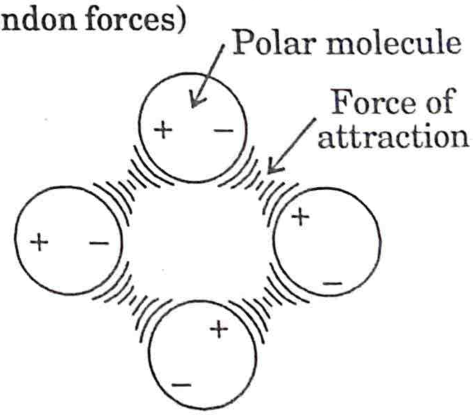


Fig. 31 : Dipole-dipole forces in polar molecules

It is called as **orientation effect** because molecule orient itself under the influence of attractive force of polar molecule.

Some polar molecules given as HCl, H_2O, NH_3, HF, HBr, HI etc.

2. **Dipole-induced dipole interaction :–** Dipole induced dipole interaction studied by Debye in 1920.

   The kind of forces existing between the two molecules, one molecule is polar while other molecule is non polar. The non polar molecules do not have any dipole moment. So polar molecule induced polarity in them by distorting their electron cloud fig.-32. Such a interaction between polar molecule with a non-polar molecule is called dipole Induced dipole interaction.

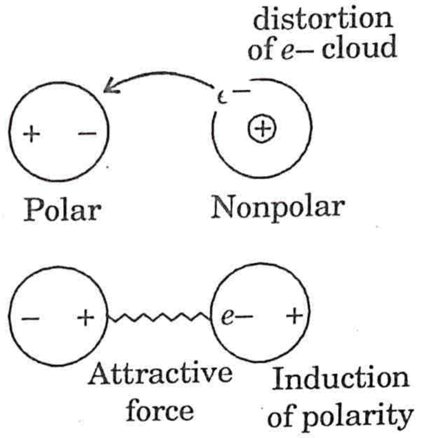


Fig. 32 : Intermolecular forces

It is called as **induction effect**, due to induction of polarity in nonpolar molecules.

3. **Instantaneous dipole- instantaneous induced dipole interaction (London forces)** :– The kind of forces noticed by the Fritz London in Noble gases. In this type of interaction, a non-polar molecule attracted by other non polar molecule. The interaction of this type is called instantaneous dipole induced dipole interaction. It is also called as **dispersion forces.**

   Origin of forces :– Atoms of noble gases are uncharged due to the presence of symmetrical electron cloud. Due to motion of electrons, the electron clouds remain no longer symmetrical. So instantaneous dipole is produced (Fig. 33).

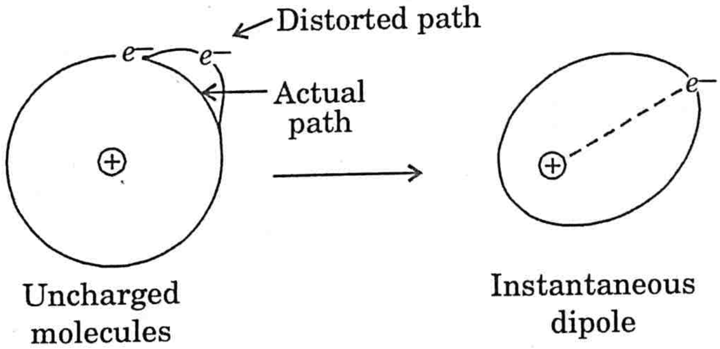


Fig. 33 : London forces in non-polar molecules

The instantaneous dipole, induces dipole in the neighbouring molecule (Fig. 34). So a weak interaction is set up known as London forces.

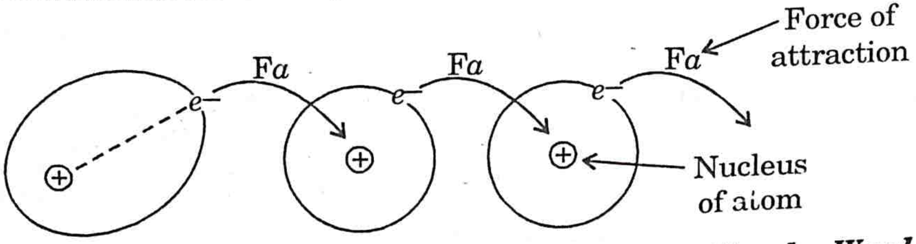


Fig. 34 The non polar atoms or molecules interact via Vander Waal Forces

Some examples of non-polar molecules are H_2, Cl_2, Br_2, I_2, F_2, CH_4 , CCl_4, CBr_4, CF_4 , SF_6, BF_3, BCl_3, BBr_3, BI_3, CO_2, C_6H_6 etc.

There are many factors on which the magnitude of vander waal forces depend. These factors are :

1. **Size of the molecule** : Large sized molecule posseses large surface area. Therefore, has greater chance of distortion of their electron cloud. As a result, attractive force of the nucleus cannot hold their electron cloud no more symmetrical.

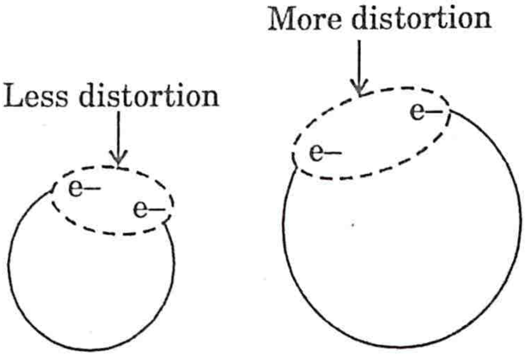


Fig. 35 : VWF and molecular sizes

Evidence :– The boiling points of hydride of G-14 given Table-4.

Table-4 : B.Pt of Some molecules

Molecules	Boiling point(K)
CH_4	111.5
SiH_4	161
GeH_4	183
SnH_4	221
PbH_4	260

2. **Number of Electrons** :– Greater the number of electrons, more will be chance of distortion because nuclear force cannot hold large electron cloud in a symmetrical manner.

For example : Increase in boiling point of noble gases with increase in number of electrons (Table-5) (fig. 36).

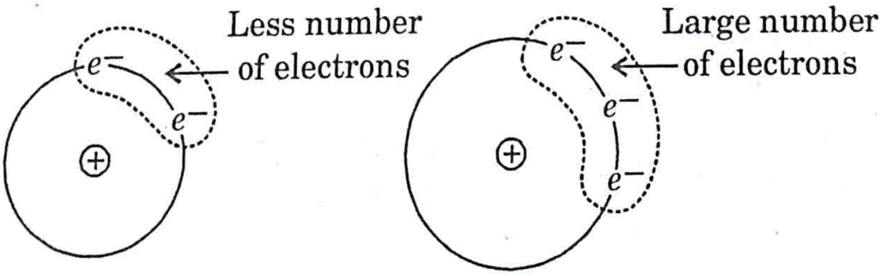


Fig. 36 : Distortion in atoms of noble gases

Table : 5 B.Pt. of Noble gases

Noble gases	He	Ne	Ar	Kr	Xe	Rn
Atomic No.	2	10	18	36	54	86
B.Pt. (K)	4.1 K	27	67.2	121	167	211

3. **Molecular Structure : In symmetrical molecule, less chance of distortion of their electron cloud than unsymmetrical molecules** (molecules with lone pair of electrons).

For example : The molecule of H_2 does not have any lone pairs of electron associates with it. Hence less chance of distortion as shown, H—H.

But on the other hand in molecule like (Br_2), $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Br}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Br}}:$ their is large number of lone pairs of electrons, that cause greater distortion.

These forces collectively called as Vander Waal Forces.

The potential energy of their interaction given as inverse of sixth power of distance between the molecules. The relation between these two given as :

$$\text{P.E. } \alpha -\frac{1}{r^6} \text{ or } = -\frac{K}{r^6}$$

where,

K— Constant of proportionality, negative sign – force of attraction

The potential energy of Vander Waal interaction given in the table-6

Table 6 : Vander Waal interactions in water and noble gases

Atom/molecule	Dipole-2	Dipole-induced dipole	Dispersion
He	0	0	1.3
Ar	0	0	5.2
Xe	0	0	21.5
H_2O	190	10	45

Easy method to know the type of interaction if the nature of molecules is known.

Nature of molecules	Interaction
(i) Polar-Polar	Dipole-2
(ii) Polar-Non-polar	Dipole induced dipole
(iii) Non-polar- Non-polar	Instantaneous dipole-induced dipole forces

IMPORTANT QUESTIONS : HYDROGEN BONDING

1 Write a note on

(i) H-bond and its applications (M.D.U. 2015)

(ii) Inter-molecular and intramolecular hydrogen bond.

2. How does hydrogen bonding affect the viscocity of a liquid?

3. Explain the following :

(i) B.P*t* of NH_3 is greater than PH_3 (ii) NH_3 is highly soluble in water

4. H_2O is a liquid while H_2S is gas.

5. NH_3 has exceptionally high M.P*t* and high B.P*t* as compared to those of hydrides of remaining elements of group-15

6. B.P*t* of H_2O is greater than H_2S. Explain it.

7. B.P*t* of water is higher than the hydrides of group-16.

8. BPt of H_2O and HF is found to be abnormally high.

9. HF is polymeric, while other halogen acids are monomeric. (HC*l*, HB*r*, HI)

10. Anhydrides HF is solid, while other hydrides of group-17 are gases. Explain it.

11. Acid salts of HF are known only.

12. Why does HF have abnormally high B.P*t*.?

13. Draw the structure of H_2O (s) *i.e.* ice.why it floats on water.

14. Oxygen and chlorine have same electronegatively, but chlorine does not from H-bond.

15. List the main uses of H-bond.

16. What are the main conditions for forming hydrogen bond?

17. What is the cause of hydrogen bonding?

18. Explain why H_2SO_4 is denser, viscous and have high boiling point.

19. Explain the solubility of organic compounds in water.

20. Carboxylic acid exist in dimeric form why? (M.D.U. 2015)

21. What is hydrogen bond? Discuss the types of hydrogen bonds. Give examples of each type. **(K.U.K 2011)**

22. Explain the following :

    (i) Ice floats over water

    (ii) H_2O is a liquid at room temperature while H_2S is gas. **(K.U.K. 2011)**

23. A chlorine derivative corresponding to KHF_2 is not possible. Comment. **(M.D.U. 2011)**

24. NH_3 has higher B.Pt than PH_3 . **(M.D.U. 2011)**

25. Explain why?

    (i) HF and H_2O have abnormally high boiling point.

    (ii) Water has maximum density at 4°C **(K.U.K . 2012)**

26. List the main conditions for forming H-bond. **(K.U.K. 2012)**

27. What types of bond present in

    (i) H_2O and HF.

    (ii) H_2O and He, show by drawing the structures in each case. **(M.D.U. 2012)**

28. Why B.Pt of water is higher than hydrogen fluoride? **(M.D.U. 2012)**

29. Define hydrogen bond and explain the cause of hydrogen bonding. **(K.U.K. 2013)**

30. Water has maximum density at 4°C. **(K.U.K. 2013)**

31. Why H_2O is a liquid while H_2S is a gas. **(MDU-2013)**

32. Explain the following :

    (i) HF has higher boiling point than HCl. **(KUK-2014)**

    (ii) H_2S is a gas at room temp. while H_2O is a liquid.

33. Define intramolecular H-bonding. **(K.U.K. 2014)**

34. Which is denser ice or water? Why? **(M.D.U. 2014)**

35. Discuss the H-bonding and its type in detail. **(M.D.U. 2014)**

VANDER WAAL'S FORCES

36. What are weak interactions? What is the role of these interactions in explaining the properties of compounds. **(M.D.U. 2015)**

37. What do you mean by the term vander waal forces?

38. Explain Xenon has higher B.Pt than Kr.

39. Discuss the various factors on which Vander Waal forces depend.

40. Which of the element in group-18 has higher boiling point. Why?

41. Discuss the solubility of noble gas in water.

42. Boiling point of Xe is greater than Kr. why?

43. What type of forces are present in (i) Polar molecules (ii) Non-polar and polar molecules.

44. Explain briefly London dispersion force.

45. Explain briefly Keesom forces.

46. Give one example of the following :

(i) dipole-2 forces

(ii) dipole-induced dipole forces

(iii) London-dispersion forces

47. Write a short note on Vander Waal's forces. **(M.U.K. 2015), (M.D.U. 2011)**

48. Define Vander waal's forces. **(K.U.K. 2011)**

49. What type of bond present in H*e* and H*e*. **(M.D.U. 2012)**

50. What are Vander Waal's forces? Describe briefly London forces. **(K.U.K. 2012)**

51. Discuss the type of interaction in He and He. **(M.D.U. 2013)**

52. Explain dipole induce dipole forces? **(K.U.K. 2013)**

53. Write brief note on London forces. **(M.D.U., K.U.K. 2014)**

54. What are Vander Waal forces? How are they helpful in explanining noble gases? **(M.D.U. 2015)**

□□

2

Metallic Bond and Semiconductors

In metallic crystals, valence electrons neither associates with ionic bond nor they are covalent in nature. The impossible nature of ionic bond is due to their tendency not to loss the electrons because no one atom can have tendency to loss the electron. While impossible nature of covalent bond is due to the fact, in metallic crystals the metal atom associates with a large number of atoms of metal. So their is peculiar type of bonding in the atoms of metal known as metallic bond. A number of models are available to explain the bonding between atoms of metal.

Some of these models are –

(1) Free electron or electron sea model

(2) Valence bond model

(3) Bond Theory of metallic bond.

I. Free electron or electron sea model

The free electron model proposed by scientist Lorentz. It is based upon the following characteristics

a. Low value of Ionization energy

The ionization energy of metal, generally found to be low. The valence electrons of metal atom loosely held by the nucleus (kernels). Therefore these valence electron can move freely under the influence of kernels. Thus electrons of metals is called **mobile electrons** (fig-1).

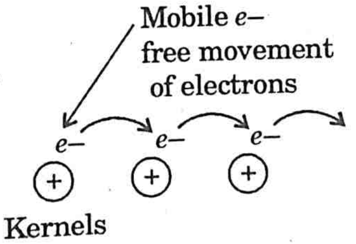


Fig.1 : free movement of mobile electrons

(b) Large number of vacant orbitals

It has been observed that number of vacant orbitals is greater than the number of valence electrons in metal atom.

For examples : The number of vacant orbitals of metal atom given in the following table:

Metal	Configuration	Vacant orbitals
Li	$1s^2\,2s^1\,2p^{\circ}$	$2p$
Na	$1s^2\,2s^2\,2p^6\,3s^1\,3p^{\circ}\,3d^{\circ}$	$3p$ and $3d$
Mg	$1s^2\,2s^2\,2p^6\,3s^2 3p^{\circ}\,3d^{\circ}$	$3p$ and $3d$
Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{\circ} 4p^{\circ}\,4d^{\circ}$	$3d$, $4p$ and $4d$

Silient features of electron sea model

1. The kernels (positive charge) of metal atom are arranged in a regular fashion (fig. 2)

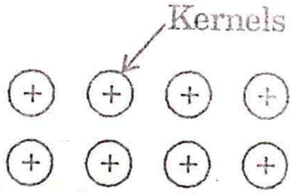


Fig. 2 . Regular arrangement of Kernels

2. Each kernel (Positive charge) in metallic crystal surrounded by large number of valence (mobile) electrons (fig. 3)

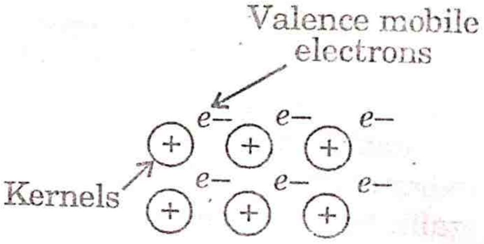


Fig. 3 : Valence e-around Kernels

3. These mobile electrons associated with metal atom can moves freely from one part of metallic lattice to other part (fig. 4).

   So we can say that there are sea of valence electrons in which positively charged kernels are immersed. Therefore, name of this model is **electron sea model.**

   Thus, metallic force is responsible for holding the atoms of metal together. It is defined as–

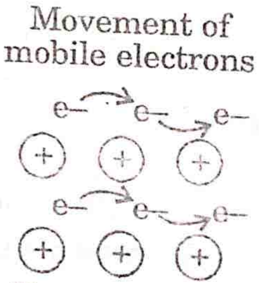


Fig. 4 : Free movements of mobile electrons

Simultaneous interaction between the mobile electrons and positive kernels that hold the metal atoms together is called metallic force (fig-5).

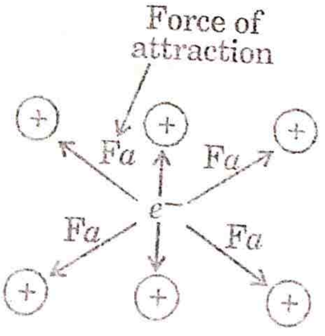


Fig. 5 : Metallic bond formation

Physical Properties of metals

The physical properties of metallic crystal can be explained on the basis of electron sea model. These properties given as –

1. Metallic lustre : The bright metallic lustre of metal is due to presence of loosely bound mobile electrons. When light falls on the surface of metal, the electron of metal atom absorb photon of light and start vibrating at frequency same as the frequency of incident light. From the emitted light, surface of metal aquires shining appearance (fig. 6).

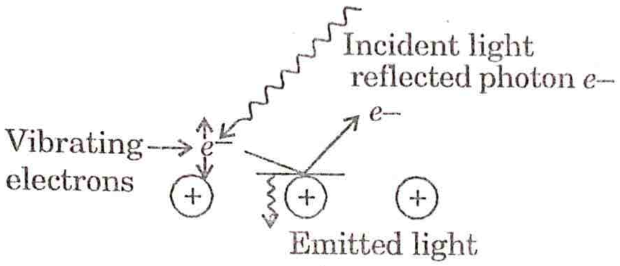


Fig. 6 : Metallic lustre

2. Electrical conductivity : The electrical conductivity of the metal due to presence of mobile electron. Under the influence of electrical potential the mobile electrons of metal moves towards the positive electrode. Thus in a metallic crystal the electrons flow from negative electrode to positive electrode (fig. 7).

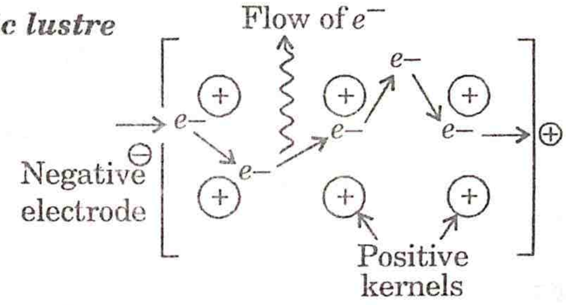


Fig. 7 : Movements of electrons

3. Heat (Thermal) Conductivity : The thermal or Heat conductivity of metal is due to the presence of mobile electrons. When a part of metal is heated, the electrons of that part aquires kinetic energy (Fig. 8).

These energetics electrons moves to the cooler part *i.e.*, towards kinetically low energetics e^-. Here they colloids with them and transfer its energy. Therefore, heat is travels from one part of metal to other part.

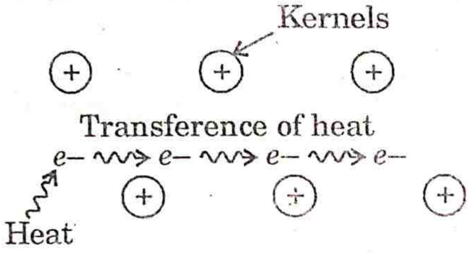


Fig. 8 : Thermal Conductivity

4. Ductility and Melleabilty : Metal can be drawn into wire (ductile) and can be beaten into sheets (malleability). The ductility and malleability of metal is due to non-directional nature of metallic bond. Wherever mechanical stress (hammering) is applied on the surface of metal, the position of kernels change without breaking the crystals (fig. 9).

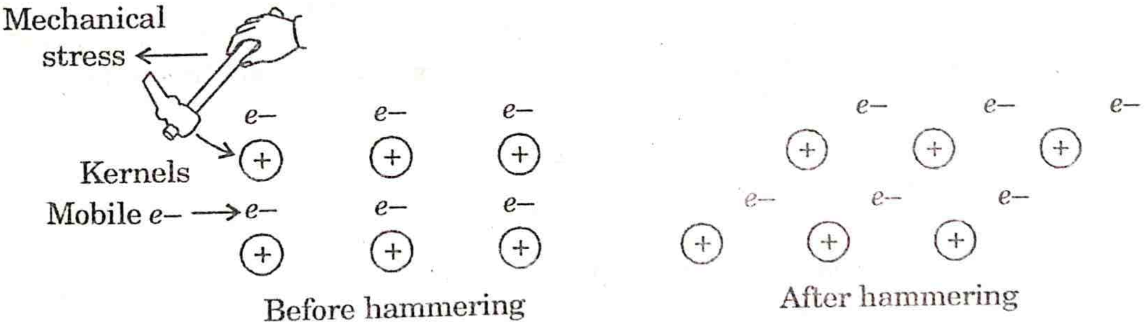


Fig. 9 : Before hammering

These metallic layers can slip over each other, so that metallic crystal get deformed. Therefore hammering simply moves the kernels from one lattice site to other lattice site and give the characteristics properties like ductility and malleability.

5. Tensile Strength : In metals their is strong electrostatic metallic force, so metal can be stretched without breaking (fig. 10)

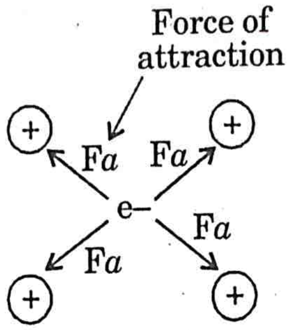


Fig.10 : Strong metallic force

6. Hardness :– The hardness of metals is due to the presence of strong electrostatic (metallic) bond.

The strength of metallic bond depend upon the following factors.

1. Size of Kernels : Smaller is the size of positive kernels greater is the attractive force for mobile electrons (fig. 11). Hence stronger is the metallic bond.

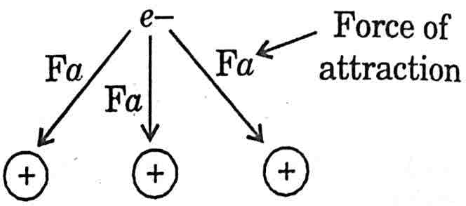


Fig. 11 : Strong metallic force

2. Number of mobile electrons : Greater the numbers of mobile electrons, more will be its delocalisation (movement) and more will be the attractive force. Hence form strong metallic bond.

Limitations of electron sea model

This theory can not explain the

1. High M.P*t* of W (3573 K)
2. Low M*pt*. of H*g* (234 K)
3. Density of Osmium is very high
4. It does not explain why some metal are good conductor than the other metal.

2. Valence Bond Theory (VBT): The valence bond theory was proposed by the Pauling. According to this theory the metallic bond is covalent in nature. This theory also called as **Resonance theory** because of resonance of *e*-pair between each metal and its nearest neighbour.

For example : In case of Li-atom, its electronic configuration is $1s^2\ 2s^1\ 2p^\circ$, so Li-atom can form only one bond, but it has been observed that each Li-atom surrounded by 8 other neighbouring L*i*-atoms. Therefore it is assumed that resonance takes place throughout the crystal. The different resonating strcuture are shown in (Fig. 12).

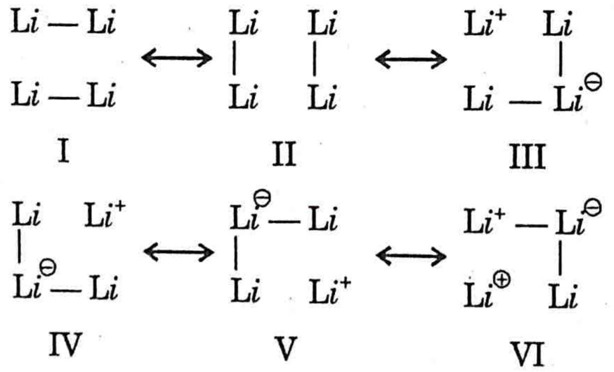


Fig. 12 Resonating structure of Li

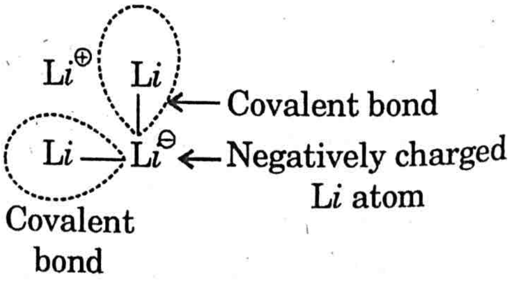


Fig. 13 : Covalent bond formed by lithium

In resonating structure III, IV, V and VI there is negative charge on L*i*-atoms which is attached with two other L*i*-atom by two covalent bonds as shown in fig. 13.

These covalent bonds is called **resonating covalent bonds.**

The formation of resonating covalent bond in Li-atom is given as

Explaination :

Consider the four Li-atoms as shown in figure-14

$$\begin{matrix} Li_x - Li_y \\ Li_a - Li_z \end{matrix}$$

Fig. 14 : Resonance bond in lithium

The electronic congiguration of each Li-atom say Li_x given as Li_x, $1s^2\,2s^1\,2p^o$, their is one valence electron in 2*s*-orbital while its all the three 2*p*-orbital are vacant, but 2*s* and 2*p*-orbitals of Li-are of comparable in energy. Thus, valence electrons of Li_x easily transferred to one of the three 2*p*-vacant orbitals of Li_z–atom to convert it into $Li_z^{\ominus}$ as shown in fig. 15

$$\begin{matrix} Li_x - Li_y \\ Li_a - Li_z \end{matrix} \longleftrightarrow \begin{matrix} Li_x^{\oplus} & Li_y \\ & | \\ Li_a - & Li_z^{\ominus} \end{matrix}$$

$$Li_x,\ 1s^2\,2s^1 \xrightarrow{-1e^-} Li_z,\ 1s^2\,2s^1\,2px^\circ\,2py^\circ\,2pz^\circ$$

$$Li_z^{\ominus},\ 1s^2\,2s^2\,2px^1\,2py^\circ\,2pz^\circ$$

Fig 15. : Formation of $Li^{\oplus}$ *and* $Li^{\ominus}$

Thus Li_z that have configuration *i.e.* $1s^2 2s^1 2px^1 2py^\circ 2p_z^\circ$ undergo *sp* **hybridization** and form two covalent bonds with Li_y and Li_a as shown in fig.-16

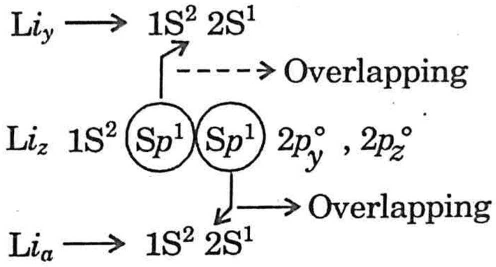
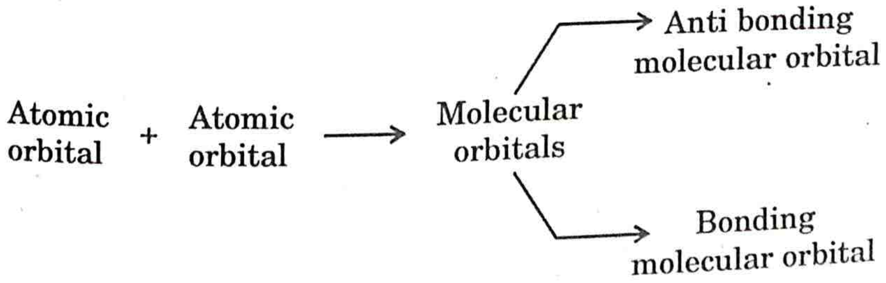


Fig. 16 : Covalent bond formation in lithium

After the formation of two covalent bonds with Li_y and Li_a, two vacant orbitals still left as in $Li_z\,(2p_y^\circ\,2p_z^\circ)$. These vacant orbital can accept electrons and responsible for metllic conduction. Therefore these two vacant orbitals $Li_z\,(2p_y^\circ, 2p_z^\circ)$ is called **metallic orbitals.**

3. Molecular orbital Theory or Band Theory : The bonding in metal can be explained by the molecular orbital theory. According to M.O.T., when two atomic orbitals overlaps with each other result in the formation of two molecular orbitals, one M.O. is of bonding type which is lower in energy while other M.O. is of anti bonding type which is of higher in energy. These two M.O.'s can be seperated from each other via. energy gap as shown –



For example

Consider Li-atoms: The electronic configuration of Li-atom is $1S^2, 2S^1$. So Li has one electron in its valence shell, its $1S^2$ electron does not takes part in the formation of bond.

In Li_2 – When two Li-atoms approaches towards each other, their 2S-atomic orbitals overlaps with each other and form two molecular orbitals, one is bonding while other is antibonding types as shown in Fig-17.

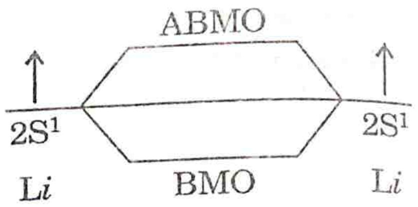


Fig. 17 : Formation of BMO and ABMO in Li

In Li_3 – Three Li-atoms approaches towards each other their 2S-atomic orbitals unites and give rise to three molecular orbitals, one is bonding, other is non-bonding and antibonding molecular orbitals.

The energy of non-bonding orbitals is same in magnitude as 2S-atomic orbital or in between B.M.O and ABMO.

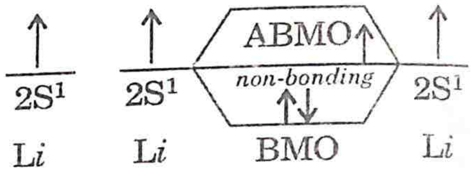


Fig. 18 : Formation of BMO, non-bonding and ABMO in Li_3

In Li_4 – Four Li-atoms give four molecular orbitals, two is bonding type while other two is antibonding type as shown in Fig. 19.

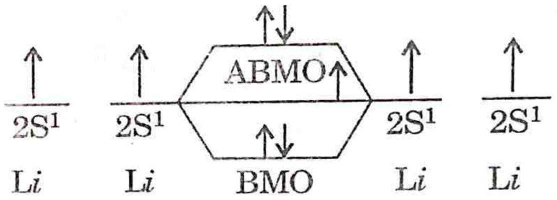


Fig. 19 : Formation of BMO and ABMO of Li_4

Similarly, **In Li_n** - n-Li-atoms overlap with each other give rise to 2n-molecular orbitals. Half of the orbitals (n) are of bonding typs while other half (n) is of antibonding types. Thus molecular orbitals formed is very large in numbers. So their energies level are close to each other as shown in Fig. 20. Such a group of energy level is known as **energy bands,** therefore its name is **Band Model** for metal.

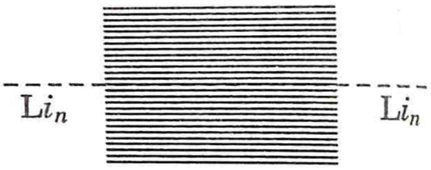


Fig. 20 : Formation of M.O.'s of Li_n

The number of energy levels in a band is equal to the number of atoms overlaps with each other. The formation of energy bands depend upon the

(1) The closeness of large number of atoms.

(2) and difference in energy between pure atomic orbitals

Formation of energy bands in Li_n

Electronic configuration of Li-atom is $1s^2 2s^1$. The '1S' orbital of lithium atom is full filled, hence doesn't participate in the formation of bond, only 2s-orbital takes part in the formation of bond.

In Li_2 the number of energy band formed is equal to two. In Li_4 the number of energy bands thus formed is equal to four. Similaly in Li_n the number of energy band is formed is equal to n.

The energy bands formed by the overlapping of 1S, 2S and 2p-orbitals of Li-atoms as shown in fig.21

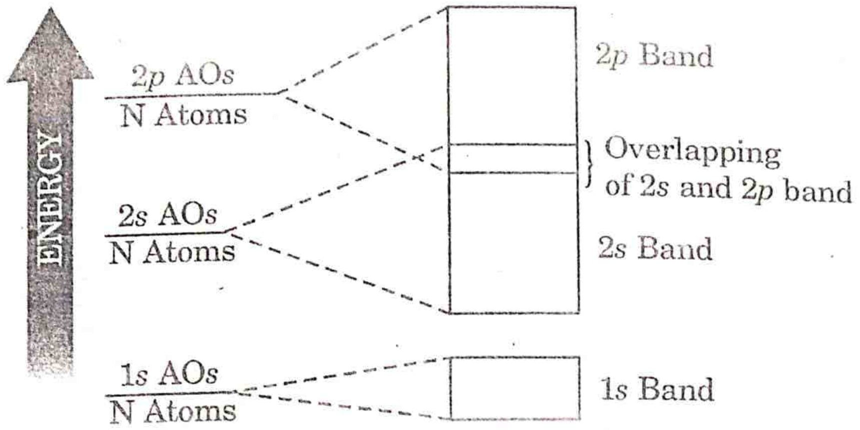
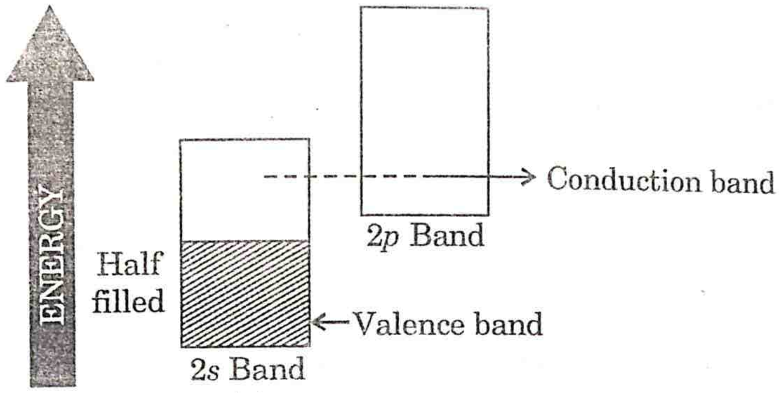


Fig. 21 : Formation of energy bands in lithium atoms.

Since in *Li*-atom their is one valence *e*-. Out of *n*-number of band, half of the bands filled with the electrons while other half of the bands remain empty (fig. 22).

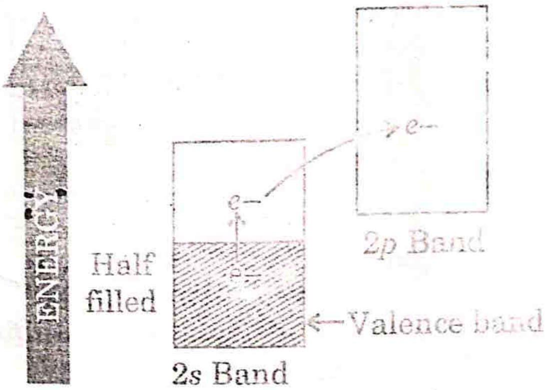
The 2p-orbital of *Li* also takes part in overlapping along with 2S-atomic orbital and give rise to large number of closely packed energy bands. Thus their are many empty bands into which electrons can move.



(a)

Fig. 22 : Band model of Li

1. Electrical conductivity :– The movement of electrons from one energy band (valence) to another energy band (conduction) responsible for an electric current as shown in fig.-23



(a)

Fig. 23 : Electrical Conductivity in Li

Thus Li is good conductor of electricity

2. Thermal conductivity :- The thermal conductivity of metal is also due to movement of electron from one band to another band by the action of heat (Fig. 24)

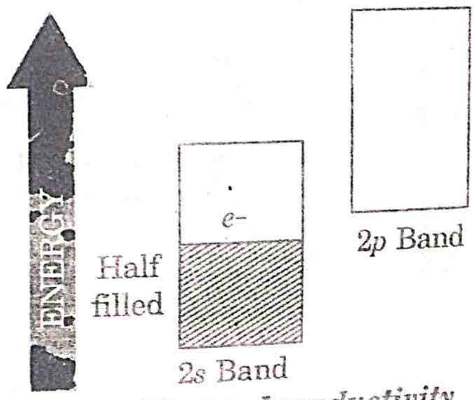


Fig. 24 : Thermal conductivity in Li

Similar explanation can be given for Na-metal

Formation of energy bands in Beryllium : The electronic configuration of Be is $1S^2\ 2S^2$. Its 2S - atomic orbital completely filled with electrons.Therefore overlapping of 2S-atomic orbitals of *Be*-does not give any empty band so we can say *Be* is bad coductor of electricity, but actually in *Be* 2*p*-orbital is empty, this empty 2*p*-orbital overlapping with 2S-orbital give many empty orbitals.

The lowest lying empty band is called **conduction band** and outermost filled band is called **valence band.**

Due to overlapping of 2S-orbital with 2p-orbitals some of the 2*p*-energy bands occupied and some of the 2*s*-energy band remain empty as shown in fig. 25.

Electrical Conductivity

The electrical conductivity of *Be* is due to movement of electrons from outermost filled band (valence) to lowest empty band (conduction) as shown in fig-26.

Similar explanation can be given for Mg-metal

3. Formation of energy band in aluminium : The electronic configuration of *Al* is $1S^2 2S^2 2P^6 3S^2\ 3P_x^1 3P_y^\circ\ .\ 3P_z^\circ$ The 3S-orbital of Al is fully filled while 3P*x* orbital is half filled while its 3py and 3pz orbitals are empty. These empty band is responsible for the electrical coductivity of *Al* i.e. movement of electrons from filled band (Valence) to empty conduction band as shown in Fig. 27

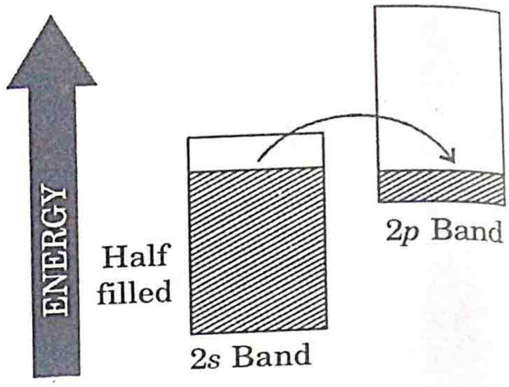


Fig. 25 : Electrical conductivity in Be

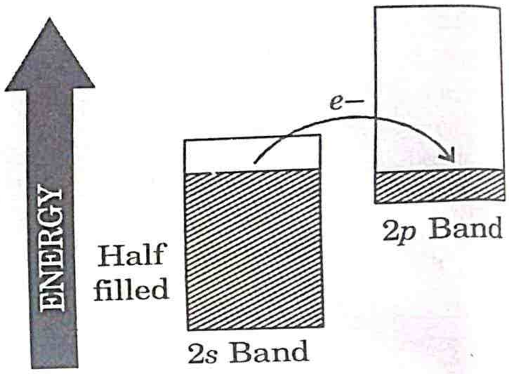


Fig. 26 :Electrical conductivity in Be

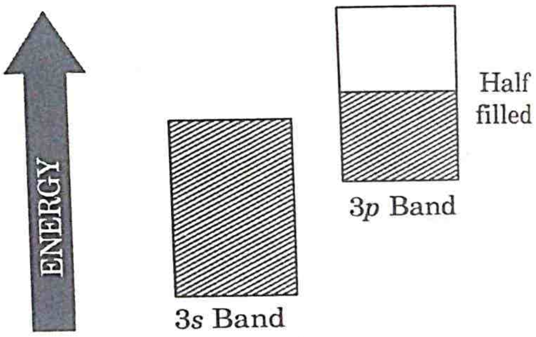


Fig. 27 : The band structure for aluminium

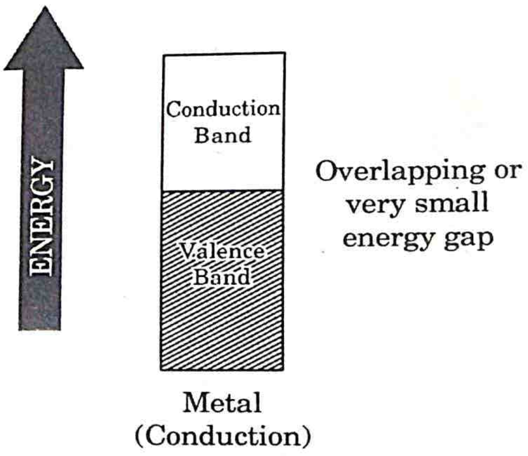


Fig. 28 : Valence band and Conduction band for metal

Energy bands (Valence and conduction bands) for metal

In metals, the energy gap between valence band to conduction band is very small, so electrons can jump easily from valence band to conduction band only at room temperature. Therefore, responsible for electrical conductance. (fig. 28)

Energy band for non-metals (Insulator)

In non-metals, the energy gap between valence band to conduction band is larger than energy gap of metal and semi-metal. Even at high temperature electrons cannot jump from valence band to conduction band. Hence, non-metals are bad conductor of electricity (fig. 29).

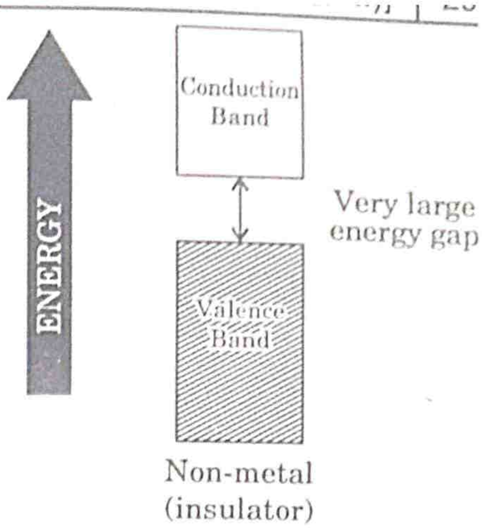


Fig. 29 : Valence band and conduction band for non metal

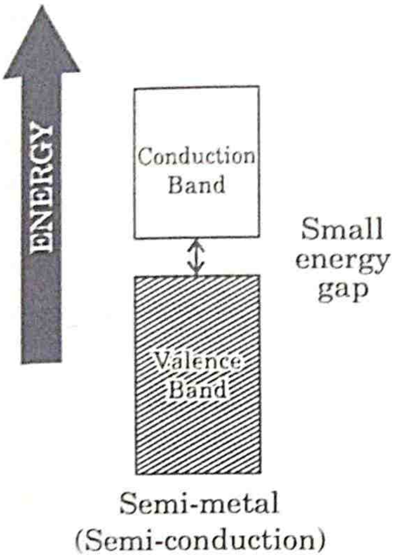


Fig. 30 : Valence band and conduction band for semimetal

Enegy band for semimetal:

The energy gap of semimetal lying between metals and non-metals. At room temperature electrons cannot jump from valence band to conduction band but on increasing temperature some of the electrons get energy and move from valence band to conduction band and responsible for increasing the electrical conductivity. Therefore, substance behave as semiconductor (fig. 30).

The energy gap of elements of Group-14 given in the table.

Table 1 : Bond energies of Carbon family

Energy in	C	Si	Ge	Sn
KJ mol^{-1}	508	105	57	8

Thus, from the energy gap given in the table we can say Sn is metal, Carbon is insulator while Si and Ge are semiconductor.

Semiconductors

The electrical conductivity of semiconductor at normal temperature lie in between conductor and insulator. The condutivity range of 10^2 to 10^{-9} ohm^{-1} cm^{-1}.

Semi conductors are very important materials have many applications.

The conductivity of a substance depend upon the energy gap between valence band and conduction band. The energy gap of various materials at zero K given in the table 2.

Table 2 : Band gaps of semicondcutors at 0K.

Compound	Energy gap E_g (KJ mol^{-1})	Compound	Energy gap Eg (KJ mol^{-1})
a-Sn	0	GaAs	145
Te	29	CdS	251
Ge	68	Cu_2O	212
Si	106	GaP	278
		ZnSe	269
PbTe	19	ZnO	328
PbS	29	ZnS	376
InAs	39		
InP	125	AIN	441

Semi conductors have a very small differences between the filled valence band and empty conduction band. On cooling these substances at absolute zero, all the electrons occupies the lowest energy level. The conduction band remain totally empty and the materials are perfectly insulator.

At room (normal) temperature, some of the electrons transferred from valence band to conduction band, hence they can conduct electricity upto small extent. Moreover, the conductivity of semiconductors also depends upon the numbers of electrons in the conduction band.

Germanium-*Ge* and silicon-*Si* are most important examples of semi-conductors.

The crystal structure of both similar to diamond. The elements *Si* and *Ge* have four electrons in their valence shell, thus form four covalent bonds. At a very low temperature the valence band of *Si* and *Ge* are fully filled with electrons and their conduction band are empty, under these conditions they are insulators.

The energy gap between valence band and conduction band of *Si* and *Ge* are 106 KJ mol^{-1} and 68 KJ mol^{-1} respectively at room temperature.

Types of Semi-conductors

They are of two types :–

1. Intrinsic semiconductors
2. Extrinsic semiconductor

1. Intrinsic semiconductors :– Intrinsic semiconductor are those substances in which conductivity produced due to effect of high temperature.

For example :–

In *Si* and *Ge*, the outermost electronic configuration is ns^2np^2 . Thus each atom of *Si* and *Ge* surrounded by four covalent bonds in the crystal structure. Therefore each atom associated with 8 *e*-and hence, is stable as shown in fig. 31

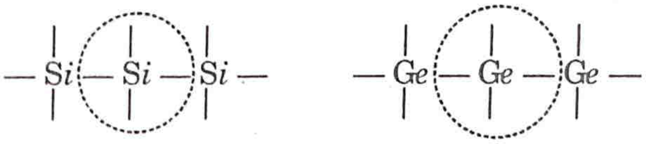
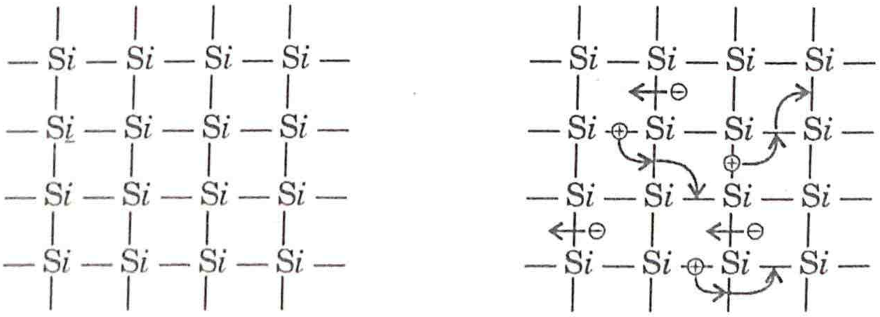


Fig. 31 : Perfect structure of Si and Ge

When temperature is very low say 0k. Their is no movement of electrons of covalent bond due to their fixed position. However on increasing the temperature one or more covalent bond break and release electrons creates a positive hole at the site of missing electrons as shown in fig-32.



(a) Network of pure silicon

(b) Intrinsic semiconductor in silicon

Fig. 32 : (a) Pure silicon (b) Silicon showing positive holes and negative electron.

The positive hole thus formed get electrons from near by covalent bond and a fresh hole is formed as shown in fig. 33.

The process run continue throughout the crystals. Thus crystal of Si and Ge conduct electricity. The movements of electorns are in one direction and movement of holes are in opposite directions. Therefore presence of positive hole responsible for conduction of electricity in the crystal of Si and Ge at high temperature. But their conductivity lies between conductor and insulator, so these elements generally act as semiconductors.

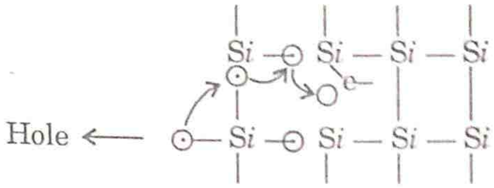


Fig. 33 : Movement of holes in silicon

Band Model of Intrinsic semiconductor

According to band model the energy gap between valence band and conduction band is not so large, this small energy gap can be overcome by the application of temperature (Thermal energy) fig-34. On increasing temperature some of the electrons jump from valence band to conduction band. Hence, substance generally act as semiconductor.

Effect of temperature on conductivity of semi-conductor

If the temperature increase the conductivity of semiconductors also increases, due to jumping of electrons from valence band to conduction band.

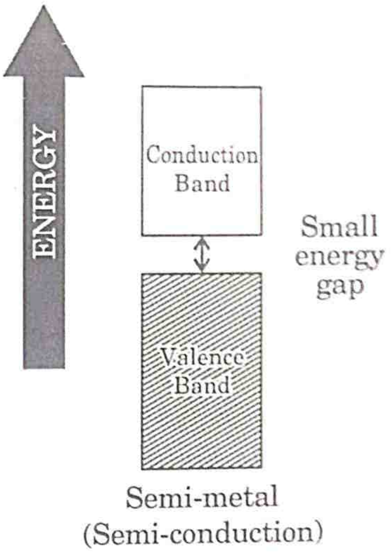


Fig. 34 Valence band and conduction band of semi-metal

2. Extrinsic semiconductor :– The conductivity of extrinsic type of semiconductor is due to the addition of foreign substance (impurities) in the crystal structure of other. It is also called as **doping** (fig. 35)

For the preparation of semiconductors of Si and Ge, they must be obtained in highly purified form.

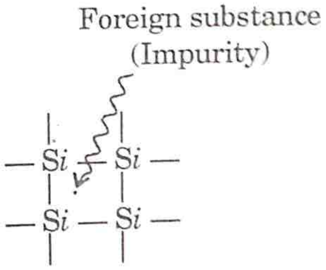


Fig. 35 Silicon doped with impurity

Preparation of Pure silicon :

Reduction of SiO_2 with C in the electric furnance at 1900°C give impure silicon (98%)

$$SiO_2 + C \xrightarrow{1900°C} \underset{(98\%)}{3Si} + CO_2$$

This silicon (98%) further purified by reacting it with HCl forming trichloro silane $SiHCl_3$. which may be purified by distilling and on decomposition give pure silicon as shown

$$Si + 3\,HCl \xrightarrow{350°C} SiHCl_3 + H_2$$

$$SiHCl_3 \xrightarrow[\text{Heat}]{\text{Strong}} Si$$

On increasing the temperature electrons are excited from valence band to (acceptor) impurity band and creating positive holes in the valence band. The motion of positive holes is responsible for conduction of electricity.

Application of Semi-conductors

Semi-conductors have wide range of application. These are used as rectifier, photovoltaic cells, photoelectrolytic cells, transistor and in integrated circuits etc.

Some important application of semi-conductors are discussed here.

1. Rectifier : A rectifier allow the current to flow from an outside source in one direction. Rectifier converting alternating current-(AC) into direct current-(DC). It is simply used as a diode which is a transistor with two zone whose one end is p-type and other end is n-type, so that p-n junction is formed as shown in fig. 43

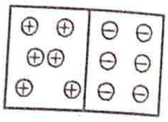


Fig. 43 : Diode

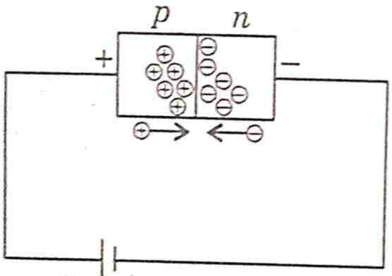


Fig. 44 : Behaviour of diode

Let a positive voltage is applied to the p-type of region and negative voltage is applied to the n-type of region (forward bias) so in p-type of region the positive holes will move towards the p-n junction and electrons also move towards the p-n junction. At the junction two destroy the effect of each other as shown in fig. 44

So we can say, the moving electrons fill the vacant space of positive hole. Therefore current will flow as long as external voltage is used.

If voltage are reversed the positive holes (p-region) and electrons (n-region) migrates away from the junction, so no current can flow. It is called reverse bias as shown in Fig. 45.

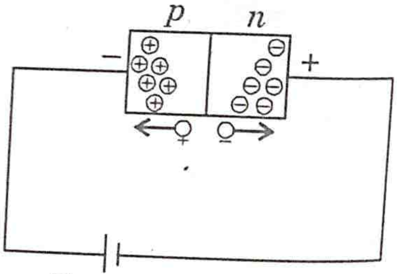


Fig. 45 : Behaviour of diode

2. Photovoltaic cell : In photovoltaic cell, p-n junction is irradiated with a source of light, if the energy of light source exceed than the energy gap, then some of the bond will break, produce positive hole and electrons. These electrons are promoted from valence band to conduction bands. These excess electrons make n-type region of conduction band more negative, while in p-type region the electrons are trapped by positive hole.

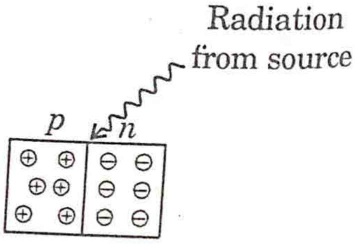


Fig. 46 : Diode irradiated with light

If these two region are connected by an external circuit then electrons flow from n-type region to p-type region while the current flow from p-type region to n-type region.

Thus, this device generate electricity from light.

Efferts are made by the scientist to prepare economically efficient cell to harnness solar energy.

3. Photoelectric cell :– In PEC's light energy used as a source of energy for electrolysis of water (fig. 47) producing dihydrogen and electrical energy, which can be used as a source for fuel. In PEC, when a n-type of semiconductor is placed in a solution containing redox couple (x^+/x), few numbers of electrons of semi conductor near the surfaces react with oxidising agent (x^+) by absorption of photon of light and promote an electron from valence band to conduction band and creates holes in the valence band. Due to movements of electrons they separate from each other *i.e.* holes remain at the surface while electrons moves towards the bulk of semi conductor. If the reduction potential of solution is low then, the species x of redox couple give electrons to hole according to the following reaction.

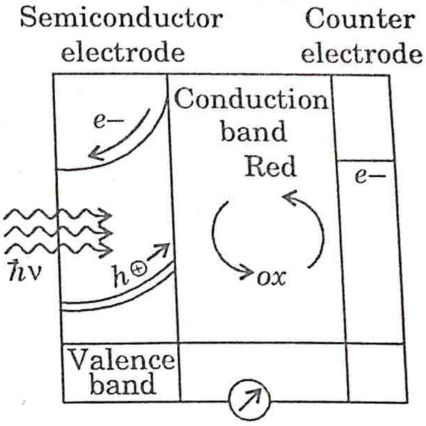


Fig. 47. PEC–General

$$x + h^+ \rightarrow x^{\oplus}$$

Now excited electron move through the wire of semiconductor to non photo electrode and reduce the oxidised species

$$y^{\oplus} + 1e^-, \rightarrow y$$

Thus overall reaction for the production of electrical energy given as

$$x + y^+ \rightarrow x^+ + y$$

For example :

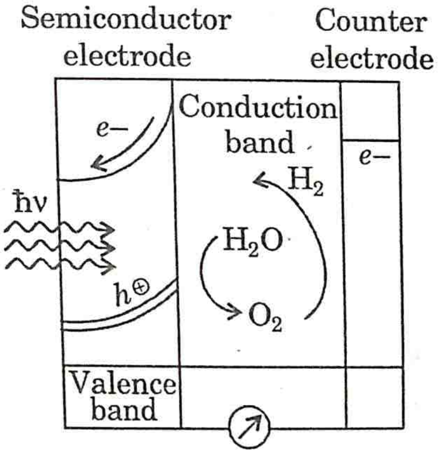
Similarly, in H_2O/O_2 and H^+/H_2 couples the following reaction occurs (fig-48).

$$H_2O \rightleftharpoons 2H^+ + \frac{1}{2}O_2 + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_2$$

Thus, net reaction given as

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$



3

s-Block Elements

The elements belong to group-1 and group-2 of the periodic table are called as S-block elements. The elements of group-1 are called as alkali's metal while the elements of group-2 are called as alkaline earth metals. These elements are placed towards the left side of the periodic table as shown in (fig. 1)

←s-block element→		←p-block element→						
IA (I)	IIA (2)		IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	Zero (18)
H_1 Li_3 Na_{11} K_{19} Rb_{37} Cs_{55} Fr_{87}	Be_4 Mg_{12} Ca_{20} Sr_{38} Ba_{56} Ra_{88}	↔ d-Block Element	B_5 Al_{13} Ga_{31} In_{49} Tl_{81}	C_6 Si_{14} Ge_{32} Sn_{50} Pb_{82}	N_7 P_{15} As_{33} Sb_{51} Bi_{83}	O_8 S_{16} Se_{34} Te_{52} Po_{84}	F_9 Cl_{17} Br_{35} I_{53} At_{85}	He_2 Ne_{10} Ar_{18} Kr_{36} Xe_{54} Rn_{86}

Fig. 1 Location of s-and p-block elements

The general electronic configuration of elements of group-1 is ns^1 while group-2 is ns^2. The alkali's metal are six in number namely lithium-(Li), Sodium-(Na), Potassium-(K), Rubidium-(Rb) Caesium-(Cs) and Francium-(Fr) while the number of alkaline earth metals are also six these are: Berylium-(Be), Magnesium-(Mg), Calcium-(Ca), Strontium-(Sr), Barium-(Ba) and Radium-(Ra).

