THE *P*-BLOCK ELEMENTS

SYLLABUS

General Introduction to p-Block Elements

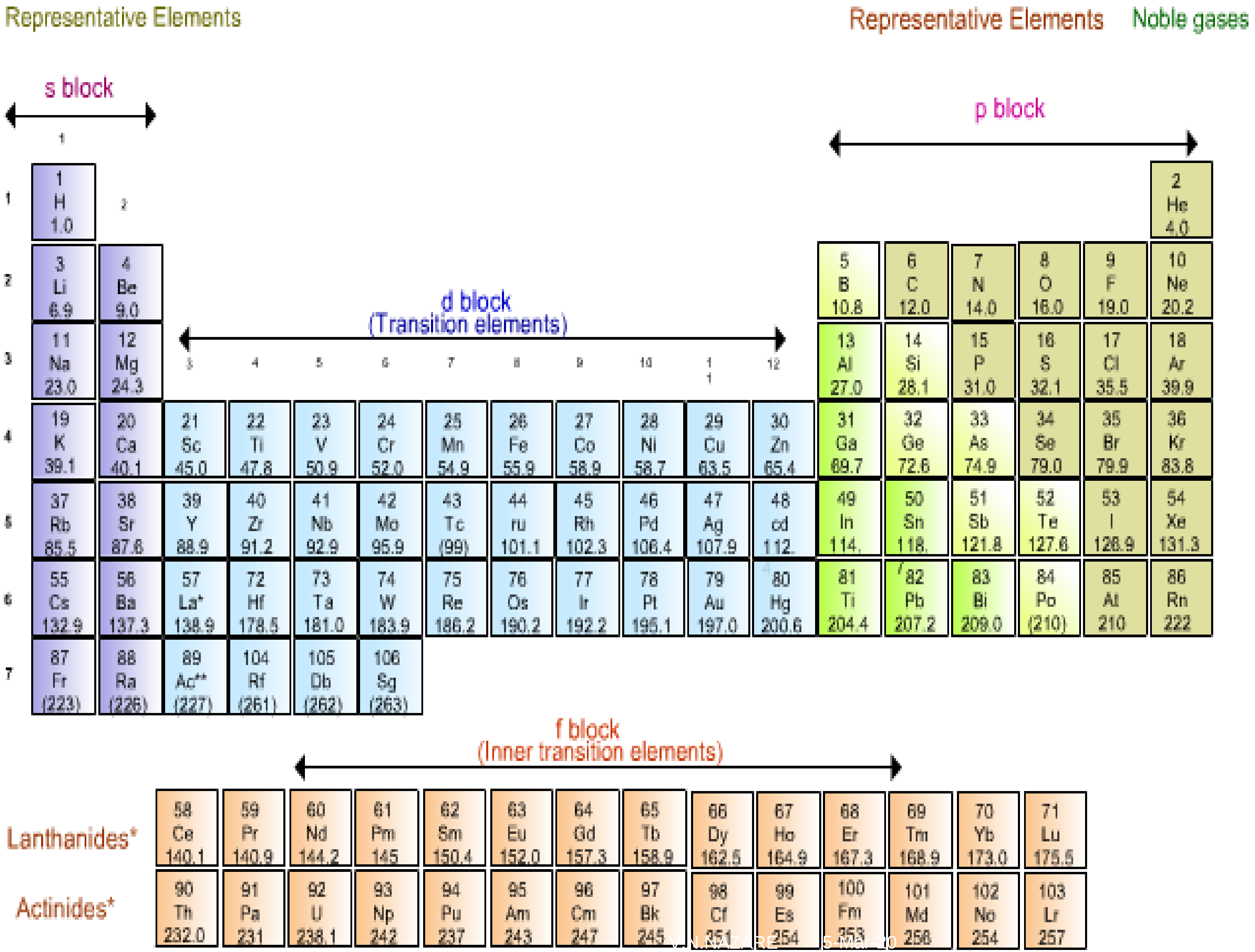
Group 13 elements: General introduction, electronic configuration, occurrence, variation of properties,

oxidation states, trends in chemical reactivity, anomalous properties of first element of the group;

Boron – physical and chemical properties, some important compounds: borax, boric acids, boron hydrides. Aluminum: uses, reactions with acids and alkalis.