In this present unit we shall make a study of their variations in moving down in each group

Group-1 Elements (S-block elements)

Group-1 of the periodic table contains six elements which are :-

$_3$Li-lithium
$_{11}$Na-Sodium
$_{19}$K-Potassium
$_{37}$Rb-Rubidium
$_{55}$ Cs-Caesium
$_{87}$ Fr-Francium

These are known as alkali's metals because their hydroxides are alkaline (water soluble base) in nature.

These elements have only one *e*- in their outermost shell ∴ its general electronic configuration is ns^1

The name of alkali's metals derived as *i.e.* the name of sodium derived from word **'soda'** which means **to split apart**, potassium from **potash** which means the **ash of plants**, Rubidium named after **ruby colour of spectral line**, caesium means **sky blue** due to formation of blue lines in the spectrum while name francium is derived in the honor of (M.M. Perey) her native land. It is a radioactive element. Its longest lived isotopes has a half life 21 minutes.

Occurance

The alkali's metals not found in free state in nature due to their highly reactive nature. They react violently with air so these elements are found in the combined state. The metal sodium exist as sodium chloride (as sea water or as large deposite on earth) while main source of potassium is carnalite - $KCl. MgCl_2.6H_2O$.

The main source of Li, Rb and Cs is **alumino silicate** yet in small quantities. F*r*-not found in nature due to its radioactive nature. The earth crust abundance of elements of group-1 given in the table1.

Table 1 : Abundance of an elements in the earth crush

Elements	ppm	(%)	Relative abundance
Li	18	0.0018	35
Na	22700	2.27	7
K	18400	1.84	8
Rb	78	0.0078	23
Cs	2.5	0.00025	46

Comparative study of alkali metals, group-1

The physical properties of an elements of group-1 given in the table-2

Table 2. Pysical properties of Alkali metals.

Property	**Li**	**Na**	**K**	**Rb**	**Cs**
Atomic number	3	11	19	37	55
Atomic mass	6.94	22.99	39.10	85.48	132.91
Density (g cm^{-3}) at 20°C	0.53	0.97	0.86	1.53	1.90
Melting point (K)	454	370.8	336.2	312.0	301.5
Boiling point (K)	1620	1154	1038.5	961.0	978.0
Atomic radius (pm)	123	157	203	216	237
Ionic radius (pm)	60	95	133	147	169
Ionisation energy I	520	496	419	403	376
(kJ mol^{-1}) II	7298	4564	3051	2633	2230
Electronegativity	0.98	0.93	0.82	0.82	0.79
Oxidation state	+1	+1	+1	+1	+1
E° value (V) [$M^+(aq) + e^- \rightarrow M(s)$]	–3.04	–2.71	–2.93	–2.99	–3.00
Flame coluration	Crimson red	Golden yellow	Pale violet	Violet	Bluish

1. Electronic configuration : The electronic configuration of alkali's metals given as in table-3

Table 3 : Group 1 (Alkali metals) configuration

Elements	At. No.	Electronic configuration
Lithium, Li	3	[He]$2s^1$
Sodium, Na	11	[Ne]$3s^1$
Potassium, K	19	[Ar]$4s^1$
Rubidium, Rb	37	[Kr]$5s^1$
Cesium, Cs	55	[Xe]$6s^1$
Frencium, Fr	87	[Rn]$7s^1$

These metls have one electron in their outermost shell. Therefore their general configuration is ns^1, Here (n = 2 – 7)

2. Physical state : All these metals are exist as solid. The alkali's metals are soft solid except Li and are malleable and ductile in nature. They can be cut with Knife in fresh form. They give metallic lustre that tarnished in air after sometime due to their highly reactive nature.

3. Atomic and ionic radii : Alkali's metals have largest size in whole of the periodic table. They have large atomic radii and largest ionic radii in their respective period (fig. 2).

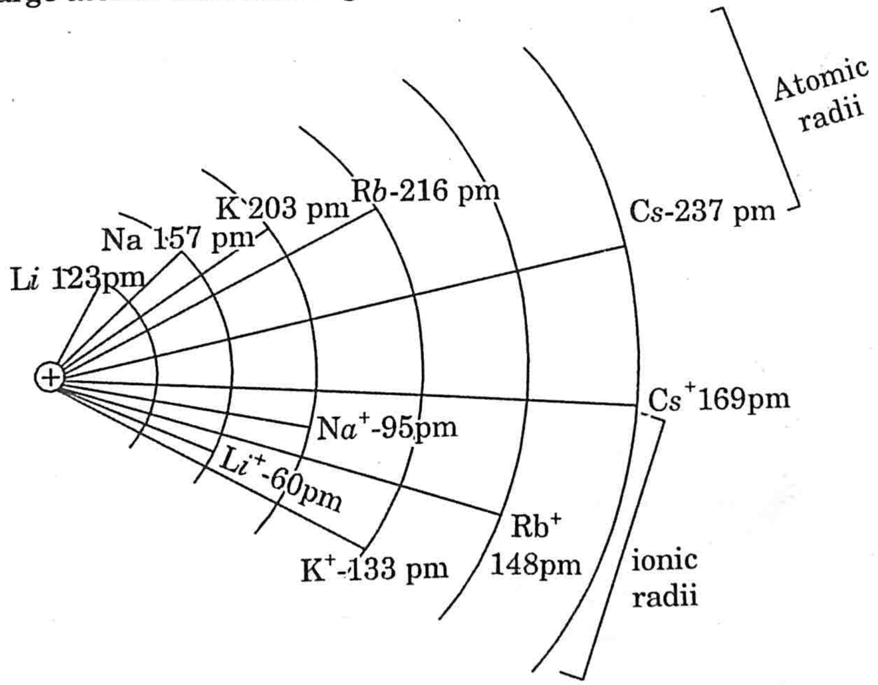


Fig. 2 : Atomic / ionic radii of alkali's metal

The atomic and ionic radii of an elements of group-1 in their respective period generally decreases due to increase in magnitude of effective nuclear charge (fig. 3).

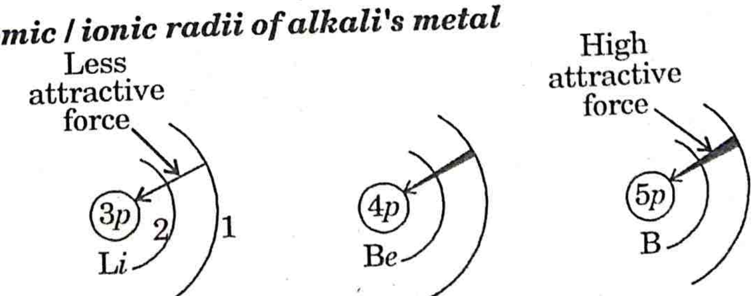
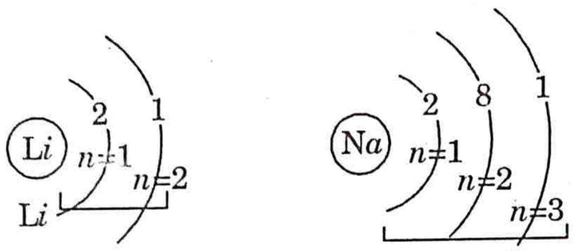


Fig. 3 : Variation of atomic radii in period

The atomic and ionic radii generally increases in group, due to increase in number of shells and screening effect and decrease in effective nuclear charge as shown in fig. 4.



2-Shells 3-Shells

Fig. 4 : Variation in atomic radii in group

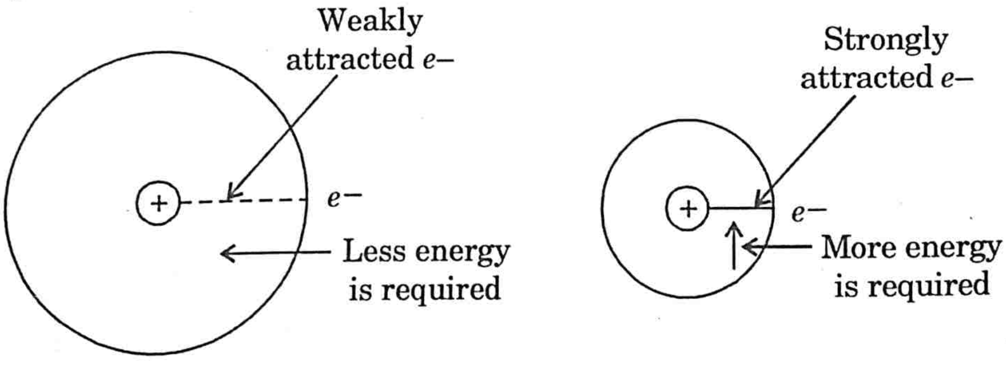
4. Ionization energy (KJ/mol^{-1})

Table 4 : I.E. of Group-I

Elements	Li	Na	K	Rb	Cs
IE$_1$ IE$_2$	520 7298	496 4564	419 3051	403 2633	376 2230

Alkali's metal have lowest value of I.E. in their respective period, because in period the size of alkali's metals is large ∴ its valence electron loosly held by the nucleus. Hence can be removed easily.

Moreover, the atom of alkali's metals after removing their valence electron aquires stable noble gas configuration as shown in fig. 5.



Alkali metal Other metal

Fig. 5 : Comparison of I.E. of alkali metal with others

The ionization enthalpy of alkali's metals decreases in group, because of increase in number of shells, screening effect and decrease in magnitude of effective nuclear charge. After loss of one electron, the alkali's metals aquires stable noble gas configuration as shown in fig. 6.

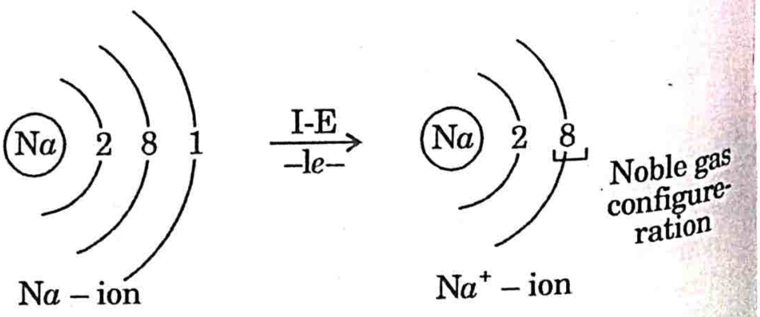


Fig 6. : Aquirance of noble gas configuration

The metals of group-1 loss their one electron only, so they form stable monovalent cation

$$Na \xrightarrow{496 \text{ KJ mol}^{-1}} Na^+ + le^-$$

But the second ionization enthalpy of alkali's metal are very-very high.

This is because, after removing one electron, the alkali's metals aquire stable noble gas configurtion. So, it is difficult to remove electron easily from noble gas core. Here 2nd I.E. of alkali metals are very high (fig-7).

IE_1 and IE_2 of Na-atom.

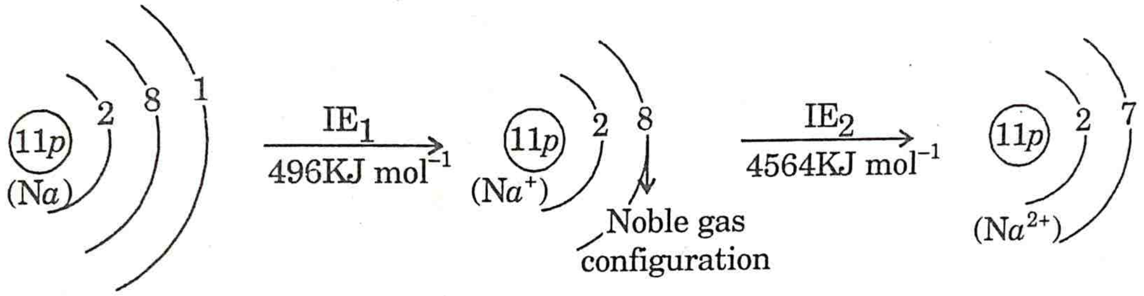


Fig. 7 : IE_1 and IE_2 of sodium metal

5. Melting point and Boiling Point

Table-5 : M.*pt*/B.*pt* of alkali's metals

M.P*t*	L*i*, 454 K	N*a*, 370.8K	K, 336 K	Rb, 312 K	C*s*, 301.5K
B.P*t*.	L*i*, 1620 K	N*a*, 1154 K	K, 1038.5K	Rb, 961 K	C*s*, 978 K

The alkali's metals generally have low M.P*t* and B.P*t*. This is due to their large size and less number of valence electrons, they do not form strong metallic bond (Fig. -8)

Moreover **M.*pt*. and B.*pt*. generally decreases in groups** due to increase in size of alkali's metals and decrease in strength of metallic bond.

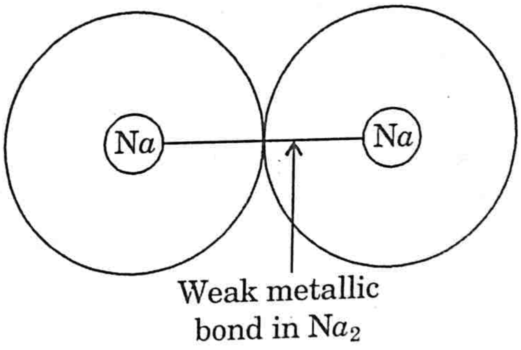


Fig. 8 : Metallic bond in Na_2

6. Density

Table-6 : Density of alkali's metal at 20°C

	L*i*	N*a*	K	R*b*	C*s*
At 20°C	0.53 g/cc	0.97	0.86	1.53	1.90

Alkali's metals are lighter than other metals some of the metals (L*i*, Na, K) floats on the surface of water

Density of alkali's metals generally increases in group (Fig-9)

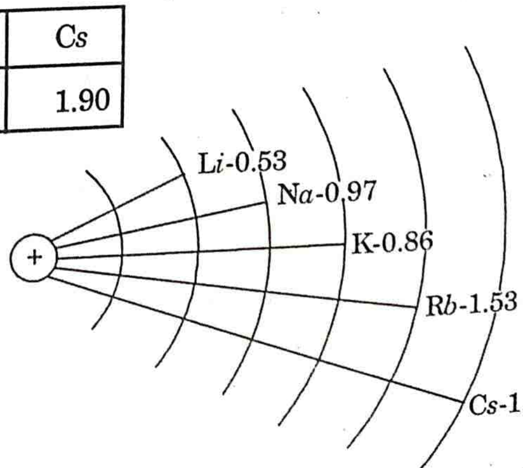


Fig. 9 : Densities of alkali's metal

Explanation : In group both atomic masses and atomic volume increases.

But magnitude of increase in atomic masses is greater than increase in atomic volume, so density is directly related with atomic masses acc. to equation, $d = m/v$. Therefore, density increases in group

Density of K (0.86 *g/cc*) is less than *Na* (0.97 g/cc) (fig.-10)

Explanation : The density of K, is less than *Na*, due to unexpected increase in volume, in case of K (203 pm), which is greater than *Na* (157 *pm*), This increase in volume is greater than increase in masses, so that density decreases.

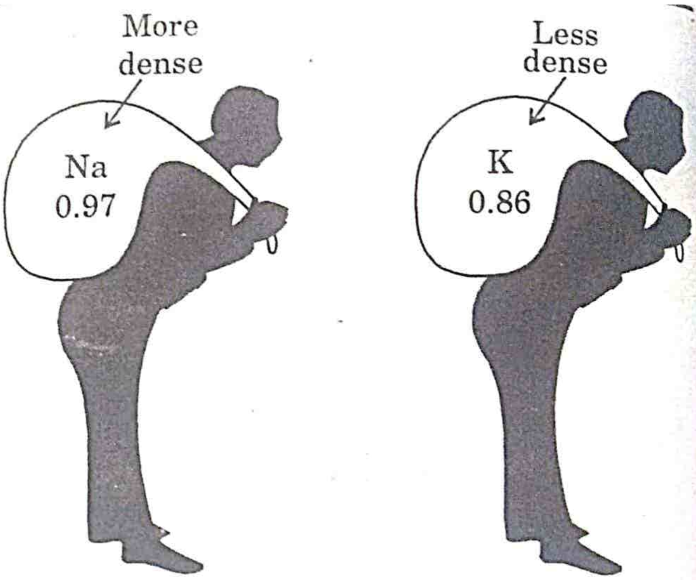


Fig. 10 : Density of Na and K

7. Electropositive Nature : All the alkali's metals strongly metallic in nature because size of alkali's metal is large. So they easily loses their valence electron with a supply of very small amount of ionization energy as shown in fig. 11.

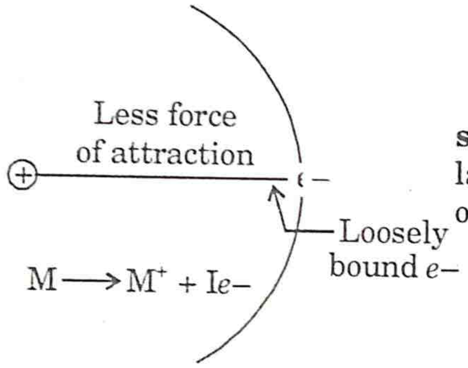


Fig. 11 : Electropositive nature of alkali's metals

The **metallic nature generally increase in group,** this is due to decrease in magnitude of I.E. with the increase in size of alkali's metals (fig. 12)

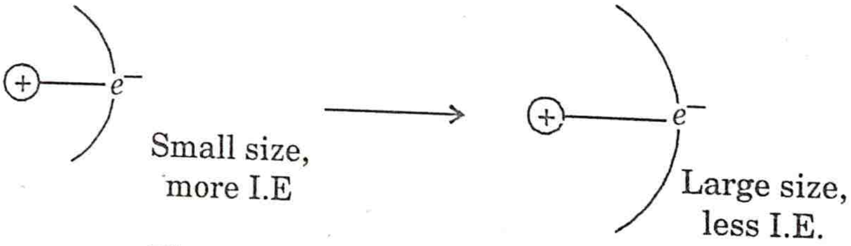


Fig. 12 : Metallic nature in Group

8. Oxidation State : All the alkali's metals exhibits the oxidation state of +1 in all the compounds.

As given $M \longrightarrow M^{\oplus} + ie^{-}$ (M = L*i*, N*a*, K, R*b*, C*s*)

This is because of large size of alkali's metals and less value of their I.E. They losses their one e^- readily and aquires stable noble gas configurtion. So that these elements exhibits the oxidation state of +1.

9. Flame colouration : All the alkali's metals and their salt imparts characteristics colour on the flame of bunsen burner.

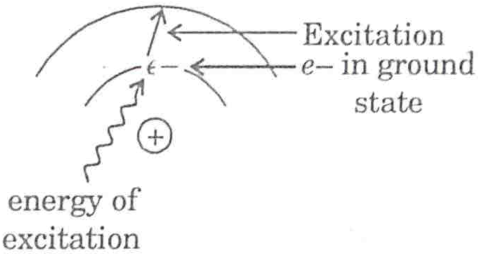


Fig. 13 : Excitation of e^-

Explanation

Alkali's metals have low value of I.E.

So energy of bunsen burner is sufficient to excite the electrons of alkali's metals. The excited state is the highest energetics state that is unstable. The life time of e^- of alkali's metals is very small (i.e. 10^{-8} sec) in the excited state, when this electrons jump back (ground or normal state) gives the corresponding colour (fig. 14)

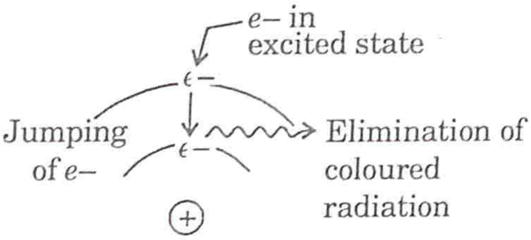


Fig. 14 : Production of Colour

The characteristics colour of alkali's metal given in the table-7

Table 7 : Colour of alkali's metals

Li	Crimson Red
Na	Golden yellow
K	Pale violet
Rb	Red violet
Cs	Blue

As the size of alkali's metals increases, the frequency or energy of the emitted light also increases. The different colour emitted by the alkali's metals is due to different amount of excitation energy is required for different alkali's metals.

The colours thus emitted by the alkali's metals are complementary. The complementary coloured charts is given as

For exmaple : If an element emit blue colour it will absorb orange (complementary) colour and so on. (Fig. 15)

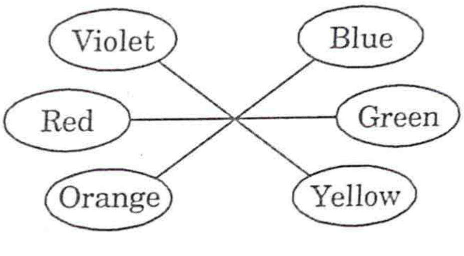


Fig 15 : Complementary Colour Chart

10. Photoelectric effect : Alkali's metals show the phenomenon of photoelectric effect. The ejection of *e*- from the surface of metal when radiation of suitable frequency falls on its surface. (Fig. 16)

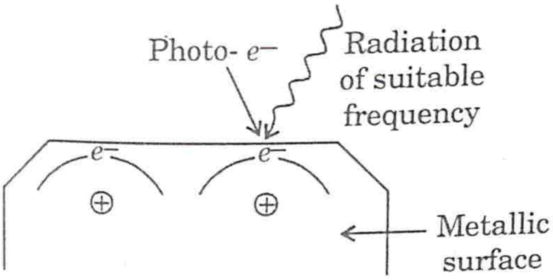


Fig. 16 : Photoelectric effect

Explanation : Alkali's metals have low value of their ionization enthalpy, when radiation of suitable frequency fall on its surface. They eject or emit their electron. Caesium is the alkali's metal that show the photoelectric effect, due to their large atomic size and low I.E. Therefore generally used in photo voltaic cell.

11. Nature of Compounds : The alkali's metals generally form an ionic compound with the atoms of non metal. But Li generally form covalent bond due to their small size and high electron density around the nucleus. Therefore it can easily polarize anion and form covalent bond. ($LiCl$, $LiBr$, LiI)

Explanation : This is due to large size of alkali's metals they loss their electron readily and form ionic compound .The tendency to form ionic bond generally increases in group, due to increase in size of alkali's metals and decrease in value of I.E.

12. Lattice energy : The salts of alkali metals made up of cation and anion

$$\underset{\text{Salt}}{MX} \longrightarrow M^{\oplus} + X^{-}$$

These ions held with each other via strong electrostatic forces of attraction, so large amount of lattice energy (*i.e.*, amount of the energy is required to dissociate one mole of ionic solid into its constituents ions) is required to break their crystal structure. The magnitude of lattice enthalpy incrases if attractive force among the ionic solid increases.

Factors on which magnitude of lattice energy depends.

The lattice energy depends upon the size of ions and charge on the ions

1. If the anion is same and cation of same nuclear charge but difference in their size is considered, the lattice enthalpy given in the table-8 :

Table 8 - Salt and its lattice enthalpies

Salt	Lattice enthalpy (KJ mol^{-1})
$LiCl$	803
$NaCl$	759
KCl	681
$RbCl$	661
$CsCl$	619

2. Similarly if cation is same and anion of same nuclear charge is considered, but have difference in their size, their lattice enthalpy given as in the table-9.

Table 9 : Salt and its lattice enthalpy

Salt	Lattice enthalpy (KJ mol^{-1})
NaF	895
$NaCl$	759
$NaBr$	715
NaI	669

So we can concluded that the lattice enthalpy decreases with increase in the size of either cation or anion, due to decrease in magnitude of attrative force.

13. Electrolysis of aqueous solution of salt of alkali metals : Generally alkali metals cannot be obtained from their aqueous solution of salt.

Explanation : Consider, the salt $NaCl$, when $NaCl$ dissolve in water. It dissociates in the following manner (fig. 17).

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

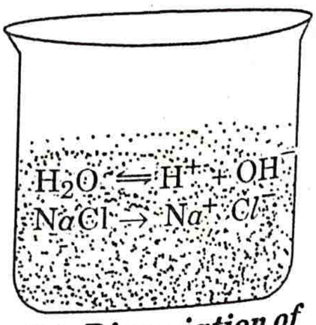


Fig. 17 : Dissociation of NaCl in water

Along with $NaCl$ small amount of water also get decomposed as shown

$$H_2O \longrightarrow H^+ + OH^-$$

Therefore, four types of ions (Na^+, Cl^-, H^+ and $\bar{O}H$ are present in the aqueous solution of salt ($NaCl$)

On Electrolysis both cation (Na^+, H^+) moves towards cathode but discharge potential or mobility of H^+ ion is greater than Na^+ ion, So H^+ ion liberated at the cathode and form $H_2(g)$.

$$2H^+ + 2e^- \longrightarrow H_2$$

While Na^+ ion remain in the solution. Similarly, both Cl^- and $\bar{O}H$ moves towards anode, but discharge potential or mobility of Cl^- ion is greater than $\bar{O}H$ ion.

So, Cl^- ion liberated at the anode and form $Cl_2\,(g)$

$$2Cl^- \longrightarrow Cl_2(g) + 2e^-$$

14. Heat of atomisation

Alkali is metals have low heat of atomisation, due to presence of weak interatomic bond in alkali metals.

Chemical Properties :

1. Reducing Nature : All the alkali metals are strong reducing agent.

Explnation : This is due to their low value of I.E.. They loss electrons quickly (fig. 18)

In gas phase caesium is strongest reducing agent.

Explanation : This is due to largest size of caesium atom and its low I.E. They loss electron quickly and generally act as reducing agent. The reducing nature of following alkali's metals given as

$$Cs > Rb > K > Na > Li$$

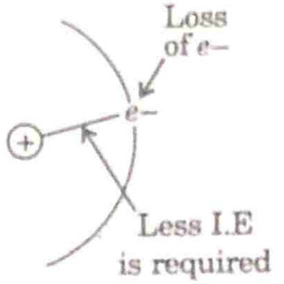


Fig. 18 : Loss of e^- by the alkali metal

In aqueous phase 'Li' is strongest reducing agent

Explanation : Lithium is strongest reducing agent in aqueous solution because in aqueous solution Li^+ ion is highly hydrated with the molecules of water as shown in Fig. 19 and release large amount of hydration energy (531 KJ mol^{-1}). Thus, hydration energy compensate the I.E. and make the Li atom strongest reducing agent.

$$Li \longrightarrow Li^+ + 1e^-$$

$$Li^+ + xH_2O \longrightarrow Li^+\,(aq) + \text{Hydration energy}$$

$$Li + \text{Hydration energy} \longrightarrow Li^+ + ie^-$$

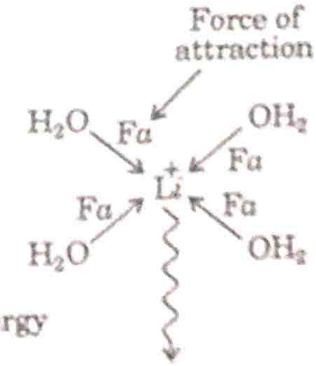


Fig. 19 : Interaction of Li^+ ion with the molecule of water

Therefore, the order given as

$$Li > Cs > Rb > K > Na$$

All the alkali is metals are strongest reducing agent, than hydrogen and therefore, react with the compounds containing acidic hydrogen and liberates $H_2(g)$.

$$2M + HCl \longrightarrow 2MCl + H_2$$

$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + \frac{1}{2}H_2$$

$$Na + CH \equiv CH \longrightarrow CH \equiv C^- Na^+ + \frac{1}{2}H_2$$

The reduction potential of alkali's metals given in the table-10

Table 10 : Reduction potential of alkali's metal

S.No.	Elements	Reduction reaction	Reduction potential
1.	Lithium	$Li^+ + 1e^- \longrightarrow Li$	– 3.04 V
2.	Sodium	$Na^+ + 1e^- \longrightarrow Na$	– 2.71 V
3.	Potassium	$K^+ + 1e^- \longrightarrow K$	– 2.93 V
4.	Rubidium	$Rb^+ + 1e^- \longrightarrow Rb$	– 2.99 V
5.	Cesium	$Cs^+ + 1e^- \longrightarrow Cs$	– 3.00 V

2. Reactivity : **Alkali's metal are highly reactive metals in whole of the periodic table.**

Explanation : This is due to their large size and less value of their I.E. They are highly reactive towards non-metals and generally form ionic bond.

The reactivity in **group generally increases.**

Explanation : This is due to increase in size of alkali metals and decrease in value of I.E., so we can concluded that Li react slowly, Na react vigorously while K, Rb and Cs react violently.

The order of reactivities of alkali is metals given as

$$Cs > Rb > K > Na > Li$$

3. Reaction with air : **All the alkali's metals react vigorousoly with air or oxygen when alkali's metals exposed to air or oxygen then get tarnished due to formation of oxide on its surface,** the oxide thus formed on the surfaces of alkali is metals are of three types.

(i) Normal oxides containing O^{2-} ion

(ii) Peroxides containing O_2^{2-} ion

(iii) Superoxides containing O_2^- ion

(I) Oxides

Oxides of lithium – Li_2O

Pure Li_2O is formed by decomposition of Li_2O_2 at 450°C

$$Li_2O_2 \xrightarrow{450°C} Li_2O + \frac{1}{2}O_2$$

Li_2O is white in colour and stable upto 500°C.

Oxide of sodium – Na_2O

It is prepared by the action of Na metal on NaOH, Na_2O_2 and $NaNH_2$

$$NaOH + Na \longrightarrow Na_2O + \frac{1}{2}H_2$$

$$Na_2O_2 + 2Na \longrightarrow 2Na_2O$$

$$NaNH_2 + 3Na \longrightarrow 2Na_2O + \frac{1}{2}H_2$$

It is also white in colour. It is stable upto 500°C.

Oxides of other alkali's metals : K_2O, Rb_2O, Cs_2O

These are prepared in similar manner as mentioned in case of Li and Na

When alkali's metals burned in air, Li form only simple oxide- Li_2O

Explanation : This is due to the fact that small cation can stabilize the small anion. Lithium ion is very small in size, therefore has strong positive field around it so it can stabilize only a small anion $(O^2)^-$. The stronger positive field of Li^+ ion prevent the spreading of negative charge towards another oxygen atom. Thus form simple oxide only

Moreover, Li^+ ion small in size. ∴ has less surface area, so less numbers of oxygen atom can attack ∴ form simple oxide only

(II) Peroxide (O_2^{2-})

Peroxide of lithium – Li_2O_2

It is prepared by the reaction of lithium hydroxide monohydrate LiOH. H_2O with H_2O_2, the product thus formed decomposes and give Li_2O_2 as shown.

$$LiOH.H_2O + H_2O_2 \longrightarrow LiOOH.H_2O + H_2O$$

$$2\,LiOOH.H_2O \longrightarrow Li_2O_2 + H_2O_2 + H_2O$$

Li_2O_2 is white cyrstalline solid, it is stable upto 200°C.

Peroxide of sodium Na_2O_2

It is prepared by reacting sodium metal in the presence of dry air, the product thus formed react further and give sodium peroxide

$$2\,Na + ½\,O_2 \xrightarrow{\Delta} Na_2O \xrightarrow{H_2O} Na_2O_2$$

It is pale yellow powder

Peroxide of other alkali metals, Rb_2O_2, Cs_2O_2

These are prepared by the oxidation of alkali's metals in liquid ammonia

$$M + x + y\,(NH_3) \longrightarrow M^+(NH_3)_x + e^-(NH_3)_y$$

$$O_2 \xrightarrow[\text{electron}]{\text{ammoniated}} O_2^- \xrightarrow[\text{electron}]{\text{ammoniated}} \underset{\text{Peroxide}}{O_2^{2-}}$$

When alkali's metals burn in air only sodium metal form peroxide.

Explanation : The size of sodium ion is large ∴ it can stabilize large anion. The positive field around the sodium ion is weak and doesn't prevent the spreading of negative charge over other oxygen atom. Thus, form peroxide.

Moreover, the sodium ion large in size therefore, possess large surface area, so large number of oxygen atom can attack, and form peroxide.

(III) Superoxide (O_2^-)

Sodium superoxide – NaO_2

It is prepared by reaction of Na - Metal with liquid NH_3 and air

$$Na + x + y\,(NH_3) \longrightarrow Na^+(NH_3)_x + e^-(NH_3)y$$

$$O_2 \longrightarrow \xrightarrow[\text{electron}]{\text{ammoniated}} O_2^-$$

Superoxide of other alkali's metals K, *Rb* and *Cs*.

They are obtained by burning these metals with oxygen.

Only K *Rb* and Cs from superoxide

Explanation : K, Rb and Cs ion large in size. Therefore, their positive field is very weak, these ion cannot prevent the spreading of negative charge on oxygen atoms and form superoxide.

Moreover, due to large size of these metals and large surface area, large number of oxygen atom can attack simultaneously. Therefore exist as superoxide ion as shown in fig. 20

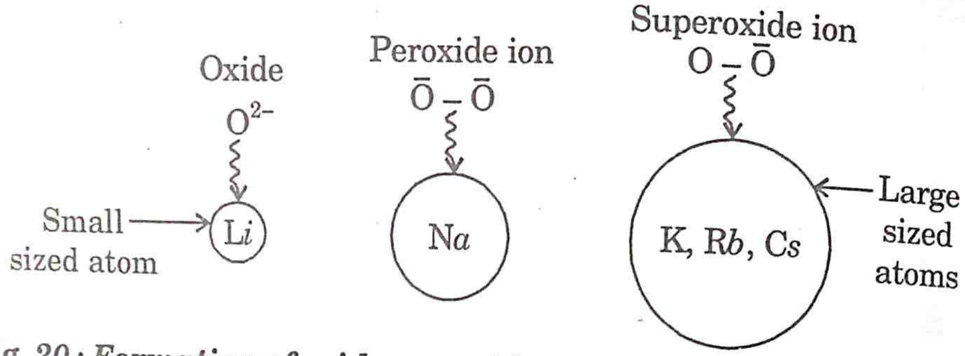


Fig. 20 : Formation of oxide, peroxide and superoxides of alkali's metal

4. Reaction with Hydrogen

All the alkali is metals react with hydrogen to form hydrides of general formula (M^+H^-)

$$2M + H_2 \longrightarrow 2M^+H^- \; (M - Li, Na, K, Rb, Cs)$$

The hydrides of alkali metals are generally ionic is nature.

1. Reactivity : The reactivity of alkali's metals with hydrogen in group generally increases.

Explanation : This is due to increase in size of alkali metals the value of I.E. decreases.

II. Nature : Ionic nature of hydrides generally increases in group.

Explanation : This is due to increase in size and decrease in I.E., the valence electron of alkali metals is easily available for H-atom to form Hydride (H^-) easily.

III. Stability : Stability of hydride in a group generally decreases.

Explanation : This is due to increase in size of alkali's metal, M—H bond strength decreases (fig.-21), so bond cleave easily. Therefore stability of hydride decrease.

Li-H	Cs — H
Bond length - less	Bond length-large

Fig. 21 : M-H bond length of alkali's metals

IV. Reducing Nature : Reducing Nature of hydrides generally increases in a group.

Explanation : This is due to increase in size of alkali is metal. The strength of M-H bond decreases (fig. 22), so bond cleave easily. Therefore reducing nature of hydride increases.

Li—H	Cs———H
Bond length	Bond length

Fig. 22 : M–H bond strength of alkali's metal

(V) Action of water : Hydride of alkali metals ion reaction with water liberates H_2 gas

$$MH + H_2O \longrightarrow MOH + H_2$$

*Li*H — is use as a source of hydrogen for meterological observation.

5. Reaction with water

All the alkali's metal react with water to form metal hydroxide and $H_2(g)$

$$M + H_2O \longrightarrow MOH + ½ H_2$$

Reaction of Li with water is slow but other alkali metals react vigorously with water. So that $H_2(g)$ evolved immediately and catch fire. The alkali metals normally kept in kerosene oil.

Explanation : The reaction of alkali metals with water vigorously. Therefore, the hydrogen gas thus evolved immediately catch fire, so we kept alkali's metal in kerosene oil.

Kerosene oil make a covering on the surface of alkali's metals. So only a small part of alkali's metals in direct contact with moisture.

The hydroxide of alkali metals are basic in nature.

Explanation : The hydroxide of alkali's metal formed by the reaction of alkali's metal with water

$$M + H_2O \longrightarrow MOH + ½ H_2$$

They are ionic in nature. The M—OH bond is weak that cleaves easily and give $\overline{O}H$ (Hydroxide) ion. Therefore are basic in nature.

Basic nature of hydroxide of alkali metals generally increases down the group.

Explaination : In group size of alkali metals generally increase, it also increases the bond length of M——OH bond (Fig. 23)

So bond became weak and dissociate easily and release $\overline{O}H$ ion.

∴ basic nature generally increase. The order of basic strength given as

$CsOH > RbOH > KOH > NaOH > LiOH$

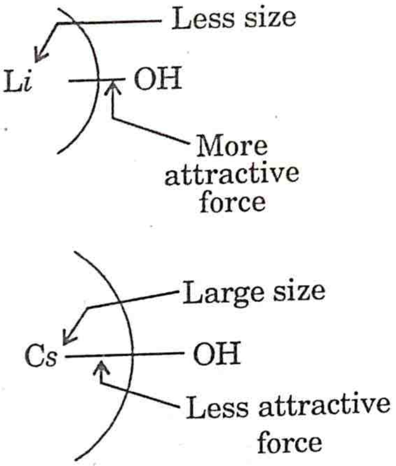


Fig. 23 : M—OH bond strength

6. Reaction with halogen

The alkali metals react with halogen and form halide of general formula

$$M + X \longrightarrow M^+X^-$$

(M = Li, Na, K, Kb, Cs) (X = F, Cl, Br, I)

The reactivity of alkali's metal towards halogens increases on moving down in group.

Explanation : This is due to increase in size of the alkali metals and decrease in magnitude of I.E.

Alkali's metal hydride generally ionic in nature

Explanation : The ionic nature of halide is due to large size of metals and their less I.E. While halogen atom are highly electronegative elements accept electrons from alkali's metal immediately.

LiI generally covalent in nature.

Explanation : Because Li^+ ion small in size. Therefore possesses high polarizing power while size of Iodide ion (I^-) is very large. Therefore, possess high polarisability

LiF generally insoluble in water.

Explanation : This is due to the fact their high value of lattice enthalpy (small cation, Li^+ and small anion, F^-). The bond formed between Li^+ ion and F^- ion is strong.

7. Solubility in liquid ammonia

Alkali's metals dissovle in liquid ammonia give deep blue solutions.

Explanation :

In liquid ammonia the alkali's metals dissociate in the following manner.

$$M + (x + y)\,NH_3 \longrightarrow M+ (NH_3)\,x + e^- (NH_3)y$$

This ammoniated electron absorb red wave length of light and get excited. When this excited e-jump back it reflect blue light. ∴ solution of alkali metals in liquid ammonia blue in colour (Fig. 24)

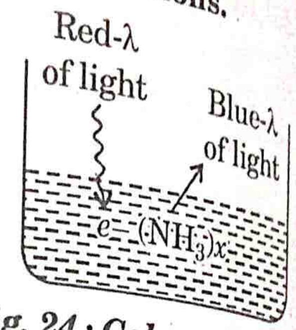


Fig. 24 : Colour of alkali's metal in $NH_3(l)$

The solution of alkali's metals in liquid ammonia are conducting in nature.

Explanation : The conducting nature of solution is due to presence of ammoniated cation $M(NH_3)_x$ and ammoniated e^-, $(e\!-(NH_3)y)$. Under the influence of electric field both cations and anion show movements.

The dilute solution of alkali's metal generally paramagnetic in nature but in concentrated solution paramagnetic character generally decreases.

Explanation : In dilute solution their is unpaired e^- in the solution of metal in ammonia. As the concentration of solution increases, the unpaired e^- get pair up.

$$2e^- (NH_3)y \longrightarrow [e^- (NH_3)y]_2$$

The solution of alkali is metal in ammonia generally act as good reducing agent.

Explanation : This is due to the presence of ammoniated e^- $(NH_3)y$ they reduce O_2 into (O_2–) superoxide ion and O_2– to O_2^{2-} (peroxide ion)

On standing the solution of alkali's metal liberates $H_2(g)$.

Explanation : On standing the solution dissociation in the following manner :

$$2M + 2NH_3 \longrightarrow 2\,MNH_2 + H_2$$

Anomalous behaviour of Li

The behaviour of Li is different than other member of alkali metals group. This is mainly due to following reason :

1. Lithium atom and Lithium ion are in small size.
2. The I.E. of Li is very high.
3. Li^+ ion has high polarising power *i.e.* charge/size. Therefore have high tendency to form covalent bond.
4. It does not have vacant d-orbital in its valence shell.

Therefore some properties of Li that make it differ from the rest of the elements of group Their characteristics properties given below :

1. The polarising power of Li^+ ion is very high. Therefore has tendency to form covalent compound and are soluble in organic solvent while other members are insoluble in organic solvent.
2. Lithium is largest metal while other metals are soft.
3. The M.Pt and B.Pt of Li is very high.
4. It is least reactive towards water.
5. Li from monoxide only.
6. It react with nitrogen and form nitride

$$Li + N_2 \longrightarrow Li_3N$$

7. Li react with silicon and form lithium silicide, Li_6Si_2
8. It is least reactive metals.
9. Li react with carbon and form carbide.
10. Its Hydroxide is unstable decomposes on heating

$$2\,LiOH \longrightarrow Li_2O + H_2O$$

11. Its carbonate is also unstable and decomposes on heating.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

12. $LiNO_3$ on heating produce NO_2 while other member do not give NO_2

$$4\,LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$NaNO_3 \xrightarrow{\Delta} NaNO_2 + 1/2O_2$$

13. LiH, is more stable and act as source of H_2.
14. LiOH is least basic than other alkali metals hydroxide.
15. Li^+ ion due to their small, size highly hydrated with the molecules of water. Thus give large amount of hydration energy.
16. LiF sparingly soluble in water.
17. LiCl is deliquescent and form $LiCl.2H_2O$
18. Its hydrogen sulphide (LiSH) is unstable.
19. Li on heating with ammonia form imide Li_2NH while other alkali's metal form amide MNH_2.
20. Only LiCl undergo hydrolysis.

Diagonal Relationship : It has been observed that elements belonging to period second show similarities in properties with the elements of next group and next period placed diagonally is called diagonal relationship.

Few diagonal relationship shown below :

$$\begin{tikzcd} \text{Second Period} & Li \arrow[dr] & Be \arrow[dr] & B \arrow[dr] & C \\ \text{Third Period} & Na & Mg & Al & Si \end{tikzcd}$$

Thus Li diagonally related with Mg, Be releated with Al while B diagonally related with Si and so on.

Cause of Relationship

The similarities in properties of an element Li with element of Mg due to following reason :

1. **Electropositive character** : **Electropositive characters of both Li and Mg almost same.**

Explanation : In period, size of an element generally decreases while in group, size of a element generally increases on moving diagonally the increased size and decreased size cance the effect of each other. As a result electropositive character remains same.

2. Polarising power : In period, the magnitude of polarising power generally increas due to decrease in size of ion while in period polarising power decreases (fig. 25) due to increas in size of metals.

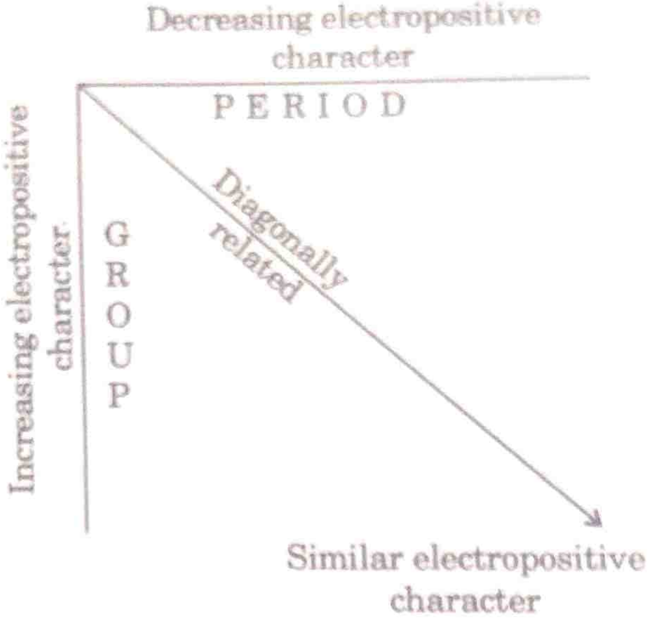


Fig. 25 : Diagonal relationship

GROUP-2

Group-2 of the periodic table contains six elements these are

$_4Be$ $_{12}Mg$ $_{20}Ca$ $_{38}Sr$ $_{56}Ba$ $_{88}Ra$

These are known as **alkaline earth metals** because their oxides are alkaline in nature and remain unaffected by the action of fire and heat and also exist in earth's crust. The element of Group-2 has two electrons in its valence shell. Therefore its electronic configuration is ns^2 ($n = 2\text{-}7$).

Occurance

These elements do not occur in free state in nature because of their high reactivity. Elements Be is present in very small qunatity (2 ppm). It is found in minerals like **Beryl**, $Be_3Al_2S_6O_{18}$. Mg is sixth most abundance elements in earth crust. Salt of Mg occur in sea water. It occur mainly in minerals **dolomite**, $MgCO_3.CaCO_3$.

Calcium is fifth most abundant elements in earth's crust. The main source of Ca is $CaCO_3$. Sr and Ba is less abundance. Sr and Ba mainly expected from $SrSO_4$ and $BaSO_4$. But Ra is present in very-very **rare amount due to their radioactive in nature.** The earth crust abundance of elements of group-2 given in the table-11

Table 11 : Abundance of an elements in the earth crust

Elements	ppm	Relative abundance
Be	2.0	51
Mg	27640	6
Ca	46600	5
Sr	384	15
Ba	390	14
Ra	1.3×10^{-6}	—

Comparative study of alkaline earth metals. The physical properties of an alkaline earth metals given in the table-12

Table 12 : Physical properties of alkaline earth metals

Property	Be	Mg	Ca	Sa	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic mass	9.14	24.31	40.08	87.62	137.34	(226)
Atomic radius (pm)	112	160	197	215	222	—
Ionic radius (pm)	27	72	100	118	135	148

Property	Be	Mg	Ca	Sa	Ba	Ra
Ionic (g cm–3)	1.85	1.74	1.05	2.03	3.62	5.5
Ionisation energy (kJ not^{-1}) IE$_1$	899	738	590	549	503	509
IE$_2$	1757	1451	1146	1064	965	979
IE$_3$	14849	7733	4910	—	—	3281
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.90
Oxidation state	+2	+2	+2	+2	+2	+2
Melting point (K)	1560	920	1112	1041	1000	973
Boiling point (K)	2770	1378	1767	1654	2123	1800
E° (V)	–1.70	–2.37	–2.87	–2.89	–2.90	–2.92

1. Electronic configuration : The electronic configuration of alkaline earth metals given as in table-13

Table13. Group 2 (Alkaline earth metals) electronic configuration

Element	At. No	Electronic configuration
Beryllium, Be	4	$[He]2s^2$
Magnesium, Mg	12	$[Ne]3s^2$
Calcium, Ca	20	$[Ar]4s^2$
Strontium, Sr	38	$[Kr]5s^2$
Barium, Ba	56	$[Xe]6s^2$
Radium, Ra	88	$[Rn]7s^2$

These metals have $2e^-$ in its valence shell. Therefore their general electronic configuration is ns^2 ($n = 2–7$).

2. Physical Properties : These elements are malleables and ductiles and also have greyish white lustre (when cut Freshly).

3. Atomic and ionic radii : Their atomic and ionic radii generally smaller than an elements of group-1 (Table 14)

Table 14 : Atomic/ionic of Group-1 and Group-2 element (in pm)

Li (123, 60)	Na (157, 95),	K (203, 133)	Rb (216, 148)	Cs (273, 169)
Be (112, 27)	Mg (160, 72)	Ca (197, 100)	Sr (215, 118)	Ba (222, 135)

Explanation : The nuclear charge in alkaline earth metals is greater than alkali metals. Therefore, the attraction of electrons is more towards the nucleus. As a result atomic and ionic raddi smaller than alkali's metals.

In Group : The atomic and ionic radii in group, generally increases.

Explanation : This is because of increase in number of shells, so effective nuclear charge decreases. ∴ atomic and ionic radii increases in group.

4. Ionization enthalpy (in KJ mol^{-1})

The value of IE_1, IE_2, IE_3 given in the table-15

Table 15 : Values of I.E. for elements of group-1 and group-2

IE_1	Li-520	Na-496	K-419	Rb-403	Cs-376	
IE_1	Be-899	Mg-738	Ca-590	Sr-549	Ba-503	Ra-509
IE_2	Be-1757	1451	Ca-1146	1064	965	979
IE_3	14849	7733	4910	—	—	3281

The I.E. of alkaline earth metals are low.

Explanation : This is due to large size of their atoms.

The alkaline earth metals have higher value of I.E. than Group-I (Table-16)

Explanation : This is because of their small size, the electrons attracted more towards the nucleus. Therefore IE_1 of alkaline earth metals is greater than IE_1 of alkali's metals.

The IE_2 of alkaline earth metals smaller than those of alkali metals

Table 16-IE_2 of elements of group-I and group-2 in KJ mol^{-1}

Li-7298	Na-4564	K-3051	Rb-2633	Cs-2230
Be-1757	Mg-1451	Ca-1146	Sr-1064	Ba-965

Explanation : Consider the alkali's metals such as Na, Its electron configuration is given as (Fig. 26)

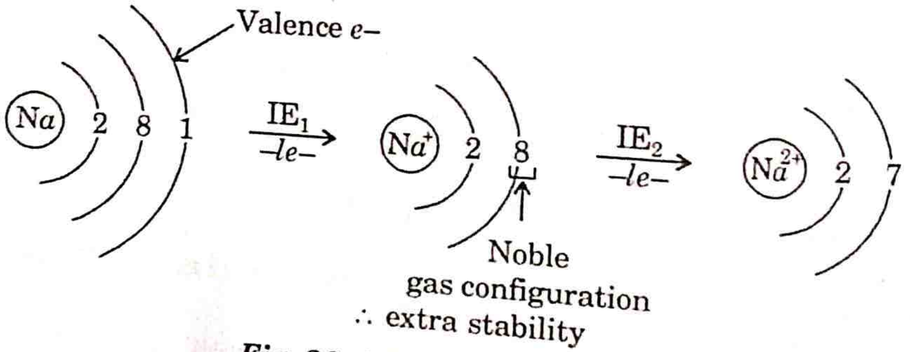


Fig. 26 : IE_1 and IE_2 of Na-atom

$$\underset{2,\,8,\,1}{Na(g)} \xrightarrow[IE_1=496]{-1e} \underset{2,8}{Na^+(g)} \xrightarrow[IE_2=4564]{-1e} \underset{2,7}{Na^{2+}(g)}$$

In case of alkali's metal (Na), 2nd e^- must be removed from noble gas core. Hence, requires large amount of I.E.

While in case of alkaline earth metals. Consider, the case of Mg (fig.27)

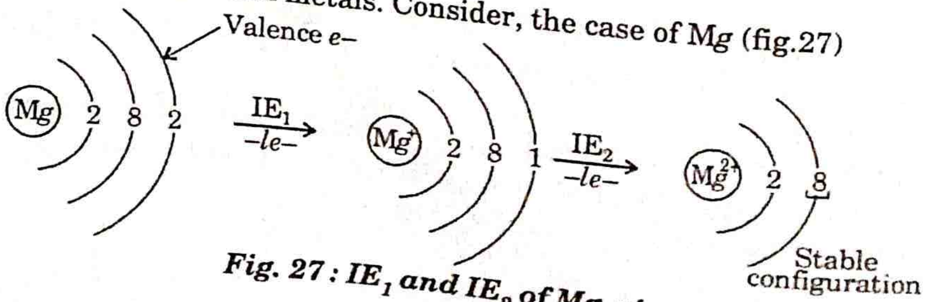


Fig. 27 : IE_1 and IE_2 of Mg-atom

$$\underset{2,8,2}{Mg(g)} \xrightarrow[IE_1=738]{-e} \underset{2,8,1}{Mg^{+}} \xrightarrow[IE_2=1451]{-e} \underset{2,8}{Mg^{2+}(g)}$$

In Mg, after removing 2^{nd} e^-, it acquires stable noble gas configuration. Therefore, it loss 2nd e- quickly.

3rd, IE of Mg is very-very high (fig. 28)

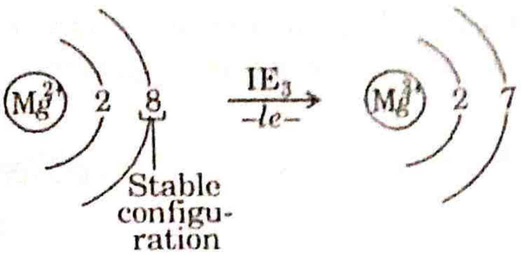


Fig. 28 : Comparison of IE_2 and IE_3 of Mg

$$Mg^{2+} \xrightarrow[-e]{IE_3=7233} Mg^{3+}$$

Explanation : This is because after removing 2nd e^-, the elements of group-2 aquires noble gas configuration. Therefore 3rd e^- must be removed from the noble gas core. Therefore, possesses high value of I.E.

I.E. alkaline earth metal in group decreases.

Explanation : This is because in group size of an atom increases and that decrease the magnitude of attractive force, ∴ I.E. decreases.

5. Melting point and Boiling Point :

Alkaline earth metal have low value of Mpt and Bpt.

Explanation : This is because of their large size and less bond dissociation energy.

The Mpt and Bpt of Group-2 elements gretaer than Group-1 (fig-29)

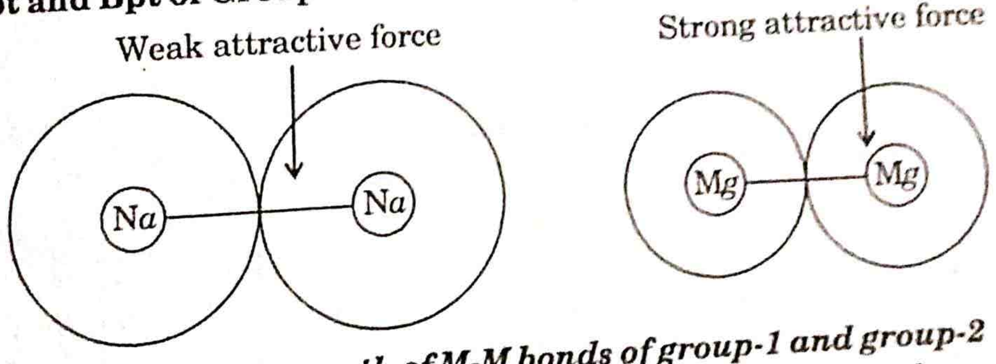


Fig. 29 : Strength of M-M bonds of group-1 and group-2

Explanation : The elements of group-2 are smaller in size than elements of group-1, therefore attracted more towards each other.

6. Density : Alkaline earth metals are more dense than alkali's metals.

Explanation : This is because of their atomic size which is smaller than an elements of group-1.

Density of elements of group-2 generally increases.

Explanation : This is because of increase in mass of an elements. The density is directly related with atomic masses of an elements.

The density of Ca is smaller than Mg.

Explanation : In case of Ca, there is unexpected increase in volume as compared to mass.

7. Electropositive Nature : Alkaline earth metals are strongly electropositive in nature.

Explanation : This is because of their large size and less value of I.E.

The electropositive nature in group generally increases.

Explanation : In group, the size of alkaline earth metals generally increases, so that value of I.E. decreases that increase their electropositive nature.

8. Oxidation State : The alkaline earth metals shows the oxidiation state of +2.

Explanation : The +2, oxidation state of group-2 elements due to following reasons :

1. After loss of two electrons the elements of group 2 aquires stable noble gas configuration.
2. In aqueous solution the M^{2+} ions are highly hydrated and release large amount of hydration energy.

$$\underset{\substack{\text{Alkaline}\\\text{earth}\\\text{metals}}}{M} \xrightarrow[-e]{IE_1+IE_2} M^{2+} + aq \longrightarrow M^{2+}(aq) + \text{Hydration Energy}$$

This hydration energy compansate the I.E.

3. In solid state, the magnitude of lattice energy is so high that it can compensate the $IE_1 + IE_2$.

$$\underset{\text{Strong bond}}{X-M-X} \xrightarrow{L.E} M^{2+} + 2X^-$$

9. Flame Colouration : Salt of alkaline earth metals impart colour in bunsen flame (Fig. 30)

Explanation : The colour of alkaline earth metals are due to, when their metallic salt burnt, their electrons get excited, when this excited e^- jump back give corresponding colour.

The different colours given by the alkaline metals in table-17

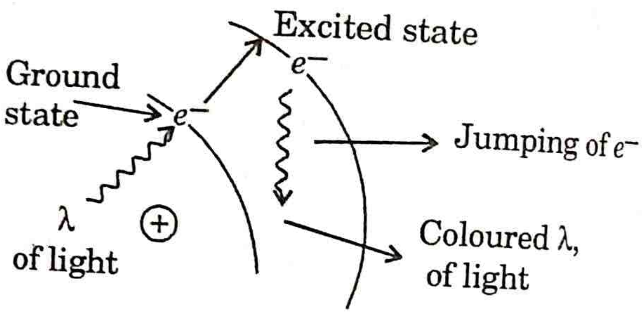


Fig. 30 : Colour production from element of group-2

Table 17 : Colour of alkaline earth metals

Ca	Brick Red
Sr	Crimson Red
Ba	Apple green
Ra	Crimson Red

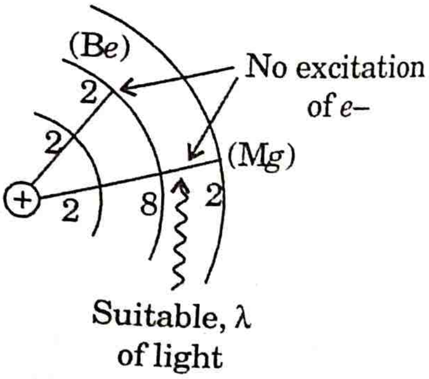


Fig. 31 : Non production of colour by Be and Mg

Be and Mg do not impart colour in bunsen flame. (fig.31)

Explanation : This is because, Be and Mg smaller in size, their I.E. is very high. So energy of the flame unable to excite the electrons of Be and Mg. Hence these metals (Be and Mg) do not give any colour in bunsen flame.

10. Nature of compounds : Be and Mg generally form covalent compounds (fig. 32)

Explanation : This is according to Fajan's rule, the size of their cations (Be^{2+} and Mg^{2+}) is small, therefore it can polarised the anion to greter extent, as compared to other alkaline earth metals. Hence form covalent compounds.

But the other elements of this group have less tendency to form covalent compounds (fig. 32)

Explanation : This is because these elements large in size and have less I.E. There fore they loss electrons quickly. Moreover there cation is also large in size, It cannot polarise the anion to greater extent. Thus form ionic compounds.

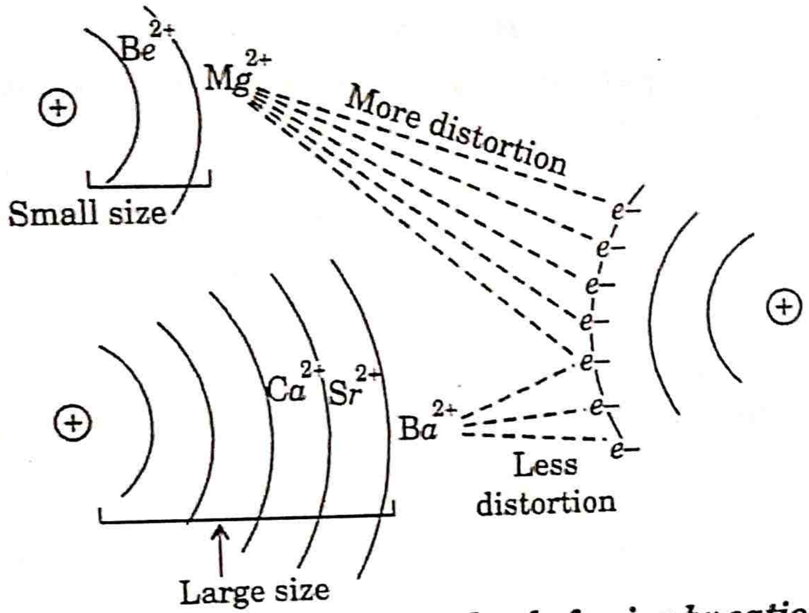


Fig. 32 : Distortion of e⁻ cloud of anion by cations

11. Conductivity : The alkaline earth metals are good conductor of heat and electricity.

Explanation : This is because, the alkaline earth metals have 2e^- in its valence shell. These electrons move freely throughout the crystals. Therefore, becomes good conductor of heat and electricity.

12. Hydration energy (in kJ mol^{-1}) : The magnitude of hydration energies of alkaline metals generally decrease in group.

Be^{2+} – (2494), Mg^{2+} (1953.9), Ca^{2+} (1577), Sr^{2+} (1443), Ba^{2+} (1352)

Explanation : This is because, in group atomic and ionic radii generally increases. So, attractive force between ions and molecules of water decreases. So, less amount of hydration energy is released.

The hydration energy of M^{2+} ions greater than M$^+$ ions (Fig. 33)

Explanation : This is because the magnitude of nuclear charge on M^{2+} ions greater than M$^+$ ions. So, force of attraction created by M^{2+} ions greater than M$^+$ ion. Consequently, M^{2+} ions has greater hydration energy than M$^+$ ions.

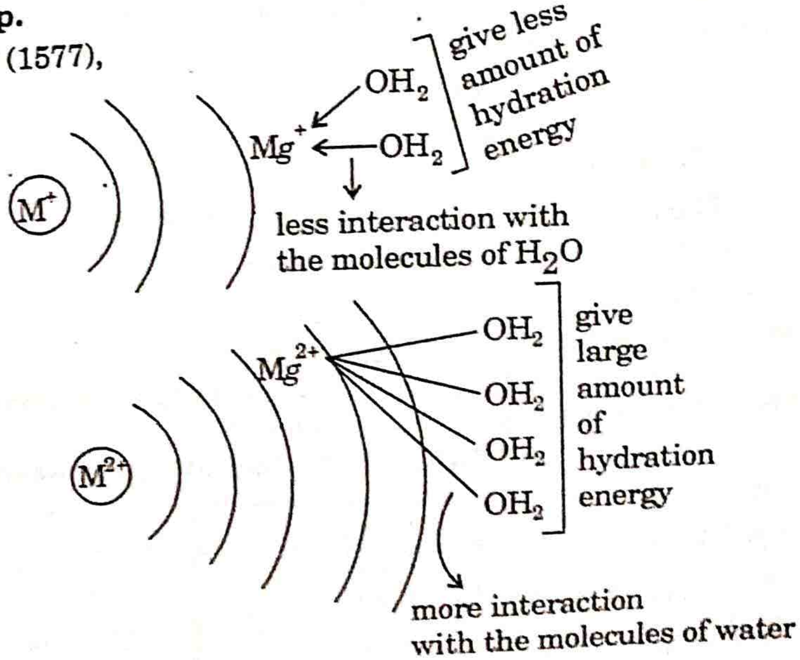


Fig. 33 : Magnitude of Hydration energy for M$^+$ and M^{2+} ions.

Chemical Properties

Reducing Nature : The alkaline earth metals are strong reducing agent.

Explanation : The reducing nature of earth metals are due to their large size and less value of their I.E. The earth metals loss their electrons quickly. Therefore, generally act as strong reducing agents.

$$M \xrightarrow{\text{I.E.}} M^{n+} + ne^-$$

The reducing nature of alkaline earth metals generally increases in group.

Explanation : The reducing nature of alkaline earth metals increases in group due to increase in size of metals and decrease in value of I.E. They loss electrons quickly.

The elements of group-2 is weak reducing agent as compared to elements of group-1.

Explanation : This is because the size of alkaline earth metals generally smaller than elements of group-1. So the attractive force created by the elements of group-2 is more as compared to elements of group-1. Therefore possesses high values of their I.E. Hence do not loss electrons quickly and act as weak reducing agent.

2. Reactivity : The earth metals are less reactive than alkali's metals.

Explanation : The less reactivity of earth metals is due to their small size and high I.E.

The reactivity of earth metals increases in group.

Explanation : The increase in reactivity of alkaline earth metals is due to increase in size and decrease in I.E.

The order of reactivities of elements of group-2 is given as

$Ra > Ba > Sr > Ca > Mg > Be$

Radium is highly reactive metals while Be is a least reactive.

3. Reaction with air : The elements of group-2 react with air slowly as compared to elements of group-1. Their reactions with oxygen are slow and form two type of oxides

(i) Normal oxide containing, O^{2-} ion (ii) Peroxide containing, O_2^{2-} ion

Oxides : Alkaline earth metals specially Be, Mg and Ca react with oxygen and form simple oxides.

$$2M + O_2 \longrightarrow \underset{\text{Monoxide}}{2MO}$$

(M = Be, Mg, Ca)

The monoxide can also be prepared by the decomposition of their carbonates

$$MCO_3 \xrightarrow{\text{Heat}} MO + CO_2 \quad (M = Be, Mg, Ca, Sr, Ba)$$

The oxides (BeO and MgO) insoluble in water due to their high value of lattice energy while other oxides are soluble in water.

Nature of oxides :– The nature of oxides of earth metals are different in aqueous solution. The nature of various oxides given as

Table 18 : Nature of oxides of elements of group-2

BeO	amphoteric
MgO	Weakly basic
CaO	Basic
SrO	Basic
BaO	Basic

The basic nature of oxides in group increases, due to increase in ionic nature. These oxides liberates $\overline{O}H$ ions easily. Therefore becomes basic in nature while the amphoteric nature of BeO can be supported via following reaction *i.e.*, it can react with acid as well as with base

$$BeO + HCl \xrightarrow{} BeCl_2 + H_2O$$

Basic

$$BeO + NaOH \xrightarrow{} Na_2BeO_2 + H_2O$$

Acidic Sod. beryllate

Be, *Mg* and *Ca* form only simple oxides

Explanation : Because the size of Be, *Mg* and *Ca* are small. These elements have high polarising power of their ions, so there positive field are strong enough and attract oxide ion, so strongly that it prevent the spreading of negative charge over other oxygen atoms. Therefore, form simple oxides.

Peroxides : These are formed by the reaction of metals with air

$$2M + O_2 \xrightarrow{Heat} MO_2 \ (M = Sr, Ba)$$

***Sr* and *Ba* form peroxides**

Explanation : This is because the elements *Sr* and *Ba* possesses large size and less polarising power, there positive field is very weak so cannot prevent the spreading of electrons cloud of oxygen atom to other oxygen atom. Hence from peroxides.

4. Reaction with Hydrogen : Be form hydrides in the following manner :

$$2BeCl_2 + 2LiH \xrightarrow{ether} BeH_2 + 2LiCl$$

$$2\,BeCl_2 + LiAlH_4 \xrightarrow{} 2\,BeH_2 + LiCl + AlCl_3$$

BeH_2 – It is covalent in nature, generally has polymeric structure $(BeH_2)n$ as shown in fig. 34.

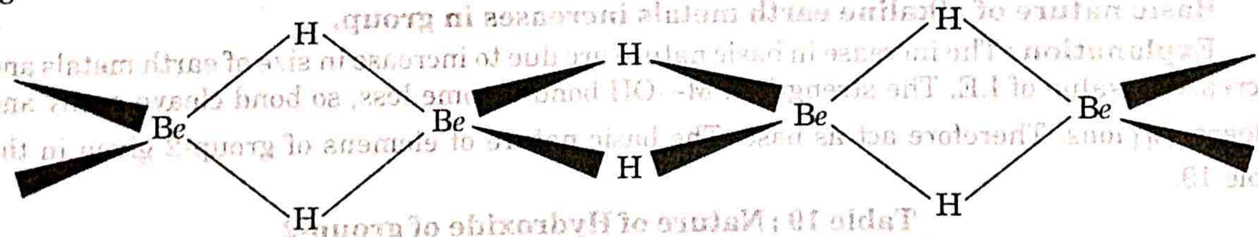


Fig. 34 : Structure of polymeric BeH_2

$BeCl_2$ has a special type of bonds known as **three centre-two electrons bond** or **banana bond or Tau bonds**. It is an electron deficient hydrides in which atom, Be attached with four hydrogen atom. It is represented as H.....Be.....H. Hydrides of *Mg* and other metals are formed by direct heating the metals in the presence of hydrogen as shown

$$M + H_2 \xrightarrow{} MH_2$$

Hydride of *Mg*, partially ionic and polymeric in nature *i.e.*, $(MgH_2)_n$

Hydride of *Ca*, *Sr*, *Ba* are generally ionic in nature formed in the same manner as the hydride of *Mg*

$$M + H_2 \xrightarrow{} MH_2$$

(M = *Ca*, *Sr*, *Ba*)

CaH_2 is called **hydrolith**

The ionic nature of hydrides in group generally increases.

Explanation : This is due to increase in size of metals and decreases in I.E., they give electrons to the hydrogen atom and form ionic hydride.

Hydrides generally act as reducing agent.

Explanation : Reducing nature of hydrides due to their reaction with water and give $H_2(g)$

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

The reducing nature of hydrides generally increases in group.

Explanation : The reducing nature of hydride increases in group due to increase in size and decrease in the value of I.E., so the strength of M— H bond decreases and release $H_2(g)$ easily. Therefore reducing nature increases

Hydrides of elements of group-2 is less reducing than the hydride of group (1).

Explanation : This is due to the size of the elements of group-2 generally less than the elements of group-1. Therefore bond strength of hydrides of group-2 is greater than group (1). Therefore M— H bond do not cleave easily so, there reducing nature become less.

5. Reaction with water : Alkaline earth metals is less basic than alkali metals hydroxide.

Explanation : This is due to the following reason because alkaline earth metals have

(i) small size (ii) high I.E.

(iii) dipositive charge on metal ion

6. Reaction with Water : These metals have less tendency to react with water and form metal hydroxides. Their reaction with water is slow. Be react with water very slowly while Mg not react with cold water but react with hot water while the reaction of other metals of this group fairly high

$$M + 2H_2O \longrightarrow M(OH)_2 + H_2 \; (M = Be, Mg, Ca, Sr, Ba)$$

Basic nature of alkaline earth metals increases in group.

Explanation : The increase in basic nature are due to increase in size of earth metals and decrease in value of I.E. The strength of M—OH bond become less, so bond cleave easily and release $\bar{O}H$ ions. Therefore act as base. The basic nature of elemens of group-2 given in the table-19.

Table 19 : Nature of Hydroxide of group-2

$Be(OH)_2$	amphoteric
$Mg(OH)_2$	mild basic
$Ca(OH)_2$	Basic
$Sr(OH)_2$	
$Ba(OH)_2$	

There order of basic strengh is given as :

$$Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$$

The solubility of hydroxide of alkaline earth metals generally increases in group.

Explanation : This is due to increase in size of metal or metal ion, the magnitude of lattice enthalpy decrease, but the magnitude of hydration energy increases, so solubilities also increases given as (Table 20)

Table 20 : Solubility of hydroxides of group-2

$Be(OH)_2$ $Mg(OH)_2$	Insoluble
$Ca(OH)_2$	Sparingly soluble
$Sr(OH)_2$ $Ba(OH)_2$	Fairly soluble

$Be(OH)_2$ and $Mg(OH)_2$ are insoluble in water.

Explanation : This is because of their small size and high magnitude of lattice energy. So (M — OH) bond do not cleaves easily.

Alkaline earth metals are less basic than alkali's metals

Explanation : This is due to the following reasons, because alkaline earth metals have

(i) small size
(ii) high I.E.
(iii) dispositive charge on metal atom of group (2)

All these factors increases the M—OH, bond strength, so that M—OH bond does not cleave easily, so become less basic than alkali metals hydroxide.

Reaction with halogens : Halides of elements of group-2 are obtained by reacting either metal atom with halogen or from their oxides, carbonates and hydroxides by reacting these with halogen acid as shown

$$M + X_2 \longrightarrow MX_2 \ (X - Cl, Br, I)$$

$$MO + 2HX \longrightarrow MX_2 + H_2O$$

$$M(OH)_2 + 2HX \longrightarrow MX_2 + H_2O$$

$$MCO_3 + 2HX \longrightarrow MX_2 + CO_2 + H_2O$$

Halide of Beryllium are prepared by some special methods as given

$$BeO + C + Cl_2 \xrightarrow{873-1073\ K} BeCl_2 + CO$$

$$2BeO + CCl_4 \xrightarrow{1073\ K} 2\,BeCl_2 + CO_2$$

$BeCl_2$ in solid state posseses polymeric structure as shown in fig. 35

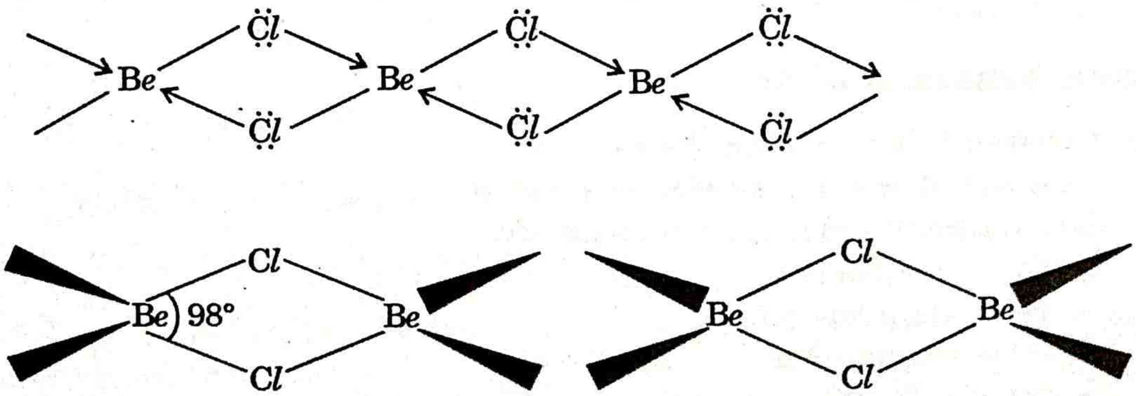


Fig. 35 : Structure of $BeCl_2$ in the solid state

In the polymeric form atom of Be undergo sp^3 hybridisation

It has a special type of bonding *i.e.* 3-centre-2-electrons bond or banana or Tau bond. The bond angle between Cl-Be-Cl is approximately 98°.

But in vapour phase it exist in dimeric form as shown in fig. 36

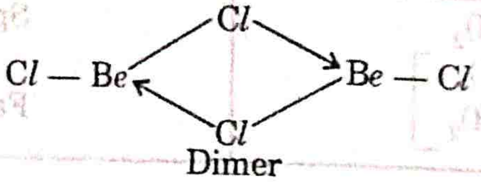


Fig. 36 : Chloro bridged dimer of $BeCl_2$

On heating this dimeric form at elevated temperature, it exist in monomeric form as shown in Fig. 37

$$Cl - Be - Cl$$

Fig. 37 : Monomeric structure of $BeCl_2$

In monomeric form the atom of Be undergo sp-hybridisation and generally, has linear structure.

Halide of Be, generally covalent in nature.

Explanation : This is due to their small size, the polarising power of Be^{2+} ion is very high. So, it disperse the electrons cloud of halide ions strongly, that favour it for the formation of covalent bond.

Halide of alkaline earth metals other than Be generally form ionic bond.

Explanation : This is because of their large size and less polarising power, they cannot disperse the electron cloud of halide ions so strongly, thus unable to form covalent bond. Therefore, form ionic bonds.

Halide of alkaline earth metals other than Be are good conductor of electricity in fused state.

Explanation : The good conductivity of halide, in aqueous and in fused state due to increase in size of earth's metals. So that their ionic nature increases.

The solubility of halide generally decrease in group.

Explanation : The decrease in solubility due to decrease in lattice enthalpy and hydration energy. But decrease in lattice enthalpy is less than decrease in hydration energy. Thus solubility of halide decrease in group.

Halide of alkaline earth metals generally exist in hydrated form as shown

$BeCl_2.4H_2O$, $MgCl_2.6H_2O$, $SrCl_2.6H_2O$

$BaCl_2.2H_2O$, $RaCl_2.2H_2O$, $CaCl_2.6H_2O$ etc.

Anomalous behaviour of Be

The anomalous behaviour of Be due to following reason :

1. Be has small size of their atom and their ion.
2. Be has high IE and high electronegativity
3. Be do not has *d*-orbital
4. Its polarising power is high
5. Be is hard metals than other alkali metals
6. M.Pt and B.Pt of Be greater than other metals of the group
7. Be generally form covalent bond
8. Be doesn't react with water even at high temp.

9. Hydride of Be formed by indirect method

10. On reaction with alkali, it gives $H_2(g)$

$$Be + 2\,NaOH \longrightarrow Na_2BeO_2 + H_2(g)$$

11. Oxides and hydroxide of Be are amphoteric in nature.

12. Carbide of Be on hydrolysis give $CH_4(g)$

$$Be_3N_2 + H_2O \longrightarrow 2\,Be(OH)_2 + CH_4$$

13. Be_3N_2 — Beryllium nitride is volatile in nature.

14. Hydration of Be is greater than other alkali's metals.

15. Be form stable complexes like $|BeF_4|^{2-}$ and $|BeF_3|^{-}$ etc.

Diagonal Relationship of Be

Both Be and *Al* are diagonally related with each other and both possesses same physical parameters *i.e.*

(i) Same atomic radii, Be–170 pm *Al* –167 pm

(ii) Same electronegativity, Be – 1.5 *Al* = 1.5

(iii) Same covalent radii, Be – 125 pm *Al* = 130 pm

The various properties of Be and *Al* discussed below :

1. Be and *Al* form covalent bond
2. Be and *Al* are passive towards the action of nitric acid
3. Both Be and *Al* form fluorocomplexes $|BeF_4|^{2-}$ and $|AlF_4|^{-}$
4. Halides of both in vapour phase are polymeric in nature
5. Nitride of Be and *Al* give $NH_3(g)$

$$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

6. Carbide of Be and Al on hydrolysis give $CH_4(g)$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 10\,H_2O \longrightarrow 4Al\,(OH)_4 + CH_4$$

7. Oxides (BeO, Al_2O_3) and hydroxides [$Be(OH_2)$, $Al(OH)_3$] of both are amphoteric in nature
8. Both Be and *Al* react with alkalies and evolved $H_2(g)$

$$Be + NaOH \longrightarrow Na_2BeO_2 + H_2$$

$$Al + NaOH \longrightarrow NaAlO_2 + H_2$$

Solvation and Complexation tendencies

When simple salts dissolve in water, they dissociates into ions and their solution conduct electricity. Out of alkali's metals ions, the Li^+ ion due to its small size might be expected to conduct electricity upto large extent as compared to other ions (Na^+, K^+, Rb^+ and Cs^+). But the measurements of ionic mobility of aqueous solution shown that the opposite result as shown :

$$C_s^+(aq) > Rb^+(aq) > K^+(aq) > Na^+(aq) > Li^+(aq)$$

Explanation : When alkali's metal ion (Li^+) dissolve in water, it attracted by the molecules of water and form complexes and form primary solvation shell as shown in fig. 38.

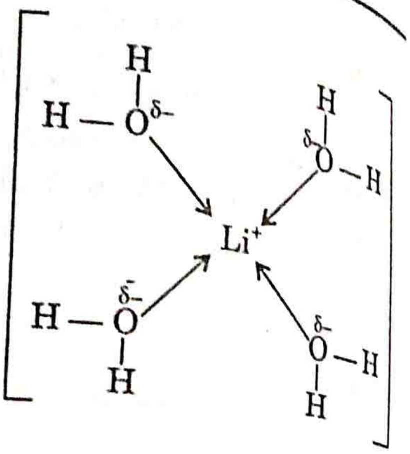


Fig. 38 : Hydration of Li+ with water

Each Li^+ ion in primary solvation shell tetrahedrally attracted by the four molecules of water and form $|Li(H_2O)_4]^+$. Thus hydrated ion is formed. Due to small size of Li^+ ion it also attracted by the additional layer of solvent molecule and form secondary solvation shell, so hydrated radius becomes very large.

Similarly, Na^+ and K^+ ions also surrounded by the four molecules of water and Rb^+ and Cs^+ ion surrounded by six molecules of water. These ions due to less attractive influence not attracted by the molecules of water. Their secondary solvation shell is poor and their hydrated radius become less.

Thus Li^+ ion hydrated to maximum extent while Cs^+ ion hydrated to minimum extent. The decreasing order of hydrated radius given as (Table 21)

$L^+ (aq) > Na+ (aq) > K^+ (aq) > Rb^+ (aq) > Cs^+ (aq)$

While their ionic mobility follow the order give as $Cs^+ (aq) > Rb^+ (aq) > K^+ (aq) > Na^+ (aq) > Li^+(aq)$

Table 21 : Hydration of aqueous ions of group–1

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radius (Å)	0.76	1.02	1.38	1.52	1.67
Hydrated radius (Å)	3.40	2.76	2.32	2.28	2.28
Approx. hydration numbers	25.3	16.6	10.5	10.0	9.9
Hydration energy (kJ mol^{-1})	–506	–406	–330	–310	–276
Ionic mobility at infinite Dilution ($ohm^{-1}\ cm^2\ mol^{-1}$)	33.5	43.5	64.5	67.5	68.0

Elements of group-2 hydrated to greater extent.

Explanation : This is because of smaller size of alkaline earth metals and their greater nuclear charge. The attractive force between metal ion and molecules of water is more (4-5 times more than alkali metals). Thus hydration energy decrease in group due to increase in size of alkaline earth metals just in similar manner as alkali's metals. The hydrated ionic radius and hydration energy of alkaline earth metals given in the table 22.

Table 22 : Ionic radii and hydration energies of alkaline earth metal ions.

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius (Å)	0.31*	0.72	1.00	1.18	1.35
Hydration energy ($KJmol^{-1}$)	–2494	–1921	–1577	–1443	–1305

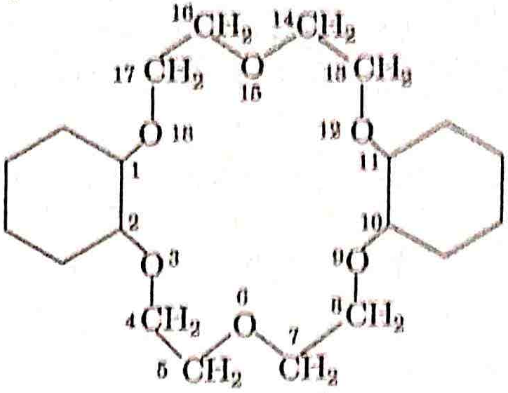
The important role of solvated metal ions is in the exchange material and passage of ions through the cell walls

Complexation of alkali's metal ions by cyclic polyether

C.J. Pederson shows that alkali's metals ion form stable complexes with cyclic polyether. These are also called as **crown ether** because of crown shaped arrnagement of cyclic ether with metal ion.

The stability of complex depend upon the number of oxygen atoms and their geometrical arrangement, sizes and shapes of polyether and to the size of metal ion.

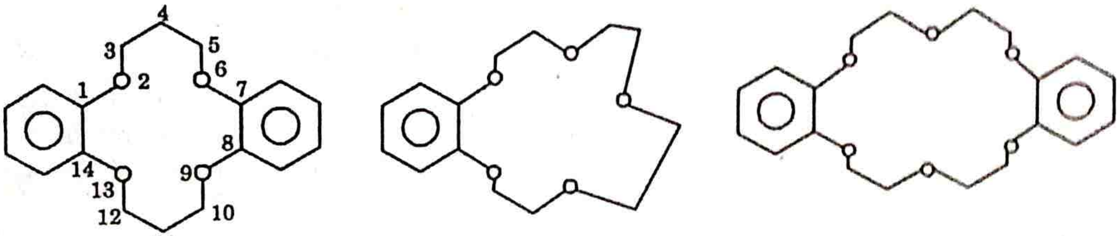
The structure of polyether **Dicyclohexyl-18-crown-6** given as in this figure (fig. 39) the prefix-18 is the number of atoms in heterocycle while suffix-6-indicates the number of oxygen atoms.



Dicyclo hexcyl - 18

Fig. 39 : Dicyclohexyl-18 crown 6 cyclic polyether

Some other examples of polycyclic ethers given as fig. 40



Dibenzo-14-crown-4 Benzo-15-crown-5 Dibenzo-18-crown-6

Fig. 40 : Structure of some poly cyclic ether

The electrostatic forces between metal ion and oxygen atoms make the complex stable. The stability of the complexes lies in the fact that the ring size of complex that can fit exactly the cation in its cavity.

The size of metals ion and their corresponding polycyclic ether cavity shown in table 23.

Table 23 : Comparison of ionic diameter and crown ether hole size

Cation	Ionic diameter	Polyether ring	Hole size
Li	1.52 Å	14-Crown-4	1.20–1.50 Å
Na	2.04 Å	15-Crown-5	1.70–2.20 Å
K	2.76 Å	18-Crown-6	2.60–3.20 Å
Rb	3.04 Å	21-Crown-7	3.40–4.30 Å

Cryptates : The meaning of cryptates in Greek is "Hidden" it means the metal ion hidden in the cavity of these strcuture.

The cryptates are polycyclic ligand that contains in addition to oxygen atom the other donor atoms (N,S,P)

The cryptates are more selective and much stronger than polycyclic ether

The structure of cryptates shown in fig. 41

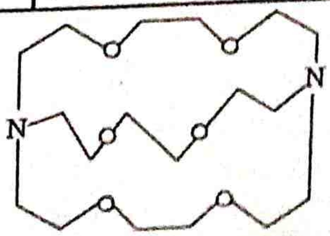


Fig. 41 : 2, 2, 2-crypt ligand

Sodium form compound [Na (2, 2, 2, crypt]$^+$ Na$^-$ in a solution of ethyl amine. This is golden yellow substance and diamagnetic in nature in solid form and stable at low temp. such as 263 K.

This cryptate contain Na$^-$ ion *i.e.* sodide ion. It is formed by the transference of electron between two sodium atoms as shown :

$$2\,Na \longrightarrow Na^+ + Na^-$$

The large sized cavity of cryptates shield the Na$^+$ ion and prevents its combination with Na$^-$ (sodide ion).

Characteristics of crown ether and cryptates

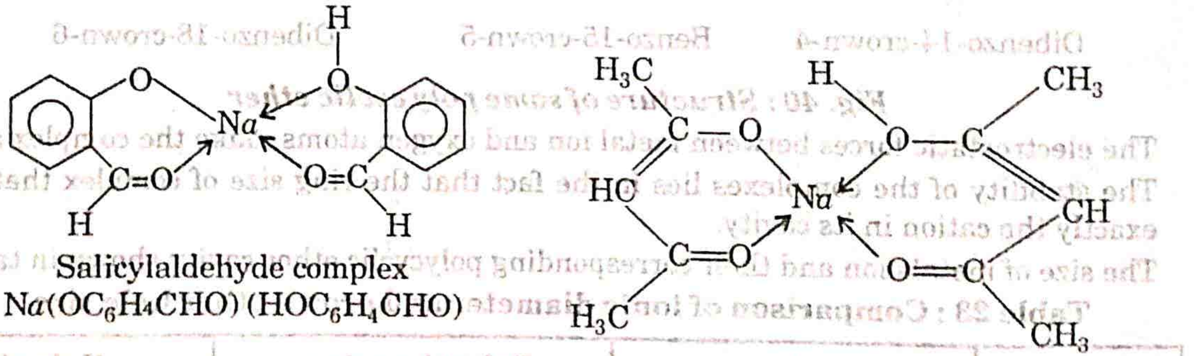
1. Both have unusual solubilities in organic solvent. For example- Na and K in ether form dilute solution with a concentration of 10^{-4} M. Whenever cryptates and crown ether is added the concentration of Na and K becomes upto 10^3 to 10^4 M.
2. Both, cryptates and crown ether stabilizes large anion by shielding the cation in their cavity. So, stable complex is formed.

Difference between the stability of cryptates and polyether

1. Cryptates are better complexing agent and are more selective than polyether this is due to the presence of donor atoms (N, P, S) in addition to oxygen atom.
2. These hetero atom surrounds the metal ions more firmly.

Alkali's metals have poor tendency to form complexes

Explanation : This is due to large size of their ions and low charge density on it. They have poor electrons acceptor capacity. Hence, do not form large number of complexes. Some of the complexes of alkaline metals with a coordination number of 4 or 6 given as fig. 42.



Salicylaldehyde complex
Na(OC$_6$H$_4$CHO) (HOC$_6$H$_4$CHO)

Fig. 42 : a : Complex formation by sodium *b: Complex formation of sodium*

Cs$^+$ also form 6-coordinated complexes as shown in fig. 43

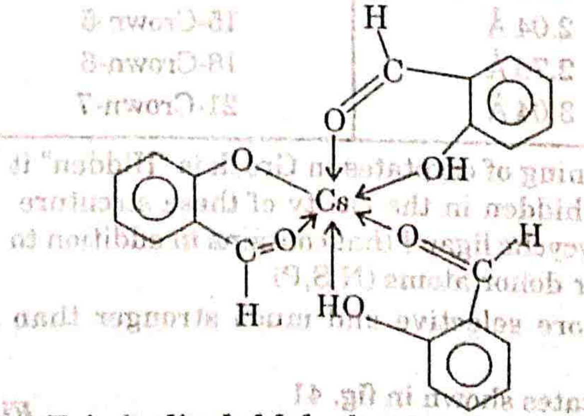


Fig. 43 : Tris (salicylaldehydato) cesium complex

Complexation tendency of alkaline earth metals

Alkaline earth metals have greater tendency to form complexes.

Explanation : This is because of their small size and high nuclear charge density, the attractive power between metal ion and ligand is strong. So form stable complexes. Be^{2+} form complex with oxalate as shown in fig. 44.

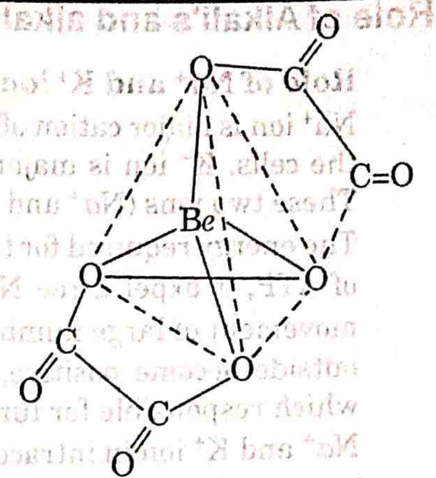


Fig. 44 Structure of beryllium oxalate $[Be(ox)_2]^{2-}$

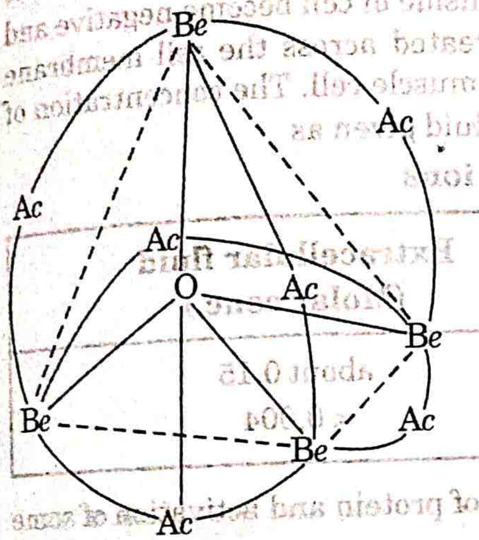


Fig. 45 : Structure of basic beryllium acetate $Be_4O(CH_3COO)_6$

Similarly, other complex of Be, basic Beryllium acetate $[Be_4O(CH_3COO)_6]$. In this structure centrally located oxygen atom tetrahedrally surrounded by four Be-atoms and six acetate groups arranged along the six edges of tetrahedron as shown in fig-45.

Mg^{2+} ion form complex with chlorophyll. Chlorophyll is the green pigment of plants. It helps in the process of photosynthesis. In chlorophyll Mg^{2+} ion located at the centre of heterocyclic porphyrin ring in which four nitrogens are bonded to the Mg^{2+} ion as shown in fig. 46.

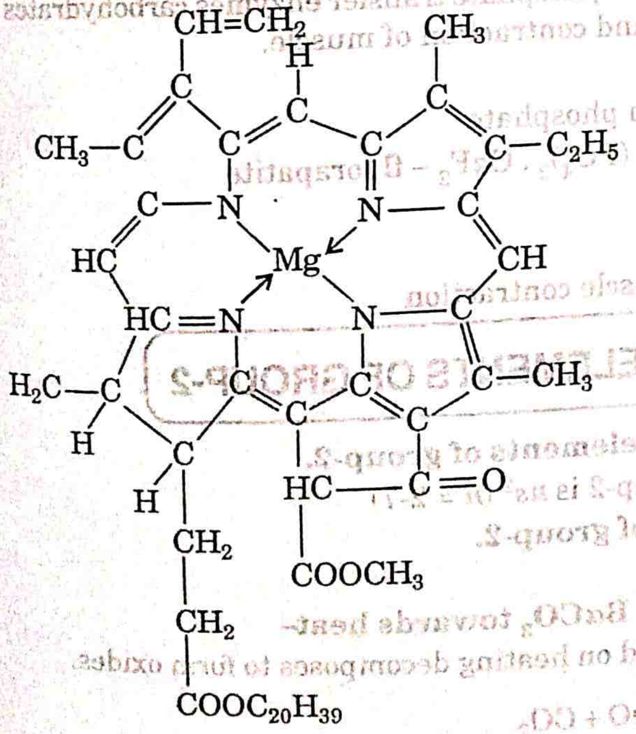


Fig 46 : Structure of chlorophyll

Complex with E.D.T.A.

Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} all these ions form complexes with EDTA as shown in fig.-47

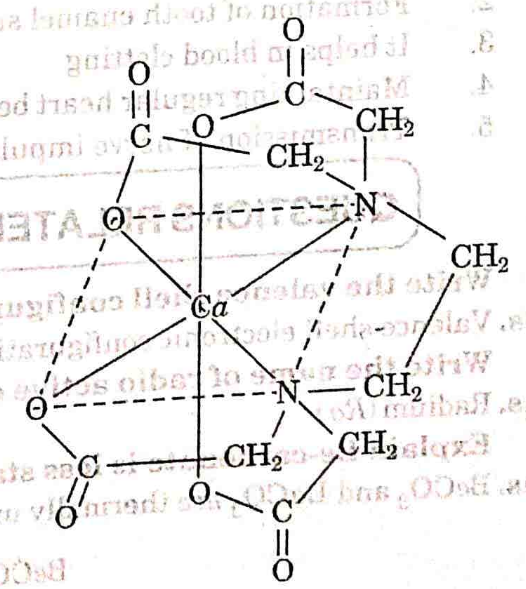


Fig 47 : Structure of EDTA complex of Ca^{2+} ion.

Role of Alkali's and alkaline's earth metals in biological system

Role of Na^+ and K^+ ion

Na^+ ion is major cation of extracellular fluid in living organism. It is actively expelled from the cells. K^+ ion is major cation of intracellular fluid and actively taken inside the cell. These two ions (Na^+ and K^+) run via sodium pump with the help of carrier protein.

The energy required for transportation comes from ATP i.e., with the cost of one molecules of ATP, it expel three Na^+ ions out the cell and two K^+ ion inside the cell. So due to movement of large number of Na^+ out side the cell, the inside of cell become negative and outside become positive, so a potential difference is created across the cell membrane which responsible for functioning of nerve impulse and muscle cell. The concentration of Na^+ and K^+ ion in intracellular fluid and extra cellular fluid given as

Table 24 : Conc. of Na^+ and K^+ ions

Ions	Intracellular fluid (Molar conc.)	Extracellular fluid (Molar conc.)
Na^+	about 0.01	about 0.15
K^+	about 0.15	< 0.004

The K^+ ion also help in metabolism of glucose, synthesis of protein and activation of some enzymes.

Role of Mg^{2+} and Ca^{2+} ion

Ca^{2+} ion is the major ion in intracellular fluids while Mg^{2+} ion is the major ion in extra cellular fluids. These ions also creates potential difference across the cell membrane just like sodium pump.

Mg^{2+} ion help in photosynthesis and also activate phosphate transfer enzymes carbohydrates metabolism, transmission of nerve impulse and contraction of muscle.

Ca^{2+} ion essential for :

1. Formation of bone and teeth as calcium phosphate
2. Formation of tooth enamel such as $Ca_3(PO_4)_2 \cdot CaF_2$ – fluorapatite
3. It helps in blood clotting
4. Maintaining regular heart beat
5. Transmission of nerve impulse and muscle contraction

IMPORTANT QUESTIONS : ALKALI METALS

1. Alkali's metals are good reducing agent. Explain.
2. Why alkali's metals not found in nature.
3. Sodium is less reactive than potassium.Explain. **(K.U.K. 2015)**
4. Why are alkali metals kept in paraffins or kerosene. **(M.D.U. 2012)**
5. Alkali metals are paramagnetic while their salt are dimagnetic in nature.
6. Alkali metals are obtained by electrolysis of their salt (molten state), not obtained from their aqueous solution.
7. On exposure to air, sodium hydroxide becomes liquid and after some time it changes to white power.

8. $NaCl$ is not hygroscopic but table salt on exposure to air damp up explain.

9. Alkali metals impart colour to ammonia solution. The solution also possess strong reducing nature. Explain. (K.U.K. 2015)

10. Lithum salt are more covalent than other alkali metals salts.

11. Li^+ ion smaller in size than Cs^+ ion, but the conducting power of Cs^+ ion greater than Li^+ ion.

12. Lithium from normal oxide, sodium form peroxide and rest an alkali metals form superoxides. Explain. (K.U.K. 2011) (K.U.K. 2013)

13. Li and Mg are placed in different group of the periodic table, yet they resemble each other to show diagonal relationship. Explain. (K.U.K. 2013 (2012) (M.D.U. 2011, 2012, 2015)

14. Sodium and potassium donot form complex ions. Explain.

15. Among LiF and LiI which is more covalent in nature and why.

16. LiF has lowest solubility in water. Explain.

17. Lithium differ from rest of metals in many of its properties. Explain. (M.D.U. 2013) (K.U.K. 2014)

18. Alkali metals loss metallic lustre on exposure to air. Explain.

19. MP.t and B.Pt of alkali metals decreases from Li to Cu. Explain.

20. Superoxide of alkali metals are coloured and paramagnetic in nature. Explain it.

21. Why sodium fire in the laboratory not extinguished by water.

22. Bottle containing $NaOH$ solution are not closed by glass cork. Explain.

23. Lithium and magnesium show similar properties. Why.

24. How will you explain flame colouration in group one alkali metals.

25. Solution of alkali metals in liquid ammonia are blue and conducting in nature. Explain. (M.D.U. 2013)

26. In group-1
    (i) Hydrated ion of which element is large in size.
    (ii) Which element is used in photovoltaic cell

27. In group-1
    (i) Which element form peroxide
    (ii) Which element is strongest reducing agent

28. What is the role of Na^+ and K^+ ion, in biological system?

29. K, Rb, Cs from superoxides. Explain.

30. In group-1, lithium has highest value of ionization energy yet it is strongest reducing agent. Why?

31. What do you understand by term (i) perioxide and (ii) superoxides? Explain.

32. Which element of group-1 is hard. Why?

33. Why are alkali metals are soft and have low melting points. (K.U.K. 2011)

ALKALINE EARTH METALS

41. Why do alkaline earth metals do not form monovalent ions?
42. The atomic radius of Mg is smaller than sodium. Explain.
43. Alkaline metals salt are diamagnetic in nature. Explain.
44. Why NaCl is added to anhydrous $MgCl_2$ before electrolysis?
45. M.Pt of calcium halides decreases in the order $CaF_2 > CaCl_2 > CaBr_2 > CaI_2$
46. Mpt. of group (2) elements greater than group-1 elements. Explain.
47. Group-2 elements are weaker reducing agent than group-1 elements.
48. Be form covalent bond while other alkali metals form ionic bonds.
49. $IE_1 < IE_2$ in elements of group-2. Explain.
50. $Ba(OH)_2$ is much stronger than $Be(OH)_2$.
51. Why $BeCl_2$ is easily hydrolysed.
52. Be and Mg donot give flame colouration explain it. **(K.U.K. 2010, 2011)**
53. Anhydrous $CaSO_4$ used as drying agent. Why?
54. The reaction of marble and dilute H_2SO_4 stop soon. Explain.
55. Mg– metal burns in air to give a white ash. when this ash is treated with water the odour of ammonia can be detected. What is the reason?
56. The hydroxide of Group-2 elements are weaker the group-1 elements. Explain.
57. Ba^{2+} ion is poisonous, yet $BaSO_4$ is given to patient-prior to taking stomach, X-ray.
58. Be does not exhibit a covalency beyond it.
59. BeH_2 and $BeCl_2$ have polymeric structure in solid state. Why.

4

CHEMISTRY OF NOBLE GASES

The elements Helium (He), Neon (Ne), Argon (Ar) krypton (Kr), Xenon (Xe) and Radon (Rn) belongs to Group number 18 of the periodic table. The element of this group denoted by short term 'R A I N' *i.e.*

R–stand for, **rare gas** because they were found in rare amount but today, this name have been proved to be wrong because these gases no more rare.

A–stand for, **aerogens** because these gases were found in air.

I–Stand for **inert gas** because at ordinary temperature these gases donot have chemical reactivity. However now a day these gases particularly Xe and Kr from large number of compounds. Therefore they are not regarded as completely next.

N–stand for, **noble gases**, this is because these gases have some reactivity.

These gases are chemically inert, so they always occur in free state *i.e.*, in atomic state except radon, which is radioactive in nature. (it decay very repidly).

Position of These Gases in the Periodic Table

When Mandeleev arranged his periodic table in 1869, these gases were not known at that time. Therefore no place alloted to these gases at that time. Whenever, these gases, discovered, their position in the periodic table were assigned according to their physical and chemcial characteristics. It to be noted that these gases were found to be chemically unreactive. Therefore on the basis of their non reactive nature and chemically inertness, Ramsay proposed a new group called **zero group.**

The zero group is due to their zero valency.

But before the discovery of noble gases, the various elements were arranged in the periodic table according to their chemical reactivity i.e. electropositive elements were placed towards left side of periodic table while electronegative element were placed towards right hand side of the periodic table. Therefore by studying the properties of these gases, (In between electropositive and electronegative elements) it has been confirmed that these gases must be placed in between these border lines.

The position of these gases finally confirmed by Moseley who suggested that atomic number is the fundamental property to classify the elements.

Due to these conclusive reason these gases ware placed in the last column on the extreme right side of the perodic table i.e. in Group–18.

The Discovery of Noble Gases

The names of noble gases were given due to their interesting behaviour or on the basis of source from which they were obtained.

Helium– It is first time detected in the spectrum of sun in 1868, hence its name derived from Greek : **helios** – *i.e.* **sun.**

Argon–This gas discovered by Lord Rayleigh by measuring the density of nitrogen sample from different sources. He observed that samples of air was always denser than obtained from decomposition of ammonia.

Similarly Ramsay confirmed the experiment performed by Rayleigh, by burning Mg in nitrogen of air.

Therefore it comes from Greek, word argos which means the 'idle one'.

Similarly the name of neon, kypton and Xenon were derived from Greek word given as

Neon – **the new one**

Krypton – **the hidden one**

Xenon – **the stranger**

While the name radon comes from its radioactive nature.

The name of discoverer and the percentage abundance of various noble gases given the table–1

Table - 1 %tage abundance of noble gases.

Gas	Year of discovery	% by volume in air	Discovered by
Helium	1895	6.2×10^{-4}	Sir William Ramsay
Neon	1898	1.8×10^{-3}	Sir Willian Ramsay, M.W. Travers
Argon	1894	0.93	Sir William Ramsay, Lord Rayleigh
Krypton	1898	1.4×10^{-3}	Sir William Ramsay, M.W. Travers
Xenon	1898	8.7×10^{-6}	Sir William Ramsay, M.W. Travers
Radon	1900	Radioactive	Friedrich Dorn.

General Characteristics of Noble gases

Some of the important physical properties of noble gases given in the table - 2. These various properties discussed one by one.

Table-2 Physical parameter of noble gases

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
Electronic configuration	$1s^2$	[He] $2s^2$ $2p^6$	[Ne] $3s^2$ $3p^6$	[Ar] $3d^{10}$ $4s^2$ $4p^6$	[Kr] $4d^{10}5s^2$ $5p^6$	[Xe] $4f^{14}$ $4p^{10}6s^2 6p^6$
Vander Waal's radius (pm)	131	173	189	210	215	—
First Ionisation energy (kJ mol^{-})	2372	2081	1521	1351	1170	1037
M.Pt (K)	—	24.5	83.7	116.7	161.7	202.2
B.pt. (K)	4.2	27.2	87.3	121.3	166.2	211.0
Heat of vapori sation (kJ mol^{-1})	0.08	1.77	6.51	9.02	12.6	16.4
Density, g/L	0.178	0.899	1.783	3.736	5.891	9.960
Abundance in atomosphere (% moles)	0.00052	0.0015	0.930	0.00011	0.0000084	Trace

1. Electronic Configuration : The electronic configuration of noble gases given in the table - 3.

Table-3 Electronic configuration of noble gases

Element	Symbol	Atomic Number	Electronic configuration
Helium	He	2	$1s^2$
Neon	Ne	10	$1s^2\ 2s^2\ 2p^6$
Argon	Ar	18	$2s^2\ 1s^2\ 2p^6\ 3s^2\ 3p^6$
Krypton	Kr	36	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
Xenon	Xe	54	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
Radon	Rn	86	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

The electronic configuration of He is $1s^2$ where as all other elements have general electronic configuration of $ns^2\ np^6$. Where n is the period number or Principle Quantum number.

Thus all the noble gases except He have $8e^-$ in its valence shell.

2. Existence: All the noble gases are mono atomic in nature. The mono atomic nature is due to their stable noble gas configuration *i.e.* 8 electrons in its valence shell, so these gases are not capable to combined with each other.

Moreover their values of Cp/Cv (*i.e.* molar heat capacity at constant pressure and can stant volume) is equal to 1.66 (for monoatomic gases)

All these gases are colourless and odourless

3. Atomic Radii: In noble gases, their atomic radii are Vander Waal radii (Fig-1). **The atomic radii of noble gases generally increase in group.**

Explanation–The increase in atomic radii is due to increase in number of shells and screening effect, so effective nuclear charge between nucleus and valence electrons decrease. As a result, atomic size increases.

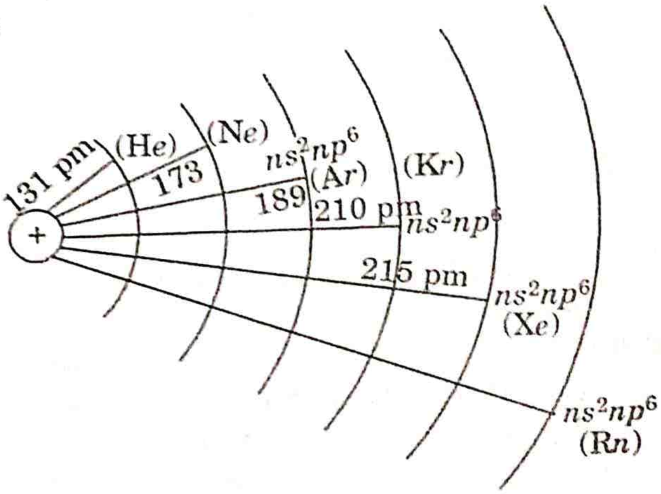


Fig-1 Atomic radii of noble gas

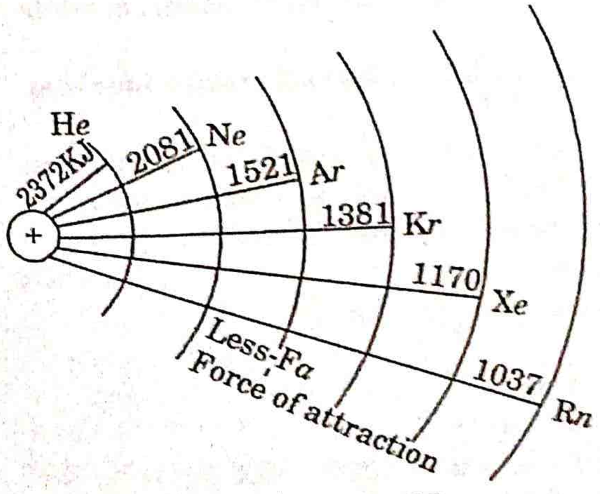


Fig-2 : I.E. *of noble gases*

4. Ionization Energy : The ionization enthalpy of noble gases are very high.

Explanation – This is because their stable noble gas configuration.

Ionization energy of noble gases in group generally decreases (Fig-2).

Explanation–The decrease in the value of Ionization energy is due to increase in size of noble gases and decrease in magnitude of force of attraction.

5. Electron Affinity: Noble gases generally have no tendency to accept electrons.

Explanation–This is due to their stable noble gas ($ns^2\ np^6$) (Fig-3) configuration. These gases have no tendency to accept any extra electrons. Therefore electron affinity of noble gases is found to be zero.