Group 14 elements: General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first element. Carbon – catenation, allotropic forms, physical and chemical properties; uses of some important

compounds: oxides.Important compounds of silicon and a few uses: silicon tetrachloride , silicones, silicates and zeolites.



Representative Elements

Representative Elements

Noble gases

s block

p block

d block
(Transition elements)

f block
(Inner transition elements)

	1	2	3	4	5	6	7	8	9	10	1 1	12						
1	1 H 1.0																	2 He 4.0
2	3 Li 6.9	4 Be 9.0											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
3	11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
4	19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.8	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
5	37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 ru 101.1	45 Rh 102.3	46 Pd 106.4	47 Ag 107.9	48 cd 112.	49 In 114.	50 Sn 118.	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Ti 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At 210	86 Rn 222
7	87 Fr (223)	88 Ra (226)	89 Ac** (227)	104 Rf (261)	105 Db (262)	106 Sg (263)												

Lanthanides*	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.5
Actinides*	90 Th 232.0	91 Pa 231	92 U 238.1	93 Np 242	94 Pu 237	95 Am 243	96 Cm 247	97 Bk 245	98 Cf 251	99 Es 254	100 Fm 253	101 Md 258	102 No 254	103 Lr 257

THE *P*-BLOCK ELEMENTS

The ***p*-Block Elements** comprise those belonging to Group 13 to 18 and these together with the ***s*-Block Elements** are called the **Representative Elements or Main Group Elements**.

THE *P*-BLOCK ELEMENTS

The outermost electronic configuration varies from

ns^2np^1 to ns^2np^6 in each period.

- Group 13 elements--- ns^2np^1
- Group 14 elements--- ns^2np^2

THE *P*-BLOCK ELEMENTS

Main points (properties)

- **Most of p-Block elements are non-metals.**
- **They have variable oxidation states.**
- **They form acidic oxides**
- **They impart no characteristic colour to the flame**
- **Generally they form covalent compounds. Halogens form salts with alkali metals**

THE *P*-BLOCK ELEMENTS

Main points (properties) cont…d

- **They have high ionization potentials.**
- **They have very large electron gain enthalpies.**
- **They are solids/liquids/gases at room temperature (Br is liquid)**
- **The aqueous solutions their oxides are acidic in nature.**

THE *P* -BLOCK ELEMENTS

- why p-block elements consist of only six groups?
- The number of p orbitals is three therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six.
- Therefore, there are six groups of p–block elements in the periodic table numbering from 13 to 18.

The *p*-Block Elements

- Boron, carbon, nitrogen, oxygen, fluorine and helium head the groups.

- Their valence shell **electronic configuration is** ***ns^2np^{1-6}(except for He).***