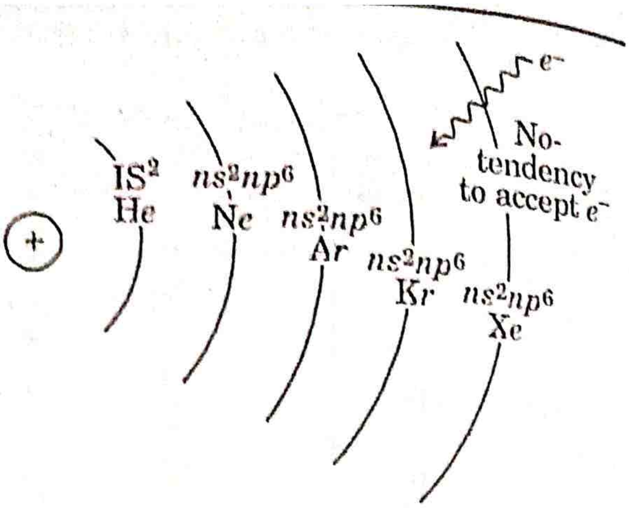


Fig-3 Valence shell configuration of noble gases

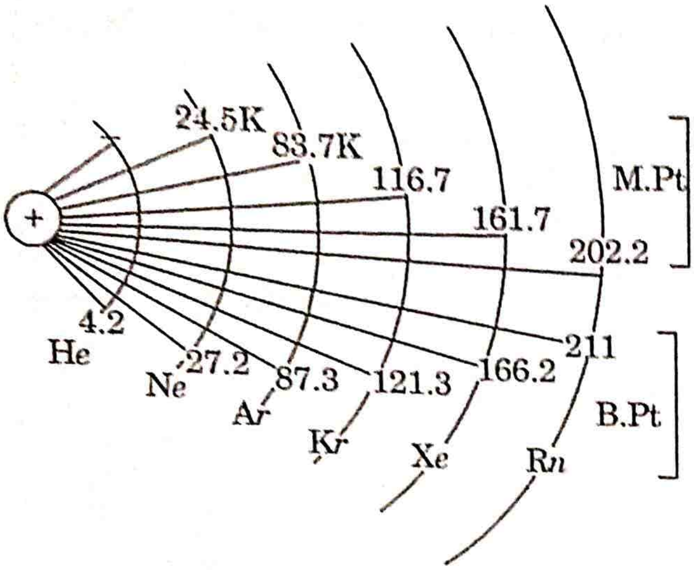


Fig-4 **M.Pt.** *and* **B.Pt.** *of* **Noble gases**

6. Melting point and Boilng point: The M.Pt. and B.Pt. of noble gases are very low.

Explanation–This is due to their large size and weak Vander Waal forces of attraction between the atoms of noble gases in solid and liquid state

M.Pt. and B.Pt. of noble gases generally increases in group.

Explanation–The increase in MPt. and BPt. of noble gases in group is due to increase in size of noble gases and increase in surface area so, magnitude of Vander Waal forces also increases, so that Mpt. and Bpt. also increases.

7. Ease of Liquifaction: The noble gases not liquified easily.

Explanation–This is because due to presence of only weak Vander Waal forces of attraction. So, that atoms of noble gases not hold strongly with each other.

Ease of liquifaction of noble gases increases in group.

Explanation–This is due to increase in size of noble gases so, that their surface area also increases. These factors increases the magnitude of attractive force. Therefore, atoms of noble gases come close to each other and exist as liquid.

8. Solubility in Water : These are slightly soluble in water their solubility increase in group.

Explanation–In group the magnitude of vander waal forces increases so, interaction with the molecules of water also increases. As a result solubility of noble gases also increases.

9. Chemical Characteristics : Generally noble gases are unreactive.

Explanation. This is because of the following reason :

(i) Their valence shell are completely filled with electrons ($ns^2\ np^6$).

(ii) I.E. of noble gases are also very high.

(iii) The electron affinity of noble gases are almost zero.

That's why the noble gases found to be unreactive in nature.

But the above reason discouraged by chemist, Neil Bartlett in 1962, while studying the chemistry of Platinum (VI) fluoride (PtF_6) which is red crystalline solid. It is powdered oxidising agent. He observed that, when PtF_6, is exposed to oxygen or air a solid ionic compound $O_2^+ Pt F_6^-$, which is yellow in colour is formed :

$$\underset{\curvearrowright\, e^-}{O_2 + PtF_6} \longrightarrow O_2^+[PtF_6]^-$$

Yellow solid
Dioxygenyl hexa fluorido
platinate (V)

In the above reaction the O_2 is oxidised to O_2^+

$$O_2 \rightarrow O_2^+ + 1e^-$$

So Bartlett noticed that the IE_1 for Xe (1170 kJ mol^{-1}) was almost identical to that of O_2 1175 kJ mol^{-1}.

With this assumption, Bartlett mix PtF_6 with Xe in gas phase and obtained orange yellow coloured solid substance which is ionic in nature *i.e.* $Xe^+PtF_6^-$

$$Xe + PtF_6 \rightarrow Xe^+PtF_6^-$$

orange yellow
Xenon hexa fluorido platinate (V)

This was the first noble gas compound and becomes centre of attraction for many scientist for further researches.

With in few months scientist synthesized large number of compound of Xe with O_2 and F_2.

Some of the compounds listed below in table - 4

Table-4 Stable compounds of Xenon.

Oxidation state	**Compounds**
+2	XeF_2, Xenon difluoride
+4	XeF_4, Xenon tetrafluoride $XeOF_2$, Xenon oxydifluoride
+6	XeF_6, Xenon hexafluoride $XeOF_4$, Xenon oxytetrafluoride XeO_2F_2, Xenon dioxydifluoride
+8	XeX_8, Xenon octafluoride XeO_4, Xenon tetroxide

Before discussing the chemistry of noble gases we must know about the following questions :

(i) What are the factors responsible for the late discovery of compounds of noble gases.

(ii) Why does Xenon form the maximum number of compounds with fluorine and oxygen.

1. Late discovery of compounds of noble gases

Explanation–Before 1962, it was believed that the noble gas were not reactive at all because of its :

(i) Stable Configuration (ii) High I.E.

(iii) Zero electron affinity

So all the attempts to synthesize the compounds of noble gases become faulty. French chemist Henry Moisson in 1895, noticed that there was no chemical reactivity between fluorine and argon. So, Ramsay concluded that noble gases are chemically inert. On the basis of chemica inertness of noble gases. Lewis, in 1916, give an important rule i.e. octet rule. According to this rule every atoms want to gain a stable noble gas configuration.

To get stability, atom either loss or gain the electrons.

Therefore compounds of noble gases not discovered in early time.

Why do most of the compounds of Xenon, only with fluorine and oxygen?

Explanation–The I.E. of noble gases are very high, only Xe has ionization enthalpy, comparable to C, N and O. Therefore Xe, has maximum tendency to loss their electrons.

But Xe can give an electron to that atom only which should be highly electronegative or must have strong tendency to accept electron from Xenon atom (high electron affinity value)

So, in the periodic table only two elements (O and F) have these above mentioned tendencies.

It is for this reason Xenon from compound with fluorine and oxygen.

Xenon form a variety of compounds, with F and oxygen as shown in the table-5.

Table-5 Stable compounds of Xenon

Oxidation state	Compounds
+2	XeF_2, Xenon difluoride
+4	XeF_4, Xenon tetra fluoride $XeOF_2$, Xenon oxy fluoride
+6	XeF_6, Xenon hexa fluoride $XeOF_4$, Xenon oxytetra fluoride $XeOF_2$, Xenondioxy difluoride
+8	XeO_4, Xenon tetroxide XeF_8, Xenon octa fluoride

Let us discuss the method of preparation of compound of Xenon.

1. Xenon difluoride, XeF_2

There are many method to synthesize the compound of Xenon.

(1) It is prepared in laboratory by heating a mixture of Xe and F_2 in ratio of (2 : 1) at 400°C in a sealed nickle tube.

$$Xe + F_2 \xrightarrow[400°C]{Ni} XeF_2$$

Xenon always taken in excess amount otherwise XeF_4 is formed.

(2) It can be prepared by mixing a mixture of Xe and F_2 in molar ratio of 2 : 1 in electric discharge.

$$Xe + F_2 \xrightarrow[\text{discharge}]{\text{electric}} XeF_2$$

(3) Photo chemical combination of Xe and F_2 in the presence of Hg–vapours also give XeF_2

$$Xe + F_2 \xrightarrow{\text{Hg-vapours}} XeF_2$$

(4) Qualitatively, it can be synthesized by fluorination of Xenon by O_2F_2 at – 78°C

$$X_e + O_2F_2 \xrightarrow{-78°C} XeF_2 + O_2$$

Properties :

(1) XeF_2 is colourless crystalline solid

(2) Its M.Pt is 129°C

(3) It is least volatile

(4) It is stable when pure and in dry state can be stored in nickle vessel.

(5) It react with H_2 and give HF and Xe

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

(6) XeF_2 dissolve in HF.

(7) XeF_2 show substitution reaction with protonic acids such as $HClO_4$, CF_3COOH and HSO_3F etc.

$$XeF_2 + 2HX \rightarrow XeX_2 + 2HF$$

$$(X = ClO_4^-\ CF_3COO^-, SO_3F^-)$$

(8) It hydrolysed slowly in the following manner.

$$XeF_2 \xrightarrow{H_2O} 2Xe + 4HF + O_2$$

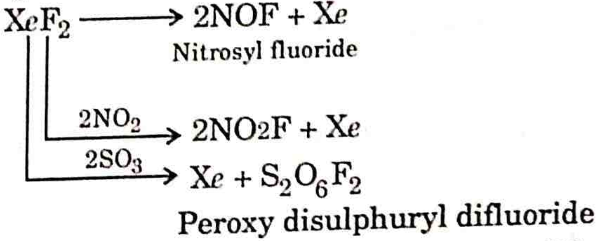
But in acidic and alkaline medium it give fast response

$$2XeF_2 + 4NaOH \rightarrow 2Xe + 4NaF + O_2 + 2H_2O$$

(9) It react with I_2 in the presence of BF_3

$$XeF_2 + I_2 \xrightarrow{BF_3} 2IF + Xe$$

(10) It react with NO, NO_2 and SO_3 to give, Xe



$$XeF_2 \longrightarrow 2NOF + Xe$$

Nitrosyl fluoride

$$XeF_2 \xrightarrow{2NO_2} 2NO2F + Xe$$

$$XeF_2 \xrightarrow{2SO_3} Xe + S_2O_6F_2$$

Peroxy disulphuryl difluoride

(11) It act as mild fluorinating agent. It react with ethylene to give 1, 2–difluoro ethane

$$CH_2 = CH_2 + XeF_2 \rightarrow FCH_2 - CH_2F + Xe$$

1,2–difluoro ethane

(12) XeF_2 react with AsF_5 and to form the compound in molar ratio of 1 : 1 as shown

$$XeF_2 + MF_5 \rightarrow XeF_2 - MF_5$$

$$(M = As, Sb, Bi)$$

The compound $XeF_2 \cdot MF_5$ exist in ionic form $XeF^+ MF_6^-$

If the ratio of XeF_2 to MF_5 is 1 : 2, the compound, thus formed have composition i.e. $XeF_2 \cdot 2MF_5$. These compounds has been shown to contain $XeF^+ Sb_2F_{11}^-$ ions. The bonding between XeF^+ and $Sb_2F_{11}^-$, Shown in the following figure-5.

The reaction of XeF_2 with AsF_5 can also give the product of composition $2XeF_2 \cdot AsF_5$. This compound exist as $|Xe_2F_3|^+|AsF_6|^-$.

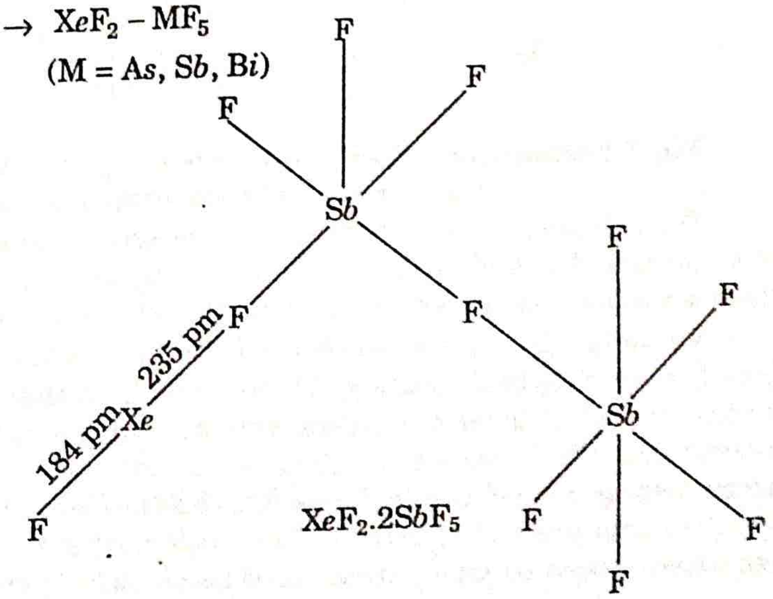


Fig-5 Structure of $XeF^+ Sb_2F_{11}^-$

The geometry of $Xe_2F_3^+$ is linear around Xe as shown in Fig-6 and angular geometry around Xenon fluoride.

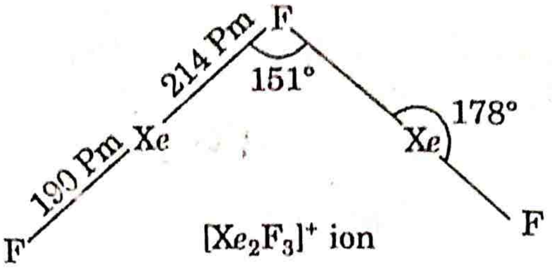


Fig-6 Structure of $Xe_2F_3^+$

(13) XeF_2 readly react with Pt, S_8 and Ir and give

$$Pt + 3XeF_2 \xrightarrow{HF} PtF_6 + 3Xe$$

$$S_8 + 24XeF_2 \xrightarrow{HF} 8SF_6 + 24Xe$$

$$16Ir + 5XeF_2 \longrightarrow 10IrF_5 + 5Xe$$

(14) It also oxidise BrO_3^- to BrO_4^-

$$BrO_3^- + XeF_2 + H_2O \rightarrow Xe + 2HF + BrO_4^-$$

Structure and Shape of XeF_2

One the basis of spectroscopy, the geometry of XeF_2 has been found to be linear. The geometry of XeF_2 can be explained on the basis of valence bond theory as shown in Fig-7.

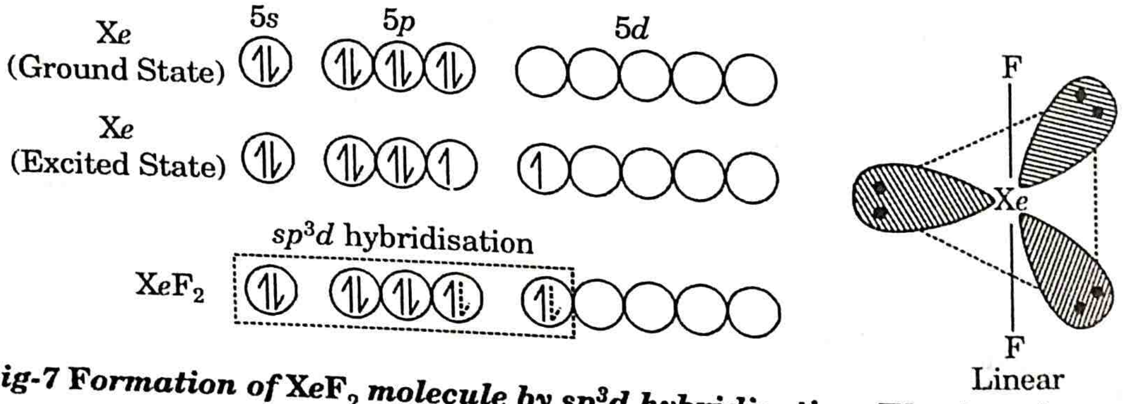


Fig-7 Formation of XeF_2 molecule by sp^3d hybridisation. The dotted arrows represent electrons supplied by fluorine atoms.

The valence shell electrtonic configuration of Xe in ground state is $5s^25p^6$, one of the electron of Xe promoted to higher energy state form 5p orbital to 5d–orbital. Therefore in excited state their are two unpaired electrons in Xe, (One in 5p and other 5d–orbital)

Therefore five orbital hybridised (One 5s, three–5p, and one – 5d) with each other and give five sp^3d hybrid orbitals. These Sp^3d hybridised orbitals adopt trigonal bipyramidal geometry. Out of these five hybrid orbitals, the two orbitals that have one unpaired electron, overlaps with the unpaired electron of fluorine atoms and forming two Xe—F bonds. Both the atoms arranged itself axially. These form **linear** Geometry, while the equitorial position occupied by three lone pairs of electrons. Thus, lone pair are located on the equitorial positions. Thus repulsion caused by lone pair on axial bond-pairs is found to be negligible.

The important properties of of XeF_2 summerised as in Fig-8.

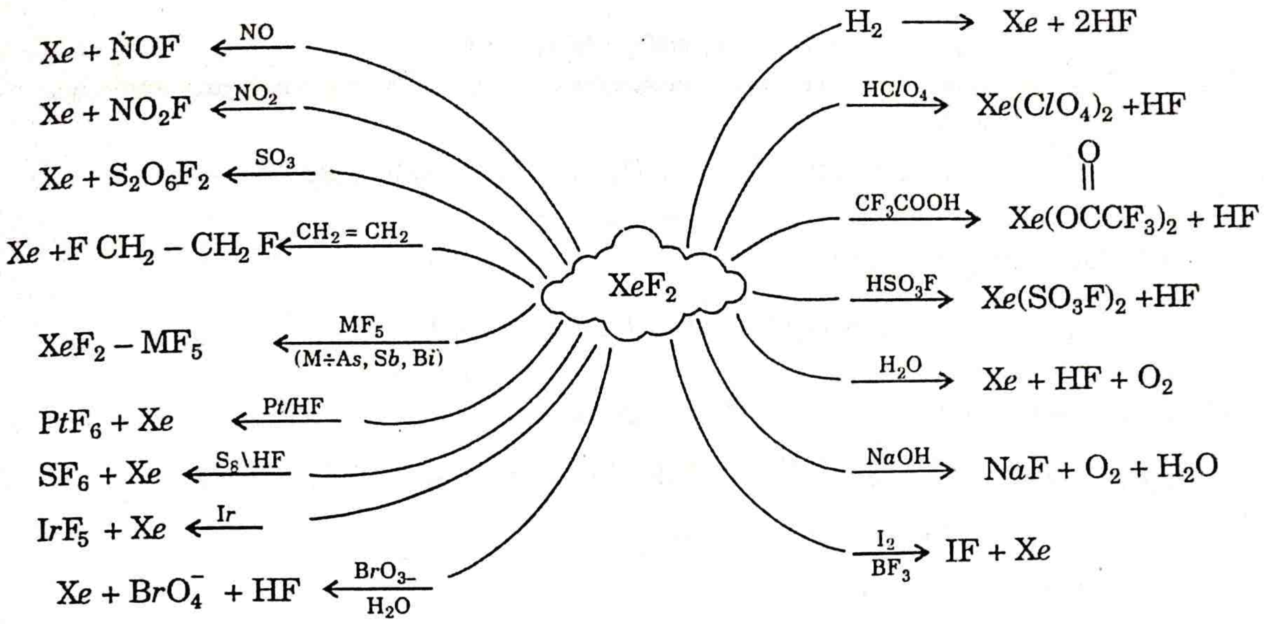


Fig-8 Summery of chemical properties of XeF_2.

Xenon Tetra Fluoride → (XeF_4)

Preparation : XeF_4 can be prepared by the following methods.

(1) It is prepared by mixing of Xe and F_2 in the molar ratio of (1 : 5) in a vessel of nickle at a temperature of 400°C and pressure of 5 – 6 atm.

$$Xe + 2F_2 \xrightarrow[5\text{–}6\text{atm.}]{400°C} XeF_4$$

The yield of XeF_4 in this method is good.

(2) It is also prepared by mixing Xe with F_2 in the molar ratio of 1 : 2 at, – 78°C and a pressure of 3 – 15 mm of Hg by passing electric discharge

$$Xe + F_2 \xrightarrow[-78°C]{\text{electric discharge}} XeF_4$$

Properties: The physical and chemical properties of XeF_4 given below

(1) XeF_4 is colourless and crystalline solid.
(2) Its melting point is 117°C.
(3) It sublime easily.
(4) It is soluble in HF and IF_5 without any reaction.
(5) It react with H_2 and give HF at a temp. of 30°C.

$$XeF_2 + H_2 \rightarrow Xe + 4HF$$

(6) It is strong fluorinating agent and show a variety of reaction

$$Pt + XeF_4 \rightarrow Xe + PtF_4$$
$$NO_2 + XeF_4 \rightarrow NO_2F + Xe$$
$$2SF_4 + XeF_4 \rightarrow 2SF_6 + Xe$$
$$2Hg + XeF_4 \rightarrow Xe + 2HgF_2$$
$$NO + XeF_4 \rightarrow NOF + Xe$$

(7) It react with BCl_3 and give BF_3

$$3XeF_4 + 4BCl_3 \rightarrow 4BF_3 + 6Cl_2 + 3Xe$$

(8) (i) XeF_4 show disproportionation reaction with water and give highly explosive compound such as XeO_3

$$3XeF_4 + 12H_2O \rightarrow \underset{\text{(explosive)}}{2XeO_3(s)} + 4Xe + 24HF + 3O_2$$

(ii) But if temp. is – 80°C it gives Xenon oxy fluoride

$$XeF_4 + H_2O \xrightarrow{-80^\circ C} \underset{\text{Xenon oxy fluoride}}{XeOF_2} + 2HF$$

(9) If form addition product with SbF_5 as shown.

$$XeF_4 + SbF_5 \rightarrow XeF_4 \cdot SbF_5 \text{ or } |XeF_3|^+|SbF_6|^-$$

$$XeF_4 + 2SbF_5 \rightarrow XeF_4 \cdot 2SbF_5 \text{ or } |XeF_3|^+|Sb_2F_{11}|^-$$

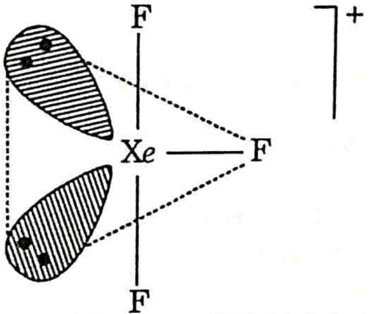


Fig-9* T-*shaped* XeF_3^+ *ion

The geometry of XeF_3^+ is T–shaped. The element Xe, is generally Sp^3d hybridised. Its two equitorial position, occupied by two lone pair of electrons as shown in Fig-9.
It react with TaF_5 and give $Xe(TaF_6)_2$ i.e. straw-in-colour

$$XeF_4 + 2TaF_5 \rightarrow Xe(TaF_6)_2 + F_2$$

Structure of XeF_4

Spectroscopic techniques has shown that the structure of XeF_4 is square planer (Fig-10) Their square planer geometry described *via*, valence bond theory.

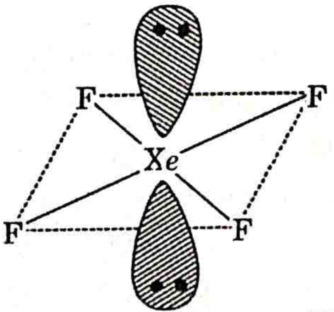


***Fig-10 Square planar of* XeF_4**

The ground state electronic configuration of XeF_4 is $5S^25p^6$ (Outer most shell) To create four unpaired electons for, four fluorine atoms, its two 5p-electrons promoted into vacant 5*d*-orbitals as shown in figure-11.

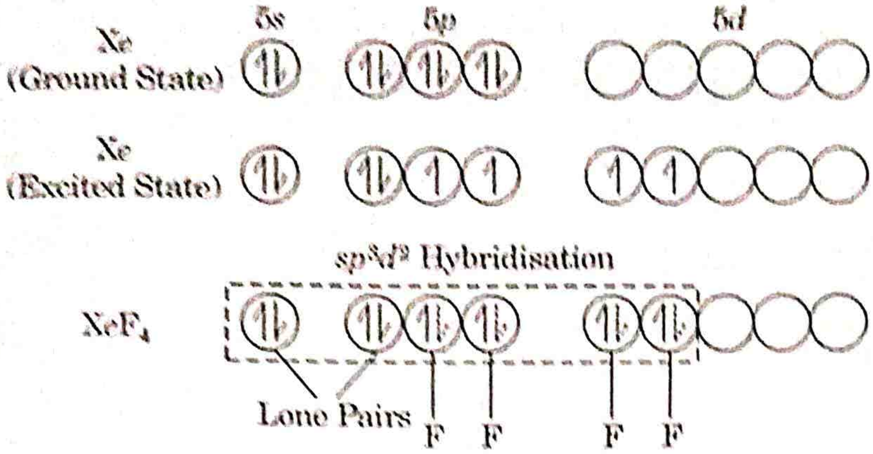


Fig-11 Formation of XeF$_4$ molecule involving sp^{3}d^2 hybridisation. The dotted arrow represent electrons supplied by fluorine atoms.

Thus their six orbitals (one 5*s*, three 5*p*, and two 5*d*) got hybridised and form *sp*^{3}*d*^{2} hybrid orbitals and gave octahedral geometry. Their four unpaired electrons overlaps with 2*p*-orbitals of four fluorine atoms and form four Xe-F bonds, while the remaining two octahedral position especially on axis occupied by the lone pair of electrons. Thus XeF$_4$ has square planer shape.

The important properties of XeF$_4$ summerised in Fig-12.

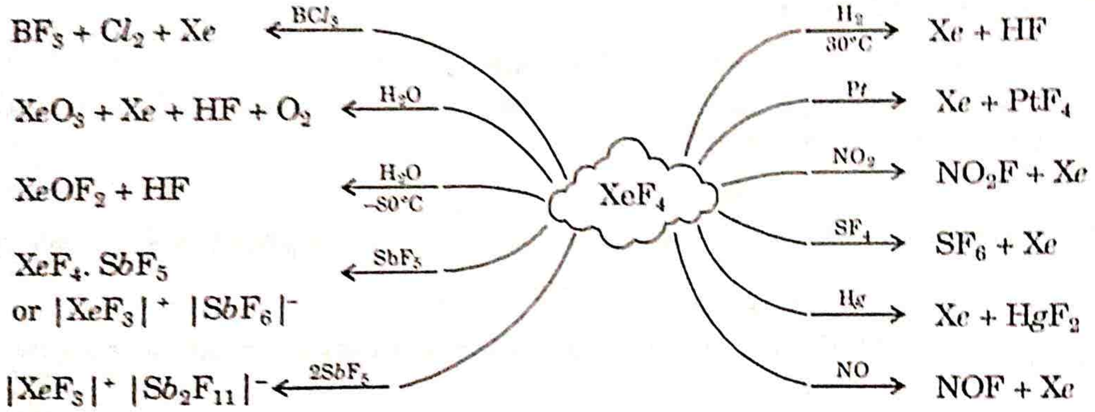


Fig-12 Summery of chemical properties of XeF$_4$

(3) Xenon Oxydifluoride, XeOF$_2$

It is synthesized by slow and partial hydrolysis of XeF$_4$ at a temperature of –80°C

$$XeF_4 + H_2O \xrightarrow{-80^\circ C} XeOF_2 + 2HF$$

It is unstable compound.

Structure of XeOF$_2$

The ground state electronic configuration of XeOF$_2$ is 5S^{2}5P^6 (outer most shell configuration).

To create four unpaired electrons two for fluorine atoms and two for one oxygen atom. *Xe* promote their two electrons from 5p-orbitals to vacant 5d-orbitals as shown in the Fig-13.

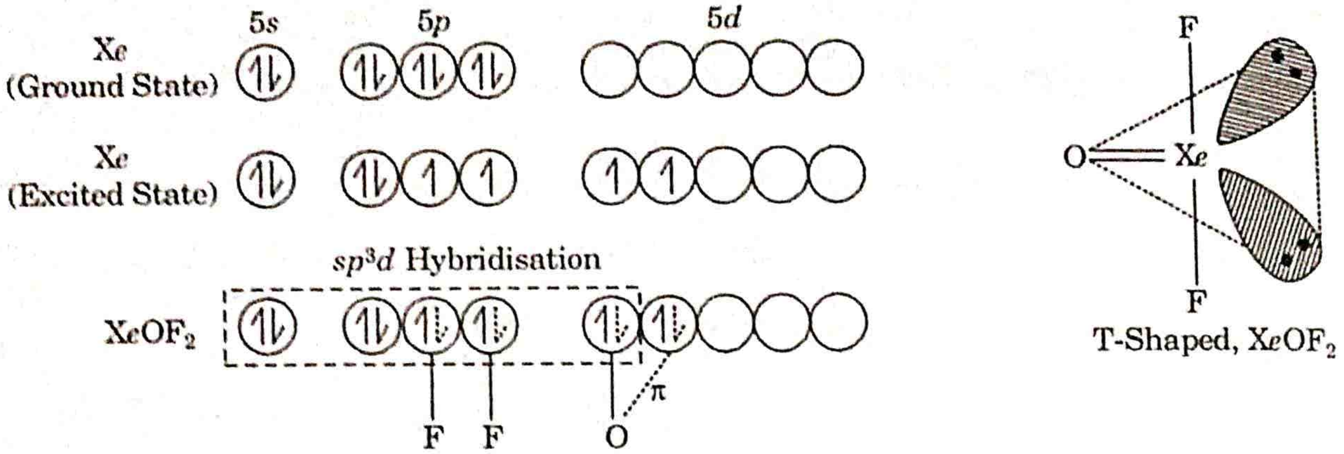


Fig-13* T-*shaped structure of* $XeOF_2$ *molecule involving sp³d hybridisation.

Thus their five orbitals (one 5*s*, three 5*p* and one 5*d*) get hybridised and to form five *sp*³*d* hybrid orbital for the overlapping with four unaired electrons of fluorine and oxygen atoms. But one of the 5*d*-orbital electron does not takes part in hybridisation, that form an additional π-bond with oxygen atom. Due to *sp*³*d* hybridisation in $XeOF_2$ its geometry should be trigonal bipyramidal but due to presence of two lone pairs of electrons. The compound, $XeOF_2$ has **T-shaped structure**, its two equitorial position occupied by the two lone pairs of electrons.

Xenon Hexafluoride-XeF_6

Synthesis–It is synthesized by the following methods.

1. It is formed by treating Xe with F_2 in the ratio of (1 : 20), in a nickle vessel at 300°C and at a pressure of 50-60 atm.

$$Xe + 3F_2 \rightarrow XeF_6$$

2. It is formed by the oxidation of XeF_4 with O_2F_2 under pressure at a temp. of –130°C

$$XeF_4 + O_2F_2 \xrightarrow{-130^\circ C} XeF_6 + O_2$$

3. It can also be obtained by passing electric discharge through a mixture of Xe : F_2 (1 : 3) at low temp.

$$\underset{1:3}{Xe + 3F_2} \xrightarrow[\text{temperature}]{\text{low}} XeF_6$$

It can be separated from XeF_2 and XeF_4 by the following reaction

$$XeF_6 + 2NaF \xrightleftharpoons{T=17^\circ C} Na_2XeF_8$$

on warning Na_2XeF_8 at 120°C pure XeF_6 is obtained

$$Na_2XeF_8 \xrightarrow[\text{Warm}]{T=120^\circ C} XeF_6 + 2NaF$$

Properties

1. It is a crystalline solid.
2. It melts at 50°C.
3. It is highly voltile fluoride form a solution, which act as good conductor of electricity due to formation of ions

$$HF + XeF_6 \rightarrow XeF_5^+ + HF_2^-$$

5. By the action of H_2, NH_3 and HC*l*, it reduce to Xe

$$XeF_6 + 3H_2 \rightarrow Xe + 6HF$$

$$XeF_6 + 8NH_3 \rightarrow Xe + 6NH_4F + N_2$$

$$XeF_6 + 6HCl \rightarrow Xe + 3Cl_2 + 6HF$$

6. It undergoes slow hydrolysis with moisture and form highly explosive XeO_3

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

On partial hydrolysis it gives, $XeOF_4$

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

7. It also react with glass, if stored in glass

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \rightarrow 2XeO_3 + SiF_4$$

In the above reactions highly explosive substance XeO_3 is formed.

8. It reacts with F–ion acceptor and to form adduct

$$XeF_6 + PtF_5 \rightarrow XeF_6 \cdot PtF_5 \text{ or } |XeF_5|^+|PtF_6|^-$$

$$XeF_6 + SbF_5 \rightarrow XeF_6 \cdot SbF_5 \text{ or } |XeF_5|^+|SbF_6|^-$$

$$XeF_6 + AsF_5 \rightarrow XeF_6 \cdot AsF_5 \text{ or } |XeF_5|^+|AsF_6|^-$$

In the above reaction XeF_6 act as fluorinating agent.

Structure of XeF_5^+ : XeF_5^+ has square pyramidal geometry. It undergoes sp^3d^2 hybridisation in Xe. Its structure given below :

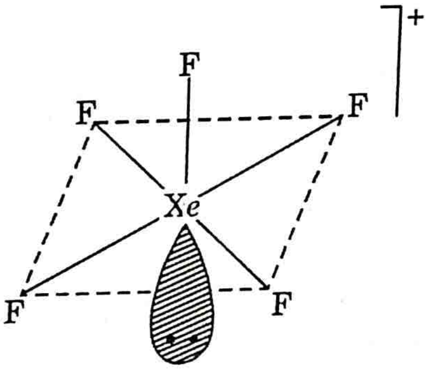


Fig-14 Square pyramidal structure of XeF_5^+ ion

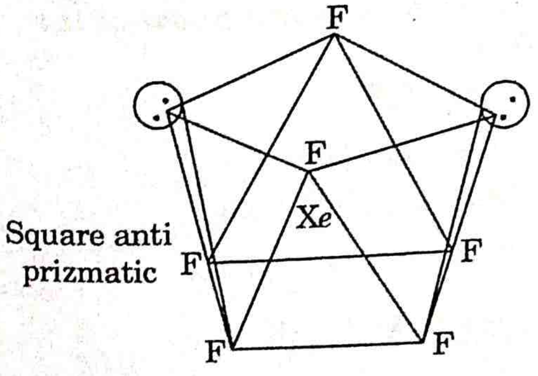


Fig-15 Structure of XeF_6^{2-}

9. It form XeF_7^- and XeF_8^{2-} by reacting with CaF and RbF (F-ion donor)

$$CsF + XeF_6 \rightarrow CsF \cdot XeF_6 \rightarrow 2Cs^+ |XeF_8|^{2-}$$

$$2RbF + 2XeF_6 \rightarrow 2RbXeF_7 \rightarrow 2Rb^+ |XeF_8|^{2-}$$

Structure of XeF_6^{2-} (Fig-15)

It has square antipriszmatic geometry.

Structure and Shape of, XeF_6–The ground state electronic configuration of Xe is $5s^25p^6$. Three of $5p$–e^- are promoted to $5d$–orbitals so that there are six unpaired e^-(three e^- in $5p$–orbitals and three e–in $5d$–orbitals)

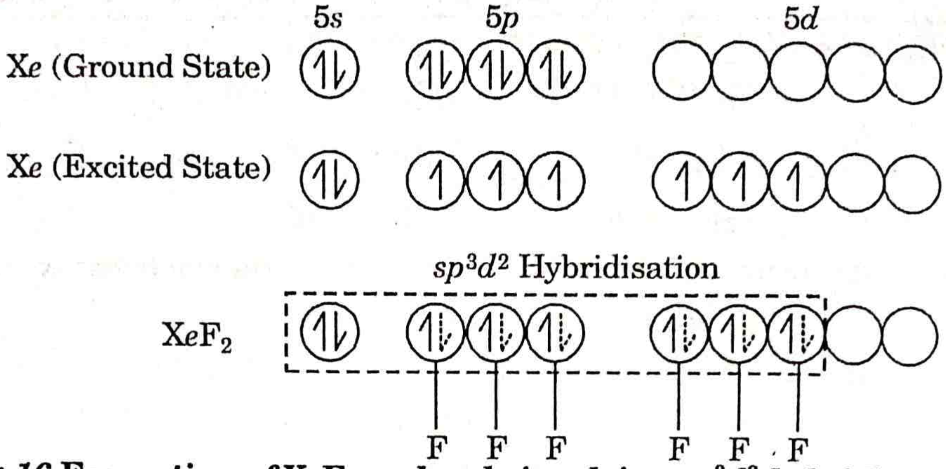


Fig-16 Formation of XeF_6 molecule involving sp^3d^3 hybridisation. The dotted arrows represent electrons supplied by fluorine atoms.

Here the seven orbitals (one *s*, three-*p* and three-*d*) hybridise to form Sp^3d^3 hybrid orbitals (Fig-16). The compound XeF_6 adopt pentagonal bipyramidal geometry. Out of these seven orbitals six orbitals form single, σ bonds with six fluorine atoms. But one position of Xe is occupied by lone pair of electron. So due to presence of this lone pair of electron the pentagonal bipyramidal structure get slightly distorted Fig-17(a). Therefore, the structure become **distorted octahedral shape** Fig. 17(b).

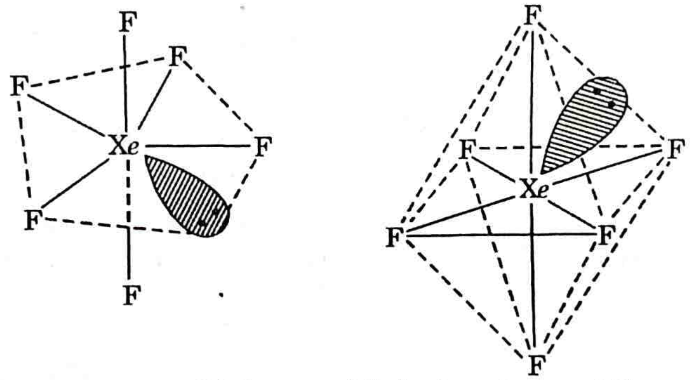


Fig-17 (a) Distorted pentagonal bipyramidal structure with one position occupied by a lone pair. (b) Distorted octahedral structure with lone pair present at the centre of a triangular face.

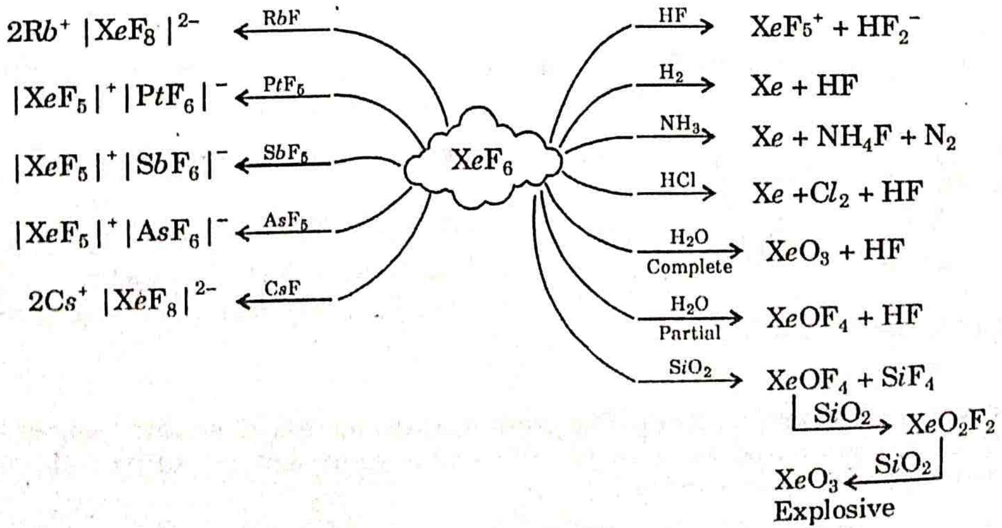


Fig-18 Summery of chemical properties of XeF_6

Xenon Oxytetrafluoride - $XeOF_4$

Synthesis : $XeOF_4$ synthesized by the following methods.

(1) It is prepared by the partial hydrolysis of XeF_6

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

(2) Silica on reacting with XeF_6 at 50°C give $XeOF_4$

$$\underset{\text{Silica}}{SiO_2} + 2XeF_6 \xrightarrow{50^\circ C} XeOF_4 + SiF_4$$

(3) It can also be prepared by mixing Xe and F_2 (in molar ratio of 1 : 4) in the presence of excess of O_2 at 230°C.

$$Xe + O_2 + 4F_2 \rightarrow 2XeOF_4$$

It can be purified by the vacuum distillation method.

Properties

(1) It is a colourless compounds. Its M.Pt is –46°C.

(2) $XeOF_4$ react with H_2 and reduce to Xe

$$XeOF_4 + 3H_2 \rightarrow Xe + H_2O + 4HF$$

(3) $XeOF_4$ react with silica and give XeO_2F_2, which react further and give explosive compound XeO_3

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \rightarrow \underset{\text{explosive}}{2XeO_3} + SiF_4$$

4. Oh hydrolysis $XeOF_4$ give XeO_2F_2, which react further and give XeO_3 (explosive compound)

$$XeOF_4 + H_2O \rightarrow XeO_2F_2 + 2HF$$

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

5. $XeOF_4$ act as fluornating agent react with F^- ion acceptor as shown

$$XeOF_4 + SbF_5 \rightarrow XeOF_3^+ + SbF_6^-$$

$$XeOF_4 + 2SbF_5 \rightarrow XeOF_3^+ + |Sb_2F_{11}|^-$$

The compound $XeOF_3^+$, **cation undergo sp^3d** hybridisation. Therefore posseses trigonal bipyramidal structure but has a lone pair of electron on equitorial position as shown in fig. - 19

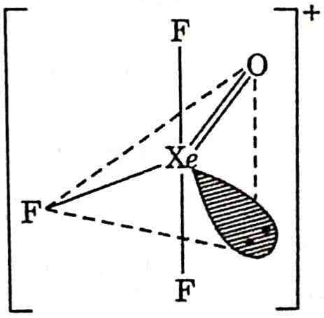


Fig-19. Structure of $XeOF_3^+$

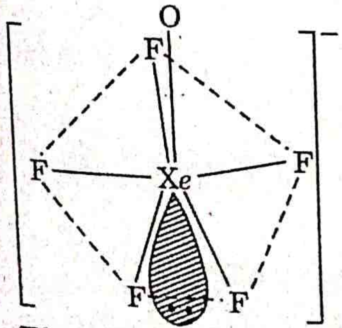


Fig-20. Structure of $XeOF_5^-$

6. On reaction with Nitrosyl fluoride (NOF), the $XeOF_4$ give $NO^+(XeOF_5)^-$

$$XeOF_4 + NOF \rightarrow NO^+(XeOF_5)^-$$

In $XeOF_5^-$ ion, the atom –Xe is generally Sp^3d^3 hybridised. Thus has pentagonal bipyramidal geometry but with a lone pair of electron as shown in Fig-20.

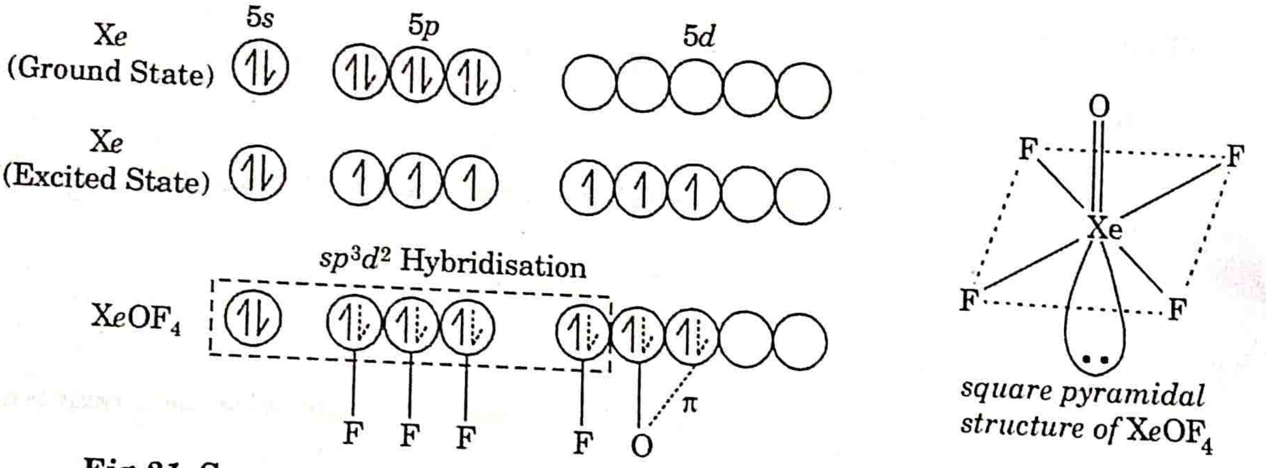
The oxygen atom occupy the optical position. While Xe-atom located slightly above the plane of five fluorine atoms.

Structure and Shape of $XeOF_4$ molecule

The ground state electronic configuration of Xe is $5s^2 5p^6$. The number of unpaired electrons required are six (four for F^--atoms and two e-for oxygen atom). So, three 5p-electrons of Xe promoted to 5d-orbitals shown in fig-21.

The six orbitals of Xe(one-5s, three-5p and two-5d-orbitals) hybridise and give sp^3d^2 hybridised orbitals. One of the 5d-electrons donot takes part in hybridisation, it form π-bond.

The singly occupied orbitals of Xe form five sigma bonds (four with fluorine atoms and one with oxygen atom). The unpaired electron of Xe, that does't takes part in hybridisation forms a π-bond (double bond) with oxygen atom. Due to presence of a lone pair of electron the molecule has square pyramidal structure.



square pyramidal structure of $XeOF_4$

Fig-21. *Square pyramidal structure of* $XeOF_4$ *molecule involving* sp^3d^2 *hybridisation.*

The important chemical propeties of $XeOF_4$ summerised in fig-22.

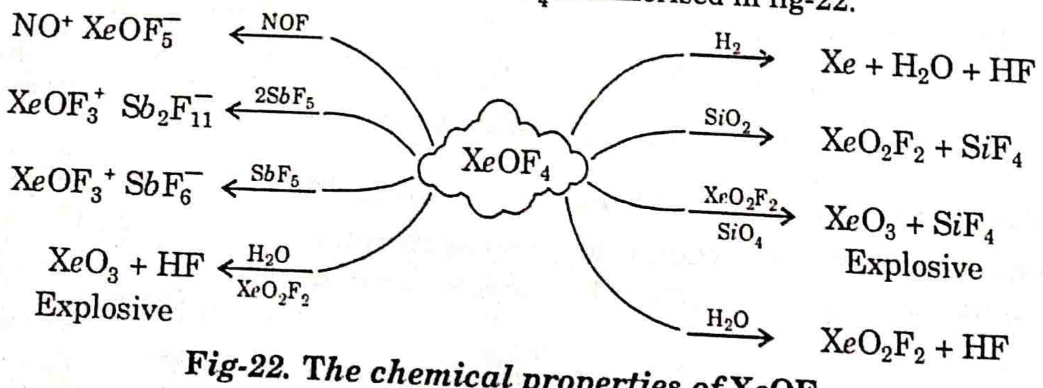


Fig-22. *The chemical properties of* $XeOF_4$.

Xenon Dioxydifluoride, XeO_2F_2

Synthesis

(1) It is synthesized by mixing XeO_3 and $XeOF_4$ at a temperature of –78°C

$$XeO_3 + XeOF_4 \xrightarrow{-78°C} 2XeO_2F_2$$

Fractional distillation is the technique by which we can purify the XeO_2F_2.

$F_2 + 2HF$

(3) It is synthesized by the reaction of $XeOF_4$ with silica

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

Properties

(1) XeO_2F_2 is colourless solid
(2) Its melting point is 30.9°C.
(3) On hydrolysis give XeO_3 (explosive)

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

(4) It is thermodynamically unstable, on heating it give XeF_2 and O_2

$$XeO_2F_2 \rightarrow XeF_2 + O_2$$

(5) On reaction with SbF_5, it give white ionic solid

$$XeO_2F_2 + 2SbF_5 \rightarrow XeO_2F^+ Sb_2F_{11}^-$$

The compound $XeO_2F^+ Sb_2F_{11}^-$ is unstable and decomposes as to $XeF^+ Sb_2F_{11}^-$ and O_2 of room temperature.

Structure of XeO_2F^+

In XeO_2F^+-ion, the atom Xe is generally sp^3-hybridised. Therefore has tetrahedra geometry. But one of the tetrahedral position occupied by the lone pair of electron. Thus aquires **pyramidal shape** as shown in fig-23.

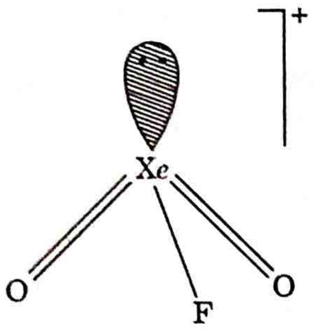


Fig-23. Structure of XeO_2F^+

Structure and Shape of XeO_2F_2.

XeO_2F_2 undergoes sp^3d hybridisation. In XeO_2F_2 the total number of unpaired electrons required for the formation of six bonds (two with F-atoms and four with O-atoms) is obtained by exciting, three of the 5*p* electrons. Thus XeO_2F_2 has **trigonal bipyramidal** geometry, as shown in fig-24.

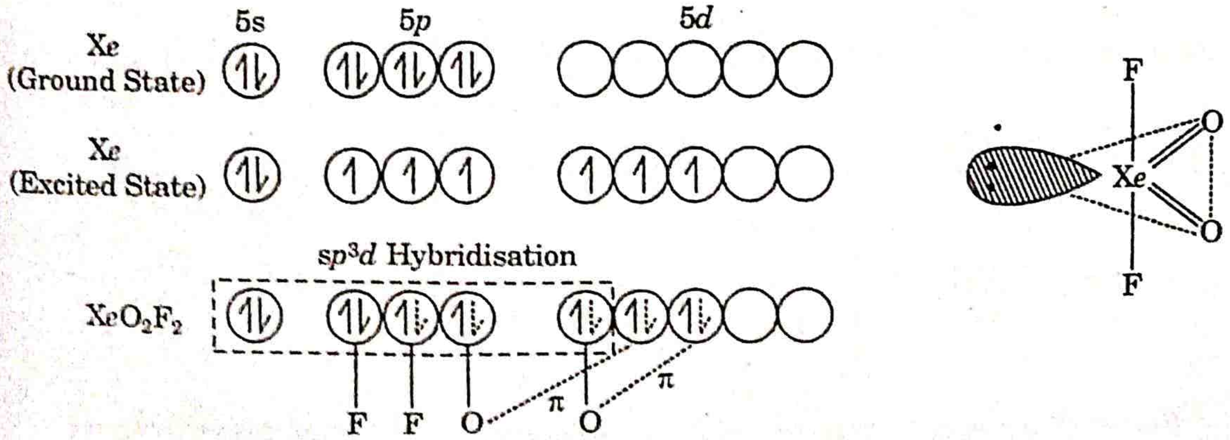


Fig-24. Distorted trigonal bipyramidal structure of XeO_2F_2 molecule involving sp^3d hybridisation.

Thus Xenon form four σ bonds with fluorine atoms and oxygen atoms. After forming four σ bonds, its two of the 5*d*-orbitals are left unhybridised. These unhybridised orbitals of Xe form π-bonds with the two oxygen atoms. But the molecule XeO_2F_2 does not have regular geometry. The irregularity is due to the presence of a lone pair of electron at one of the equitorial position.

7. Xenon trioxide–XeO_3

Synthesis

XeO_3 synthesized by the hydrolysis of XeF_6 or XeF_4

$$6XeF_4 + 12H_2O \rightarrow 2XeO_3 + 4Xe + 6HF + 3O_2$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

XeO_3 is highly explosive compounds, it should be handled carefully.

Properties

(1) It is white non volatile solid.

(2) It is soluble in water and stable in their aqueous solution.

(3) In dry state, XeO_3 explodes violently

$$XeO_3 \rightarrow Xe + {}^3/_2O_2 + 400\text{ kJ}$$

It give 400 kJ of energy, thus are explosive in nature.

(4) In acidic medium it act as powerful oxidising agent and convert $\overset{3+}{Pu}$ to $\overset{4+}{Pu}$ ions–

$$6Pu^{3+} + XeO_3 \xrightarrow{H^+} 6Pu^{4+} + Xe + 3H_2O$$

(5) XeO_3 when dissolve in NaOH undergoes disproportionation reaction and form sodium perxenate

$$2XeO_3 + 4NaOH + 6H_2O \rightarrow Na_4XeO_6 \cdot 8H_2O + Xe + O_2$$

Sodium perxenate, on dissolving in an acidic solution give XeO_3 and O_2

$$Na_4XeO_6 + 4HCl \rightarrow H_4XeO_6 + 4NaCl$$

$$2H_4XeO_6 \rightarrow 2XeO_3 + 4H_2O + O_2$$

Structure of XeO_3

The outer most electronic cnfiguration of Xe in ground state is $5s^25p^6$. In compound XeO_3, the atom Xe is generally sp^3 hybridised. This have tetrahedral geometry. In order to creates six unpaired electron for three oxygen atom, Xe promoted, three of the 5*p*-electrons to 5*d*-orbitals. Therefore total number of unpaired electrons in Xenon is six as shown in fig-25.

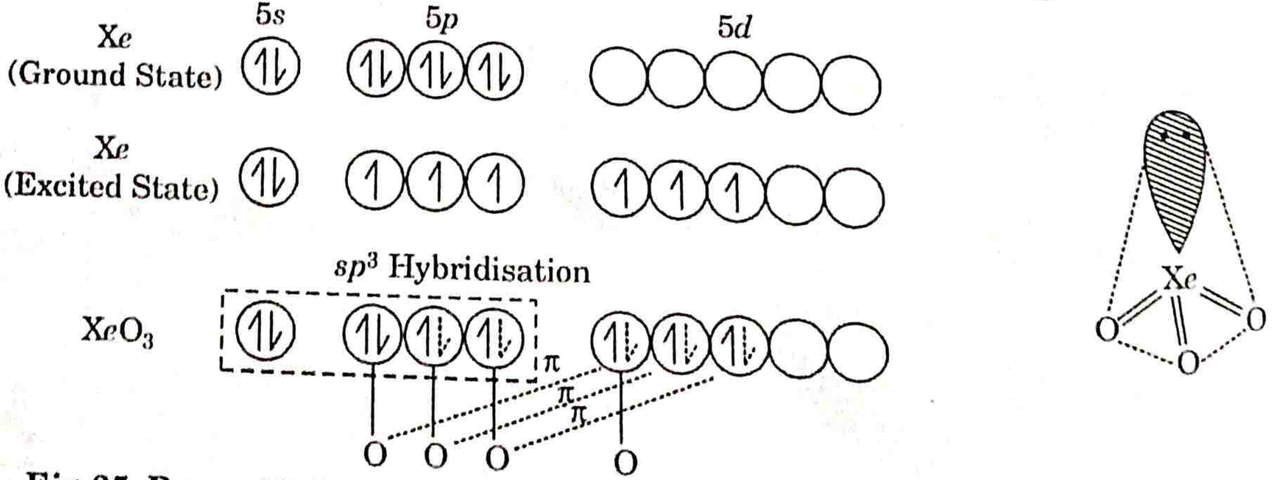


Fig-25. Pyramidal structure of XeO_3 molecule involving sp^3 hybridisation.

Tha atom-Xe-form three σ bonds with three oxygen atoms. The remaining (unhybridised) electrons of Xe-from π-bonds with three oxygen atoms (one π-bond with each oxygen atoms).

The geometry of XeO is not exactly tetrahedral, due to presence of one lone pair of electrons to one of the tetrahedral position. Consequently the molecule has a pyramidal structure.

Xenon (VIII) Compounds: The suggested compounds of Xenon are as

XeF_8, XeO_4, $XeOF_6$, XeO_3F_2 and XeO_2F_4.

These compounds donot have any confirmatory existance except XeO_4.

Synthesis: XeO_4 is synthesized by the action of conc. H_2SO_4 on sodium xenate –Na_4XeO_6 or Barium Xenate – Ba_2XeO_6. It is purified by vacuum distillation method at –78°C

$$\underset{\left(\begin{array}{c}\text{Conc.}\\ H_2SO_4\end{array}\right)}{XeO_6^{4-} + 4H^+} \rightarrow H_4XeO_6 \xrightarrow{-2H_2O} XeO_4$$

It is highly unstable compound and decomposes to Xe and O_2. It is highly explosive compounds and explode at (–40°C) a very low temperature.

$$XeO_4(g) \rightarrow Xe + 2O_2 + 640\text{ kJ}$$

Its geometry is tetrahedral, due to sp^3 hybridisation in Xenon. Its expected structure given as in fig-26.

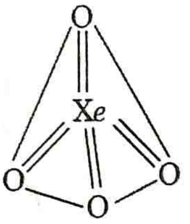


***Fig-26. Structure of* XeO_4**

IMPORTANT QUESTIONS : NOBLE GASES

1. Name the molecular geometry of $XeOF_4$.
2. Name the molecular geometry of XeO_3.
3. Which compound led to the discovery of compounds of noble gases?
4. Why do noble gases form compounds with fluorine and oxygen only?
5. Draw the structure of XeF_2 molecule.
6. Draw the structure of XeF_4 molecule.
7. He is used in diving equipment.
8. Explain why structure of Xenon fluoride cannot be explained by valence bond approaches.
9. Draw the structure of XeF_6.
10. Complete the following equation

$$XeF_4 + SbF_5 \rightarrow$$

11. Complete the equation

$$XeF_4 + O_2F_2 \xrightarrow{150\text{ K}}$$

12. Why do noble gases have very low boiling point.
13. Complete the following equation **(M.D.U. 2015)**

$$XeF_6 + \underset{\text{(excess)}}{H_2O} \rightarrow$$

14. Complete the following equation

$$XeF_2 + PF_5 \rightarrow$$

15. XeF_2 is a linear molecule not bent.
16. Noble gases are least reactive elements.
17. What happens when XeF_6 is hydrolysed.
18. Complete the equation

$$XeF_6 + KF \rightarrow$$

19. Of the noble gases only Xenon is known to form stable compounds Explain it.
20. Write the chemical equation of PtF_6 with Xe.
21. Why noble gases form compounds with fluorine and oxygen only.
22. Write the balanced chemical equations for obtaining XeO_3 and $XeOF_4$ from XeF_6.
23. How does Xenon atom form compounds even though, the Xe atom has a closed shell electronic configuration?
24. How are following compounds are prepared from XeF_6?
    (i) $XeOF_4$ (ii) XeO_3
25. Discuss the structure of $XeOF_2$ and XeF_6. **(M.D.U. 2011)**
26. What caused delay in the study of chemistry of noble gases? **(M.D.U. 2011)**
27. Why most of noble gas compounds involve F and O? **(K.U.K. 2014, 2013) (M.D.U. 2012, 2011)**

5

p-BLOCK ELEMENTS

The elements whose last electrons enter in the *p*-orbitals is called *p*-block elements. These elements belonging to group 13 to group-18. The valence shell electronic configuration of Group-13 to 18 given as in Table-1.

Table -1 General electronic configuration of Group-13 to Group-18

Group Number	Electronic Configuration
13	ns^2np^1
14	ns^2np^2
15	ns^2np^3
16	ns^2np^4
17	ns^2np^5
18	ns^2np^6

Thus their general electronic configuration given as $ns^2\ np^{1-6}$

Here $n = 2-7$

Together with *s*-block elements these elements are called as representative elements.

The comparative study of elements belonging to G-13 to 18 are discussed below–

GROUP - 13 : BORON FAMILY

The elements of group-13 are Boron-(B), Aluminium-(A*l*), Galium-(G*a*), Indium (In) and Thallium-(T*l*). Boron is non metal while rest of the elements have some metallic characters.

Occurance– The element boron present in rare amount, while the element–Aluminium is most abundant element of this group (*i.e.*, Third most abundant element).

Galium also occur in rare amount but double the amount as boron.

But Indium and thallium are less common

Comparative Study of the Elements of Group - 13

Electronic Configuration: The General electronic configuration of elements of group-13 given as ns^2np^1. These elements have only one electron in *p*-orbitals and two electrons in *s*-orbital.

The electronic configuration of elements of group-13 given in the Table-2

Table-2 Electronic configuration of Group 13 elements.

Element	Symbol	Atomic No.	Electronic configuration
Boron	B	5	[He] $2s^2\ 2p^1$
Aluminium	*Al*	13	[Ne] $3s^2\ 3p^1$
Gallium	*Ga*	31	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Indium	*In*	49	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Thallium	*Tl*	81	[Xe] $5d^{10}\ 6s^2\ 6p^1$

General Properties of Elements of Group-13: The important data of physical properties of an element of group-13 given in the Table-3

Table-3 Physical data of group 13 elements.

Element		B	*Al*	*Ga*	*In*	*Tl*
Atomic number		5	13	31	49	81
Atomic radius (pm)		85	143	135	167	170
Ionic radius (pm) M^{3+}		27	53.5	62.0	80.0	88.5
Density (g cm^{-3})		2.35	2.70	5.90	7.31	11.85
Ionisation energy	I	800	577	579	558	589
(kJ mol^{-1})	II	2427	1816	1979	1820	1971
	III	3659	2744	2962	2704	2877
Electronegativity		2.0	1.5	1.6	1.7	1.8
Oxidation states		+3	+3	+1, +3	+1, +3	+1, +3
Melting point (K)		2453	933	303	430	575
Boiling point (K)		3923	2740	2676	2353	1731

1. Atomic and ionic Radii : The atomic and ionic radii of an element of group-13 are smaller than corresponding elements of group-2.

Explanation

This is because in group-13, the magnitude of nuclear charge is greater than an element of group-2. So effective nuclear charge experienced by the valence electrons of elements of group-13 greater than an elements of group-2 (Fig-1)

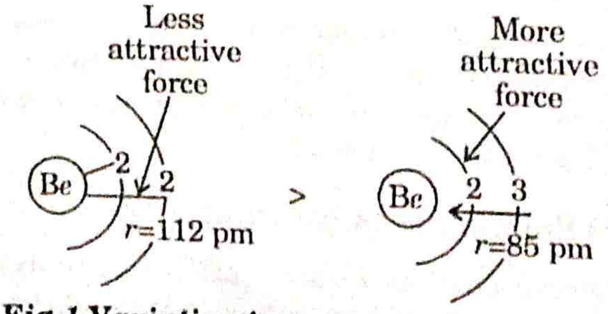


Fig-1 Variation in atomic radii in period

As we move from left to right in the periodic table, the number of electrons added to the same shell. Since electrons in the same shell have less screening effect on each other, so atomic or ionic radii decreases.

In Group-13 atomic and ionic radii generally increases. (fig-2)

Explanation

This is due to increase in number of shells in group, and decrease in magnitude of effective nuclear charge, so size of an elements generally increases.

The atomic radii of *Al* (143 pm) is slightly greater than that of Ga (135pm) (fig 3).

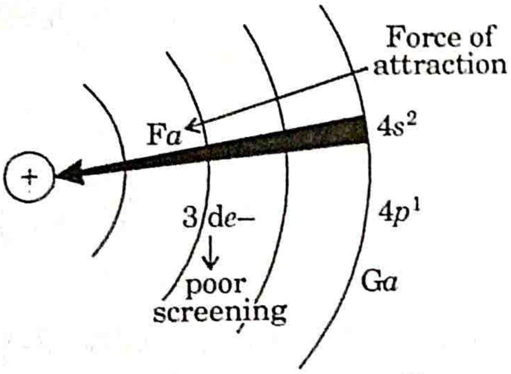


Fig-3. Atomic radii of Galium

2. Boiling Point

The boiling points (fig.-4) of elements of group-13 generally decreases in group.

Explanation

The decrease in boiling point is due to increase in size of an elements (atoms). (fig-5) With increase in size of an atoms bond length also increase, that decreases the bond dissociation energy ∴ bond cleaved easily and molecules boiled at low temperature.

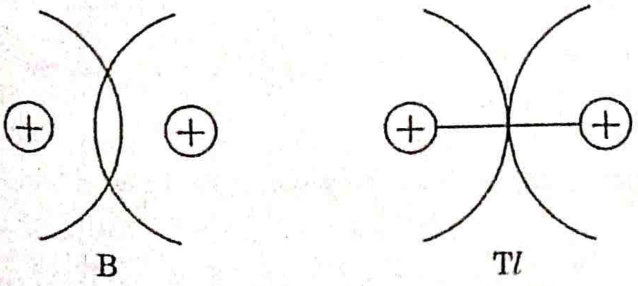


Fig-5. Size of B *and Tl*

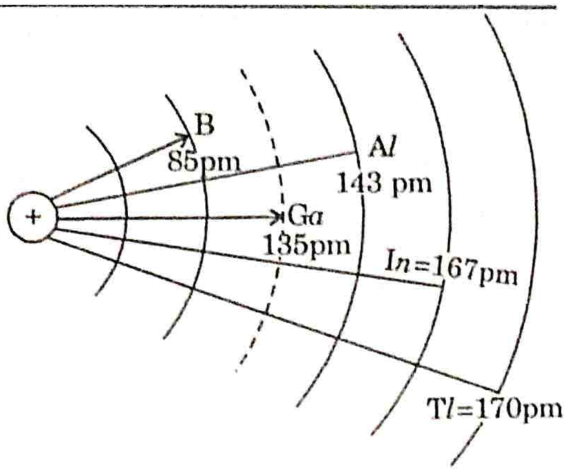


Fig-2. Atomic radii in group-13

Explanation

Atomic radii of Galium smaller than aluminium due to inert pair effect i.e. imperfect screening by innervenning *d*-orbitals electrons so that valence electrons experienced more attraction than the valence electrons of aluminium.

More over the penetrating power of *d*-orbitals electron is poor.

Therefore effective nuclear charge felt by the electrons of gallium greater than valence electrons of aluminium. Thus atomic radii slightly decreases.

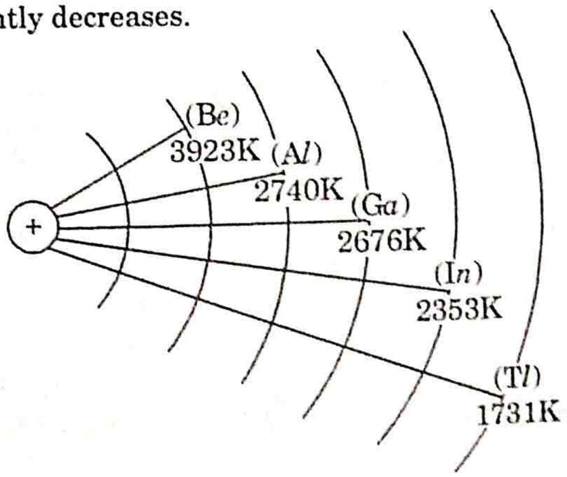


Fig-4 B.pt of Group-13 elements

(3) Melting Point

In group melting point generally decreases but decreases in melting point is not regular as shown in fig-6.

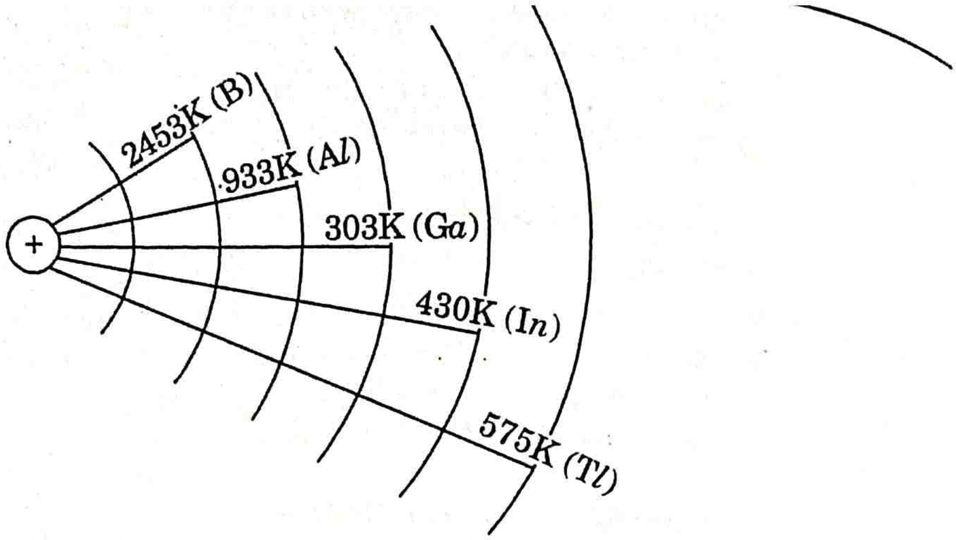


Fig-6* M.P*t of an elements of* Group-*13.

(4) Ionization energy : The first ionization energy of elements of group-13 less than an elements of group-2. (fig-7)

Explanation: This is because in case of an elements of group-13 the valence shell electronic configuration is ns^2np^1 while elements of group-2 have valence shell configuration of ns^2. Therefore in group-13, the electron will be removed from np-orbitals which is higher in energy as compared to valence electrons of group-2 (ns^2). Thus electron in *p*-subshell weakly held by the nucleus, hence removed easily.

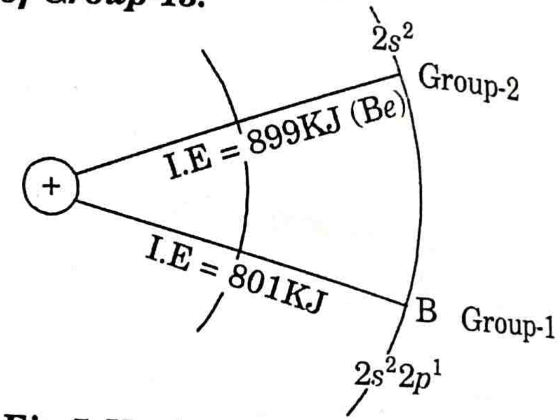


***Fig-7. Variation in* I.E. *of* Be *and* B.**

Moreover, the valence electrons of group-2 are in *ns*-orbitals, that *ns*-orbital has more penetrating power, thus feel more effective nuclear charge.

The 2nd and 3rd Ionization enthalpy of an elements of group-13 greater than first ionization energy. (fig-8).

Explanation: The IE_2 , IE_3 are greater than IE_1 because, when electron is removed from *np*-orbitals, its *ns*-orbital becomes fully filled with electrons. Thus aquires extra stability.

More over the number of protons become greater than number of electrons so *ns-e*-feels greater effective nuclear force. As a result value of I.E. increases.

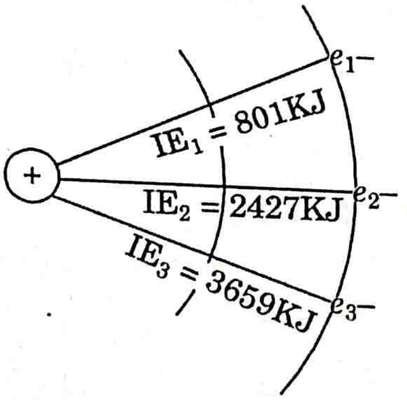


***Fig-8. Variation in values of* IE_1, IE_2 *and* IE_3**

The Ionization enthalpy of Boron is highest in Group-13.

Explanation

This is because of small size of boron atom. The effective nuclear charge felt by the valence electron is greater in magnitude than other members of group-13.

So that the value of Ionization enthalpy is found to be highest.

In group-13 the value of I.E. not regularly decreases but show irregular trend as shown in the Fig-9.

Explanation

Generally I.E. decreases in group because of increase in sizes, the effective nuclear charge felt by the valence electrons become less.

The irregularity in the values of I.E. is due to Inert pair effect i.e. poor shielding of innervenning *d* and *f* orbitals electrons. So that valence electrons attract strongly by the nucleus, that increase the values of Ionization enthalpy as it can be seen in Galium and Thallium.

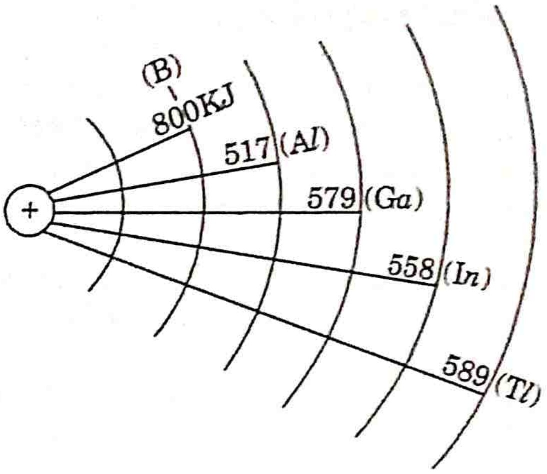


Fig-9 **I.E.** *of an elements of group-13.*

5. Oxidation State

- The number of valence electrons in the element of group-13 are three. (two in 2*s*-orbital and one-in 2*p*-orbital)

Thus elements of this group shows the maximum oxidation state of +3. (fig-10)

But +1 oxidation state becomes more stable as we goes down in group from B to Tl or moreover. The +1 oxidation state of Tl is more stable than +3 oxidation state. (fig-11).

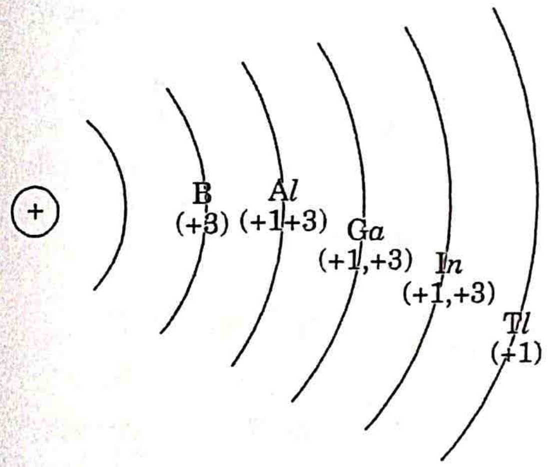


Fig-10 Oxidation state of an elements of a-13.

Explanation

According to Aufbau principle the order of filling various orbitals with electrons given as

$6s \rightarrow 4f \rightarrow 5d \rightarrow 6p$

After entering the electrons in 6*s*-orbitals, these electrons are attracted strongly by the nucleus because of no electrons in 5*d* and 4*f*-orbitals i.e. no screening or imperfect screening or poor screening by the 5*d* and 4*f*-orbitals electron (Inert pair effect)

Lastly electrons enters in the 6*p*-orbitals after filling the 4*f* and 5*d*-orbitals with electrons, Now these orbitals creates screening effect for 6*p*-electrons. Thus 6*p*-electrons weakly attracted by the nucleus and takes part in the formation of bond and shows the oxidation state of +1.

So we can say that +1 oxidation state of Thallium is more stable than +3 oxidation state.

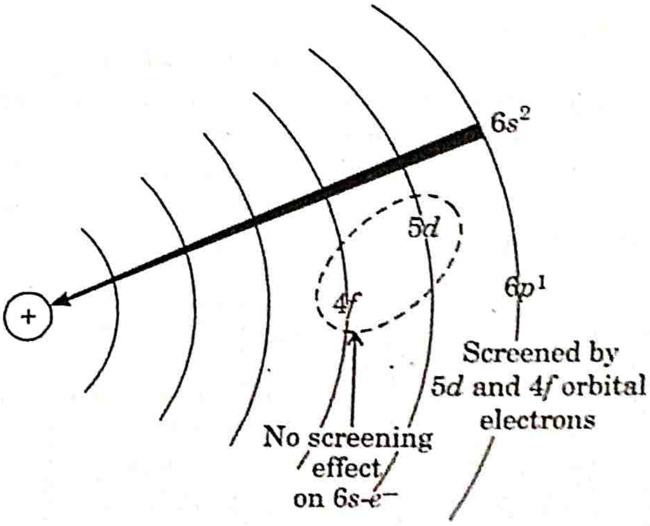


Fig-11. Oxidation state of Tl.

Similarly the the stability of +1, oxidation state explain why thallous compounds $TlOH$, $TlClO_4$ Tl_2O, TlX are more stable than thallic compounds [$Tl(OH)_3$, $Tl(ClO_4)_3$, Tl_2O_3 and TlX_3]

5. Electro Positive Nature–(Metallic Nature)

B is non metal, Al and Ga have some metallic characters while In and Tl are typically metallic in nature.

Explanation : Boron is non metal because of its small size and high ionization enthalpy, it donot loss electron quickly as shown in fig-12.

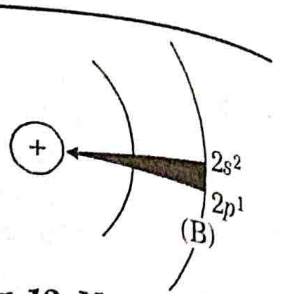


Fig-12. Non metallic nature of Boron.

While on moving down the group the size of an elements increases (fig-13) and ionization energy decrease. Therefore tendency to loss electrons increases.

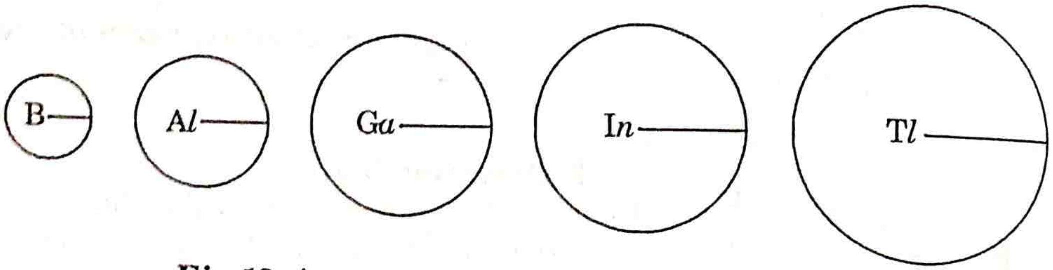


Fig.13. Atomic sizes of elements of group-13.

6. Tendency to form covalent bonds

Boron generally form covalent bonds.

Explanation : This is because of small size of trivalent (B^{3+}) ion. (Fig. 14)

It has greater polarising power and tend to pull off the electrons of neighbouring anions and show covalent characters.

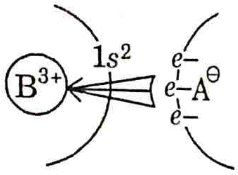


Fig. 14. Polarizing power of B^{3+} ion.

The elements Al, Ga, In and Tl exhibits ionic characters

Explanation : This is due to increase in atomic size and decrease in magnitude of polarising power. They cannot withdraw the electrons from anion strongly.

Note – The compounds formed by aluminium show ionic as well as covalent characteristic.

For example – Anhydrous – $AlCl_3$ – covalent

Hexaaqua aluminate – $[Al(H_2O)_6]^{3+}$ is ionic

Hydrides : The compounds of elements of Group-13 with hydrogen are called as Hydrides.

Hydrides of Boron

The compounds of boron with hydrogen are called boranes. The number of hydrides formed by boron are miximum. Boron form two series of hydride with a general formula of B_nH_{n+4} and B_nH_{n+6}. These are given in Table-4.

Table-4 Hydrides of Boron.

	B_nH_{n+4}		B_nH_{n+6}
$n = 2$	B_2H_6 - Diborane-6	$n = 4$	B_4H_{10} - Tetraborane-10
$n = 5$	B_5H_9 - Pentaborane-9	$n = 5$	B_5H_{11} - Pentaborane-11
$n = 6$	B_6H_{10} - Hexaborane-10	$n = 6$	B_6H_{12} - Hexaborane-12
$n = 10$	$B_{10}H_{14}$ - Decaborane-14	$n = 9$	B_9H_{15} - Nonaborane-15

The number expresses the number of H-atoms in borane. The hydrides of boron have multicentre bonds. Diborane is the simplest hydride of boron.

Hydride of Aluminium : The hydride of Aluminium is polymeric in nature with general formula of $(AlH_3)_n$. When it is heated at a temperature above 200°C, it decomposes–

$$(AlH_3)_n \rightarrow Al + H_2$$

It react with water and liberates $H_2(g)$. It is strong reducing agent

Hydride of Galium – GaH_3

It is a viscous liquid. It decomposes at room temperature into Galium and hydrogen.

Hydrides of Indium and Thallium – These are highly unstable hydrides.

The elements of group-13 also form complex hydrides.

For examples–The complex hydrides are lithium aluminium hydride $Li[AlH_4]$, lithium boron hydride $Li[BH_4]$, lithium gallium hydride $Li[GaH_4]$

Explanation : The formation of complex hydrides is due to presence of vacant p-orbitals in boron.

$$_5B\ \underline{1s^2 2s^2 2px^1 2p_y^0 2p_z^0}$$

These vacant p-orbitals can take pair of electrons from the hydride ion(H^-). The H^--hydride ion act as electron pair donor.

For examples :

$$BH_3 + H^- \rightarrow BH_4^-$$

$$AlH_3 + H^- \rightarrow AlH_4^-$$

$$GaH_3 + H^- \rightarrow GaH_4^-$$

The $Li[BH_4]$ is covalent in nature due to small size of Li^+ ion, its polarizing power is high. It react violently with water and liberates $H_2(g)$.

$$Li(BH_4) + 2H_2O \rightarrow LiBO_2 + 4H_2$$

Due to liberation of $H_2(g)$, it act as powerful reducing agent

The geometry of BH_4^- is tetrahedral as shown (fig. 15)

$Na|BH_4|$ generally ionic in nature but react slowly with water and can be crystallises from cold water.

$K|BH_4|$ is stable in water. Their stability associated with ionic nature of hydride-as shown

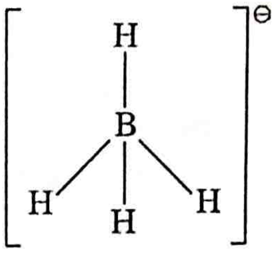


Fig. 15 Geometry of BH_4^- ion

$$K|BH_4|^- \rightarrow K^+ + \underbrace{BH_4^-}_{\text{Stable hydride}}$$

$LiAlH_4$ can be synthesized by the following method

$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

In this method LiH react with $AlCl_3$ in the presence of ether.

2. Oxides and hydroxides : All the elements of group-13 form the oxides and hydroxides of general formula M_2O_3 and $M(OH)_3$ i.e. B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3 and Tl_2O_3, $B(OH)_3$, $Al(OH)_3$, $Ga(OH)_3$, $In(OH)_3$ and $Tl(OH_3)$.

Oxide of Boron : B_2O_3 is also called as Boric oxide or anhydride of ortho boric acid. B_2O_3 is obtained by dehydration of boric acid at a temperature of about 100°C.

$$2H_3BO_3 \xrightarrow[\text{Heat}]{100°C} B_2O_3 + 3H_2O$$

B_2O_3 is highly stable oxide but on hydrolysis with water give boric acid.

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3 \text{ or } 2B(OH)_3$$

The oxide and hydroxide of boron are weakly acidic in nature and reacts with alkalies in the following manner.

$$B_2O_3 + 2NaOH \rightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$H_3BO_3 \text{ or } B(OH)_3 + 3NaOH \rightarrow \underset{\text{Sodium borate}}{Na_3BO_3} + 3H_2O$$

Oxide of Aluminium: It is obtained by heating aluminium with oxygen

$$4Al + 3O_2 \rightarrow \underset{\text{aluminium oxide}}{2H_2O_3}$$

It is commonly called as alumina. In nature it occus in two form

(i) α-Al_2O_3-corundum

(ii) γ-Al_2O_3-activated alumina

Oxide and hydroxide of aluminium are amphoteric in nature.

They dissolve in alkalies as well as in acid.

$$Al_2O_3 + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Sodium metaaluminate}}{2NaAlO_2} + H_2O$$

$$Al(OH)_3 + \underset{\text{Base}}{NaOH} \rightarrow NaAlO_2 + 2H_2O$$

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

$$Al(OH)_3 + 6HCl \rightarrow AlCl_3 + 3H_2O$$

Oxide of Gallium – Ga_2O_3: It is obtained by direct combination of Gallium with oxygen at moderate temprature

$$4Ga + 3O_2 \xrightarrow[\text{Heat}]{\text{moderate}} 2\,Ga_2O_3$$

It is white crystalline solid. Both Ga_2O_3 and $Ga(OH)_3$ are amphoteric in nature i.e. dissolve in acid as well as in alkalies

Oxide of Indium – In_2O_3

It is obtained by heating the metal sulphate and metal nitrate.

$$In_2(SO_4)_3 \xrightarrow{\text{Heat}} In_2O_3$$

$$In(NO_3)_3 \xrightarrow{\text{Heat}} In_2O_3$$

It is yellow solid. It is basic in nature.

Oxide of Thallium – Tl_2O, Tl_2O_3: Thallium form two types of oxides Tl_2O – Thallium monoxide and Tl_2O_3 – Thallium trioxide.

But Tl_2O is more stable than Tl_2O_3.

Explanation – In Tl_2O, the oxidation state of Tl is + 1, it is stable, due to inert pair effect as compared to + 3 oxidation state in Tl_2O_3.

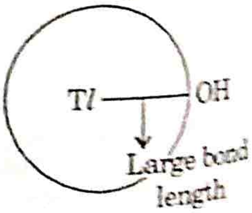


Fig. 16. Bond length of Tl–OH bond.

Thallium hydroxide – TlOH, generally basic in nature.

Explanation : The basic nature of, TlOH on is due to large size of thallium atom.

The Tl–OH bond length become large, (Fig. 16) its bond dissociation energy become less Therefore it cleave easily and release $\overline{O}H$ ion readily and act as base.

The Base nature of oxides and hydrocides given in table - 5.

Table -5 Basic nature of oxide and hydroxide of G-13.

B_2O_3, $B(OH)_3$]	acidic
Al_2O_3, $Al(OH)_3$ Ga_2O_3, $Ga(OH)_3$	amphoteric
In_2O_3, $In(OH)_3$ Tl_2O_3, $TlOH$	Basic Strongly basic

Oxo acids of Boron: Boron form large number of oxo acid but ortho boric acid is an important one.

The various oxo acids of boron given as :

(i) Orthoboric acid – H_3BO_3
(ii) Metaboric acid – HBO_2
(iii) Pyroboric acid – $H_6B_4O_9$
(iv) Tetraboric acid – $H_4B_4O_7$

Structure of Boric acid – H_3BO_3 or $B(OH)_3$

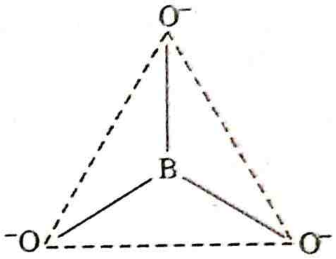
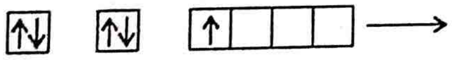


Fig.17. Structure of BO_3^{3-} ion

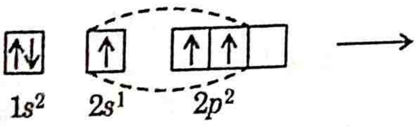
In Boric acid – H_3BO_3, the atom boron generally sp^2 hybridised. The unit of boric acid is BO_3^{3-} (borate ion) fig. 17.

The electronic configuration of Boron atom in ground state given as

$$B - 1s^2\ 2s^2\ 2p^1$$



The boron atom promotes its one electron from 2s-orbital to 2p-orbital , as a result number of unpaired electrons in boron atom becomes three as given



The boron atom under go sp^2 hybridisation and each sp^2 hybridised orbital of boron atom overlaps with the 2p-orbital of O^-, ion and forming three B–O^- bonds. Thus BO_3^{3-} ion has planer structure as shown in the Fig. 18.

The boric acid H_3BO_3 exist as two dimension sheet in which BO_3^{3-} units bonded togther via-H–bonds (i.e. each boron atom bonded to three oxygen atom while each oxygen atom bonded to a hydrogen atom).

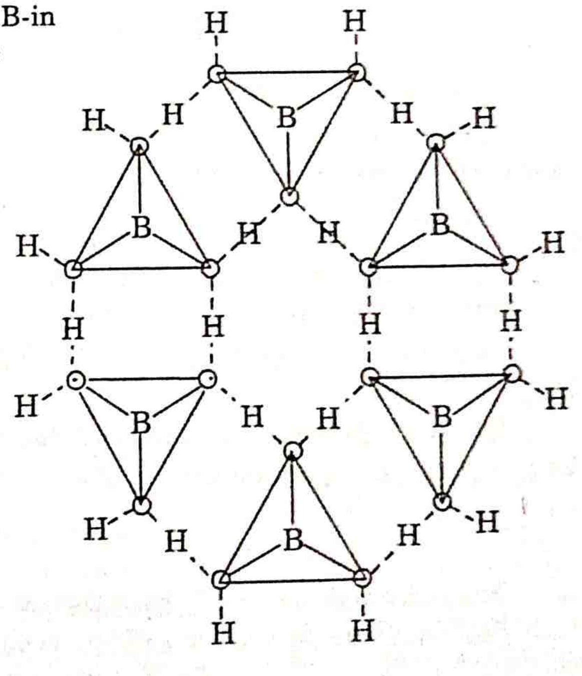


Fig. 18. Hydrogen bonded structure of orthoboric acid.

Halides: All the elements of group-13 are capable for forming halides.

Trihalides:

Boron; The trihalides of Boron are :

BF_3 BCl_3 BBr_3 BI_3

They are generally covalent in nature

Aluminium: The trihalides of aluminium are

AlF_3 $AlCl_3$ $AlBr_3$ AlI_3

Out of these four, AlF_3 is ionic in nature while remaining three trihalide are covalent in nature.

Gallium :

GaF_3 – It is non volatile, and melt at high temperature i.e. at above 1000°C.

$GaCl_3$ – It is white solid its melting point is 790°C. $GaCl_3$ vaporises at 500°C and exist as dimer Ga_2Cl_6.

Indium :

InF_3 It can be synthesized by the thermal decomposition of $(NH_4)_3InF_6$ at a temperature of 150°C to 300°C.

$$(NH_4)InF_6 \xrightarrow{150°C} NH_4InF_4 \xrightarrow{300°C} InF_3$$

InF_3 is non volatile, has high melting point.

$InCl_3$ – It does't exist in dimeric form. Its ionic nature is greater than $GaCl_3$.

InI_3 It exist in dimeric form. It is less ionic than $TlCl_3$.

Thallium:

TlF_3 It is prepared by the direct fluorination of Tl_2O_3 with F_2 at a temp. of 300°C.

$$Tl_2O_3 + 3F_2 \rightarrow 2TlF_3 + \frac{3}{2}O_2$$

It is stable upto 500°C

$TlCl_3$ It does't exist in dimeric form, it is more ionic than $InCl_3$, on heating at a temp. above 50°C it decomposes into $TlCl$ and Cl_2

$$TlCl_3 \xrightarrow{50°C} TlCl + Cl_2$$

$TlBr_3$ – At room temperature it slowly converted into $Tl^I[Tl^{III}Br_4]$

TlI_3 – It is ionic in nature and has the $Tl(I)$ and I_3^- ion.

Dihalide – General formula of dihalides of Boron are B_2X_4 = B_2F_4, B_2Br_4, B_2Cl_4, and B_2I_4.

Boron – The dihalide of boron can be snythesized by the passing electric discharge through BCl_3 vapour between mercury or copper electrodes.

$$2BCl_3 + 2Hg \xrightarrow[\text{discharge}]{\text{electric}} B_2Cl_4 + Hg_2Cl_2$$

These dihalide generally have planer structure and are less reactive.

Gallium The dihalide of gallium is obtained by reacting elemental Ga with $GaCl_3$

$$GaCl_3 + Ga \rightarrow 2GaCl_2$$

Indium The dihalids of Indium can be obtained by treating elemental In with $HCl(g)$

$$2In + HCl(g) \rightarrow 2InCl_2$$

Monohalide

Boron : Monohalide of Boron are polymeric in nature have composition $(BX)_n$ $n = 4$ or $8 - 12$

For examples : B_4Cl_4, B_8Cl_8 B_9Cl_9 $B_{10}C_{10}$ etc.

The structrure of B_4Cl_4 is closed cage like as shown in Fig. 19.

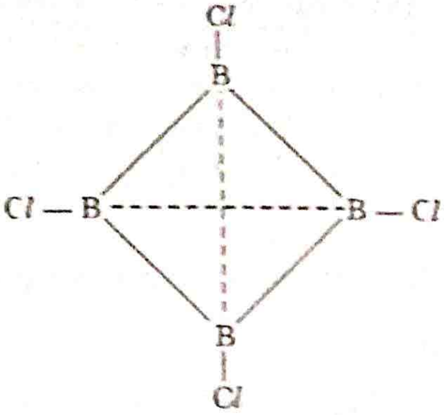


Fig. 19. Structure of B_4Cl_4

Aluminium : It is formed in gas phase at high temp. as shown.

$$AlF_3 \rightarrow 2Al + AlF$$

AlF is an unstable gas

It is also prepared as by heating metal with trihalide.

$$MX_3 + 2M \xrightarrow{\text{Heat}} 3MX$$

Galium : It is also prepared as, by heating trihalide with metal atom

$$GaCl_3 + 2Ga \xrightarrow{\text{Heat}} 3GaCl$$

The stable monohalide of Ga are GaCl, GaBr and GaI than GaF.

Indium : It is also prepared as, by heating trihalide with metal atom

$$InCl_3 + 2I_n \xrightarrow{\text{Heat}} 3InCl$$

It can also be prepared by heating medium, in a current of halogen or heating with mercuric halide

$$2In + X_2 \xrightarrow{\text{Heat}} 2InX$$

$$2In + 2HgX_2 \xrightarrow{> 300°C} Hg_2X_2 + 2InX$$

Thallium (I) halide is most stable

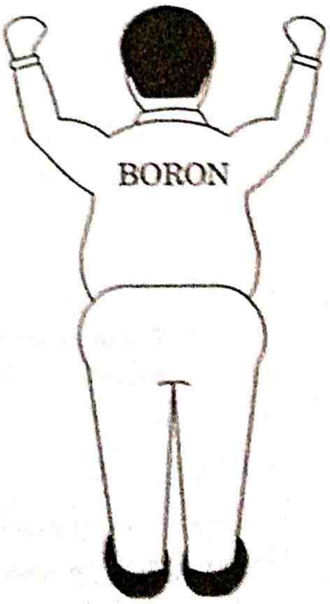
It can be obtained by reacting Tl(I) salt with acid or with alkalies

$$TlOH + HNO_3 \rightarrow TlNO_3 + H_2O$$

$$TlNO_3 + NaCl \rightarrow TlCl + NaNO_3$$

$$Tl_2CO_3 + 2HF \rightarrow 2TlF + CO_2 + H_2O$$

Anomalous Behaviour of Boron



The anomalous behaviour of boron is due :

(i) its small size

(ii) its high ionization energy

(iii) The electronegativity of boron is also high

(iv) It does't have *d*-orbitals

(v) Its polarising power is high $= \dfrac{\text{Charge}}{\text{Size}}$

The above mentioned properties are responsible for the anomalous behaviour of boron. Instead of these properties boron differ from the rest of the members of group-13, in the following manner :

(1) Boron is non metal

(2) Boron generally form covalent compounds

(3) It is bad conductor of electricity

(4) Boron exits in two allotropic form i.e. amorphous and crystalline form

(5) The oxide and hydroxide of boron are acidic in nature

(6) The trihalide of Boron exist as monomers

(7) Boron form a series of stable hydrides called boranes

(8) Maximum covalency of boron is four i.e. BH_4^-

(9) Boron react with Mg and form magnesium boride

$$3Mg + 2B \xrightarrow{\text{Heat}} \underset{\text{Magnesium boride}}{Mg_3B_2}$$

(10) The M.Pt and B.Pt of B is generally high as compared to other members of group-13.

Diagonal Relationship or Similarity of B with Si

The diagonal similarity of B and S*i* are discussed below :

(1) Both B and S*i* are non metallic in nature

(2) Both posseses high melting point

(3) Electronegativity of both are high

(4) Both are poor conductors of electricity

(5) Both B and S*i* exhibits allotropy i.e. crystalline form and amorphous form

(6) Both B and Si form stable oxides such as B_2O_3 and SiO_2. These are weakly acidic in nature.

B_2O_3 and SiO_2 both react with alkalies and form metaborates and metasilicates

$$B_2O_3 + 2NaOH \rightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

$$SIO_2 + 2NaOH \rightarrow \underset{\text{Sodium Silicate}}{Na_2SiO_3} + H_2O$$

Oxides of both react with water and form basic acid – H_3BO_3 and silicic acid-H_4SiO_4

$$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$$

$$SiO_2 + 2H_2O \rightarrow H_4SiO_4$$

(7) Both B and S*i* form a large number of stable hydrides such as boranes and silanes. These are volatile in nature and immediately catch fire when exposed to air.

(8) Hydroxides of both B and S*i* are acidic in nature.

(9) Both B and S*i* react with M*g* and form borides and silicides given as

$$3Mg + 2B \xrightarrow{\text{Heat}} Mg_3B_2$$

$$2Mg + Si \xrightarrow{\text{Heat}} Mg_2Si$$

Borides and silicides on reaction with phosphoric acid–H_3PO_4 gives a mixture of boranes and silanes

$$Mg_3B_2 + H_3PO_4 \rightarrow \text{mixture of boranes}$$

$$Mg_2Si + H_3PO_4 \rightarrow \text{mixture of silanes}$$

(10) Both B and S*i* generally act as semiconductor.

(11) Both B and S*i* react with alcohols in the presence of conc. H_2SO_4 to form volatile esters.

Diborane or Boroethane, B_2H_6

Dibrane can be prepared by the following methods :

(1) Diborane can be prepared by mixing Iodine – I_2, with sodium borohydride–$NaBH_4$, in dimethyl glyoxime–*dmg*

$$NaBH_4 + I_2 \xrightarrow{dmg} \underset{\text{(yield-98\%)}}{B_2H_6} + 2NaI + H_2$$

(2) It can also be synthesized by the reaction of sodium borohydride with anhydrous phosphoric acid

$$2NaBH_4(g) + \underset{\text{(anh.)}}{2H_3PO_4(l)} \rightarrow \underset{\text{(yield-70\%)}}{B_2H_6(g)} + 2NaH_2PO_4(s) + 2H_{2(s)}$$

(3) It can also be prepared by reacting boron trifluoride with sodium borohydride in ether at room temperature.

$$4NaBH_4 + 3BF_3 \xrightarrow{\text{ether}} 3NaBF_4 + 2B_2H_6$$

(4) It can also be obtained by reducing halide of boron with reducing agents (LiH, NaH, CaH_2, $LiBH_4$, $NaBH_4$,) in ethereal solution

$$8BF_3 + 6LiH \xrightarrow{\text{ether}} B_2H_6 + 6LiBF_4$$

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

(5) By passing silient electric discharge through a mixture of BCl_3 (vapours) and H_2 at low pressure, it can be synthesized

$$2BCl_3 + 6H_2 \xrightarrow[\text{discharge}]{\text{electric}} B_2H_6 + 6HCl$$

(6) **Industrially :** Diborane – B_2H_6 is prepared by reducing a mixture of BF_3 (*g*) with sodium hydride at a temperature of 180°C

$$2BF_3 + 6NaH \xrightarrow{180°C} B_2H_6 + 6NaF$$

(7) **Stock's Method :** In this method magnesium boride – Mg_3B_2, treated with a dilute aqueous solution of HCl and as a result volatile mixtures of various boranes are obtained. The mixture mainly contain –B_4H_{10}, which on heating further decomposes as and give B_2H_6

$$2Mg_3B_2 + 12HCl \rightarrow 6MgCl_2 + B_4H_{10} + H_2$$

$$\underset{\text{Tetraborane}}{B_4H_{10}} + H_2 \xrightarrow{\text{Heat}} 2B_2H_6$$

Properties of Diboranes

Physical Properties

(1) It is colourless gas

(2) Diborane has sweet odour

(3) It is toxic in nature

(4) It is highly ractive gas

(5) Its M.Pt. is – 165°C and B.Pt is, – 92.5°C respectively.

Chemical Properties

(1) **Stability :** It is stable only at low temeprature in the absence of moisture. But at high temperatures, B_2H_6 give a mixture of higher boranes along with evolution of H_2 gas

$$5B_2H_6 \xrightarrow{114°C} B_5H_{11} + 4H_2$$

$$2B_2H_6 \xrightarrow{-100°C} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow[\text{sealed tube}]{100°C} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow{200°-300°C} 2B_5H_9 + 6H_2$$

$$5B_2H_6 \xrightarrow[\text{P=120 mm of Hg}]{250°C} B_5H_9 + B_5H_{11} + 5H_2$$

B_2H_6 , on red heating, gives B and H_2

$$B_2H_6 \xrightarrow[\text{Heat}]{\text{Red}} 2B + 3H_2$$

On passing a mixture of B_2H_6 and H_2 in a glass tube at a temperature of 200 – 250°C B_5H_{11} obtained in large quantity

$$B_2H_6 + H_2 \xrightarrow[\text{glass tube}]{200-250°C} B_5H_{11}$$

(2) **Reaction with air or oxygen :** Pure B_2H_6 donot react with dry O_2 but impure B_2H_6 burns spontaneously in dry O_2 at room temperature and also produce large amount of energy i.e. the reaction is highly exothermic in nature

$$\underset{\text{(Impure)}}{B_2H_6} + 3O_2 \rightarrow \underset{\Delta H=-2160\ \text{kJ-mol}}{B_2O_3 + 3H_2O}$$

(3) **Hydrolysis :** B_2H_6 hydrolysed readily with water and produce boric acid and hydrogen. Due to production of H_2, the B_2H_6 act as reducing agent

$$B_2H_6 + 6H_2O \rightarrow \underset{\text{Boric Acid}}{2H_3BO_3} + 6H_2$$

(4) **Reaction with alkalies :** B_2H_6 readily dissolve in alkaline solution and give metaborate and H_2

$$B_2H_6 + 2KOH + 2H_2O \rightarrow \underset{\text{Potassium metaborate}}{2KBO_2} + 6H_2$$

$$B_2H_6 + 2NaOH + 2H_2O \rightarrow \underset{\text{sodium meta borate}}{2NaBO_2} + 6H_2$$

(5) **Reaction with metals :** It react slowly with metals like *Na*, K, and *Ca*. But react fastly in ethereal solution.

$$2B_2H_6 + 2K \xrightarrow{\text{ether}} KBH_4 + \underset{\text{Pot. triborane}}{KB_3H_8}$$

(6) **Reaction with halogens :** B_2H_6 reacts with different halogens under different sets of condition.

$$B_2H_6 + Cl_2 \xrightarrow{\text{(explosive) } 25°C} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + HCl$$

$$B_2H_6 + Br_2 \xrightarrow[\text{fast}]{100°C} \underset{\text{Bromodiborane}}{B_2H_5Br} + HBr$$

$$B_2H_6 + I_2 \xrightarrow{\text{slow}} \underset{\text{Iododiborane}}{B_2H_5I} + H_2$$

(12) **Reaction with amines :** B_2H_6 react with secondary and tertiary amines and give complexes of amine–borane.

$$\begin{aligned} &B_2H_6 + 2(CH_3)_2NH \xrightarrow{-41^\circ C} \underline{2H_3B \leftarrow \overset{+}{N}H(CH_3)_2} \\ &\underbrace{2H_3B \leftarrow N(CH_3)_3}_{\text{complex}} \leftarrow 2(CH_3)_3N + \underbrace{(CH_3)N - BH_2B_2H_6}_{\text{complex}} \qquad \text{Heat} \end{aligned}$$

(13) **Reaction with Pyridine :** B_2H_6 react with pyridine and to form salt

$$B_2H_6 + 2C_5H_5N \longrightarrow 2H_3B^- \leftarrow \overset{+}{N}C_5H_5$$

(ionic salt)

(14) **Reaction with alcohols :** Diborane react with alcohols (R–OH) and form $B(OR)_3$ and $BH(OR)_2$ and H_2

$$B_2H_6 + CH_3OH \longrightarrow 2BH(OCH_3)_2 + H_2$$

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

(15) **Reaction with trimethyl aluminium – *$Al(CH_3)_3$* :** On reaction with trimethyl aluminium, diborate give aluminium boro hydride

$$2B_2H_6 + Al(CH_3)_3 \longrightarrow B(CH_3)_3 + Al(BH_4)_3$$

(16) **Reaction with trimethyl boranes :** $(CH_3)_3B \cdot B_2H_6$ react with diborane at ordinary temperature and produces methyl derivatives of diborane.

$$B_2H_6 \xrightarrow{4(CH_3)_3B} BH_2(CH_3)_4$$

Tetramethyl borane

The above reaction shows that the nature of four-H-atoms of diborane is different than the remaining two–H–atoms.

(17) **Reaction with alkenes or alkynes :** Diboranes react with alkenes and alkynes in ether solution at room temp. to form alkylboranes. This reaction is called as Hydroboration reaction

$$CH_3CH = CH_2 + B_2H_6 \longrightarrow (CH_3CH_2CH_2)_3B$$

Tri-*n*-propyl borane

The tri-*n*-propyl borane on further reaction with H_2O_2 and alkaline medium give suitable alcohols (primary alcohol)

$$(CH_3CH_2CH_2)_3B + H_2O_2/\overline{O}H \longrightarrow 3CH_3CH_2CH_2 - OH + H_3BO_3$$

Primary alcohol

Uses : Diborane is used as

(1) as a rocket fuel

(2) as a high energy fuel and rocket propellents

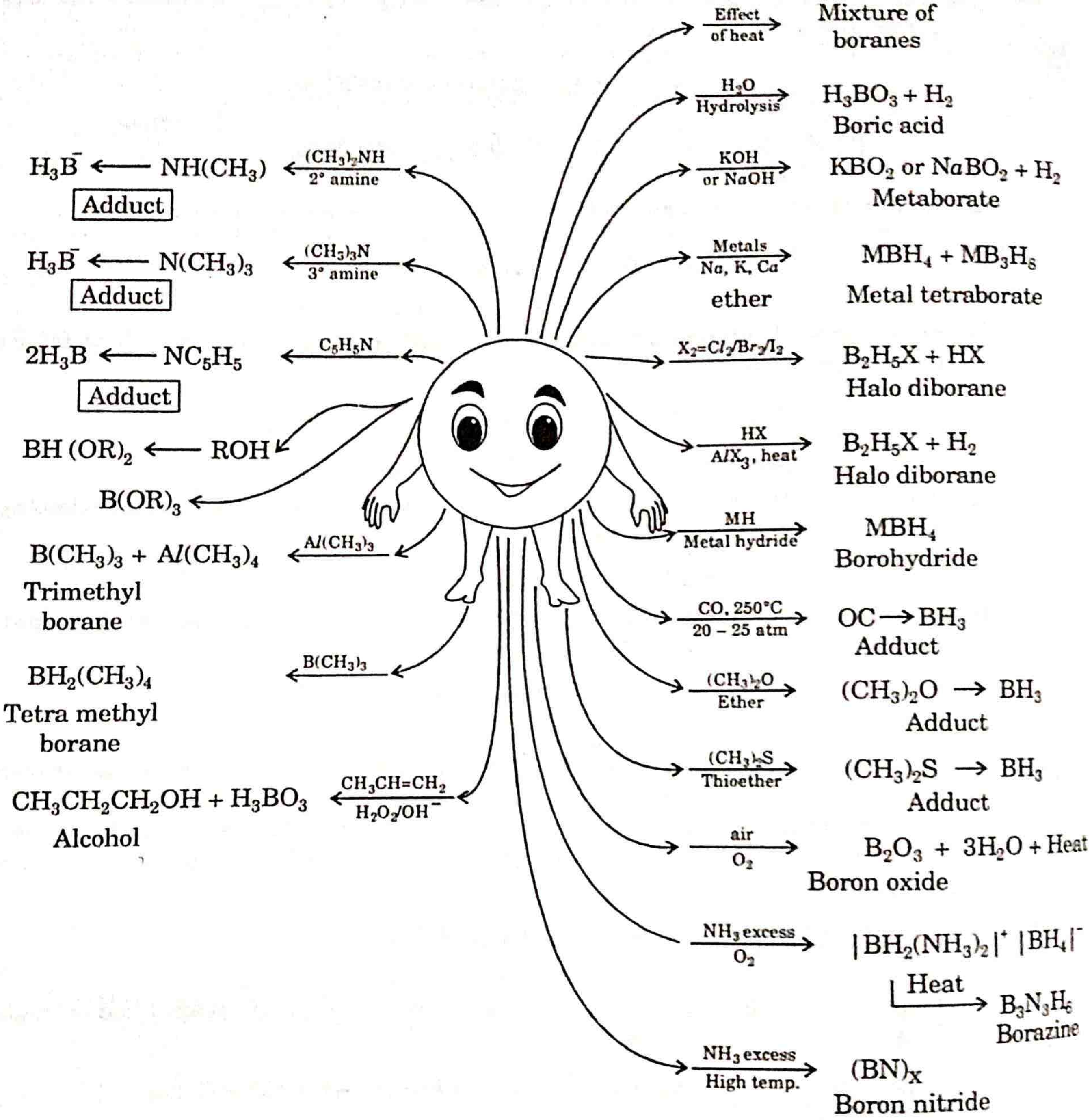
(3) synthesis of higher boranes

(4) as a reducing agent

(5) as catalyst in polymerisation reaction

(6) used for welding perposes.

Chart shown chemical properties of diborane



Structure and Bonding in Diborane – B_2H_6

Electron diffraction study of diborane–B_2H_6 molecule has shown that, the structure of B_2H_6 has hydrogen bridged structure.