THE IMPORTANT OXIDATION STATES EXHIBITED BY *P-BLOCK ELEMENTS ARE SHOWN IN TABLE*

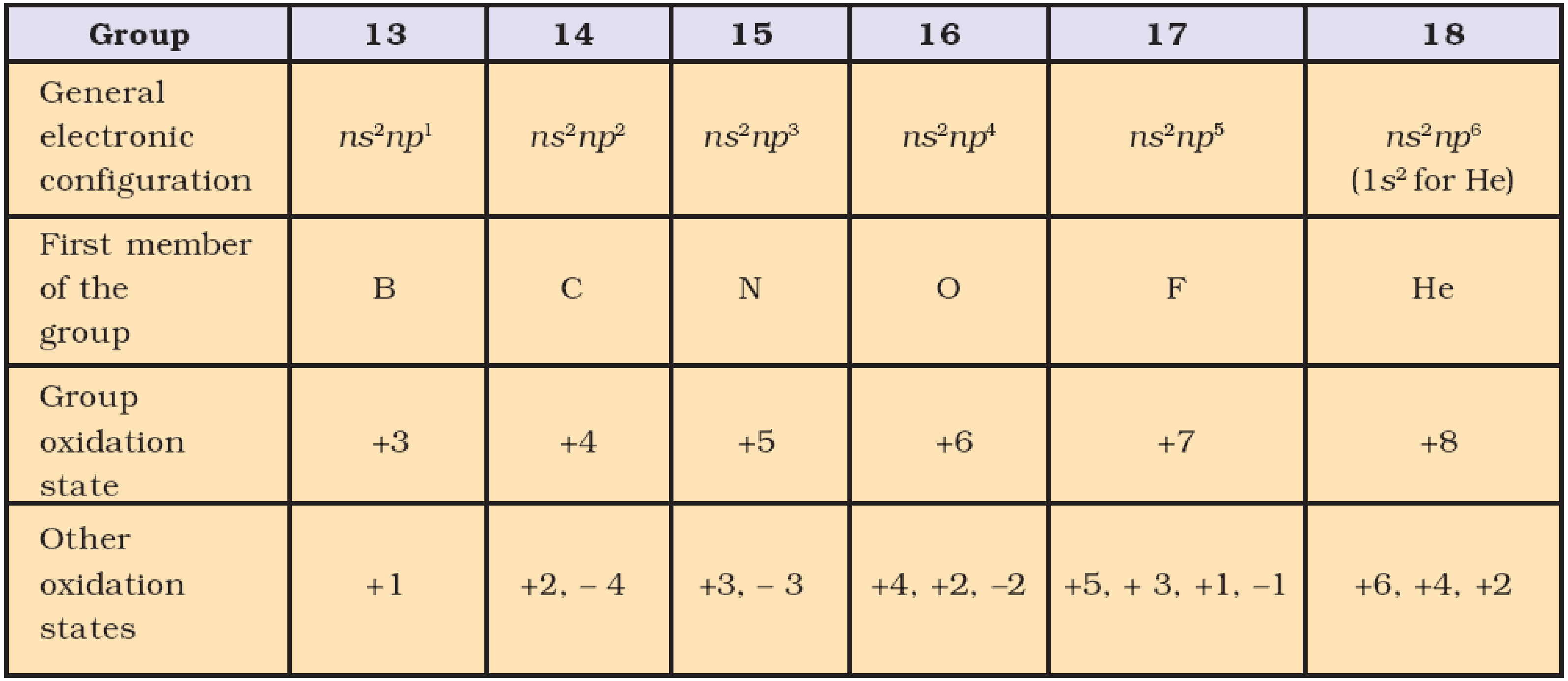


Table 11.1 General Electronic Configuration and Oxidation States of *p*-Block Elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 ($1s^2$ for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2, – 4	+3, – 3	+4, +2, –2	+5, + 3, +1, –1	+6, +4, +2

Group 13 elements

- The boron group consists of
- boron **(B)**,
- aluminium **(Al)**,
- gallium **(Ga)**,
- indium **(In)**,
- thallium **(Tl)**, and
- ununtrium **(Uut)**.

Oxidation states

- The atoms of these elements have three valence electrons, two in s-subshell and one in the p-subshell (ns^2 np^1).
- Therefore, all these elements can show maximum of +3 oxidation state.
- The common oxidation states, observed for group 13 elements are +3 and + 1.
  - The stability of the + 1 oxidation state increases in the sequence
    Al < Ga < In < Tl.

- Except boron and aluminium, the other elements also show +1 oxidation state.
- The +1 oxidation state becomes more stable as one moves down the group from boron to thallium.
- In case of last element, thallium, +1oxidation state has been found to be more stable than + 3 oxidation state.

Explanation:

- This is explained on the basis of inert pair effect. The elements of group 13 have three electrons in their valence shell (ns^2np^l) and, therefore, exhibit, oxidation state of + 3.

- However, it has been observed that in addition to + 3 oxidation state, they als exhibit oxidation state of +1. The +1 oxidation state becomes more and more stable as one goes down the group from B, Al, Ga, In to Tl.
- The +1 oxidation state of Tl is more stable than +3 oxidation state. For e.g., thallous compounds such as TlOH and $TlClO_4$ are more stable than their thallic compounds. This is attributed to the inert pair effect.