The structure of diborane discussed as :

(i) In B_2H_6, the two boron atoms represented as B^1 and B^2. Four H-atoms located at the terminal position is called as terminal H-atoms represented as *Ht* while remaining two-H-atoms form bridged called as bridged H-atoms, they are represented as *Hb* (fig. 20)

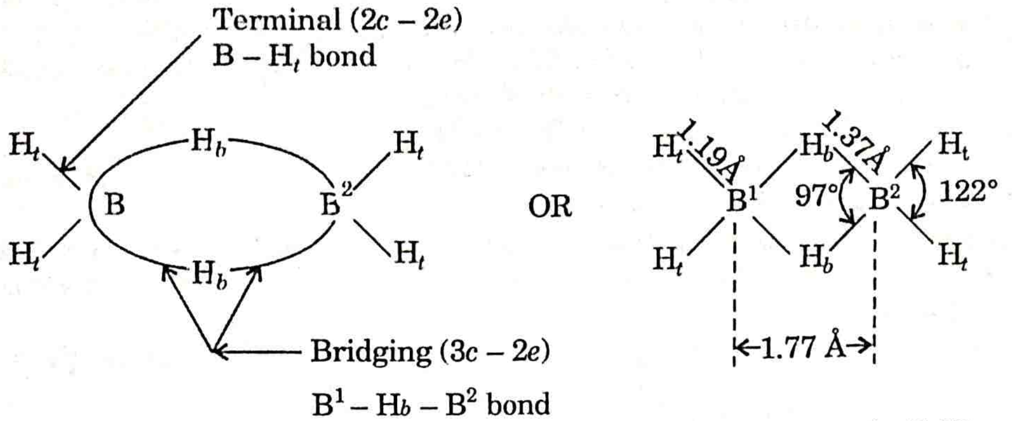


Fig. 20. **Hydrogen-bridged structure of diborane molecule, B_2H_6.**

(ii) The two Boron atoms (B^1 and B^2) and four terminal H-atoms (H*t* lie in one plane while the remaining two hydrogen atom H*b* lie in another plane. Out of two bridged H–atom one –H*b*-located above the plane while other –H*b*- located below the plane of B^1 and B^2 and H*t*.

So due to presence of different planes for H*t*–and H*b* and B^1 and B^2, the free rotation is not possible. More over presence of different types of H–atoms confirmed by NMR–spectra. NMR spectra shown that their are two types of protons in them, four H–atoms are of one kinds while two H–atoms are of other kinds.

The fact also confirmed by the nature of product formed by reaction of B_2H_6 with $B(CH_3)_3$.

$$B_2H_6 + B(CH_3)_3 \longrightarrow \underset{\text{tetra methyl borane}}{B_2H_2(CH_3)_4}$$

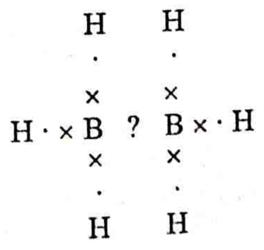
The formation of tetra methyl boranes shows that four-terminal (H*t*), H–atoms are replacable but the remaining two (H*b*), H–atoms remain unreplaced.

(iii) B^1–H_t and B^2–H_t bond length is equal to 119 pm while B^1–H*b* or B^2–H*b* bond length is equal to 137 pm and B^1–B^2 bond length is 177 pm.

The H*t* – B^1 –H*t* or H*t* – B^2 – Ht bond angle is 122° while H_b– B^1–H*b* or H_b – B^2 – H*b* bond angle is 97°.

The molecule B_2H_6 is an *e*–deficient because total number of electrons required in B_2H_6, for the formation of normal covalent bond is 14*e*–but in B_2H_6 the number of electrons present is equal to 12*e*–, so we can say that it is an electron deficient compound.

It is evident that there are no electrons left to form bond, between two Boron atoms. So there is another way by which we can represent bonding between B_2H_6.



Nature of bonds in diborane

It is proposed by Loguet – Higgins

The molecules of B_2H_6 has two types of bonds.

(a) **B – H*t* i.e. four terminal bonds :** B–H_t bond is 2-centre-–2*e*⁻ bonds (2*c*–2*e*⁻). It is formed by mutually sharing of electrons of B and H-atoms. It is normal covalent bond.

Borazine – $B_3N_3H_6$ or Borazole, $(BH_3)(NH_3)$

Borazine is isoelectronic with benzene, its physical properties and structure similar to benzene.

Therefore its name is inorganic benzene

Synthesis

(1) **By Stock's Method (1926) :** It is prepared by stock in 1926 for this, stock react ammonia with diborane – B_2H_6. The adduct thus formed, get decomposed on heating at about 200°C in a closed tube and form borazine.

$$\begin{tikzcd} \underset{(1:2)}{3B_2H_6 + 6NH_3} \arrow[r] & \underset{\text{Adduct}}{3[B_2H_6 \cdot 2NH_3]} \arrow[d, bend left=60, "200^\circ\text{C}"] \\ & 12H_2 + 2B_3N_3H_6 \end{tikzcd}$$

Stock took the B_2H_6 and NH_3 in a molar ratio of (1 : 2). The yield of this mthod is poor, due to formation of polymeric side products.

(2) It is also prepared by heating a mixture of Boron trichloride with ammonium chloride in chlorobenzene at a temperature of 140° to 150°C in the presence of catalyst such as Fe, Co or Ni. The product (B, B, B – trichloriborazine) thus formed, reduced by $NaBH_4$ in poly ether gives borazine

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{Fe,Co or Ni}]{140^\circ-150^\circ\text{C}} \underset{\text{B, B, B – Trichloro borazine}}{B_3N_3H_3Cl_3} + 9HCl$$

$$3B_3N_3H_3Cl_3 + 6LiBH_4 \xrightarrow{\text{Reduction}} 2B_2N_3H_6 + 6LiCl + 3B_2H_6$$

(3) **Laboratory Method :** It laboratory, borazine is prepared by reacting a mixture of ammonium chloride – NH_4Cl with $LiBH_4$ – lithium borohydride or $NaBH_4$ sodium borohydride in vacuum at 230°C to 240°C.

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230-240^\circ C} B_3N_3H_6 + 3LiCl + 9H_2$$

$$3NH_4Cl + 3NaBH_4 \xrightarrow{230-240^\circ C} B_3N_3H_6 + 3NaCl + 9H_2$$

The yield of this method is 30%.

Physical Properites

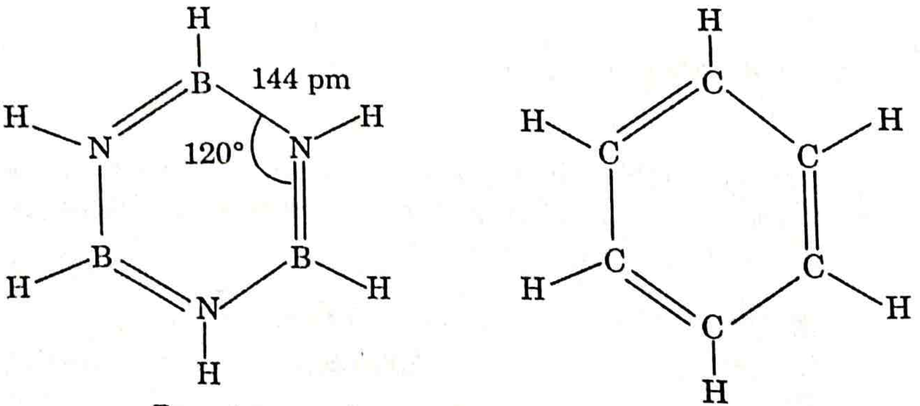
It is a colourless liquid. Its Mpt is – 58°C and BPt is 65°C. It is a light sensitive compound and can explode even in dark also. At room temperature it decomposes more rapidly into H_2, B_2H_6 and other volatile products.

Its properties similar to benzene, as shown :

	Borazine – $B_3N_3H_6$	**Benzene – C_6H_6**
Mol. wt.	80.6	78
M.Pt (°C)	– 58°C	+ 6°C
B.Pt (°C)	65°C	80°C
$\Delta H_{Vap.}$ (KJ mol^{-1})	39	31

Its properties are similar to benzene (structure, number of electrons).

Because of the similarty in structures of borazine and benzene, it is also known as inorganic benzene as shown in Fig. 26.



Borazine

Benzene

Fig. 26. Similarity in the structure of borazine and benzene.

In borazine both N and B-atoms are sp^2 hybridised. There is one lone pair associated with each–N–atom, while each boron–atom has an empty *p*–orbital. The π–bonding in borazine is coordinate or active type due to overlapping of fully filled orbital of N-atom and empty orbital of Boron atom. The structure of borazine shown in the Fig. 27. In borazine due to difference in electro negativities of N and B-atoms, the B – N bond is polar in nature

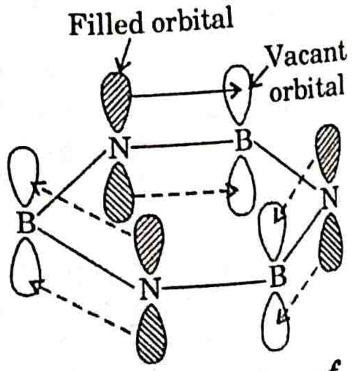


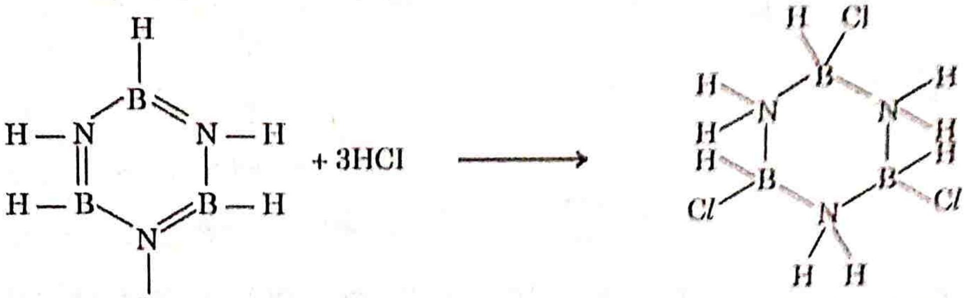
Fig. 27. Formation of dative bond in borazine

Chemical properties of Borazine : The main chemical properties of borazine are discussed here.

(1) Addition reaction

(a) **Reaction with HX (HCl, HBr) :** In addition reaction one molecule of Borazine react with three molecules of halogen acid HX (HC*l* or HB*r*) and form addition product – $B_3N_3H_9Cl_3$.

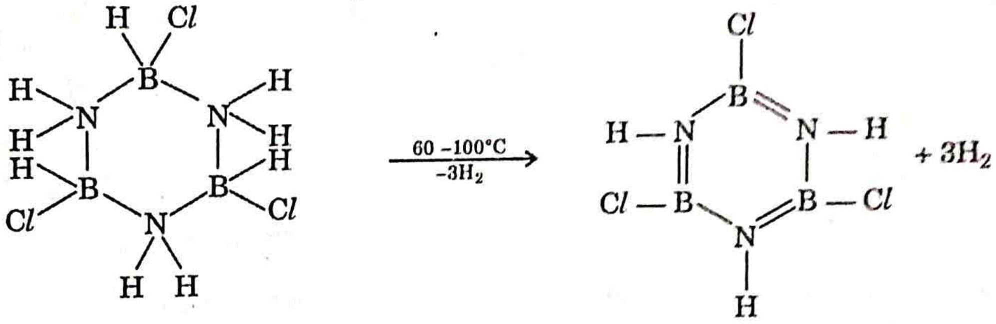
In this addition product the halogen atoms attached with Boron–atom, due to their more negative nature than N–atom.



Hydrogen chloride derivative

or $B_3N_3H_6 + 3HCl \longrightarrow B_3N_3H_9Cl_3$

when $B_3N_3H_9Cl_3$ is heated at a temperature of 60° to 100°C. It give $B_3N_3H_3Cl_3$ with a loss of three molecule of H_2

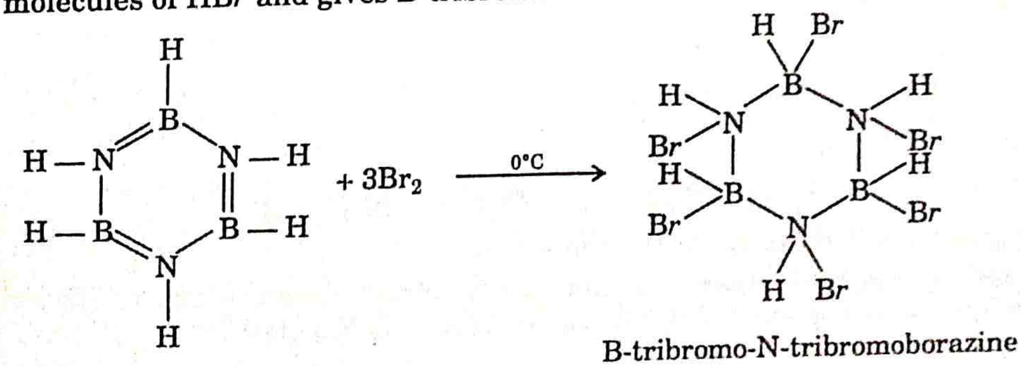


B, B, B-trichloroborazine

or $B_3N_3H_9Cl_3 \xrightarrow[-3H_2]{60-100^\circ C} B_3N_3H_3Cl_3 + 3H_2$

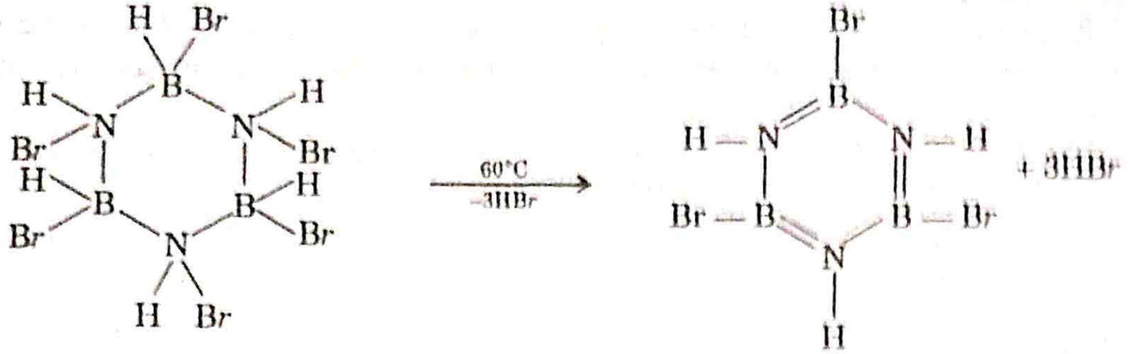
$B_3N_3H_9Cl_3$, on reduction with $NaBH_4$ form $B_3N_3H_{12}$.

(b) **Reaction with Br_2 :** One molecule of borazine react with three molecules of Br_2 at low temperature such as 0°C and give addition product i.e. B–Tribromo–N–tribromo borazine, when this addition product is heated at a temp. about 60°C, it losses three molecules of HB*r* and gives B-tribromoborazine.



B-tribromo-N-tribromoborazine

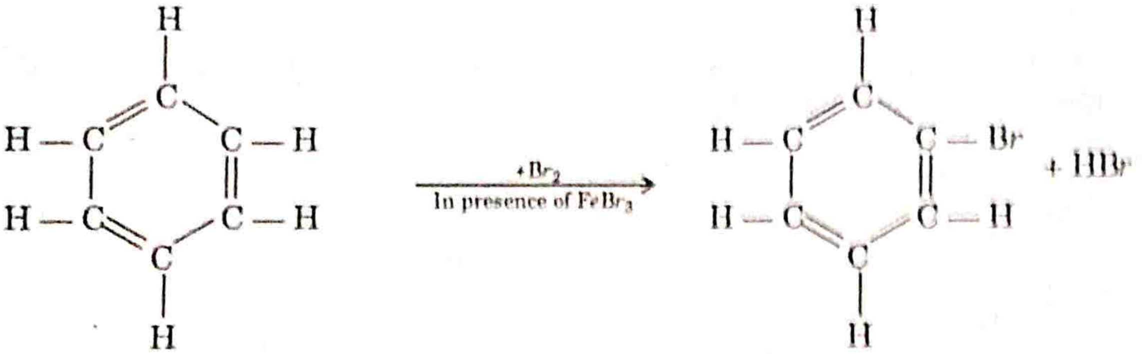
or $\underset{\text{Borazine}}{B_3N_3H_6} + 3Br_2 \xrightarrow{0^\circ C} B_3N_3H_6Br_6$



B-tribromoborazine

or $B_3N_3H_6Br_6 \xrightarrow[-3HBr]{60^\circ C} B_3N_3H_3Br_3 + 3HBr$

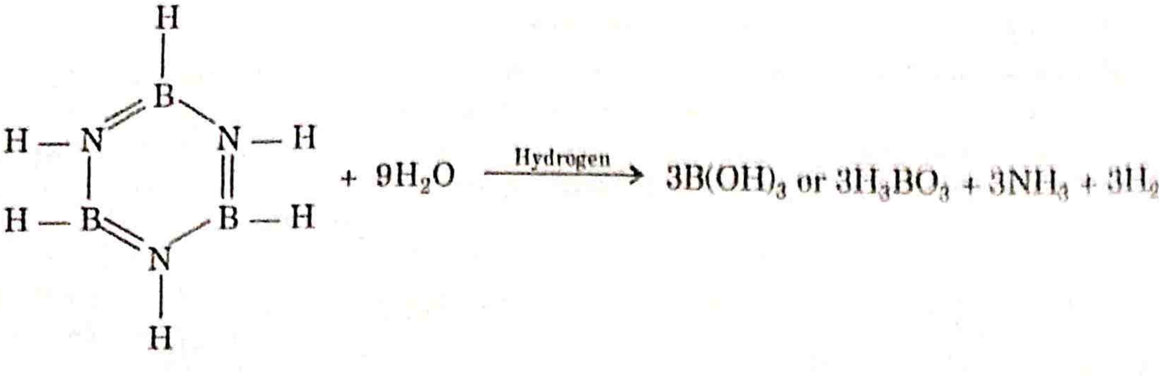
Similarly when benzene react with Br_2 it gives substitution reaction and form mono bromoderivative–C_6H_5Br.



Bromobenzene

Or C_6H_6 $+Br_2$ $C_6H_5Br + HBr$

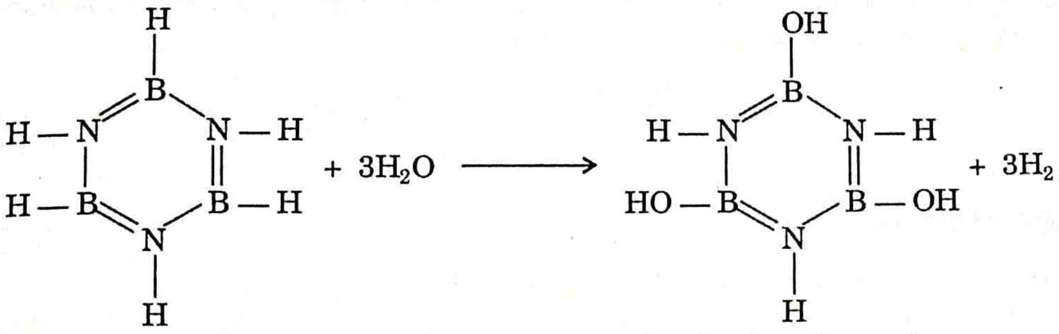
(2) (a) **Hydrolysis :** Borazine hydrolysed with water at high temperature and gives H_3BO_3, NH_3 and H_2. The reaction with water is found to be slow.



or $B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$

But benzene does't show this type of Reaction.

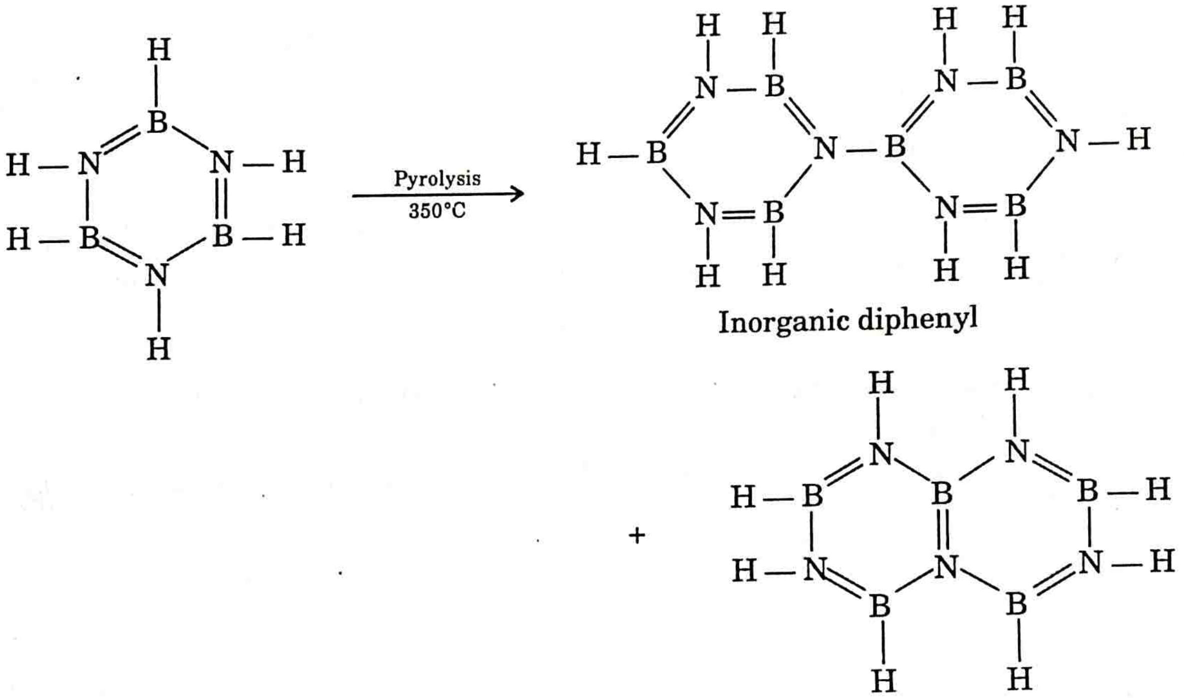
(b) **Conditional hydrolysis :** On applying condition, borazine react with water (three molecules) and gives B–trihydroxyl borazine – $B_3N_3H_3(OH)_3$



B-trihydroxyl borazine

Or $B_3N_3H_6 + 3H_2O \longrightarrow B_3N_3H_3(OH)_3 + 3H_2$

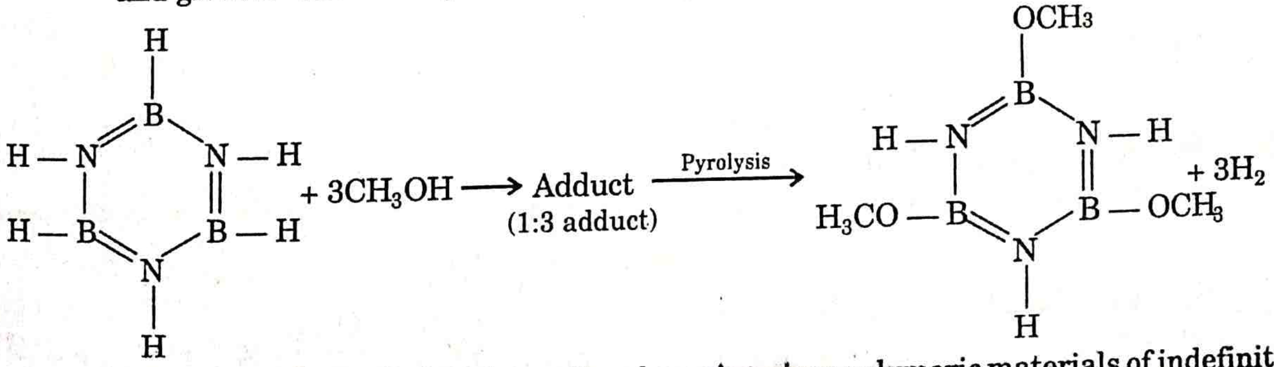
(3) **Pyrolysis :** Borazine, on pyrolysis at a temperature 350°C gives $B_6N_6H_{10}$ and $B_5N_5H_8$.



Inorganic diphenyl

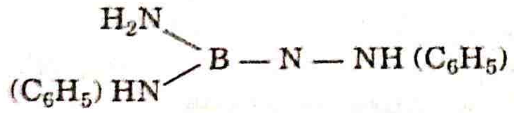
or $B_3N_3H_6 \xrightarrow[350°C]{\text{Pyrolysis}} B_6N_6H_{10} + B_5N_5H_8$ Inorganic naphthalene

(4) **Formation of addut :** Borazine form adduct with methanol. This adduct pyrolysed and gives B–tri methoxy borazine and H_2 .



(5) **Hydrogenation :** On hydrogenation, borazine gives polymeric materials of indefinite composition.

(6) **Reaction with aniline :** Borazine react with aniline and produce tri-aminoborine. The reaction is highly exothermic in nature.



Trihalide of Boron

Boron forms the following trihalides such as BF_3, BCl_3, BBr_3 and BI_3.

(a) **Boron trifluoride – BF_3 :** The BF_3 extensively used as catalyst. BF_3 can be obtained as –

(i) **Large Scale production :** It can be prepared by heating Boron oxide–B_2O_3 or borax–$Na_2B_4O_7$ with, (Na–F) sodium fluoride, Calcium fluoride–CaF_2, ammonium tetrafluoro borate, NH_4BF_4 and conc. H_2SO_4

$$B_2O_3 + 6NaF + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3H_2O + 2BF_3$$

$$B_2O_3 + CaF_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O + 2BF_3$$

$$B_2O_3 + 6NH_4BF_4 + 6H_2SO_4 \longrightarrow 6NH_4HSO_4 + 3H_2O + 8BF_3$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 2NaHSO_4 + 6CaSO_4 + 7H_2O + 4BF_3$$

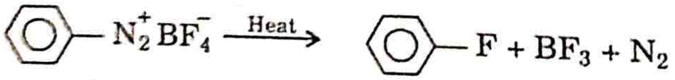
(ii) It can also be synthesized by the action of HF on B_2O_3 or sodium borate

$$B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O$$

$$Na_2B_4O_7 + 12HF + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 4BF_3 + H_2O$$

(iii) **Laboratory Method** – (Pure BF_3)

In pure form – BF_3 can be obtained by thermal decomposition of benzene diazonium tetrafluoroborate.



Benzene diazonium
tetra fluoroborate

(2) **Borontrichloride – BCl_3**

(i) It is prepared by passing chlorine gas-Cl_2, over a heated mixture of B_2O_3 and charcoal (Powdered from)

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{\text{Heat}} 2BCl_3 + 3CO$$

(ii) It can be prepared by heating B_2O_3 with PCl_5 in a sealed tube

$$B_2O_3 + 3PCl_5 \xrightarrow{\text{Heat}} 2BCl_3 + 3POCl_3$$

(3) **Boron tribromide–BBr_3**

(i) It is prepared by passing $Br_2(g)$ over a heated mixture of B_2O_3 and powdered charcoal

$$B_2O_3 + 3K + 3Br_2 \xrightarrow{\text{Heat}} 2BBr_3 + 3CO$$

(ii) It can be prepared by heating B_2O_3 with PBr_5 in a sealed tube

$$B_2O_3 + PBr_5 \xrightarrow{\text{Heat}} 2BBr_3 + 3POBr_3$$

(4) **Boron triodide – BI_3**

(i) It can be prepared by the action of Iodine on sodium borohydride

$$NaBH_4 + 4I_2 \longrightarrow BI_3 + NaI + 4HI$$

(ii) It can also be synthesized by the action of HI on BCl_3

$$BCl_3 + 3HI \longrightarrow BI_3 + 3HCl$$

Properties of Trihalide of Boron

(1) **Physical State : BF_3 and BCl_3 are the colourless gases, BBr_3 are viscous liquid while BI_3 is white solid**

Explanation : The gaseous nature of BF_3 and BCl_3 is due to small size of F and Cl, atoms. These halide have less Vander Waal interaction, so cannot come very close to each other hence, exist in gaseous form. But the size of Br–atom is large, so possesces high magnitude of Vander Waal forces as compared to BF_3 and BCl_3, so as a result they come close to each other and exist as liquid.

While in BI_3, due to large size of iodine–atom the magnitude of Vander Waal forces is very – 2 high, so the molecule of BI_3 come very close to each other. Thus exist as solid.

(2) **M.Pt and B.Pt :** The B.Pt and M.Pt of halides of Boron increase with atomic number of halogens as shown in the table-6

Table-6 : MPt and B.Pt of halides of Boron

	BF_3	BCl_3	BBr_3	BI_3
Physical state	Gas	Gas	Liquid	Solid
M.Pt. (°C)	–127.1	–107	–46	49.9
B.Pt. (°C)	–99.1	12.5	91.3	210

The order of B.Pt and M.Pt given as

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

Explanation : The increase in BPt and MPt of trihalide of Boron is due to increase in atomic number. The molecular masses of halide ion directly related with surface area and Vander Waal forces, so magnitude of these forces increases with atomic size. Thus the order of MPt and B.Pt are

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

(3) **Hydrolysis : BF_3 not hydrolysed with water but other halides hydrolyse with water.**

Explanation : $BF_3 + 3H_2O \longrightarrow$ No reaction

This is due to the fact that B-F bond is very strong because of $p\pi-p\pi$ back bonding. So bond energy of B–F bond is greater than bond energy of B–OH bond.

But BF_3 when mixed with water form hydrates of general formula $BF_3 \cdot H_2O$ and $BF_3 \cdot 2H_2O$.

On applying certain conditions BF_3 hydrolysed with water and form Boric acid as shown

$$BF_3 + H_2O \longrightarrow H_3BO_3 + 3HF$$

When excess amount of BF_3 dissolve in HF, formed in above reaction and form fluoroboric acid

$$BF_3 + HF \longrightarrow HBF_4$$

The overall reaction written as

$$4BF_3(\text{excess}) + 3H_2O \longrightarrow H_3BO_3 + HBF_4$$

other halides of boron completely hydrolysed with water and gives boric acid and halogen acid–HX as shown

$$BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX$$

(X = F, Cl, Br)

Explanation : This is because the bond energy of B–Cl, B–Br and B–I bonds are less and ineffective due to, Pπ – Pπ back donation.

(4) Monomeric nature of BX_3 : The trihalide of boron generally exist in monomeric form not in dimeric form (in vapour phase).

Explanation : This is due to the small size of boron atom. The small sized boron atom cannot accomodate four large sized halogen (fig. 28) atoms around it, so exist in monomeric form

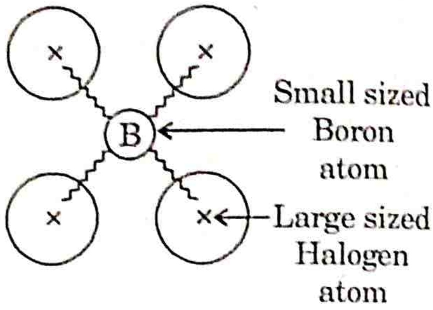


Fig. 28. Non accomodation of large sized halide ion by Boron atom

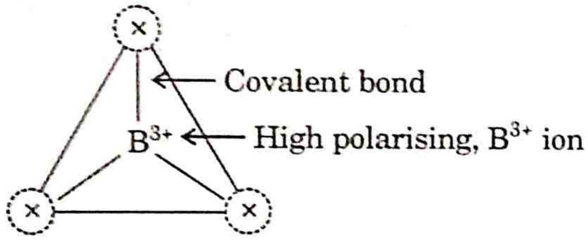


Fig. 29. Covalent nature of **BX_3**

5. Covalent nature : Trihalide of Boron are covalent in nature.

Explanation : The covalent nature of halides of boron due to small size of boron atom. B^{3+} ion possesses high charge density (high polarising power). Therefore form covalent bond (Fig. 29)

(6) Lewis acidic nature : All the trihalide of boron exist as lewis acid (Fig. 30)

Explanation : This is because all the trihalides of boron are electron deficient i.e. have incomplete octet. ($6e^-$ in valence shell). Moreover, after sp^2–hybridisation in trihalide of boron, its one p-orbital remain vacant, so boron has tendency to accept a pair of electrons from donor atoms or molecules (lewis base). Thus all the halides of boron act as lewis acid. The reaction of halide of boron with electron pair donor shown as (Fig. 31).

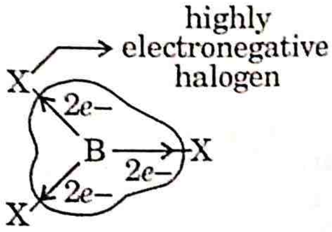
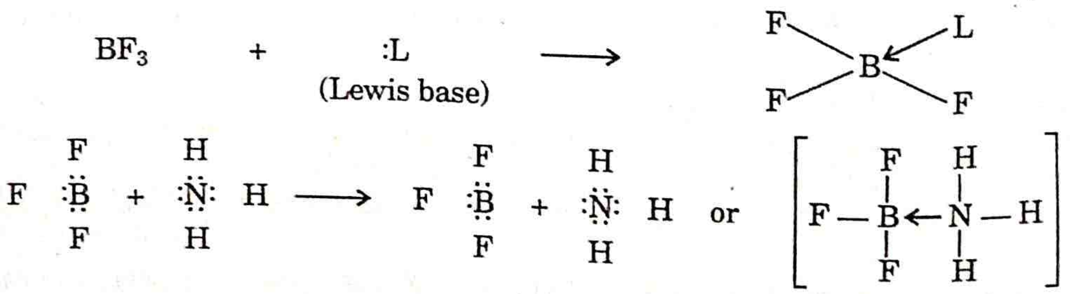
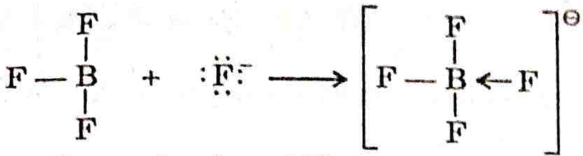


Fig. 30. Lewis acidic nature of **BX_3**





$$BF_3 + :\ddot{F}:^- \longrightarrow [F_3B \leftarrow F]^{\ominus}$$

***Fig. 31.* Reaction shown lewis acidic nature of compound of Boron**

Comparision of relative strength of lewis acids of trihalide of boron. It has been observed that **the lewis acidic strength of halide of boron are given in order as follow.**

$$\mathbf{BI_3 > BBr_3 > BCl_3 > BF_3}$$

Explaination : It is observed that the F-atom in BF_3 is highly electronegative atom, it withdraw the electron of boron atom towards itself and will make the boron atom electron deficient, So it may be act as strong lewis acid as shown in Fig. 32.

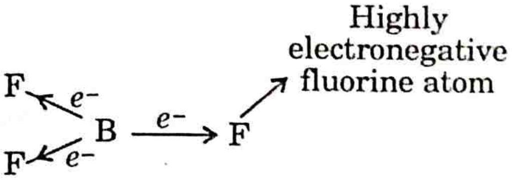


***Fig. 32.* Lewis acidic nature of** BF_3.

But back donation power of fullfilled orbital of fluorine make it weak lewis acidic. In BF_3 the 2*p*–orbitals of fluorine atom is full filled, while one of the 2*p*-orbital of boron atom is vacant. Since both the 2*p*–orbital of F and B are small in size and almost similar in energy and also close to each other, so they overlaps with each other effectively and transfer electrons from full filled orbital of F–atom to vacant orbital of B–atom easily. Thus B–F bond aquires some double bond character (Pπ–Pπ bond formation).

The type of bond thus formed is called **back donation** or dative or **π-donation** as shown in fig. 33.

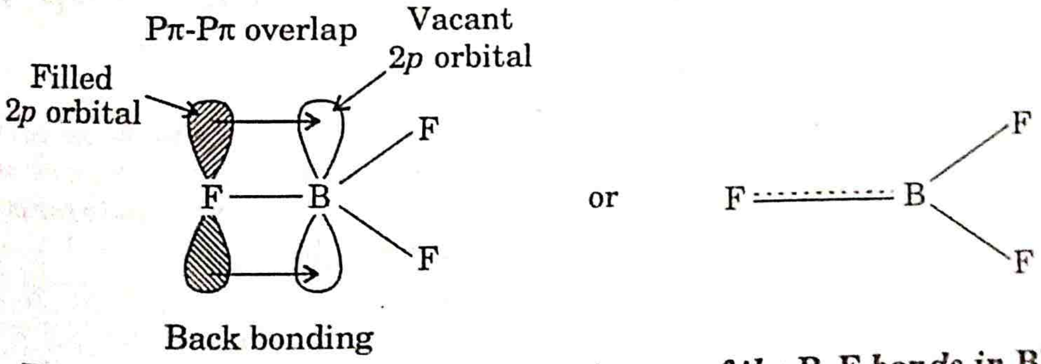


***Fig.* Formation of *pπ–pπ* back bonding in one of the B–F bonds in** BF_3.

Due to back donation power of F–atoms, it creates electron density further on boron atoms make it weak lewis acidic. The π–bond in BF_3 shows the phenomenon of resonance as shown (Fig. 34).

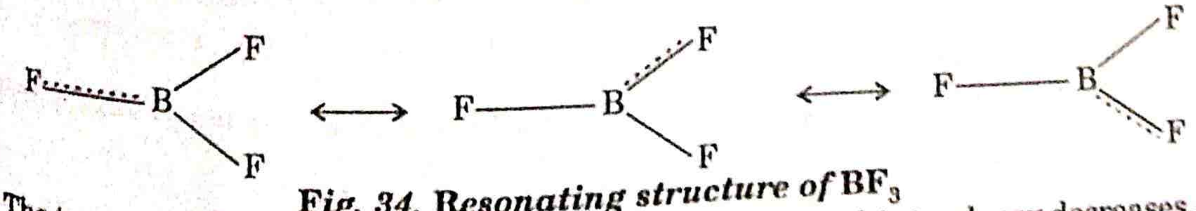


***Fig. 34.* Resonating structure of** BF_3

The tendency to form Pπ–Pπ bond in BF_3 is maximum but this tendency decreases, as the size of halogen atoms increases from ($BCl_3 \rightarrow BBr_3 \rightarrow BI_3$)

Halide of Aluminium

The halides of Aluminium given as AlF_3, $AlCl_3$, $AlBr_3$ and AlI_3.

The AlF_3 is essential ionic, $AlCl_3$ is partially ionic while $AlBr_3$ and AlI_3 are predominently covalent in nature.

Explanation : The ionic nature of AlF_3 is due to the small size of fluoride ion. The small sized F^- ion posseses less polarisability thus, cannot distort there electron cloud to greater extent and form ionic bond as shown in Fig. 38.

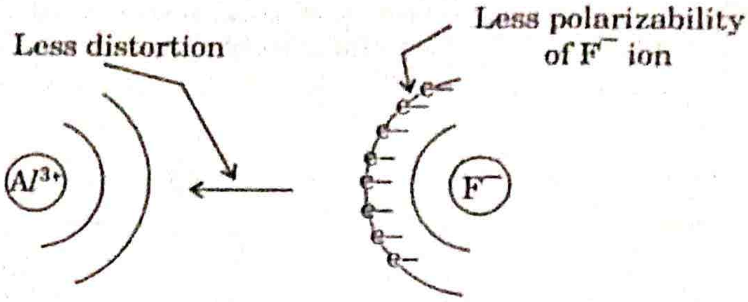


Fig. 38. Polarizability of F⁻ ion.

But I⁻ ion large in size, thus posseses more polarizability. The large sized I⁻ion can distort their electron cloud and form covalent bond as shown in Fig. 39.

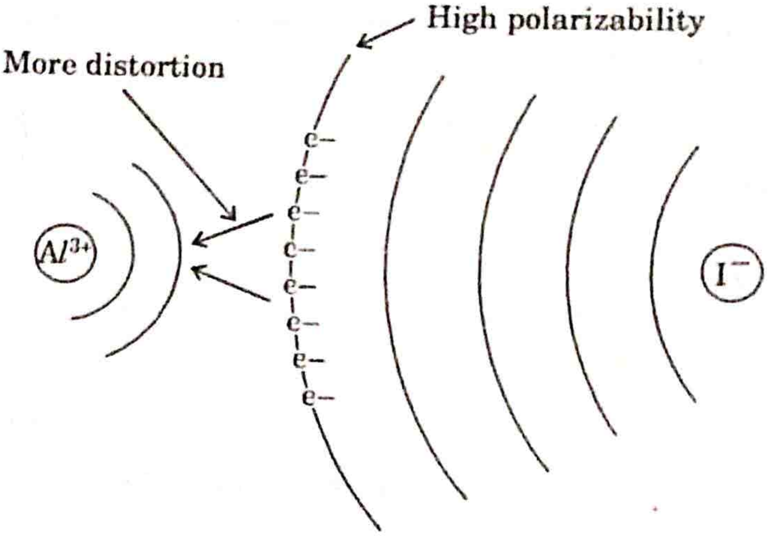


Fig. 39. Polarizability of I⁻ ion.

Synthesis

(a) AlF_3 : It is prepared by reacting Al_2O_3 with HF at 700°C.

$$Al_2O_3 \xrightarrow[700°C]{6HF} 2AlF_3 + 3H_2O$$

(b) $AlCl_3$

(i) It can be formed by direct combination of Al and X_2 or HX.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

(ii) **Large scale production :** It is obtained by heating a mixture of Al_2O_3, C and dry $Cl_3(g)$

$$Al_2O_3 + \underset{dry}{3Cl_2} + 3C \longrightarrow 2AlCl_3 + CO$$

(iii) It can also be obtained by the action of $COCl_2(g)$ or $CO(g)$ and $Cl_2(g)$ over heated Al_2O_3 at 600 – 700°C

$$Al_2O_3 + 3COCl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

$$Al_2O_3 + 3CO + Cl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

$AlBr_3$: It is obtained by direct combination of Al with Br_2 or HBr

$$2Al + 6HBr \longrightarrow 2AlBr_3 + 3H_2$$

$$2Al + 3Br_2 \longrightarrow 2AlBr_3$$

Physical properties

1. AlF_3 is ionic while other trihalides are covalent in nature.
2. The trihalides of aluminium form large number of addition compounds.

Structure of $AlCl_3$: Aluminium chloride in crystalline form or **in vapour form generally exist as dimeric form.**

Explanation: The dimeric structure of $AlCl_3$ shown as in Fig. 40.

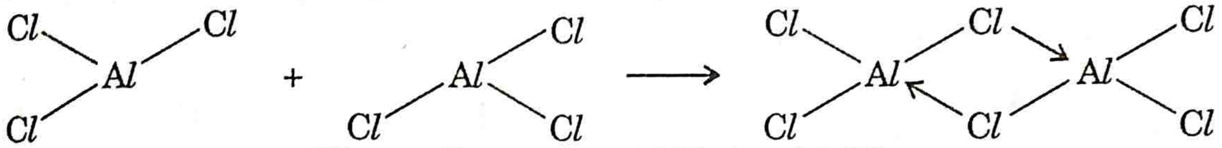


***Fig. 40* Demeric – $AlCl_3$ *i.e.* Al_2Cl_6**

In case of Al_2Cl_6. Each Al, atoms generally sp^3–hybridised. Each Al, atoms form four sp^3–hybridised orbitals these are directed towards the four corners of tetrahedron. Out of these four sp^3 hybridised orbitals of two Al atoms, three of them make normal covalent bond with p–orbital of Cl–atoms while the forth empty hybridised orbital receive a pair of electrons from Cl-atom and form coordinate bond.

Thus a bridged structure is formed. It exists in dimeric form in vapour state and at low temperature about 200°C as shown in Fig. 41.

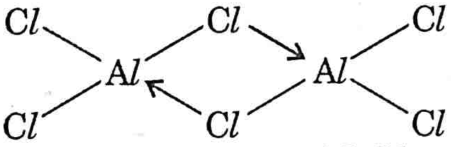


***Fig. 41.* Dimer – Al_2Cl_6**

But on increasing temperature Al_2Cl_6 dissociates to trigonal planer, $AlCl_3$ molecule, in which coordination number of Aluminium is three as shown in Fig. 42.

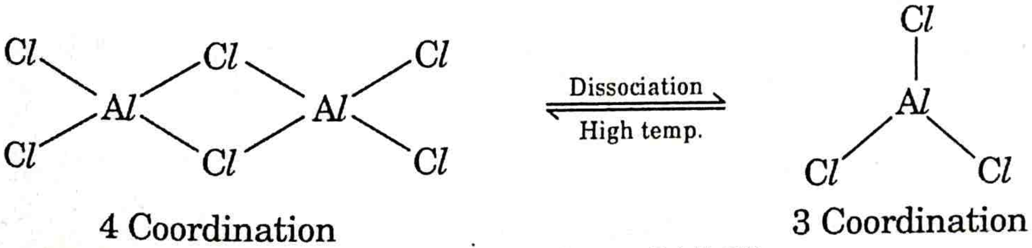


***Fig. 42. Dissociation of* Al_2Cl_6**

Just like $AlCl_3$, $AlBr_3$ also exists as dimer Al_2Br_6.

CARBON FAMILY : GROUP–14

The elements belong to G –14 are carbon (C), Silicon (Si), Germanium (Ge), tin (Sn) and lead (Pb). This group is called as Carbon family.

Occurance

Carbon : It occur in free state as diamond, graphite and coals while in combined state it occurs as hydro carbons, carbohydrates and CO_2 in atmoshperes.

Silicon : It majority occur in rocks in the form of silica and silicates.

Germanium : It is rare element.

Tin : It mainly occur as tin stone.

Lead : It is present in the form of minerals galena – PbS

Comparative study of an elements of Group – 14

The general electronic configuration of elements of G – 14 given as $ns^2\ np^2$. These elements have only two electrons in p–orbitals and two electrons in s–orbital.

The electronic configuration of elements of group – 14 given in the table – 7.

Table - 7 Electronic Configuration of group 14 elements.

Element	Symbol	Atomic No.	Electronic Configuration
Carbon	C	6	$[He]\ 2s^2\ 2p^2$
Silicon	Si	14	$[Ne]\ 3s^2\ 3p^2$
Germanium	Ge	32	$[Ar]\ 3d^{10}\ 4s^2\ 4p^2$
Tin	Sn	50	$[Kr]\ 4d^{10}\ 5s^2\ 5p^2$
Lead	Pb	82	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

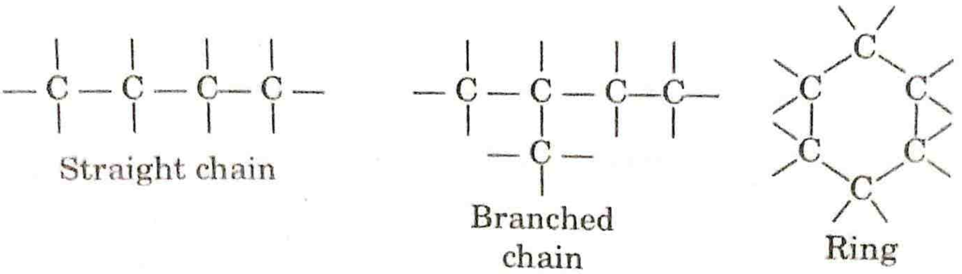
General Properties

The important data of physical properties of an elements of group – 14 given in table – 8.

Table - 8 Physical properties of elements of group 14

	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Atomic radius (pm)	77	118	122	140	146

6. Catenation : It is the self linking properties of an atom with the help of covalent bonds. The catenation tendency of carbon atom is maximum among the members of group – 14 elements. The atom, carbon form chain of different lengths as shown in the (Fig. 50.)


Straight chain

Branched chain

Ring

Fig. 50. Catenation in Carbon atom

Explanation : The properties of catenation depends upon the strength of bonds formed between the atoms. The bond strength of C—C, is very high. Thus carbon exhibits this properties to maximum extent. The chain length and bond strength of elements of group – 14 given in the table – 9.

Table - 9. $x - x$, Bond energies of elements of group – 14

Bond	C–C	Si–Si	Ge–Ge	Sn–Sn
Bond energy KJ mol^{-1}	353	226	167	155

The tendency of Catenation decreases in the order : C > Si > Ge > Sn > Pb.

Explanation : This is because with increase in size of an elements, the strength of bonds decreases, so the order are given as C > Si > Ge > Sn > Pb.

7. Tendency of form multiple bonding : The atom carbon has a unique tendency to form carbon–carbon multiple bonds. (double and triple).

Explanation : This is because of small size and high electronegativity of carbon atom.

So, *p*-orbitals of carbon atom can overlaps side wise and to form Pπ – Pπ multiple bond as shown in (Fig. 51)

Carbon can also form Pπ–Pπ bonds even with O, N and S also. The compounds of carbon is so large that they studies in a seperate branch of chemistry i.e. organic chemistry. However, Si and other members of this group have vacant *d*-orbitals in their valence shell. Thus, they have ability to form *d*π – *p*π multiple bond with elements like O and N.

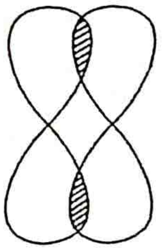


Fig. 51.* Pπ – Pπ *bond formation in Carbon atoms

Pπ – dπ bonding is also called as **back bonding** because this is due to donation of electron pair from filled 2P orbitals of N or O to the vacant *d*–orbital of Si and other elements of this group as shown in the (Fig. 52.)

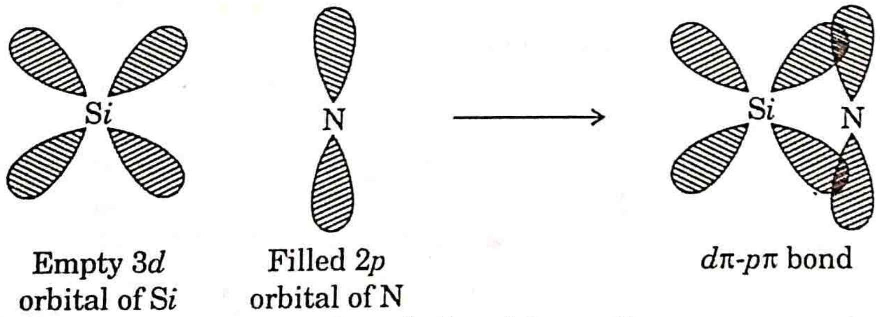


Fig. 52.* Pπ – *d*π *bond formation

Pπ – *d*π back bonding help in explaining the bonding in trimethyl amine and trisilyl amine.

Explanation : In compound trimethyl amine – $(CH_3)_3N$, the N – atom generally sp^3 hybridised, have a lone pair of electron on its tetrahedral position. Thus have pyramidal geometry as shown in the (Fig. 53)

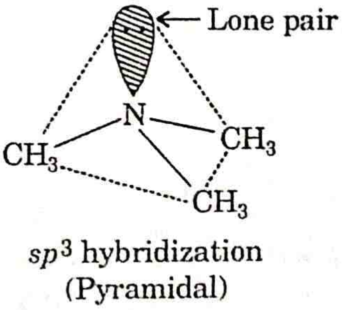
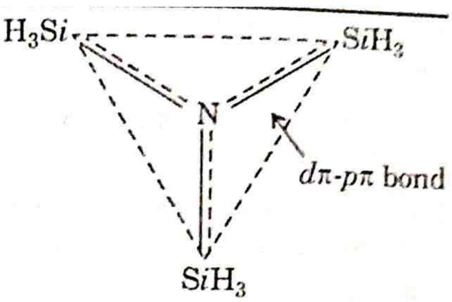


Fig. 53. Structure of trimethyl amine

Due to presence of lone pair of electron on N–atom the molecules become basic in nature while in trisilyl amine – $(SiH_3)_3N$ (Fig. 54)

N–atom generally sp^2 hybridised. Thus have trigonal planer geometry. This is because the lone pair of N–atom overlaps with the empty-d-orbital of silicon atom and form Pπ – dπ back bonding. Since due to the involvement of lone pair of N–atom in back bonding with the vacant d-orbital of silicon atom, N–atom doesn't have any lone pair of electron. As a result, the molecule does not have donor properties. Due to non availability of lone pair of electron on N–atom the molecule become non basic in nature.



sp^2 hybridisation of N(Planar)
Fig. 54. Structure of trisilyl amine

8. **Allotropy :** The existence of an element in two or more forms which have different physical properties but have similar chemical properties.

All the members of group – 14 shows the phenomenon of allotropy except lead – Pb.

Carbon exist in two allotropic forms such as diamond and graphite. These two form differ in their physical and chemical properties.

(i) The density of diamond (3.51 g/cm^3) is greater than graphite (2.23 g/cm^3)

(ii) Diamond is hard while the graphite is soft. Due to soft nature of graphite generally act as lubricant.

(iii) Diamond is bad conductor of electricity (No free electrons) while the graphite is good conductor (free electrons) of electricity.

(iv) Graphite is some what reactive form while diamond is unreactive form.

(A) Orthosilicates or Neso–Silicates

These silicates have no bridged oxygen or shared oxygen atom. These silicates have discrete SiO_4^{4-} units.

For examples :

1. **Phenacite :** (Be_2SiO_4) and willemite (Zn_2SiO_4).

In this structure of Be_2SiO_4, the metal ion are tetrahedrally coordinated.

2. **Olivine :** (9 Mg_2SiO_4, Fe_2SiO_4) They are represented by general formula M_2SiO_4 where M is the divalent metal like Mg, Fe and Mn.
3. Zircon – ($ZrSiO_4$) : In Zircon, the Zr^{4+} ion is eight coordinated i.e. each Zr atom is surrounded (Z by eight oxygen atoms.
4. **Garnet minerals** $M_3^{2+}M_2^{3+}\left[(SiO_4)_3\right]$: The general formula of garnet minerals as given, where $M^{2+} = Ca^{2+}$, Mg^{2+} or Fe^{2+} are six coordinated while $M^{3+} = Al^3$, Cr^{3+} or Fe^{3+}, are eight coordinated e.g. **crossular**–$Ca_3Al_2(SiO_4)_3$, **andradite** – $Ca_3Fe_2(SiO_4)_3$.

(B) Pyrosilicates

Silicates in which one oxygen common between two units. These have discrete $Si_2O_7^{6-}$ units. These are also called as island silicates fig. 65.

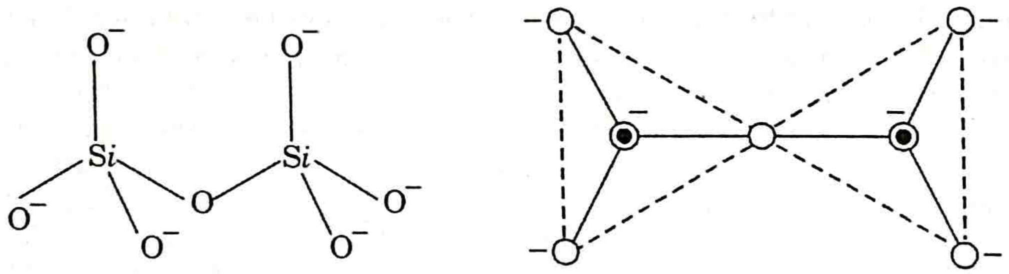


***Fig. 65. Structure of* Pyrosilicate**

For examples

(i) **Thortveitite : $Sc_2Si_2O_7$** :In thortveitite, the scandium is trivatlent and therefore, six positive charge are present on two scandium atoms which are balanced by six negative charges present on the six oxygen atoms. The seventh oxygen atom form, the bridge between two SiO_4 tetrahedra.

(ii) **Hemimorphite : $Zn_4(OH_2)Si_2O_7 . H_2O$:** In hemimorphite crystal, it contains $\bar{O}H$ ions as well as $Si_2O_7^{6-}$ ions. The $Si_2O_7^{6-}$ group are joined through ZnO_3. OH tetrahedra. The water molecule exists as isolated water molecule in the structure.

(iii) **Thalenite : $Y_2Si_2O_7$:** In thalenite, each ytterbium ion is surrounded octahedrally by oxide ions.

(iv) **Vesuvianite ($Ca_{10}Al_{14}(MgFe)_2(Si_2O_7)(SiO_4)_5(OH)_4$ and epidote – $Ca_2(Al_1 Fe)Al_2O(Si_2O_7)(SiO_4)OH$:** The structure of both contains seperate SiO_4^{4-} group as well as $Si_2O_7^{6-}$ groups.

(C) Cyclic or ring silicates

These are silicates in which two oxygen atoms are common per unit. These have general formula of $(SiO_3)_n^{2n-}$. These are of two types for examples :

(i) **Wollastonite – $Ca_3Si_3O_9$** : In this silicate, the small size ring contains three SiO_4 tetrahedra linked together as $Si_3O_9^{6-}$ ion and is present in wollastonite. Fig. 66.

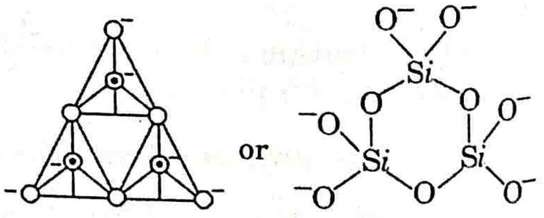


Fig. 66.Structure of $[Si_3O_9]^{6-}$ ion.

(ii) Benitoite – $BaTiSi_3O_9$: In this silicates, the rings are arranged in sheets and the SiO_4^{4-} tetrahedra are cemented by Ba^{2+} and Ti^{4+} ions. Both Ba^{2+} and Ti^{4+} are six coordinated.

(iii) Beryl – $Be_3Al_2Si_6O_{18}$: The anion of this silicate contains a ring of tetrahedra, in which an oxygen shared by one silicon. One – *Al* (six – coordinated) one Be– (four coordinated) fig. 67.

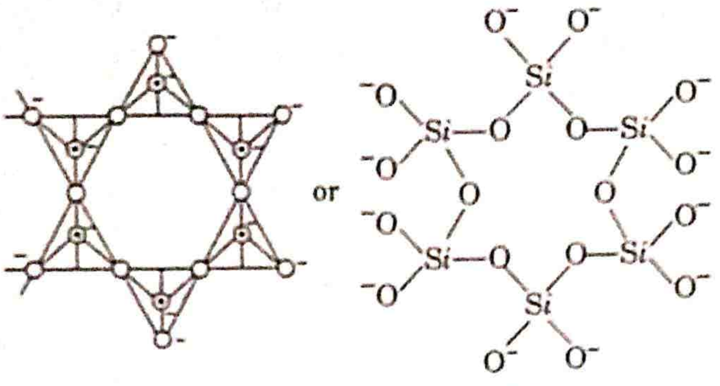


Fig. 67. Structure of $[Si_6O_{18}]^{12-}$ ion.

(D) Chain Silicates

These are of two types :

1. Single Chain Silicates : Silicates in which two oxygen atoms per unit get shared with other units. These are represented by general formula of SiO_3^{2-}. Silicates of these types are called **pyroxenes** or **metasilicates.**

For examples :

(i) Enstatite – $MgSiO_3$: In enstatite the coordination number is six for Mg.

(ii) Diopside – $CaMg(SiO_3)_2$: In dopside, the coordination number of Mg is six and Ca is eight.

(iii) Spodumene – $LiAl(SiO_3)_2$: Coordination number of *Li* and *Al* ar six fig. 68

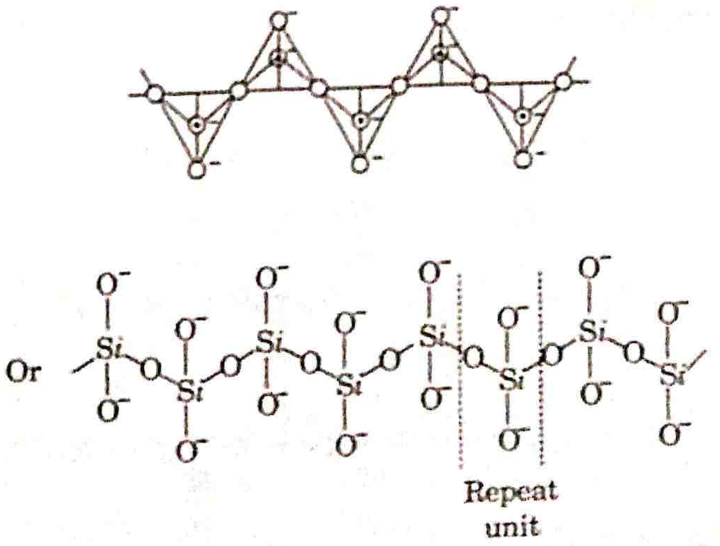


Fig. 68 Single strand chain Silicate ion, $(SiO_3)_n^{2n-}$

2. Double chain Silicates : When two single chain silicates unites with each other via oxygen atom give double chain silicate. Minerals of this type are known as **amphiboles**. Fig. 69.

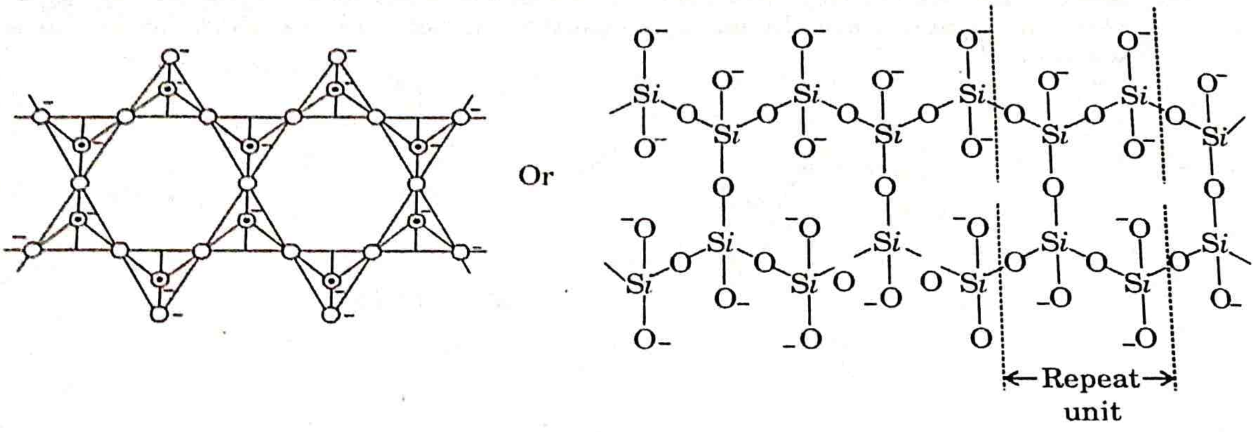


Fig. 69. Double Chain silicate ion $[Si_4O_{11}]_n^{6n-}$

These minerals contain silicates such as :

(i) Tremolite : $Ca_2 Mg_5 (Si_4 O_{11})_2 (OH)_2$

(ii) Croudolite : $Na_2 (Fe, Mg)_3 (Si_4O_{11})_3 (OH)_2$

(iii) Asbestos : $CaMg_3O (Si_4O_{11})$

(E) Sheet Silicates : The silicates which shares its three oxygen atoms with other silicate units. It give two dimensional sheet like structure. The general formula of repeating structural unit is $(Si_2 O_5)_n^{2n-}$ (Fig. 70).

For examples :

(i) Kaolinite–$[Al_2 (OH)_4 Si_2 O_5]$

(ii) Talc–$Mg_3 (OH)_3 Si_4 O_{10}$.

(iii) Halloysite – $Al_2 O_3 . 2 SiO_2 . 2H_2O$

(iv) Allophane–$Al_2 O_3 . n SiO_2 . xH_2O$

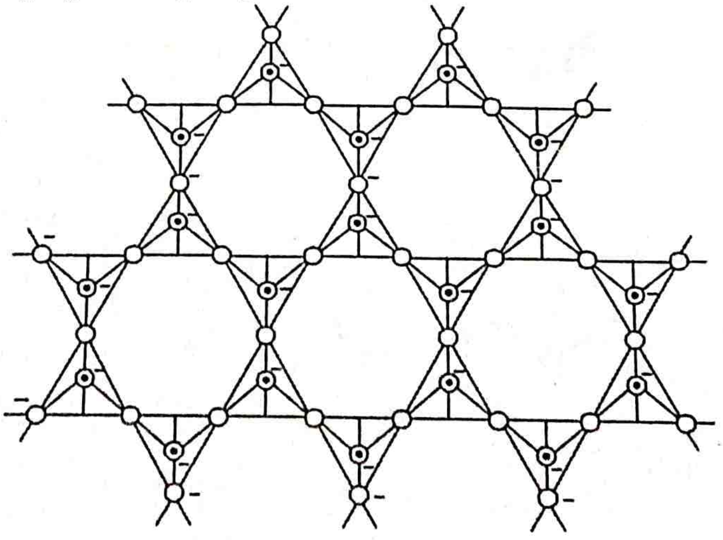


Fig. 70. (a) Structure of sheet Silicates.

or

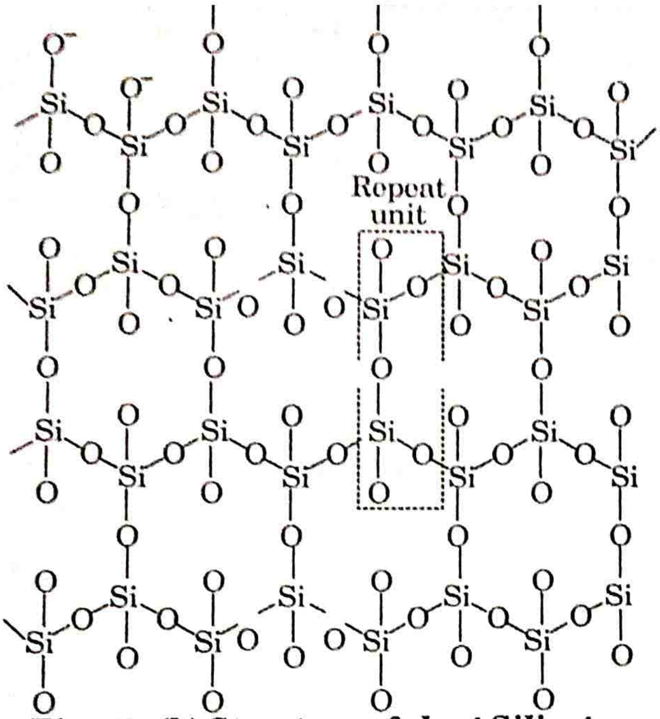


Fig. 70. (b) Structure of sheet Silicates.

(F) Three dimensional silicates : Silicates in which all the four oxygen atoms are shared with other units. These give rise to three dimensional network with a formula of $(SiO_2)_n$ as shown in fig.

The general name of these silicate is silica. Fig. 71.

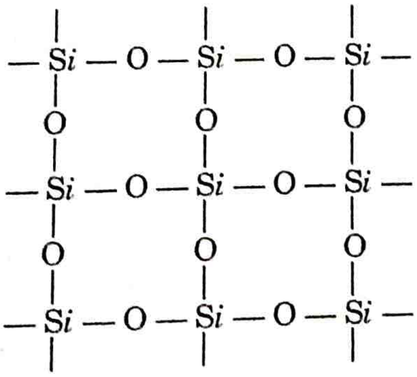


Fig. 71. Structure of Silica

Silica is high melting solid. It exists in three form : **quartz, tridymite** and **cristobalite.** All these forms have a different structure depending upon temperatures. They differ in arrangement of SiO_4 – units.

$$\begin{array}{llll} \text{Low temp. form,} & \alpha\text{ – quartz} & \alpha\text{ – tridymite} & \alpha\text{ – cristobalite} \\ & \Big\updownarrow 513\ ^\circ\text{C} & \Big\updownarrow 120\text{–}150^\circ\text{C} & \Big\updownarrow 200\text{–}250^\circ\text{C} \\ \text{High temp. form,} \xrightleftharpoons{870^\circ\text{C}} & \beta\text{ – quartz} \xrightleftharpoons[1570^\circ\text{C}]{} & \beta\text{ – tridymite} \xrightleftharpoons[1710^\circ\text{C}]{} & \beta\text{ – cristobalite} \end{array}$$

Silicones

Silicones are the organo-silicon polymer containing .... $Si - O - Si$ .... linkages. The general formula of silicones are $(R_2SiO)_n$. Here R may be alkyl or may be aryl groups. They are of many types. They may be linear, cyclic and cross linked polymer.

Synthesis of Silicones : The synthesis of silicones requires two processes :

1. Preparation of intermediates
2. Hydrolysis of intermediates

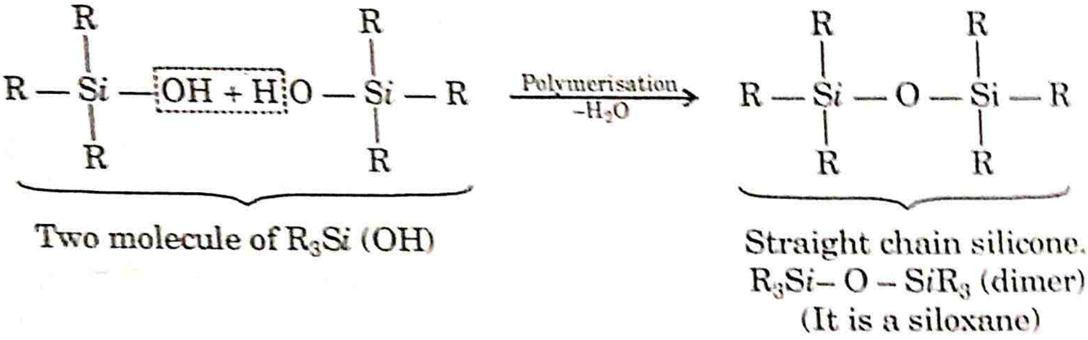
Let's discuss :

1. **Preparation of intermediates :**
   (i) **Direct Silicon process :** Methyl chloro silianes are prepared by heating methyl chloride with silicon in the presence of catalyst Cu at 300°C. This reaction give rise to a mixture of methyl chloro silanes

Formation of Silicones

The different types of silanols polymerises and give different types of silicones, given as :

(a) Straight chain Silicones : It is formed when two molecules of trialkyl monohydroxy silane – $R_3Si(OH)$ undergo polymerisation (Fig. 72).



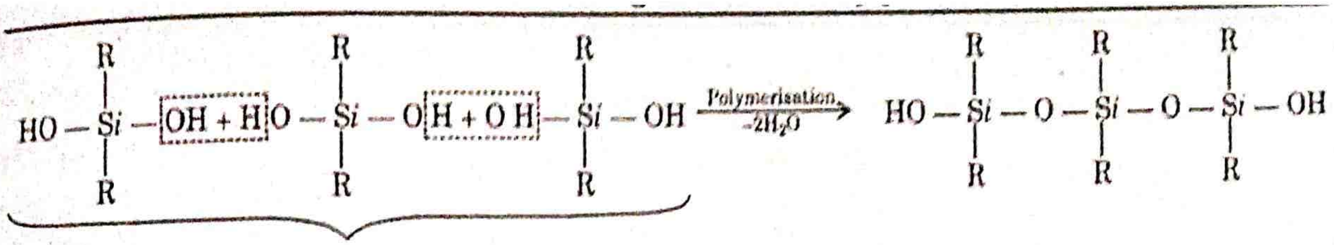
$$\underbrace{R\text{—}\underset{R}{\overset{R}{Si}}\text{—}\boxed{OH + H}O\text{—}\underset{R}{\overset{R}{Si}}\text{—}R}_{\text{Two molecule of } R_3Si\ (OH)} \xrightarrow[-H_2O]{\text{Polymerisation}} \underbrace{R\text{—}\underset{R}{\overset{R}{Si}}\text{—}O\text{—}\underset{R}{\overset{R}{Si}}\text{—}R}_{\text{Straight chain silicone.}}$$

Two molecule of R_3Si (OH)

Straight chain silicone.
$R_3Si–O–SiR_3$ (dimer)
(It is a siloxane)

Fig. 72.

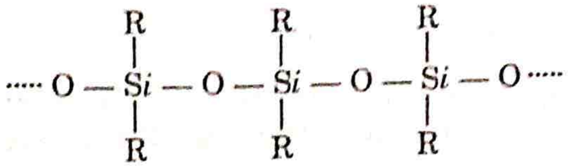
(b) Cyclic Silicones : It is formed when many molecules of R_2Si $(OH)_2$ undergo polymerisation. Fig. 73.



$$\mathrm{HO-\overset{R}{\underset{R}{Si}}-\boxed{OH + H}O-\overset{R}{\underset{R}{Si}}-O\boxed{H + O H}-\overset{R}{\underset{R}{Si}}-OH \xrightarrow[-2H_2O]{Polymerisation} HO-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH}$$

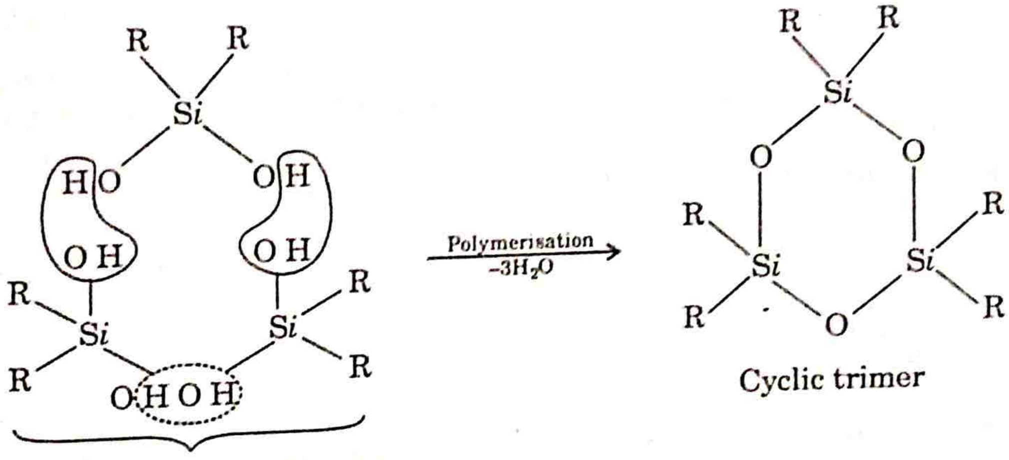
Three molecules of $R_3Si(OH)_2$

The active –OH group at each end of chain, polymerise continues and give long chain:



$$\cdots\cdots \mathrm{O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O} \cdots\cdots$$

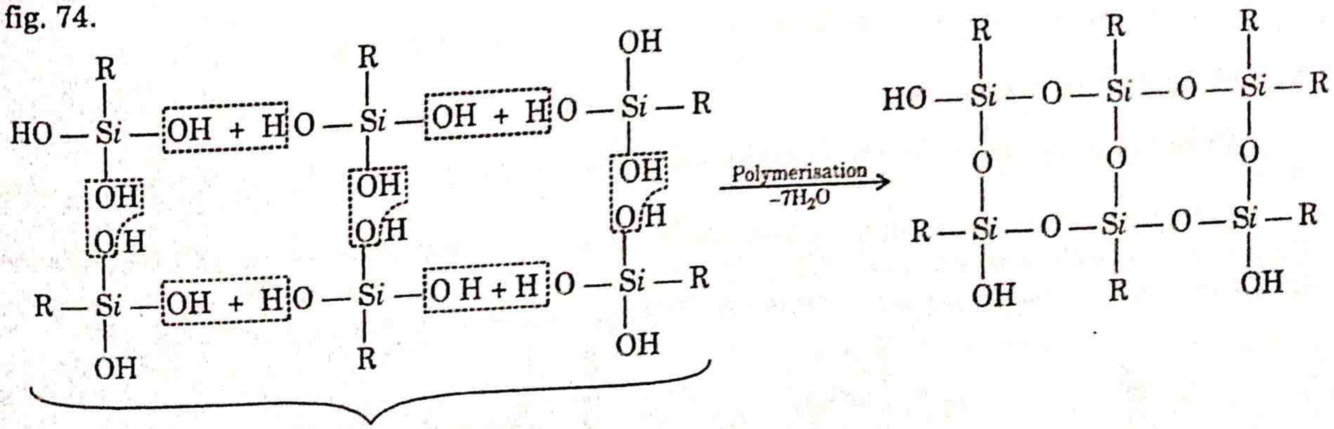
Linear or straight chain silicone
(Thermoplastic polymer)(siloxane)



Three molecules of $R_2Si(OH)_2$

Fig. 73

(c) Two–dimensional Silicones : It is formed due to polymerisation of large number of molecules of $RSi(OH)_3$ – alkyl trihydroxy silane, since – OH group an active group at each end of the chain, polymerise continues on both the ends ∴ length of chain increses as shown in fig. 74.



Six $RSi(OH)_3$ molecules

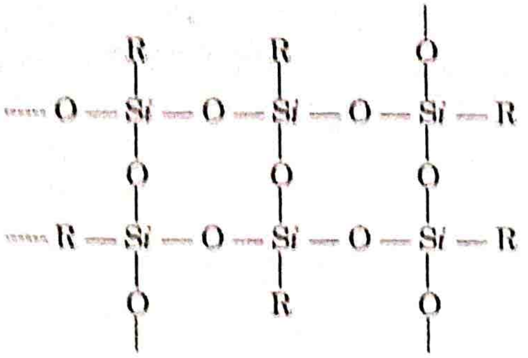


Fig. 74. Two dimensional cross-linked silicone

Factors affecting the nature of Silicones : The properties shown by the silicones depend upon the following factors :

(i) the nature of alkyl or aryl groups

(ii) the length of the chain and

(iii) the extent of cross linking.

Thus, the silicones polymers are obtained as oils, viscous liquids, resin like solid.

Generally, short chain silicones are oily liquids, medium chain are viscous liquids, while long chain silicones are highly cross linked polymers.

Properties and uses of silicones : The silicones shows the following types of properties and uses :

(i) They are thermally stable in the absence of air and can stand at a temperature such as 250°C – 300° C.

(ii) They are unaffected towards, weak acids and alkalies.

(iii) Silicones are the chemically inert.

(iv) They dissolve in non polar solvents like C_6H_6, ether and carbon tetrachloride.

(v) They generally uses as low temp., lubrication, because they donot becomes too viscous on cooling.

(vi) They are generally water repellent i.e. they are used in making water proof fabric or papers.

(vii) They generally have insulating properties thus act as insulating materials for electric appliances.

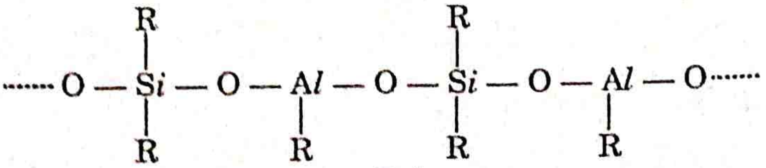
(viii) They are non toxic.

(ix) Silicones rubbers show elastic properties at low temperature.

Types of silicones

Depending upon the degree of polymerisation, silicones can be classified into following types :

1. High thermal silicones : These are obtained on hydrolysis of organosilicon halide in the presence of halide or alkoxide of Ti or Al. As a result 2–D linear or cyclic polymers is obtained. In these polymers Si–atoms are replaced by Ti or Al atoms as shown in the figures. 75



$$\cdots\cdots O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{Al}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{Al}-O\cdots\cdots$$

Linear Polymer

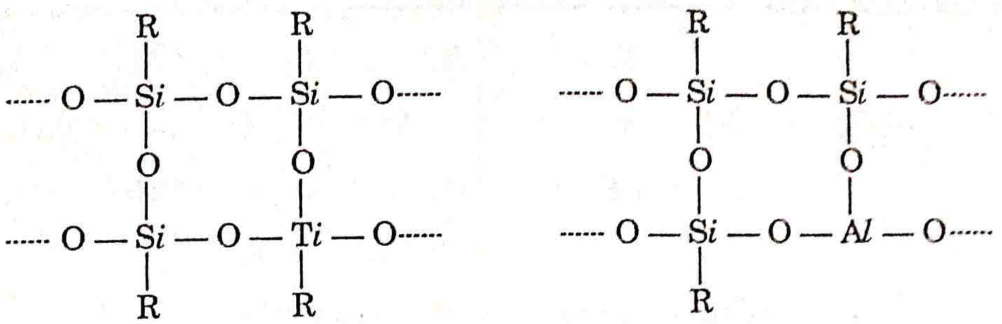


Fig. 75. **Cyclic Polymers**

The presence of T*i* and A*l* atoms in the structure of the polymers increases the thermal stability of the polymers.

Brown etal, in 1960, synthesize the highly thermally stable, linear polymer of silicones as shown fig. 76.

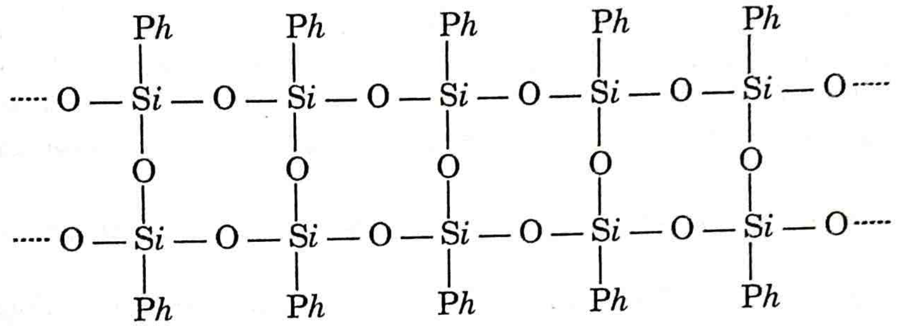


Fig. 76 **Polymers of Silicones**

2. Silicon resins : These are formed by hydrolysis of $(CH_3)_2\ SiCl_2$ in the presence of CH_3SiCl_3 ∴ extensive cross linking accompanies polymerisation. These are rigid polymers like bakelite. They are made by dissolving a mixture of $RSiCl_3$ and R_2SiCl_2 in toluene and hydrolysing with water. The partially polymerised product is washed to remove H*Cl*, then can be shaped. Finally the product is heated with quaternary ammonium salt as catalyst to condense any remaining – OH group in the structure. The final product is extensively cross linking.

The silicon resing used :

(i) as electrical insulator

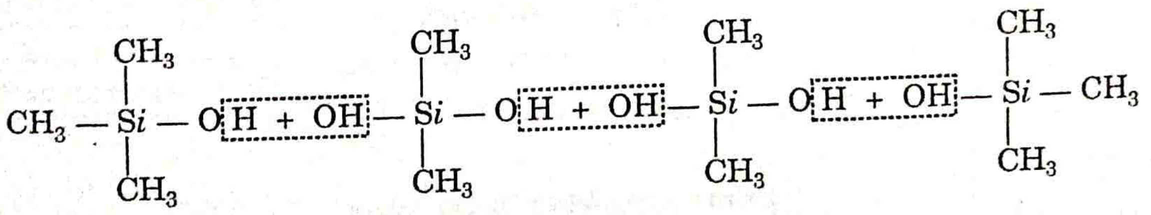
(ii) used to make printed cricuit board

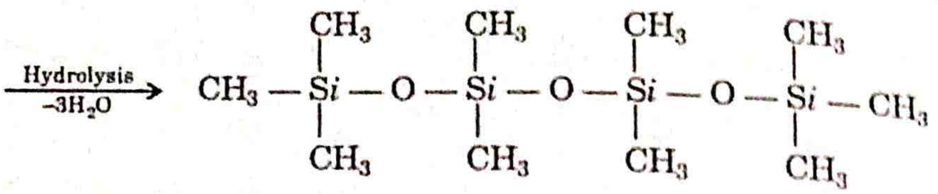
(iii) to encapsulate integrated circuit chips and resistors

(iv) Used as non-stick coating for pans.

3. Silicone fluids or silicone oils : It is a mixture of equal proportion of linear and cyclic polymers. These have low temp. coefficient of viscosity, they are generally used as hydraulic fluids. They are also used as dielectric fluids. Silicones oils are highly stable and non volatile in nature ∴ generally used as high temp. oil baths.

Generally, low mol. wt. silicones are oily liquids. The synthesis of silicones oils as shown in fig. 77.





$$\xrightarrow[-3H_2O]{\text{Hydrolysis}} CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Dimethyl silicone oil

Fig. 77. Structure of Silicon Oils

silicones oils contain $(CH_3)_3\ SiCl$ and $(CH_3)_2\ SiCl_2$ in proper ratio and hydrolysed, on polymerisation give silicone oils.

4. Silicone Rubbers : Silicones rubbers made up by polymerisation of $(CH_3)_2\ SiCl_2$. These are long chain polymers with some cross linking between the linear chains. The chain length of the polymers can be controlled by the addition of $(CH_3)_3 - Si - O - Si\ (CH_3)_3$

Silicones rubbers are elastic in nature over a temp. range of about 400°C to 550°C for 100 hours. Thus, they are generally used in sealing joint and insulating electrical parts.

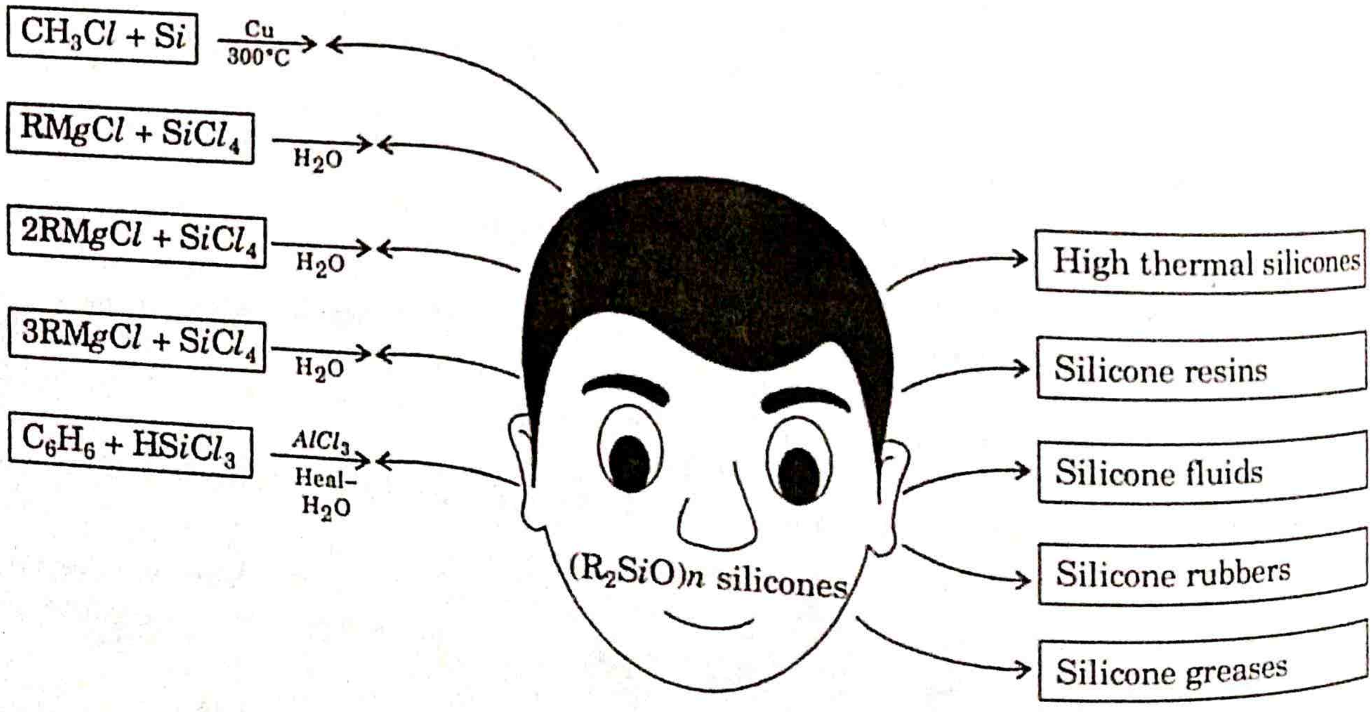
5. Silicone greases : These are made by adding carbon black special soap (lithium soap) or finally dispersed silica–SiO_2 in silicone oils.

The greases is generally used for ball bearing operating at high temperature and at high speed.

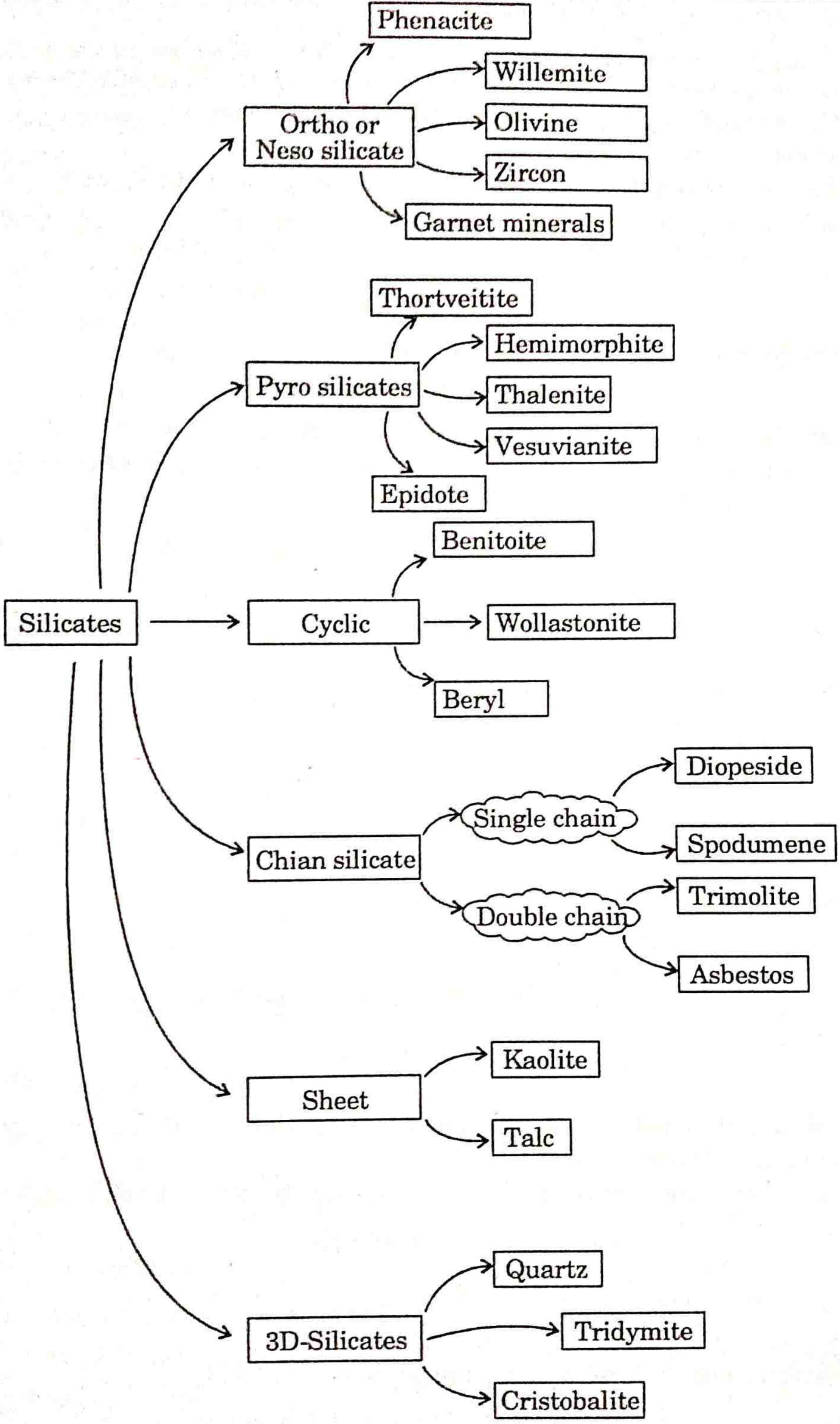
The silicone grease is just like vaseline, used as lubricants in aeroplanes parts.

Silicone greases donot melt even at low temp. of – 40° C and don't melt at high temp. even at 200°C.

Summery of Silicons



Summery chart of Silicons



Summery Chart of Silicates

Fluorocarbons

These are fluoro derivatives of hydrocarbons. These are derived from hydrocarbons by replacement of H–atoms by fluorine atoms. The following, $CClF_3$ CCl_2F_2 (freen – 12) CCl_3F, $CHClF_2$, $CF_2 = CF_2$, C_8F_{18}, C_6F_{12} are the examples of fluorocarbons.

Synthesis of Fluorocarbons :

1. **By the substitution of H–atom of hydrocarbons with F–atoms :**

(a) Fluorocarbons can be obtained by treating benezene with F_2 at a temp. of 260°C, in inert atmosphere of N_2 or He and a catalyst Cu-guaze.

$$C_6H_6 + 9F_2 \xrightarrow[Cu\ \text{guaze},\ 260^\circ C]{N_2} C_6F_{12} + 6HF$$

(b) By the action of F_2 on CH_4 given CF_4 :

$$CH_4 + F_2 \rightarrow CF_4 + 4HCl$$

2. **By the reaction of organic substance with liquid HF.**

(a) In this method organic compounds electrolysed in liquid HF in a cell of steel with Ni – anode and steel cathode.

$$C_2H_5OC_2H_5 \xrightarrow[\substack{HF \\ \text{electrolysis}}]{\text{liquid}} C_2F_5 - OC_2F_5$$

$$CH_3COOH \xrightarrow[\text{electrolysis}]{\text{liq. HF}} CF_3COOF \xrightarrow{H_2O} CF_3COOH$$

(b) By the reaction of anhydrous HF (hot) with CCl_4 in the presence of SbF_5 at a temp. of 70–100 and a pressure of 100–500 atmosphere, freon – 12 (CCl_2F_2) is obtained.

$$CCl_4 + 2HF \xrightarrow[\substack{700-100^\circ C \\ 100-500\ \text{atm}}]{SbF_5} \underbrace{CClF_3 + CCl_3F}_{\text{Small amount}} + CCl_2F_2 + 2HCl$$

(c) HF on reaction with $CHCl_3$ in the presence of SbF_3 gives teflon

$$CHCl_3 + 2HF \xrightarrow{SbF_3} CHF_2Cl + 2HCl$$

$$2CHF_2Cl \xrightarrow{800^\circ C} CF_2 = CF_2 + 2HCl$$

$$nCF_2 = CF_2 \xrightarrow{\text{Polymerisation}} \underset{\text{Teflon}}{\left(CF_2 - CF_2\right)_2}$$

3. **Reaction of metal fluoride with organic halides :** Metal fluorides, on heating with organic halides give fluarocarbons.

The metal fluorides may be LiF, NaF, CsF, AgF, AsF_3, Hg_2F_2, SbF_3, ZnF_2 etc.

$$AgF + RCl \longrightarrow AgCl + RF$$

$$AsF_3 + C_6H_5PCl_3 \xrightarrow{25^\circ C} AsCl_3 + C_6H_5PF_3$$

4. **Reaction of CCl_4 with SbF_3, the presence of $SbCl_3$**

$$3CCl_4 + 2SbF_3 \xrightarrow[\text{Heat}]{SbCl_3} 2CCl_2F_2 + 2SbCl_3$$

5. **By the fluorination of organic compound with SF_4 e.g.**

$$2R_2CO + SF_4 \rightarrow 2R_2CF_2 + SO_2$$

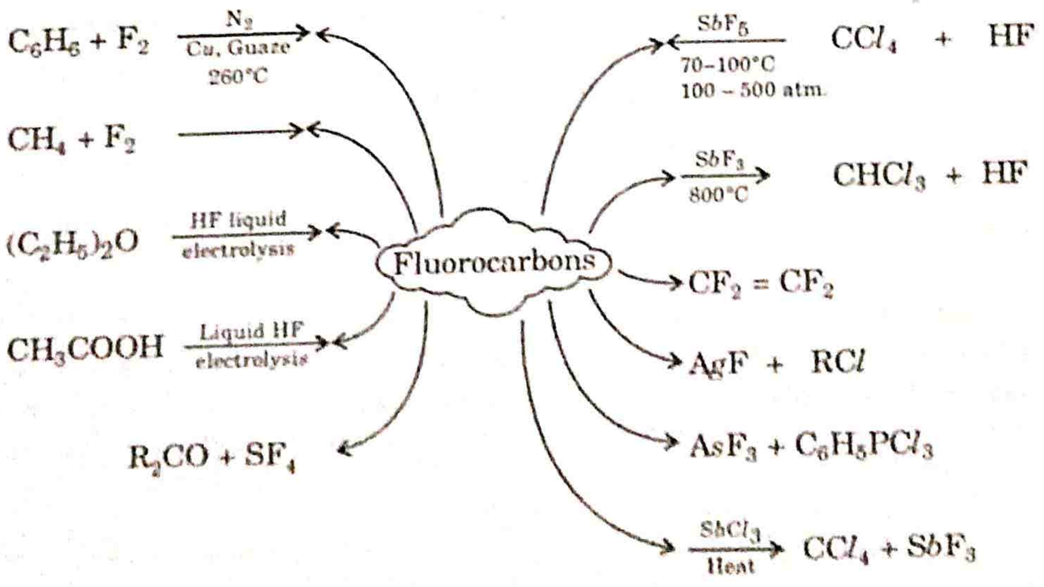
Properties of Fluorocarbons :

1. Fluorocarbons are dense, colourless, non toxic liquids.
2. Flurocarbons have unpleasant odour.
3. They generally have low melting point.
4. Flurocarbons have low viscosity and low surface tension.
5. They are generally non-inflammable.
6. They are thermally stable due to high bond energy of C – F bond.
7. Fluorocarbons are chemically inert.
8. They are unreactive towards the most of the chemical reagents i.e. acids, alkalies, oxidising agent etc.
9. They are resistant to oxidation.
10. Fluorocarbons are not able to hydrolysis.
11. They have generally low coefficient of friction.
12. Freon – 12, is colourless, non inflammable gas.
13. Teflon is white plastic like material, is used as an insulating materials for cable.

Uses of fluorocarbons

1. CFC used as refrigerants.
2. Freon – 12, is used as refrigerants and air conditioner.
3. Freon – 12 used as a solvent for DDT and insecticides.
4. Per fluoro-organic acids uses as synthetic blood for small mammals.
5. Teflon is used as electrical insulator for cables.
6. $CHClF_2$ used for preparation of Teflon.
7. $CF_3CHBrCl$ used as anaesthetics.

Summery chart of Fluorocarbons



Carbides

These are the compounds of carbons with more electropositive elements than itself. The general methods of preparation of carbides are :

1. **By heating metal with Carbon :** Many metals like Be, Ag, Mn, Fe etc reacts with carbon, at high temp., to form carbide. For example :

$$Be + 2C \rightarrow BeC_2$$
$$2Ag + 2C \rightarrow Ag_2C_2$$
$$3Mn + C \rightarrow Mn_3C$$
$$3Fe + C \rightarrow Fe_3C$$

2. **By heating metal oxide with Carbon**
For example :

$$MgO + 3C \rightarrow MgC_2 + CO \uparrow$$
$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO \uparrow$$
$$U_3O_8 + 14C \rightarrow 3UC_2 + N_2$$
$$SiO_2 + 3C \rightarrow SiC + 2CO \uparrow$$
$$CeO_2 + 4C \rightarrow CeC_2 + 2CO$$

3. **By passing acetylene gas on heated element or its oxides**

$$4Li + C_2H_2 \rightarrow Li_2C_2 + 2LiH$$
$$2Ag_2O + C_2H_2 \rightarrow Ag_2C_2 + H_2O$$

4. **By heating metallic oxide with CaC_2**

$$MgO + CaC_2 \rightarrow MgC_2 + CaO$$

5. **By passing CO over metal, at high temperature**

$$2Li + 2CO \rightarrow Li_2C_2 + O_2$$
$$6Al + 3CO \rightarrow Al_4C_3 + Al_2O_3$$

6. **By passing acetylene through the ammonical solution of metallic salt**

$$2AgNO_3 + 2NH_4OH + C_2H_2 \rightarrow Ag_2C_2 + 2NH_4NO_3 + 2H_2O$$

7. **By heating metallic carbonate with carbon in the presence of oxidisable metal**

$$BeCO_3 + C + 3Mg \rightarrow 3MgO + BaC_2$$

Classification of Carbide

Carbides can be classified into four types depeneding upon the nature of bonding. These are :

1. Salt like or ionic carbides
2. Covalent carbides
3. Interstitial carbides
4. Borderline or iron like carbides

1. **Salt like or ionic carbides :** Salt like carbides are formed by the combination of carbon with the electropositive elements of group 1, 2 and 3 (except B). These carbides are obtained by heating metal or its oxide with carbon, CO and acetylene etc.

$$2Be + C \rightarrow Be_2C$$
$$4Al + 3C \rightarrow Al_4C_3$$
$$CaO + 3C \rightarrow CaC_2 + CO$$
$$6Al + 3CO \rightarrow Al_4C_3 + Al_2O_3$$
$$2Ag_2O + C_2H_2 \rightarrow Ag_2C_2 + H_2O$$

Properties

1. These are transparent, colourless, have crystalline structure.
2. These carbides are ionic in nature.
3. They are non conductor of electricity.
4. They hydrolysed either by water or dilute acids.

Depending upon the nature of hydrocarbon formed on hydrolysis, these are classified into following types.

4. Methanides : These carbides gives methane on hydrolysis, thus these are regarded as derivative of methane and contain C^{4-} ions. Examples Be_2C and Al_4C_3 etc.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \rightarrow 4\,Al(OH)_3 + 3CH_4$$

Be_2C – Beryllium Carbide : It is prepared by heating BeO with carbon at a temp. of 2000°C as shown :

$$2BeO + 3C \xrightarrow{2000^\circ C} Be_2C + 2CO$$

Properties: Be_2C is brick red solid

It decomposes into graphite and beryllium when it is heated at a temp. of 2100°C

$$Be_2C \xrightarrow{2100^\circ C} 2Be + C$$

Structure of Be_2C : It has antifluorite structure. (Fig. 78)

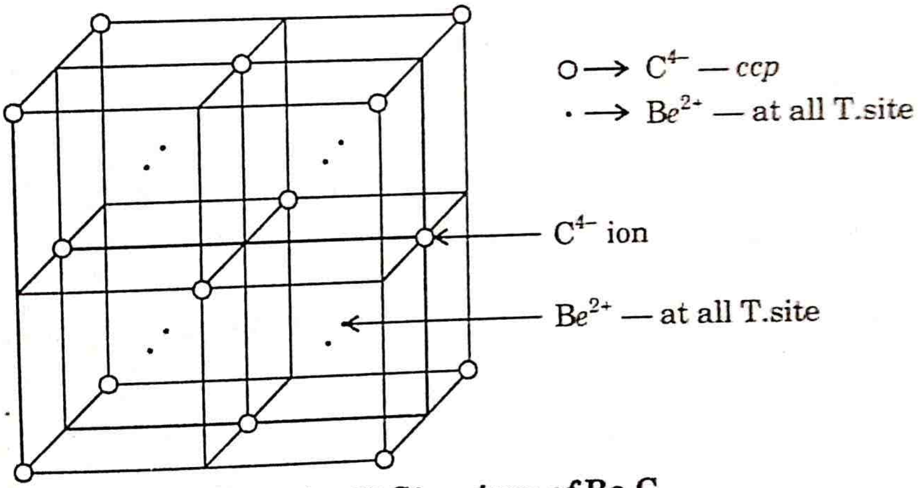


Fig. 78 Structure of Be_2C

Aluminium Carbide – Al_4C_3 : It is prepared :

(i) By heating a mixture of *Al* and C

$$4Al + 3C \rightarrow Al_4C_3$$

(ii) By heating alumina – Al_2O_3 with carbon in electrical furnace

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO\uparrow$$

(iii) By heating *Al* with CO

$$6Al + 3CO \rightarrow Al_4C_3 + Al_2O_3$$

Properties :

(i) It form Pale yellow hexagonal crystal

(ii) It sublime at 2200°C

(iii) It form Al_5C_3N with N_2 at 2000°C

(iv) It gives Al_2O_3 with O_2

$$Al_4C_3 + 6O_2 \rightarrow 2Al_2O_3 + 3CO_2 \uparrow$$

Structure : It has regular hexagonal geometry. In Al_4C_3, each Al–atom is surrounded by three C–atoms and each C—atom is surrounded by four Al–atoms i.e. Tetrahedra of two types are linked with each other and form the layer lattice. (fig. 79)

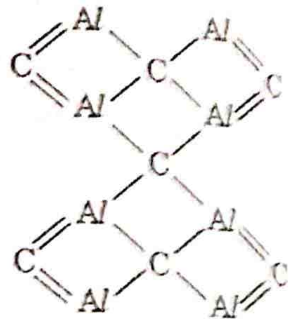


Fig. 79. Structure of Al_4C_3

6. Acetylides : These carbides give acetylene on hydrolysis. These are regared as derivative of acetylene and contain C_2^{2-} ion. Examples : BeC_2, MgC_2, CaC_2 and $Al_2(C_2)_3$ etc.

$$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$MgC_2 + H_2O \rightarrow Mg(OH)_2 + C_2H_2$$

Calcium Carbide – CaC_2 : Pure CaC_2 is colourless solid, its M.Pt. is 2300°C. It is prepared

(1) by reacting CaO with coke at 2200 – 2300°C as shown

$$CaO + 3C \xrightarrow{2200-2300^\circ C} CaC_2 + 3CO$$

It react with N_2 and give calcium cynamide

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

It act as reducing agent, it reduces MgO to Mg

$$3MgO + CaC_2 \rightarrow 3Mg + CaO + 2CO_2 \uparrow$$

Uses :

(1) It is used as oxyacetylene flame for welding perpose.

(2) It is used for manufacture of an organic compounds.

Structure : Its structure is similar to AB_2 type ionic crystal as shown in fig. 80.

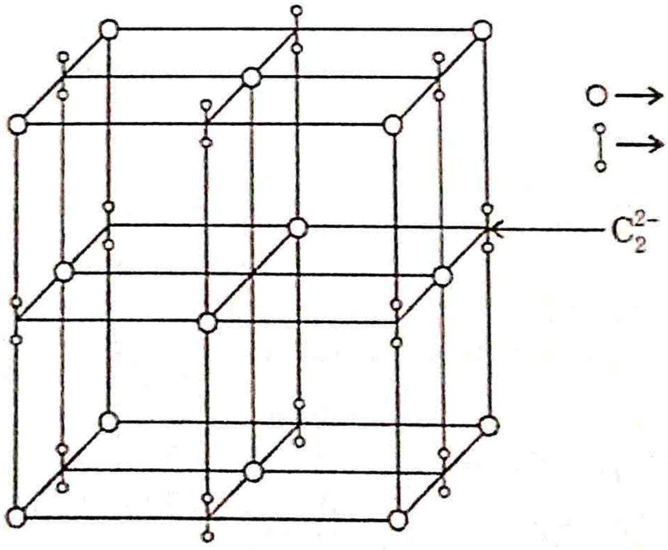


Fig. 80. Structure of CaC_2

(c) Allylides : These carbides given allylene ($H_2C = C = CH_2$) on hydrolysis, these are regarded as derivative of allylene and contain C_3^{4-} ion.

Example : Mg_2C_3

$$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + C_3H_4$$

Structure of allylide ion – C_3^{4-} : The ion C_3^{4-} is formed by the removal of four H^+ ions from allylene. Its structure given as in fig. 81

$$:\ddot{C} = C = C:$$

or

$$[:\ddot{C} = C = \ddot{C}:]^{4-}$$

Fig. 81 Structure of allylide ion

(d) Mixed Carbide : These carbides gives a mixture of hydrocarbons (acetylene, olefins and H_2) on hydrolysis

For examples : ThC_2 and UC_2.

2. Covalent – Carbides : These carbides are formed by the combination of carbon with the elements of same electronegativity as carbon or with the elements (H, S, Cl) of higher electronegativities than carbon.

Example : Silicon carbide – SiC and

Boron Carbide – B_4C

Silicon Carbide – SiC (Carborundum) : It is covalent Carbide.

Synthesis

(i) It is synthesized by mixing SiO_2 with coke in an electrical furnance at 2000°C.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

(ii) It is also synthesized by passing acetylene gas over heated silicon.

$$2Si + C_2H_2 \rightarrow SiC + H_2$$

Physical properties :

(i) It is colourless crystalline solid when pure.
(ii) Its hardness same as diamond.
(iii) It is thermally stable.
(iv) SiC is insoluble in water.

Chemical properties :

(i) It is inert, even at high temp.
(ii) It is oxidised in air at high temp. and form silica

$$SiC + O_2 \rightarrow SiO_2 + CO_2 \uparrow$$

(iii) It react with alkalies in the presence of air and to form sod. silicate.

$$SiC + 2NaOH + 2O_2 \xrightarrow{fuse} Na_2SiO_3 + H_2O + CO_2$$

(iv) It react with chlorine and give $SiCl_4$ and CCl_4

$$SiC + 4Cl_2 \xrightarrow{1000^\circ C} SiCl_4 + CCl_4$$

Uses :

(i) It is generally used in making wheel.
(ii) It is deoxidant in metallurgical processes.

(iii) It is an excellent container for fuel.

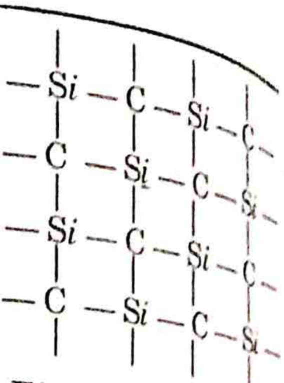


Fig. 82. Structure of Silicon Carbide

Structure : In SiC, there is 3D – array of Si and C– atoms, in which each C—atoms tetrahedrally linked by four Si–atoms and each Si–atoms tetrahedrally linked by four C–atoms as shown in fig. 82.

Boron Carbide – B_4C : It is covalent carbide.

It is prepared :

(i) By heating B with carbon in electrical furnace at a high temp. of about 2500°C

$$4B + C \rightarrow B_4C$$

(ii) By heating a mixture of B_2O_3 and coke at high temp.

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO\uparrow$$

Physical Properties :

(i) It is black coloured crystalline substance.

(ii) Its M.Pt. is very-very high 5350°C.

(iii) It is harder than SiC

(iv) It shows the electrical conductivity.

Uses :

(i) It is used for cutting diamond.

(ii) It is used for drilling holes in rockets.

(iii) It also used for making electrodes for electrical furnance.

(iv) It is used for making lamp filaments.

Structure: $B_4C \rightarrow$ generally exist in tetrameric form such as $B_{12}C_3$.

In icosahedral B_{12} unit, the 12–B atoms link together and form icosahedron and seperate B–atoms link together the B–12 units.

The structural units of linear chains of 3 – carbon atoms and B_{12} groups are arranged at the vertices of icosahedron. Thus structure of B_4C is a continuous 3 – D boron network Fig. 83.

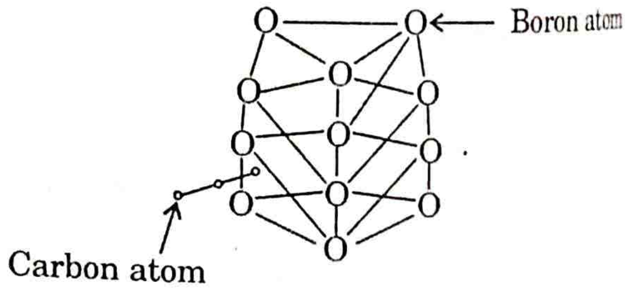


Fig. 83. Structure of B_4C *exist as tetramer i.e.* $B_{12}C_3$

3. Interstitial carbides : These are formed by the combination of carbons with metals (transition metals, lanthanides and actinides)

$$2Mn + C \rightarrow Mn_3C$$

$$3Fe + C \rightarrow Fe_3C$$

These are also formed by the reduction of metallic oxides with carbon at high temp. of about 2000°C

$$CeO_2 + 4C \rightarrow CeC_2 + 2CO\uparrow$$

$$Ag_2O + 3C \rightarrow Ag_2C_2 + CO\uparrow$$

In these carbides, the metal atom form the CCP arrangement while the carbon atoms (due to their small size) occupy the interstitial site.