GROUP 13 ELEMENTS: THE BORON FAMILY

- This group elements show a wide variation in properties.
- Boron is a typical non-metal,
- aluminium is a metal but shows many chemical similarities to boron
- Gallium,indium and thallium are almost exclusively metallic in character.

OCCURENCE

- Boron is a fairly rare element, mainly occurs as
  - orthoboric acid, (H_3BO_3),or $B(OH)_3$
    - borax, $Na_2B_4O_7 \cdot 10H_2O$, and
      - kernite, $Na_2B_4O_7 \cdot 4H_2O$.
- In India borax occurs in Puga Valley (Ladakh) and Sambhar Lake (Rajasthan).
- The abundance of boron in earth crust is less than 0.0001% by mass.
- There are two isotopic forms of boron
- 10B (19%) and 11B (81%).

OCCURENCE

- Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).
  - Bauxite, $Al_2O_3.\ 2H_2O$ and
  - cryolite, Na_3AlF_6 are the important minerals of aluminium.
- In India it is found as mica in Madhya Pradesh, Karnataka, Orissa and Jammu.
- Gallium, indium and thallium are less abundant elements in nature.

Boron.swf

PHYSICAL PROPERTIES

- Boron is non-metallic in nature.
- It is extremely hard and black coloured solid.
- It exists in many allotropic forms.
- Due to very strong crystalline lattice, boron has unusually high melting point.
- Rest of the members are soft metals with low melting point and high electrical conductivity.

PHYSICAL PROPERTIES

- It is worthwhile to note that gallium with unusually low melting point (303K), could exist in liquid state during summer.
- Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
- Density of the elements increases down the group from boron to thallium.