The radii of transition metal (r = 135 pm) sufficient to accomodate small sized carbon atoms.

These carbides melt at high temp. of about 3000° – 4000°C.

The general formula of intersitial carbides are MC or M_2C.

For example :

WC, TaC, Ta_2C, W_2C, V_2C, Nb_2C

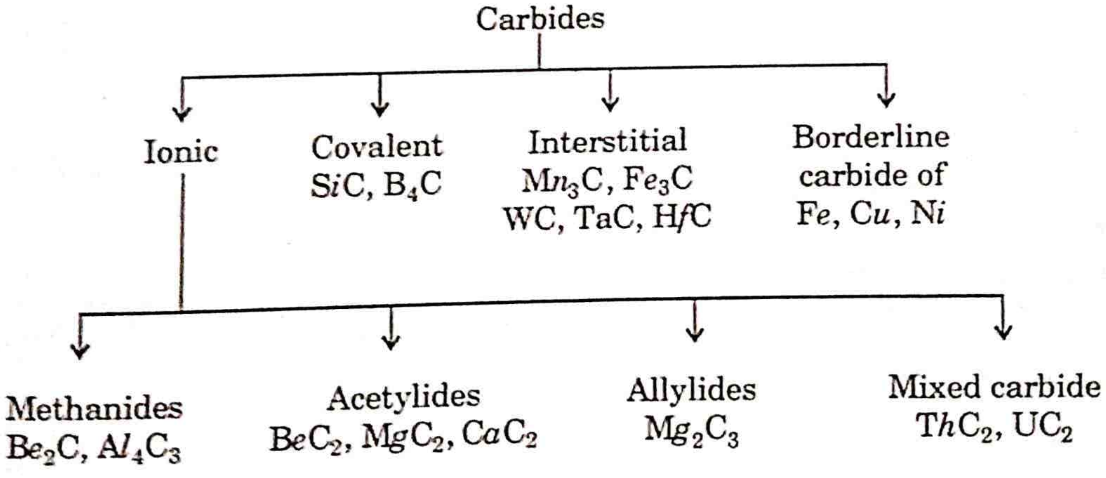
TiC, ZrC, HfC, VC etc.

The hardness of carbides is very-very high ∴ generally used for cutting tools.

4. Border line Carbides : These carbides are intermediate between ionic and interstitial carbides.

These are formed by heating the metals such as Fe, CO, Ni, Mn and Cr, because their radius is less than 135 pm, so that carbon atom can accomodated easily in their interstitial sitc. These carbides produces a greater deal of distortion, so they are less stable and highly reactive. They easily hydrolysed by the dilute minerals acids and give mixture of hydrocarbons and H_2 etc.

Flow Chart of Carbides



GROUP–15

The elements of group–15 are Nitrogen – (N), phosphorous - (P), Arsenic (As), Antimony (S*b*) and Bismuth (B*i*).

N and P are non metals, As and S*b* are metalloids and B*i* is the metal.

Occurance

Nitrogen is widely present in nature both in free state as well as in combined state. In free state, it is 75% by weight and 80% by volume in air, while in combined state, It is found as chile salt petre and Indian salt petre.

Phosphorous is found in the form of minerals such as apatite – $3Ca_3(PO_4)_2 . CaX_2$

Here X is F, C*l* and OH, if X is F then

$3Ca_3(PO_4)_2 . CaF_2$	Fluoro apatite
$3Ca_3(PO_4)_2 . CaCl_2$	Chloro apatite
$3Ca_3(PO_4)_2 . Ca(OH_2)$	Hydroxy apatite

Elements arsenic exist as arsenical nickle. (AsN*i*) and arsenical iron AsFe.

The elements antimony and bismuth exist as stibinite (Sb_2S_3) and bismuthite (Bi_2S_3).

Comparative study of an elements of group – 15.

Electronic configuration

The general electronic configuration of an elements of group – 15 given as $ns^2\ np^3$. These elements have only three electrons in *p*-orbitals and two electrons in *s*-orbital.

The electronic configuration of an elements of group–15 given in the table – 13.

Table - 7 Electronic Configuration of group 15 elements.

Element	Symbol	Atomic No.	Electronic Configuration
Nitrogen	N	7	$[He]\ 2s^2\ 2p^3$
Phosphorus	P	15	$[Ne]\ 3s^2\ 3p^3$
Arsenic	As	33	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$
Antimony	S*b*	51	$[Kr]\ 4d^{10}\ 5s^2\ 5p^3$
Bismuth	B*i*	83	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$

General Characteristics of elements of Group – 15

The important data of physical properties of an elements of group – 15 given in the table – 14

Table - 14, Physical Parameter of group 15 elements

	N	P	As	S*b*	B*i*
Atomic number	7	15	33	51	83
Atomic radius (*pm*)	70	110	120	140	150
Ionic radius (*pm*)	171 (N^{3-})	212 (P^{3-})	222 (As^{3-})	76 (Sb^{3+})	103 (Bi^{3+})
Ionisation energy IE$_1$	1402	1012	947	834	703

Oxides :

(i) All these elements form oxides of formula E_2O_3, E_2O_4 and E_2O_5.

(ii) Nitrogen forms a wide range of oxides of the formula N_2O, NO, N_2O_3, N_2O_4 and N_2O_5.

(iii) For a oxides of given oxidation state the basic nature of oxides generally increases because due to increase in metallic character. The order of acidic to basic nature given as in table – 20.

Table - 20 Nature of Oxides of elements of group – 15

N_2O_3	Acidic
P_2O_3	Acidic
As_4O_6	Amphoteric
Sb_4O_6	Amphoteric
Bi_2O_3	Basic

(iv) The acidic nature of oxides increase with increase in oxidation number of an elements as given in table 21.

Table - 21 Nature of oxides of an elements of group – 15

N	$\underbrace{N_2O, NO}_{\text{Neutral}}$	$\underbrace{N_2O_3, N_2O_4, N_2O_5}_{\text{Acidic Nature Increases}}$	$\downarrow$ Basic nature increases and acidic nature decreases
P		$\underbrace{P_4O_6, P_4O_8, P_4O_{10}}_{\text{Acidic Nature Increases}}$	
As		$\underbrace{As_4O_6, As_4O_8, As_4O_{10}}_{\text{Acidic Nature Increases}}$	
Sb		$\underbrace{Sb_4O_6, Sb_4O_8, Sb_4O_{10}}_{\text{Acidic Nature Increases}}$	
Bi		$\underbrace{Bi_2O_3, Bi_2O_4, Bi_2O_5}_{\text{Acidic Nature Increases}}$	

Oxides of Nitrogen

Nitrogen forms a number of oxides. The oxides of nitrogen are :

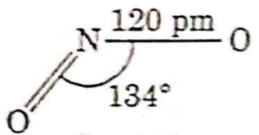
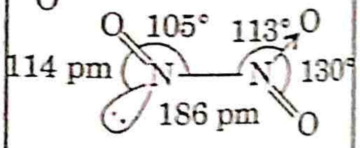
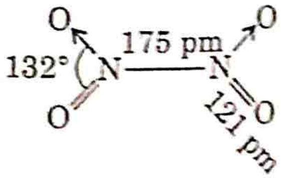
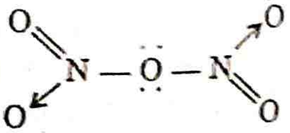
(i) Nitrous oxide, N_2O (ii) Nitric oxide, NO

(iii) Nitrogen trioxide, N_2O_3 (iv) Nitrogen tetroxide or dioxide, N_2O_4 and NO_2

(v) Nitrogen pentoxide, N_2O_5.

The names and formulae of oxides of nitrogen given in the table – 22.

Table - 22 Oxides of Nitrogen with Oxidation State and Structure

Oxides	Oxidation no of element	Property	Structure
N_2O	+1	Colourless gas with pungent smell, causes laughing hysteria	$N\equiv N-O$ 113 pm 119 pm
NO	+2	Colourless gas, paramagnetic	$:N\overset{\cdot}{=}O:$ 115 pm
NO_2	+4	brown gas with pungent odour	
N_2O_3	+3	blue liquid	
N_2O_4	+4	colourless, diamagenetic	
N_2O_5	+5	colourless ionic solid sublimes at 305 K to give gaseous molecule	

Calculation of number of bonds in the oxides of nitrogen and construction of their structures.

Method :

(i) Count the total number of atoms in the oxide of nitrogen.

(ii) Then multiply by 8.

(iii) Subtract the total numbers of valence electrons of all the atoms from 8 × No. of atoms.

(iv) Then devide the difference with two

(v) So, total number of bonds formed between the nitrogen and oxygen of oxide can be calculated.

Formula, to calculate number of bonds.

$$\text{Number of bonds} = \frac{8 \times \text{Total number of atoms} - \text{Total number of valence electrons of all the atoms}}{2}$$

For example : To calculate the number of bonds formed between N and O in NO.

By using formula, we have

$$\text{Number of bonds formed} = \frac{8 \times 2 - 5 - 6}{2} = 2.5$$

Thus number of bonds formed between N and O is 2.5

$$N \dot{=} O$$

The structure of various oxides of nitrogen discussed one by one.

(i) Nitrous oxide or Laughing gas, N_2O

Preparation : It is prepared by heating ammonium nitrate

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

Properties :

1. It is colourless gas with pungent smell.
2. It has sweet taste.
3. It is sparingly soluble in cold water.
4. It is neutral toward litmus.
5. On inhaling it cause hysterious laughing. ∴ its name is laughing gas, on inhaling in excess, it may produce insensibility.

Uses :

1. It is used as anaesthetic agent in dental in the form of mixture N_2O and O_2.
2. It is used as propellant gas in whipped bombs.

Structure : N_2O is a linear and unsymmetrical molecules. It is a resonance hybrid of two structure as shown in fig. 117. It is isoelectronic with CO_2 and its dipole moment is 0.116 D.

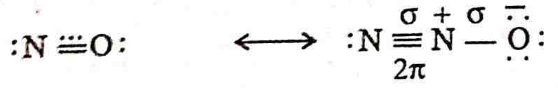


Fig. 117 **Resonating structure of N_2O**

(ii) Nitric Oxide – NO

Preparation :

1. **Laboratory Method :** It is prepared by the action of dilute–HNO_3 on copper.

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

2. **Electric arc Method :** By reacting N_2 and O_2 in electric arc.

$$N_2 + O_2 \xrightleftharpoons{\text{electric arc}} 2NO$$

Properties :

1. It is colourless gas, springly soluble in water.
2. It can be liquefied at low temp. and high pressure.
3. It is paramagnetic in nature due to presence of unpaired e^-.
4. It is neutral toward litmus.
5. It reacts with O_2 and to form brown fumes of NO_2.

$$2NO + O_2 \rightarrow 2NO_2$$

Uses :

1. It is used as in the manufacture of nitric acid.
2. It is used as catalyst for the synthesis of H_2SO_4.

Structure : The molecule NO is linear with a bond order of 2.5 (fig. 118)

***Fig. 118. Structure of* NO**

It is of paramagnetic in nature. It is a resonance hybird of (fig. 119) following structure

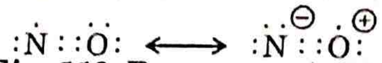


***Fig. 119. Resonance in* NO**

In solid and liquid state it exist as a dimer due to pairing of unpaired e^- as shown in fig.

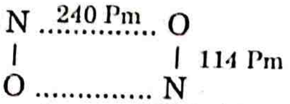


Fig. Structure of* NO *(l) or* NO *(s)

(iii) Dinitrogen trioxide or Nitrogen sesquioxide or Nitrous anhydride, N_2O_3 (Fig. 120)

Preparation :

1. **Reduction method :** In this method As_2O_3 reduced with nitric acid

$$As_2O_3 + 2HNO_3 + 2H_2O \rightarrow 2H_3AsO_4 + N_2O_3$$

2. Mixture of NO and NO_2 can be obtained by the reaction of (6N) nitric acid on Cu

$$2Cu + 6HNO_3 \rightarrow 2Cu(NO_3)_2 + \underbrace{NO + NO_2}_{N_2O_3} + 3H_2O$$

Properties :

1. It exist as blue coloured liquid at – 30°C. The N_2O_3 decomposed at room temp. and give NO and NO_2.

$$N_2O_3\,(l) \xrightarrow[\text{temp.}]{\text{room}} \underbrace{NO + NO_2}_{\text{Brown coloured gas}}$$

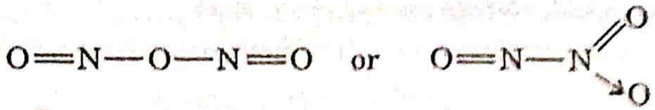
2. On reaction with water, N_2O_3 give nitrous acid

$$N_2O_3 + H_2O \rightarrow HNO_2$$

3. It react with alkalies and give nitrite

$$N_2O_3 + 2NaOH \rightarrow 2NaNO_2 + H_2O$$

Structure : N_2O_3 is unstable in liquid and gaseous state and decomposes into NO and NO_2 and thus it may be assumed to have the following electronic structure. (fig. 120) It is diamagnetic in nature.



Symmetrical form Asymmetrical form

Fig. 120. Structure of N_2O_3

(iv) Nitrogen dioxide, NO_2 or Nitrogen tetroxide, N_2O_4 : In gaseous state, it exist as NO_2, but in solid state it exist as N_2O_4 i.e. dimeric form of NO_2.

$$\underset{\text{Brown gas}}{2NO_2} \xrightleftharpoons{-10^\circ C} \underset{\text{Colourless liquid}}{N_2O_4}$$

Preparation :

1. It is synthesized by the action of conc. HNO_3 on Cu, Ag and Pb.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

2. By heating the nitrate of heavy metal

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

NO_2, condensed as a pale yellow liquid.

3. It is prepared by the oxidation of NO

$$2NO + O_2 \rightarrow 2NO_2$$

Properties :

1. It is brown coloured gas with pungent odour. It exist as dimer (N_2O_4) in liquid and solid form at low temperature.
2. On heating at temp. of 600°C,it decomposes as NO, and O_2

$$\underbrace{2NO_2}_{\text{Brown gas}} \rightleftharpoons \underbrace{2NO + O_2}_{\text{Colourless mixture}}$$

Uses : It is used as (i) manufacture of HNO_3 (ii) as a catalyst in the synthesis of H_2SO_4

Structure : NO_2 molecule possesses V-shaped structure with O—N—O bond angle 134° and N—O bond length of about 120 pm which is intermediate between a single (N—O) and a double (N = O) bond. Hence, NO_2 is supposed to be a resonance hybrid of the following two structures. (fig. 121).

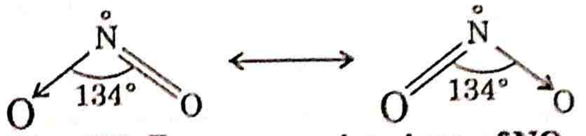


Fig. 121. Resonance structure of NO_2

The molecule has an odd electron and thus paramagnetic in nature. Due to odd electron, it is coloured and has a tendency to polymerise to form a colourless planar dimer, N_2O_4 diamagnetic in nature. (Fig. 122)

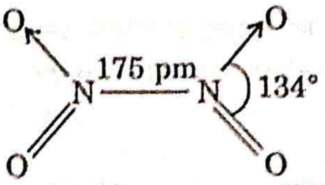


Fig. 122. Structure of N_2O_4

(v) Nitrogen pentoxide, *Nitric anhydride*, N_2O_5

Preparation : It is synthesized by distilling conc. nitric acid with P_2O_5.

$$2HNO_3 \rightarrow H_2O + N_2O_5$$

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

$$\overline{P_2O_5 + 2HNO_3 \rightarrow 2HPO_3 + N_2O_5}$$

Structure : In the gaseous state, it exists as a symmetrical molecule having the structure $O_2N—O—NO_2$. The N—O—N bond is almost linear.(fig. 123) X-ray studies reveals the ionic nature of solid N_2O_5 i.e., nitronium nitrate, $NO_2^+ NO_3^-$.

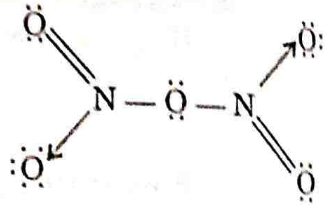


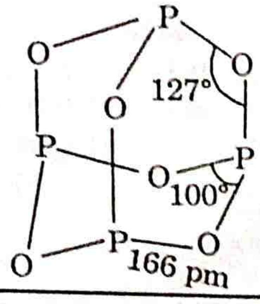
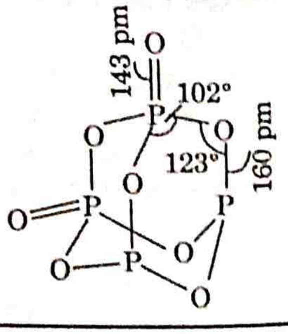
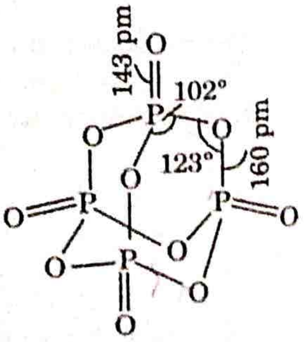
***Fig. 123* Structure of N_2O_5**

Oxides of Phosphorous : The important oxides of phosphorous are :

(i) Phosphorous trioxide, P_2O_3 or P_4O_6
(ii) Phosphorous tetrodixe, P_2O_4 or P_4O_8
(iii) Phosphorous pentoxide, P_2O_5 or P_4O_{10}

The oxides of phosphorous exist as dimers and given in the table – 23.

Table - 23 Oxides of Phosphorous

P_4O_6	+3	waxy soild, garlic odour	
P_4O_8	+4	Colourless soild, mixed anhydride	
P_4O_{10}	+5	white crystalline soild, odourless when pure	

(i) Phosphorous trioxide – P_4O_6

Synthesis : It is prepared by burning of phosphorous in limit supply of air

$$P_4 + O_2 \rightarrow P_4O_6$$

Properties :

1. It is colourless waxy solid with garlic odour and poisonous nature.
2. It is soluble in organic solvent such as chloroform and benzene
3. It decomposes on heating

$$4P_4O_6 \rightarrow 3P_4O_8 + \underset{\text{Red}}{4P}$$

4. It oxidises in air and to produce P_4O_{10}

$$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$$

5. It burns with Cl_2 and give $POCl_3$ and PO_2Cl

$$P_4O_6 + 4Cl_2 \rightarrow \underset{\text{Phosphorous Oxychloride}}{2POCl_3} + \underset{\text{Metaphosphorous Oxychloride}}{2PO_2Cl}$$

6. On dissolving in cold water and give H_3PO_3

$$P_4O_6 + \underset{\text{(Cold)}}{6H_2O} \rightarrow 4H_3PO_3$$

But in hot water, it gives violent reaction

$$P_4O_6 + \underset{\text{(Hot)}}{6H_2O} \rightarrow 3H_3PO_4 + PH_3$$

Structure of Phosphorus oxide : The vapour density data corresponds to the formula P_4O_6. In the molecule, the phosphorus atoms lie at tetrahedral positions with respect to each other and the 6 oxygen atoms are inserted between them. Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms. The bond length of P—O bond is 166 pm. Fig. 124

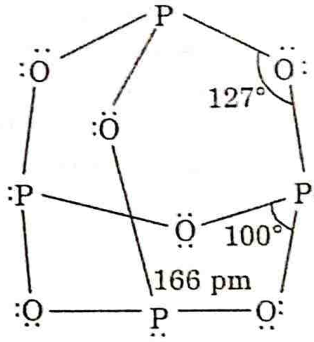


Fig. 124. Strcuture of P_4O_6

2. **Phosphorous tetroxide – P_4O_8**

Properties :

1. It is colourless solid
2. It is mixed hydride because on reaction with water it gives H_3PO_3 and H_3PO_4

$$P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$$

Structure : The structure of P_4O_8 similar to the structure of P_4O_6, the P_4O_8 has in addition, two P–atoms form coordinate bonds with their lone pair of electrons to two oxygen atom as shown in fig. 125.

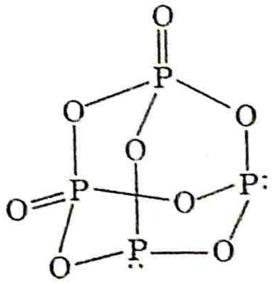


Fig. 125. Structure of P_4O_8

3. **Phosphorous pentoxide, P_4O_{10}**

Synthesis :

1. It is synthesized by heating phosphorous in free supply of air

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It is purified by sublimation. It is also called as flower of phophorous, due to there collection in the form of snowy powder.

Properties :

1. It is white crystalline substance and it is odourless in pure state.
2. It has garlic odour due to presence of small amount of impurites.
3. It sublimes on heating.
4. In the presence of water, it gives a series of reaction products as shown.

$$P_4O_{10} \xrightarrow{2H_2O} 4HPO_3 \xrightarrow{2H_2O} 2H_4P_2O_7 \xrightarrow{2H_2O} 4H_3PO_4$$

$$P_4O_{10} + 6H_2O \rightarrow 4H_3\,PO_4$$

5. It is used as powerful dehydrating agent. It removes water from
   (i) $P_4O_{10} + 2H_2SO_4 \rightarrow 2SO_3 + 4HPO_3$
   (ii) $P_4O_{10} + 4HNO_3 \rightarrow 2N_2O_5 + 4HPO_3$
   (iii) $P_4O_{10} + 4CH_3\,COOH \rightarrow 2\,(CH_3CO)_2O + 4\,HPO_3$
6. On heating with carbon, it form red phosphorous

$$P_4O_{10} + 10C \rightarrow 10CO + 4P$$

7. P_4O_{10} fuse with basic oxides, it form phosphates

$$P_4O_{10} + 6CaO \rightarrow 2Ca_3(PO_4)_2$$

Uses : As a dehydrating agent.

Structure of Phosphorus pentoxide : Its vapour density data corresponds to formula P_4O_{10}. The structure is similar to P_4O_6 with a difference that each phosphorus atom is also linked with an additional oxygen atom with the help of a coordinate linkage by lone pair of electron present on P atom. Fig. 126.

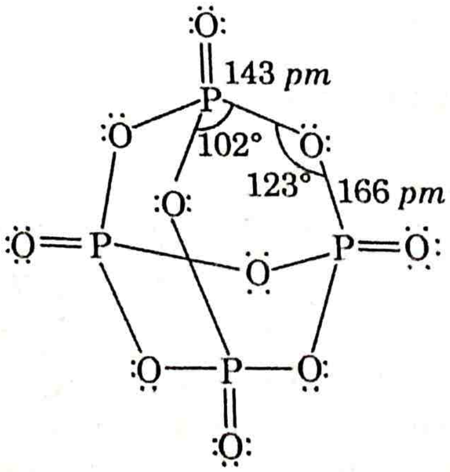
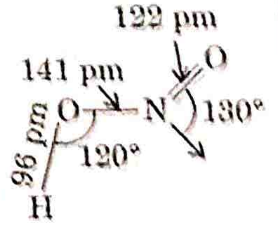


Fig. 126 Structure of P_4O_{10}

Oxoacids of Nitrogen

Nitrogen form large numbers of oxoacids some of oxoacids of nitrogen are unstable while some oxoacids are stable. The important oxoacids of nitrogen given in the table. 23

Table - 23 : Important Oxoacids of Nitrogen

Name	Formula	Oxidation state of nitrogen	Special Characteristic	Structure	Acid anhydride of oxoacid
Hyponitrous acid	$H_2N_2O_2$	+1	weak, dibasic acid, exist in cis and trans forms		N_2O
Nitroxylic acid	$H_2N_2O_4$	+2	explosive	—	—
Nitrous acid	HNO_2	+3	unstable, weak mono basic acid	H — O — N = O	N_2O_3
Nitric acid	HNO_3	+5	Stable, strong mono basic acid		N_2O_5
Peroxonitric acid	HNO_4	+7	unstable, explosive	—	—

1. **Hyponitrous acid, $H_2N_2O_2$:** In $H_2N_2O_2$ the oxidation state of nitrogen is + 1

Properties :

(i) It is white crystalline soild.

(ii) It explode on heating.

(iii) Its aqueous solution is unstable in nature and decomposes in the following manner

$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

(iv) It air it gives HNO_2 and HNO_3

$$2H_2N_2O_2 + 3O_2 \rightarrow 2HNO_2 + 2HNO_3$$

(v) It behave as weak dibasic acid

Structure : $H_2N_2O_2$ has the following structure (fig. 127)

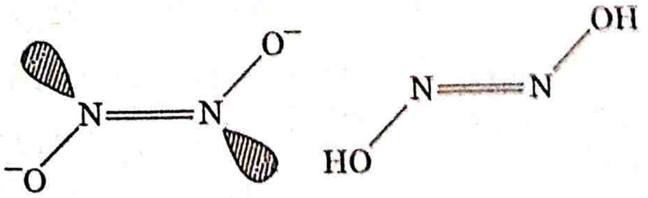


Fig. 127. Structure of $\boldsymbol{H_2N_2O_2}$

Its structure analysed from the study of IR–spectra of their silver salt.

Oxoacids of phosphorous

Phosphorous form two types of oxoacids :

(i) In this, the oxidation state of phosphorous is +1 or + 3 *i.e.* phosphorous acid

(ii) While in other, oxidation state of phosphorous are +4 and +5 *i.e.* phosphoric acid.

2. By boiling PCl_5 with H_2O

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

3. **Laboratory Method :** By heating P_4 with conc. HNO_3.

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 4H_2O + 20NO_2$$

4. **Commercially,** By decomposing $Ca_3(PO_4)_2$ with H_2SO_4

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$$

Properties :

1. It is transparent, crystalline solid.
2. It is highly soluble in water.
3. In the presence of heat it decomposes as

$$2H_3PO \xrightarrow[-2H_2O]{250°C} H_4P_2O_7 \xrightarrow{600°C} 2HPO_3 \xrightarrow{600°C} HPO_3 + 2H_2O$$

$$4H_3PO_4 \xrightarrow{\text{Strong heat}} P_4O_{10} + 6H_2O$$

4. **Acidic Nature :** It is tribasic acid. It forms three series of salts

$$\underset{\text{Salt} \longrightarrow}{H_3PO_4} \rightleftharpoons \underset{NaH_2PO_4}{H^+ + H_2PO_4^-} \rightleftharpoons \underset{Na_2HPO_4}{2H^+ + HPO_4^{2-}} \rightleftharpoons \underset{Na_3PO_4}{3H^+ + PO_4^{3-}}$$

5. It react with iodide and bromide ion and gives :

$$3NaI + H_3PO_4 \rightarrow Na_3PO_4 + 3HI$$

$$3NaBr + H_3PO_4 \rightarrow Na_3PO_4 + 3HBr$$

6. It form ammonium phosphomolybdate when heated with conc. HNO_3 and ammonium molybdate (Test for PO_4^{3-} ion)

$$H_3PO_4 + 21HNO_3 + \underset{\text{ammonium molybdate}}{12(NH_4)_2MoO_4} \rightarrow \underset{\text{ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Uses :

1. It is used for synthesis of HBr and HI.
2. It act as stabilizer for H_2O_2.
3. It is used for making phosphate fertilizers.

Structure : From the analysis, its structure is given as, in fig. 136.

It is tribasic acid due to presence of three P—OH bonds.

The crystal structure of H_3PO_4 is in the form of layers in which PO_4 units bonded via hydrogen bonds as shown in fig. 137.

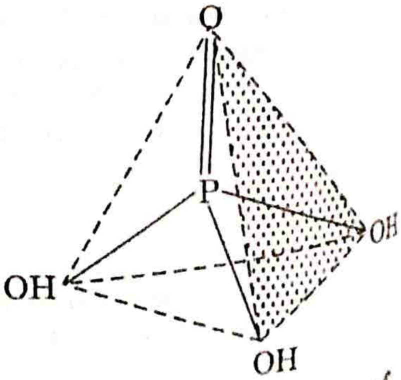


Fig. 136. Structure of H_3PO_4

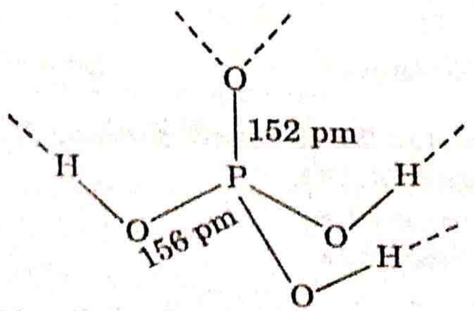


Fig. 137. H—bonding in H PO

GROUP - 16, THE OXYGEN FAMILY

The elements of Group–16 are oxygen–(O), Sulphur–(S), Selenium–(Se), Tellurium–(Te) and polonium–(Po). The elements O, S, Se and Te are non-metallic in nature while Po is metallic in nature.

Occurance

Oxygen is the most abundant element in nature. In free state oxygen form 21% by volume of air and in combined state it form 89% by weight of ocean and 46.6% of earth crust mainly as silicates. Element sulphur is less abundant is about–0.052% of earth crust.

The other elements of this group found in rare amount. Their abundance ratio given as in Table–25

Table–25 Natural abundance of an elements of group–16

Elements	**O**	**S**	**Se**	**Te**	**Po**
Abundance (ppm)	4.6×10^5	5.2×10^2	9×10^{-3}	2×10^{-3}	Radioactive in nature

Comparative study of an elements of Group–16

Electronic Configuration

The general electronic configuration of an elements of group–16 given as ns^2np^4. These elements have only four electrons in p–orbitals and two electrons in S-orbital.

The electronic configuration of an elements of group–16 given in the table–26

Table–26 Electronic configurations of group 16 elements.

Element	**Atomic No.**	**Electronic Configuration**
Oxygen, O	8	$[He]\ 2s^2\ 2p^4$
Sulphur, S	16	$[Ne]\ 3s^2\ 3p^4$
Selenium, Se	34	$[Ar]\ 3d^{10}\ 4s^2\ 4p^4$
Tellurium, Te	52	$[Kr]\ 4d^{10}\ 5s^2\ 5p^4$
Polonium, Po	84	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$

General characteristics of elements of group–16

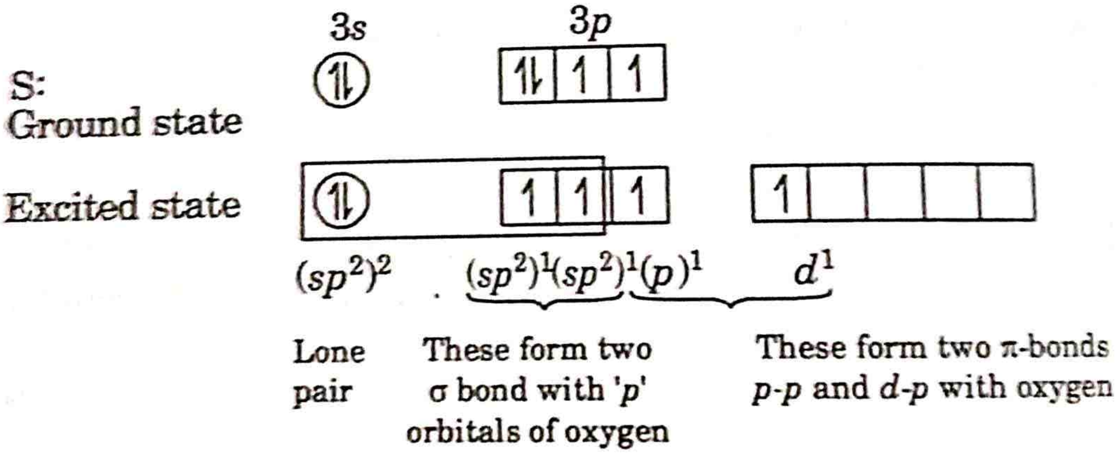
The important data of physical porperties of an elements of group–16 given in the table–27

Property	**Oxygen**	**Sulphur**	**Selenium**	**Tellurium**	**Polonium**
Atomic number	8	16	34	52	84
Atomic radius (Pm)	73	109	116	135	–
Ionic (M^{2-}) radius, (Pm)	140	185	198	221	
Ionisation energy (KJ mol^{-1})	1310	1000	940	868	–
Electronegativity	3.5	2.5	2.4	2.1	2.0

Oxide of Sulphur :

Sulphur dioxide, SO_2

Structure : S atom is SO_2 involves sp^2 hybridization



However, the bond angle O–S–O (119°) is lesser than 120° because of lone pair of electron on sulphur. Furthermore, since both the S–O bonds are identical in length (143 Pm) inspite of different overlapping (*p-p* and *d-p*), SO_2 is supposed to have the resonance hybrid of following structures. Fig. 179

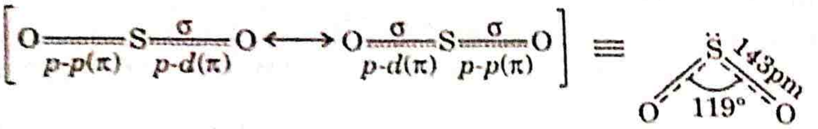


Fig. 179 Structure of SO2

The linear geometry is drawn for the sake of convenience.

Sulphur trioxide – SO_3

Structure

S atom in SO_3 involves sp^2 hybridization

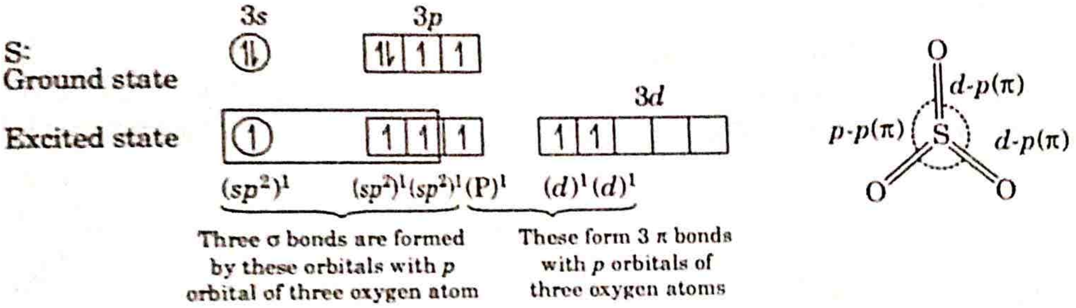


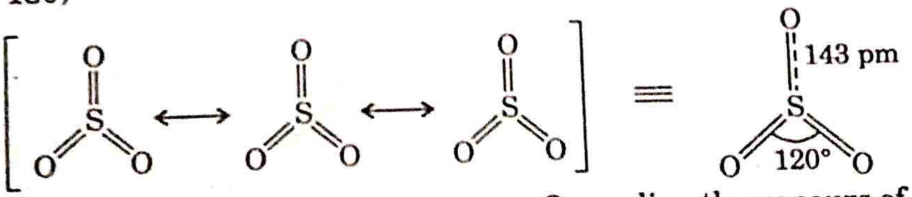
Fig.–180 Structure of SO_3

Thus, SO_3 is represented as

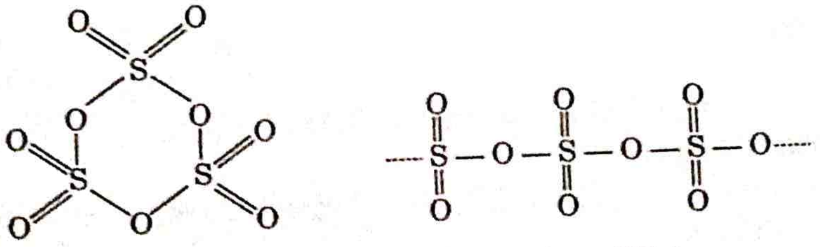
3σ bonds of S–O are of sp^2–*p* overlapping

3π bonds of S–O are of *p–p*, *d-p* overlapping.

However, since all the three bonds are identical in length (143 Pm) inspite of different overlapping [*p–p* and *d–p* (π)], SO_3 is supposed to have resonance hybrid of the following structures. (fig. 180)



Sulphur trioxide exists in three distinct forms. On cooling the vapours of SO_3, liquid SO_3 freezes to ice-like solid (*m.pt* 16.85°) i.e., γ – SO_3, a cyclic trimer S_3O_9 (a). On keeping it in presence of traces of moisture, it changes into two silky asbestos–like forms, β–SO_3 and α–SO_3. β–SO_3 have infinite helical chains made up of linked SO_4 (tetrahedral) (b) and the α-SO_3 having similar chains cross–linked into sheets. fig. 181.



(a) S_3O_9

(b) β-SO_3 or $(SO_3)n$

Fig. 181 Structure of SO_3 (a) and (b)

Hydrogen peroxide, H_2O_2 : It is discovered by the Thenard and its name also as oxyzenated water.

Physical porperties–

1. Anhydrous H_2O_2 is colourless, viscous liquid. It is soluble in water, ether and alcohol.
2. H_2O_2 is less volatile, due to presence of intermolecular H–bonding.
3. It is more dense (1.45 g/ml at 0°C) than water.
4. It form hydrate with water, $H_2O_2 . H_2O$.
5. H_2O_2 is diamagnetic in nature. It's aqueous solution are good solvent, due to their high value of dielectric constant (93.8).

Chemical properties of H_2O_2 :

1. Stability : It decomposes on standing and heating sowing an example of auto oxidation-reduction.

$$\begin{array}{lccc} & 2H_2O_2 & \rightarrow & 2H_2O + O_2 \\ \text{Oxidation Number of oxygen} & (-1) & \rightarrow & (-2) \quad (0) \end{array}$$

Presence of traces of MnO_2, carbon, alkali or finely divided metals like Pt, Au, Ag accelerates its decomposition.

2. Acidic nature : Pure H_2O_2 has weak diacidic nature but its aqueous solution is neutral towards litmus. It reacts with alkalies to form salts.

$$H_2O_2 + 2NaOH \rightarrow Na_2O_2 + 2H_2O$$

$$H_2O_2 + Ba(OH)_2 \rightarrow BaO_2 + 2H_2O$$

3. Oxidizing nature : H_2O_2 is a powerful oxidant in acidic as well as in alkaline medium.

(in acid) $\quad H_2O_2 + 2H^+ + 2e^- \xrightarrow{\text{fast}} 2H_2O \quad E^\circ_{RP} = 1.77\text{ V}$

(in alkali) $\quad H_2O + HO_2^- + 2e^- \xrightarrow{\text{slow}} 3OH^- \quad E^\circ_{RP} = 0.87\text{ V}$

Thus, H_2O_2 is more powerful oxidant in acidic medium. The simple interpretation of H_2O_2 as oxidant can be shown by the equation.

$$H_2O_2 \rightarrow H_2O + [O]$$

Following are some important examples of oxidant action of H_2O_2.

a. H_2O_2 oxidises black lead sulphide (PbS) to white lead sulphate ($PbSO_4$)

$$\begin{array}{rcl} 4[H_2O_2 & \rightarrow & H_2O + O] \\ PbS + 4\,[O] & \rightarrow & PbSO_4 \\ \hline PbS + 4H_2O_2 & \rightarrow & PbSO_4 + 4H_2O \end{array}$$

Structure of H_2O_2

From the data obtained by x-ray analysis. It has been confirmed the presence of O–O linkage (peroxide linkage). The value of dipole moment suggests that the four atoms in H_2O_2 are non-planer. The IR analysis revealed that the structure having two leaves at 90°.

The H–atoms are placed on each cover, the H–O bond angle is of 96° with O–O link. The O–O bond length is 148 pm and O–H bond length is 95 pm.

The different parameters in the structure given as fig. 195

O–O bond length	148 pm
O–H bond length	95 pm
O–O–H bond angle,	96°

Angle between planes containing H–atoms, 94°

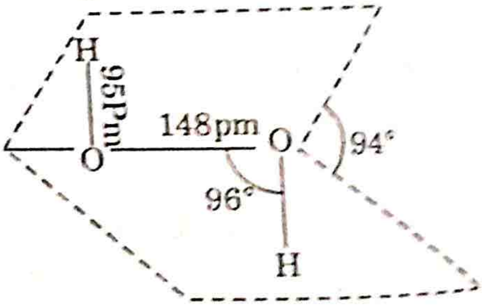


Fig. 195 Structure of hydrogen peroxide

Uses :

Aqueous solution of hydrogen peroxide is used as,

1. As germicide and antiseptic for wounds, teeth and ears.
2. As bleaching agent for wool, hair and other soft materials.
3. As preservative for milk and wine.
4. As fuel for rocket, submarine and torpedo.
5. In refreshing old oil paintings due to the formation of black PbS. H_2O_2 converts it into white $PbSO_4$

$$\underset{\text{White}}{PbO} + H_2S \rightarrow \underset{\text{Black}}{PbS} + H_2O$$

$$PbS + 4H_2O_2 \rightarrow \underset{\text{(white)}}{PbSO_4} + 4H_2O$$

6. As antichlor to remove traces of chlorine and hypochlorite.

GROUP-17 : THE HALOGEN FAMILY

The elements of Group–17 are fluorine–(F), chlorine–(Cl), Bromine–(Br), Iodine–(I) and Astatine (At). These elements are collectively known as halogens because their salts usually found in sea water.

(In Greek word–Halo means, Sea salt producer)

Occurance

All the elements of halogen family are highly electronegative and thus are very reactive. Therefore, not found in free state in nature. The important combined state of fluorine are cryolite, (Na_3AlF_6), fluorspar (CaF_2) and fluorapatite [$3Ca_3(PO_4)_2$, CaF_2].

The main source of chlorine are rock salt (NaCl), sylvine (KCl) and horn silver (AgCl). The important sources of bromine are lakes salt like (NaBr, KBr, $MgBr_2$) and Bromargyrite (AgBr) while Iodine is fused with chile salt petre ($NaNO_3$) in this it exist as 0.2% $NaIO_3$ (Sodium Iodate). The element astatine is radioactive in nature and has a short half life. The abundance of halogens in earth crust given below in Table–40.

Table 40–% abundance of Halogens

Elements	F	Cl	Br	I	At
Abundance (ppm)	800	480	2	0.33	–

Comparative study of an elements of group – 17.

The general electronic configuration of an elements of group – 17 given as ns^2np^5. These elements have only five electrons in p-orbitals and two electrons in s–orbital. The electronic configuration of an elements of group–17 given in the table–41.

Basic properties of Halogens

In the periodic table, metallic or basic properties of an elements increase on desending a group. Thus trend in basic properties of group 17 given as :

(i) Fluorine is most electronegative elements and posseses no basic properties.

(ii) Chlorine show slightly basic character.

(iii) Bromine show higher basic properties.

(iv) Iodine show strong basic character *i.e.* the tendency of iodine atoms to form cations.

Evidence for basic character of chlorine :

(i) Cl_2^+, ion can be obtained in discharge tube

(ii) $|Cl_3|^+$ can also be prepared as

$$ClF_3 + Cl_2 + AsF_5 \rightarrow [Cl_3]^+ [AsF_6]^- + F_2$$

Evidence for basic character of Bromine.

(i) $[Br_2]^+$ can be prepared by treated Br_2 with SbF_5 in the presence of BrF_5

$$SbF_5 + Br_2 \xrightarrow{BrF_5} [Br_2]^+ [Sb_3F_{16}]^-$$

(ii) $[Br_2]^+$ can be synthesized by the reaction of BrF_3 with Br_2 in the presence of AsF_5

$$BrF_3 + Br_2 + AsF_5 \rightarrow [Br_3]^+ [AsF_6]^- + F_2$$

Evidence in existence of I^+

1. I^+ is obtained, during electrolysis of ICl. When electrolysis of molten ICl is carried out the following ions are formed

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

2. Similarly it can be obtained from IBr

$$IBr \rightleftharpoons I^+ + Br^-$$

3. Positive I, is present in stable complexes of pyridine :
   I (pyridine) NO_3
   I (pyridine)$_2$ NO_3
   I (pyridine)$_2$ ClO_4
   I (pyridine) *acetate*
   I (pyridine) *benzoate*

4. *It is also formed by ionization of* ICN *in pyridine*

$$ICN \rightleftharpoons I^+ + CN^-$$

5. It is also obtained from HIO, hypoiodous acid

$$HOI \rightleftharpoons H^+ + IO^-$$

$$HOI \rightleftharpoons OH^- + I^+$$

Evidence for existence of I^{3+} Ion

1. Molten ICl_3, conducts electricity liberating Iodine and chlorine at both electrodes. Thus, its ionisation is probably

$$2\ ICl_3 \rightleftharpoons ICl^+_2 + ICl_4^-$$

Both ICl_2^+ and ICl_4^- contains I^{3+} ions.

2. It is also obtained by the oxidation of iodine by forming nitric acid in acetic anhydride, so I (acetate)$_3$ is formed. This on electrolysis using silver electrode give I^{3+}.

$$I\ (\text{acetate})_3 \rightleftharpoons I^{3+} + 3\ (\text{acetate})^-$$

3. It is also obtained by treating iodine with ozonised oxygen.

$$I_2 + O_3(O_2) \rightleftharpoons I^{3+}\ (IO_3)_3^{3-}$$

4. When iodine is dissolve in oleum, I^{3+} ions are formed

$$\underset{(H_2S_2O_7)}{I_2 + \text{oleum}} \rightleftharpoons I^{3+}$$

5. It can also be obtained by reacting iodine with HSO_3F (Fluoro sulphonic acid)

$$I_2 + HSO_3F \rightleftharpoons I^{3+}$$

6. Moreover compounds containing I^{3+} can also be synthesised as

$$I_2 + ICl + AlCl_3 \rightarrow |I_3|^+\ [AlCl_4]^-$$

$$2I_2 + ICl + AlCl_3 \rightarrow |I_5|^+\ [AlCl_4]^-$$

Interhalogen Compounds

The binary compounds formed by halogens amongest themselves are known as Interhalogen compounds. This is because of different values of their electronegativities. The less electronegative element written first.

For example : ClF-chlorine fluoride. In ClF, Cl is less electronegative than F.

Classification : They are classified into four types on the basis of their formulae. The general formula of Interhalogen compounds are AX*n*.

Where *n*, is an odd number and X is always the lighter halogen. The formulae and name of some stable interhalogen compounds given in the table–51.

Table 51–Stable interhalogen compounds

Type			
AX	AX_3	AX_3	AX_7
ClF Chlorine fluoride	ClF_3 Chlorine trifluoride	ClF_5 Chlorine pentafluoride	
BrF Bromine fluoride	BrF_3 Bromine trifluoride	BrF_5 Bromine pentafluoride	
IF* Iodine fluoride	IF_3* Iodine trifluoride	IF_5 Iodine pentafluoride	IF_7 Iodine heptafluoride

Method of preparation of halogens

Following are the important methods of preparation of interhalogen compounds.

1. By the direct combination of halogens : All the interhalogens except IF_7, could be prepared by the direct combination of halogens under appropriate conditions.

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{250°C} 2ClF$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \rightarrow 2ClF_3$$

$$I_2 + \underset{\text{(equimolar)}}{Cl_2\text{(liquid)}} \rightarrow 2ICl$$

$$I_2 + \underset{\text{(liquid and excess)}}{3\,Cl_2} \rightarrow 2ICl_3$$

$$\underset{\text{(vapour)}}{Br_2} + \underset{\text{(dilute with } N_2)}{3F_2} \rightarrow 2BrF_3$$

$$I_2 + \underset{\text{(In freon as refrigerant)}}{3F_2} \xrightarrow[\text{temp.}]{\text{low}} 2IF_3$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

(ii) From lower helogens : It is possible to prepare higher interhalogens by the interaction of lower interhalogens with halogens

$$ClF + F_2 \rightarrow ClF_3$$

$$ClF_3 + F_2\text{(excess)} \xrightarrow{\Delta} ClF_5$$

$$BrF_3 + F_2 \xrightarrow{200} BrF_5$$

$$IF_5 + F_2 \xrightarrow{250°} IF_7$$

(iii) Miscellaneous Method : Some miscellaneous method have been given by the following examples :

$$KCl + 3F_2 \xrightarrow{200°C} KF + ClF_5$$

$$3I_2 + 5AgF \rightarrow 5AgI + IF_5$$

$$8F_2 + PbI_2 \rightarrow PbF_2 + 2IF_7$$

$$PbI_2 + 6F_2 \rightarrow PbF_2 + 2IF_5$$

General properties of inter halogens.

1. **Physical state;** The interhalogens compounds exist as gases, liquid or solid depending upon the types of interactive forces existing between them
   ClF, BrF, ClF_3, IF_7, *(gases)*
   BrF_3, BrF_5, IF_5 *(liquids)*
   ICl, IBr, ICl_3, IBr_3 *(solids)*
2. **Colour :** Interhalogen compounds sepecially contains fluorine are colourless, but those made up of heavier halogens are coloured.
3. **Polar in nature :** Interhalogen compounds are covalent in nature, but have some polarity. The polarity is due to difference in their electronegativity. Greater the difference in electronegativity more will be its polarity.
   For example

   $$\underset{2.5}{I^{+\delta}} \text{———————} \underset{4}{F^{-\delta}}$$

   The bond between I and F is highly polar, due to large difference in their electronegativties *i.e.* 4 – 2.5 = 1.5.
4. **Melting point and Boiling point.**
   M.Pt. and B.Pt. depends upon the magnitude of intermolecular force of attraction, that depend upon the values of electronegativity, greater the difference in electronegativity more will be its M.Pt. and B.Pt.
5. **Thermal stability :** The thermal stability of interhalogen compounds decrease, with decrease the electronegativities, difference between halogens. The difference in electronegativity and their order of stability given as

   $$I\text{–}F\ (1.5) > BrF\ (1.2) > ClF\ (1) > ICl\ (0.5) > IBr\ (0.3)$$
6. **Reactivity :** The reactivity of interhalogens compound is greater than halogens. This is because of presence of weak forces between different halogens. This can be explained by considering an example of ClF, In ClF, the bond formed by the overlapping of half filled 3p–orbital of chlorine and half filled 2p orbital of fluorine.

   $$F \quad 1s^2 2s^2 2px^2 2py^2 (2pz^1)$$

   $$Cl \quad 1s^2 2s^2 2p^6 3s^2 3px^2\ 3py^2\ (3pz^1)$$

   But $2p_Z$ (F) and 3Pz (Cl) are not equal in sizes, therefore, there overlapping become in effective, so that bond remain weak and cleaved easily (Fig. 216)

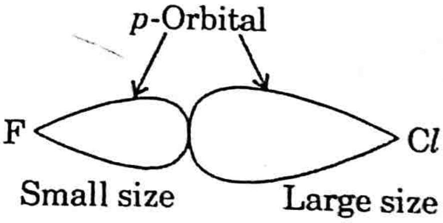


Fig. 216 overlapping of 2Pz (F) orbital with 3Pz (Cl) orbitals.

The order of reactivity of some interhalogens compounds has been found to be as

$$ClF_3 > BrF_3 > IF_7 > BrF_5 > IF_5 > BrF$$

7. **Self Ionisation :** In liquid state or in solution, the interhalogen compound, partically ionized, this is indicated by their specific conductance values.

HYDRO ACIDS OF HALOGENS

All the halogens react with hydrogen to form volatile covalent hydrides with a general formula of HX.

These hydrides are called hydracids.

Their characteristics physical parameter is given in the Table-53.

Oxoacids of chlorine

Chlorine forms large number of oxoacids in which oxidation state of *Cl* are +1, +3, +5 and +7. These oxoacids are given in table–55.

Trend in relative strength of oxoacids i.e. Acidic nature, thermal stability, oxidising Nature

1. Acidic nature of oxoacids of chlorine follow the order

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Explanation : This is due to increase in oxidation state of chlorine atom from +1 to +7, as hown in table – 56

Table - 56 Oxidation state of oxoacids of Chlorine

Acids	**$HClO$**	**$HClO_2$**	**$HClO_3$**	**$HClO_4$**
Oxidation state	+1	+3	+5	+7

Furthermore, the conjugate base of $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$ are ClO^-, ClO_2^-, ClO_3^- and ClO_4^- respectively. As the number of oxygen atoms increase, the –ve charge, dispersal become more and more from Cl–atom due to more electronegativity of oxygen atom and thus lesser is the charge on Cl–atom. Consequentely stability order of anion is $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$ as shown in resonance structure. (fig. 245)

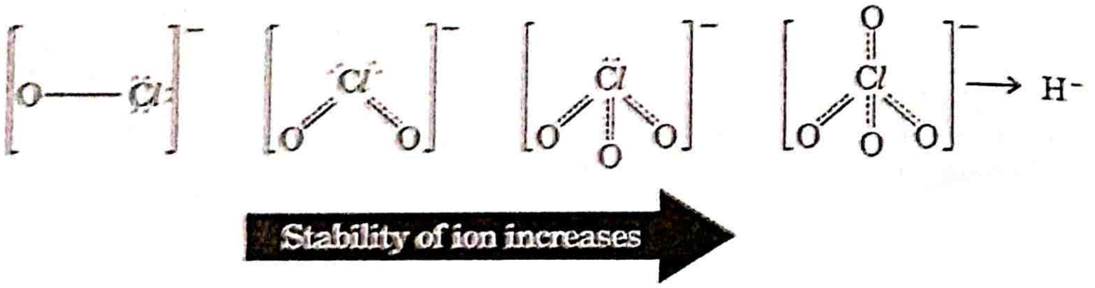


Fig. 245 Resonating structure of oxoacids anions of halogens

The acidic character of conjugate acid given as

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

(ii) The thermal stability of oxoacids of chlorine follow the order.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

It can be explained in term of oxidation state, less will be the oxidation state of chlorine, less will be the strength of Cl–OH, bonds. Thus $HClO_4$ is more thermally stable (+7, oxidation state) than $HClO$ (+1, oxidation state) fig. 246

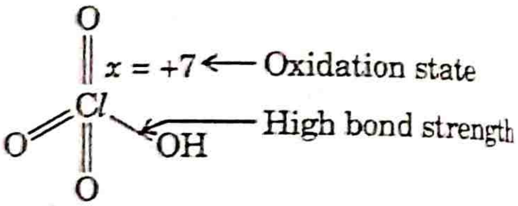


Fig. 246,. Bone length of Cl–OH, bond

(iii) Oxidising Power : The oxidising power of oxoacids follow the order

$$HClO_4 > HClO_3 > HClO_2 < HClO$$

Explanation : In can also explained in terms of oxidation state of halogen atom, greater the oxidation state of halogen, more will be its tendency to withdraw the electron towards itself given as the table – 57.

Table - 57 Oxoacids of Chlorine with Oxidation State

Oxoacids	$HClO_4$	$HClO_3$	$HClO_2$	$HClO$
Oxidation state	+7	+5	+3	+1

In $HClO_4$, the oxidation state of Cl, is +7, therefore it has strong tendency to withdraw electron toward itself and therefore act as strongest oxidising agent. Hence, it follow the order fig. 247.

$$\underset{(+7)}{HClO_4} > \underset{(+5)}{HClO_3} > \underset{(+3)}{HClO_2} > \underset{(+1)}{HClO}$$

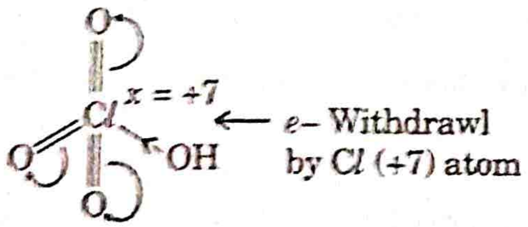


Fig. 247 Oxidising Nature of Cl in $HClO_4$