The *p*-Block Elements

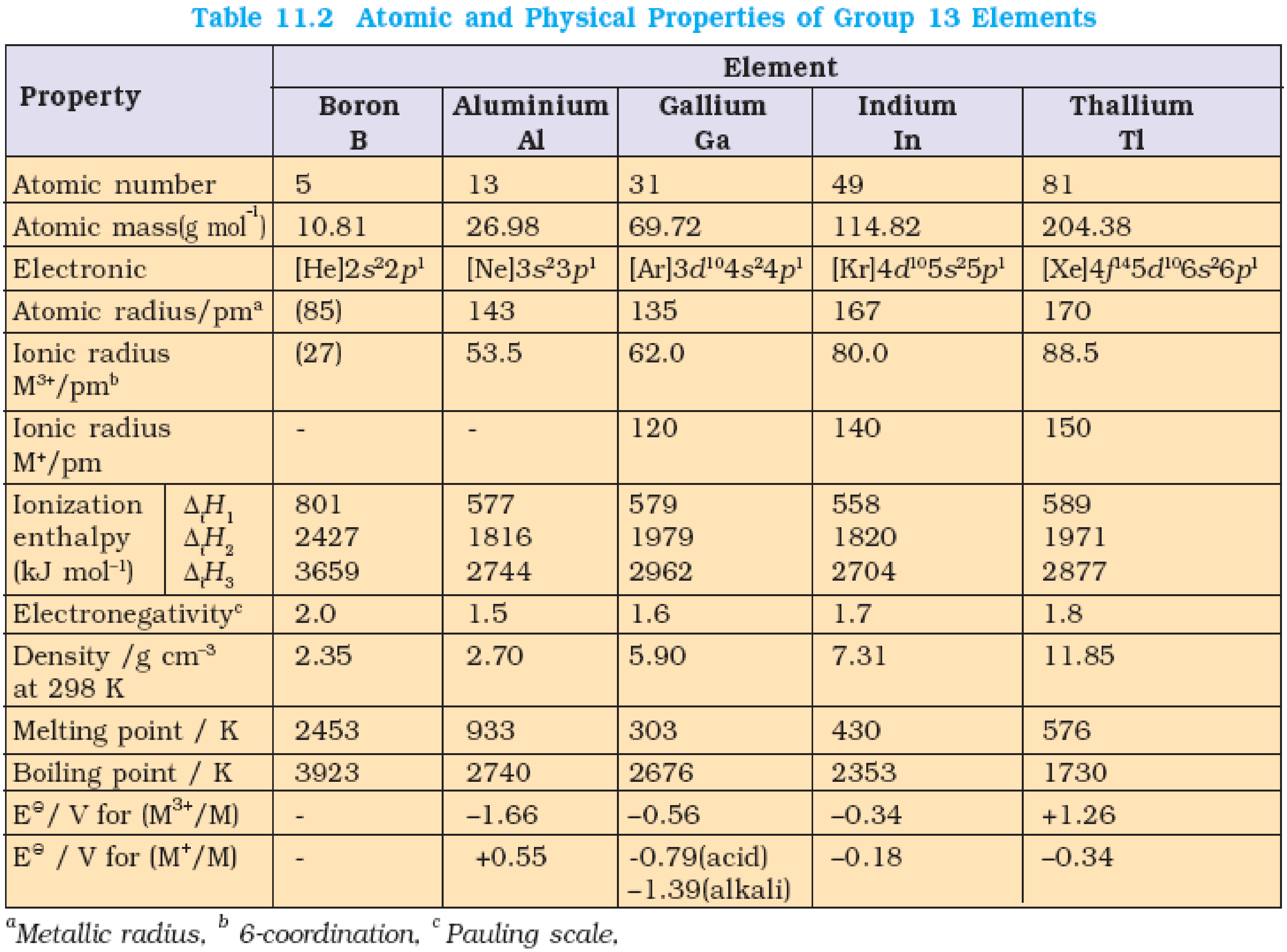


Table 11.2 Atomic and Physical Properties of Group 13 Elements

Property		Element				
		Boron **B**	**Aluminium** **Al**	**Gallium** **Ga**	**Indium** **In**	**Thallium** **Tl**
Atomic number		5	13	31	49	81
Atomic mass(g mol^{-1})		10.81	26.98	69.72	114.82	204.38
Electronic		$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10}4s^2 4p^1$	$[Kr]4d^{10}5s^2 5p^1$	$[Xe]4f^{14}5d^{10}6s^2 6p^1$
Atomic radius/pm[a]		(85)	143	135	167	170
Ionic radius M^{3+}/pm[b]		(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm		-	-	120	140	150
Ionization enthalpy (kJ mol^{-1})	$\Delta_i H_1$ $\Delta_i H_2$ $\Delta_i H_3$	801 2427 3659	577 1816 2744	579 1979 2962	558 1820 2704	589 1971 2877
Electronegativity[c]		2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730
$E^{\ominus}$/ V for (M^{3+}/M)		-	–1.66	–0.56	–0.34	+1.26
$E^{\ominus}$ / V for (M^+/M)		-	+0.55	-0.79(acid) –1.39(alkali)	–0.18	–0.34

[a]Metallic radius, [b] 6-coordination, [c] Pauling scale,

ELECTRONIC CONFIGURATION

Z	Element	No. of electrons/shell	Electronic Configuration
5	boron	2, 3	
13	aluminium	2, 8, 3	
31	gallium	2, 8, 18, 3	
49	indium	2, 8, 18, 18, 3	
81	thallium	2, 8, 18, 32, 18, 3	

ATOMIC RADII

- On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase.
- However, a deviation can be seen.

IONIZATION ENTHALPY

- The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group

ELECTRONEGATIVITY

- Down the group, electronegativity first
- decreases from B to Al and then increases marginally.
- This is because of the discrepancies in atomic size of the elements.-

WHAT IS INERT PAIR EFFECT ?

- The elements of group 13 have three electrons in their valence shell (ns^2np^1) and, therefore, exhibit, oxidation state of + 3. However, it bas been observed that in addition to + 3 oxidation state, they also exhibit oxidation state of +1.
- The +1 oxidation state becomes more and more stable as one goes down the group from B, Al, Ga, In to Tl.

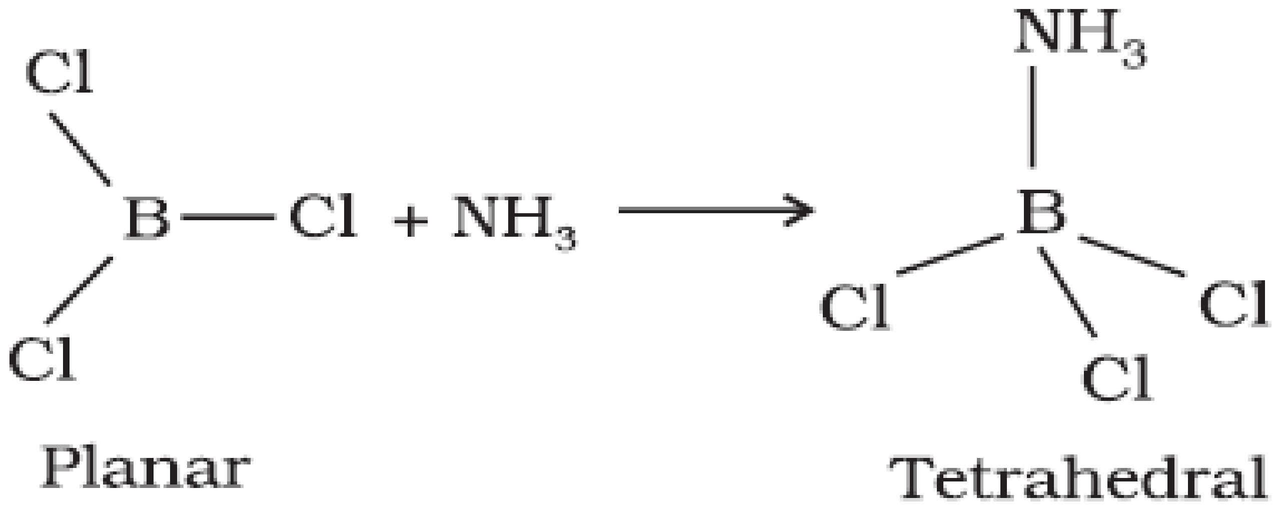
INERT PAIR EFFECT

- In the case of last element, after the removal of one electron from p-orbital, the remaining ns^2 (e.g. $6s^2$) electrons behave like stable noble gas and do not take part in bond formation. This reluctance of the s-electron pair to take part in chemical combination is called inert pair effect

ELECTRON DEFICIENT MOLECULE

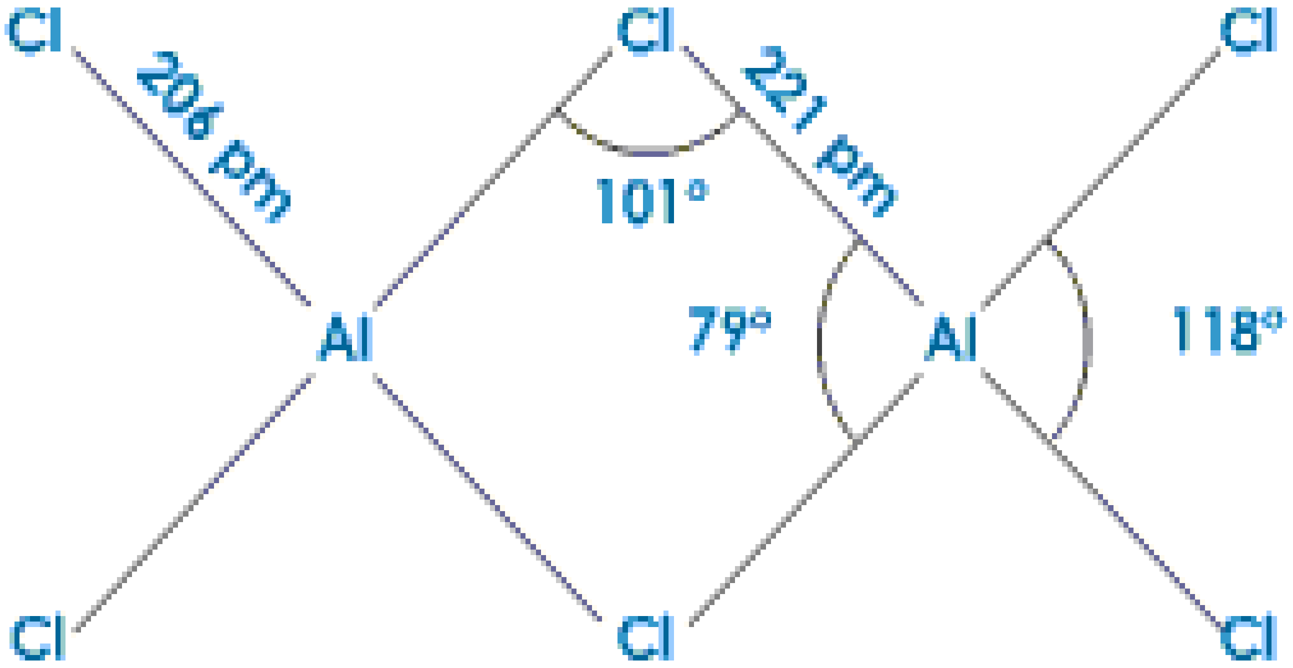
- Why does boron triflouride behave as a Lewis acid ?
- In boron triflouride , the number of electrons around the central boron atom will be only six such **electron deficient molecule have tendency** to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids.
- In boron family tendency to behave as Lewis acid decreases with the increase in the size down the group.

- BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3{\cdot}NH_3$.



Al_2Cl_6

- $AlCl_3$ achieves stability by forming a dimer



CHEMICAL PROPERTIES

Reactivity towards air

- Boron is unreactive in crystalline form.
- Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.

CHEMICAL PROPERTIES

- ***Reactivity towards air***
- Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively.

$$4\,B + 3O_2 \rightarrow 2B_2O_3$$

$$4\,Al + 3O_2 \rightarrow 2Al_2O_3$$

- With dinitrogen at high temperature they form nitrides.

$$2\,B + N_2 \rightarrow 2BN$$

$$2\,Al + N_2 \rightarrow 2AlN$$

NATURE OF OXIDES

The nature of these oxides varies down the group.

- Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates.
- Aluminium and gallium oxides are amphoteric
- and those of indium and thallium are basic in their properties.

Reactivity towards acids and alkalies

- Boron does not react with acids and alkalies even at moderate temperature;
- but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.
- Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al(s) + 6HCl_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_{2\,(g)}$$

- *concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface.*

- Aluminium reacts with aqueous alkali and liberates dihydrogen.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow 2\,Na^+[Al(OH)_4]^-_{(aq)} + 3H_{2\,(g)}$$

Sodium tetrahydroxoaluminate(III)

Reactivity towards halogens

- These elements react with halogens to form trihalides (except Tl I_3).

$$2E\,(s) + 3X_2(g) \longrightarrow 2EX_3(g)$$

X=F,Cl,Br,I

Eg. $\mathbf{2B(s)+3Cl_2(g) \longrightarrow 2BCl_3(g)}$

SOME IMPORTANT COMPOUNDS OF BORON

- Some useful compounds of boron are borax, orthoboric acid and diborane.

- Borax, $Na_2B_4O_7 \cdot 10H_2O$
- Orthoboric acid, (H_3BO_3),or $B(OH)_3$
- Diborane B_2H_6

BORAX

- It is the most important compound of boron.
- It is a white crystalline solid
- Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + \underset{\text{Orthoboric acid}}{4H_3BO_3}$$

BORAX BEAD.

- On heating, borax first loses water molecules and swells up.

- On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{Na_2B_4O_7} \xrightarrow{\Delta} 2NaBO_2 + \underset{\text{Boric anhydride}}{B_2O_3}$$

ORTHOBORIC ACID

- Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.
- It is sparingly soluble in water but highly soluble in hot water.

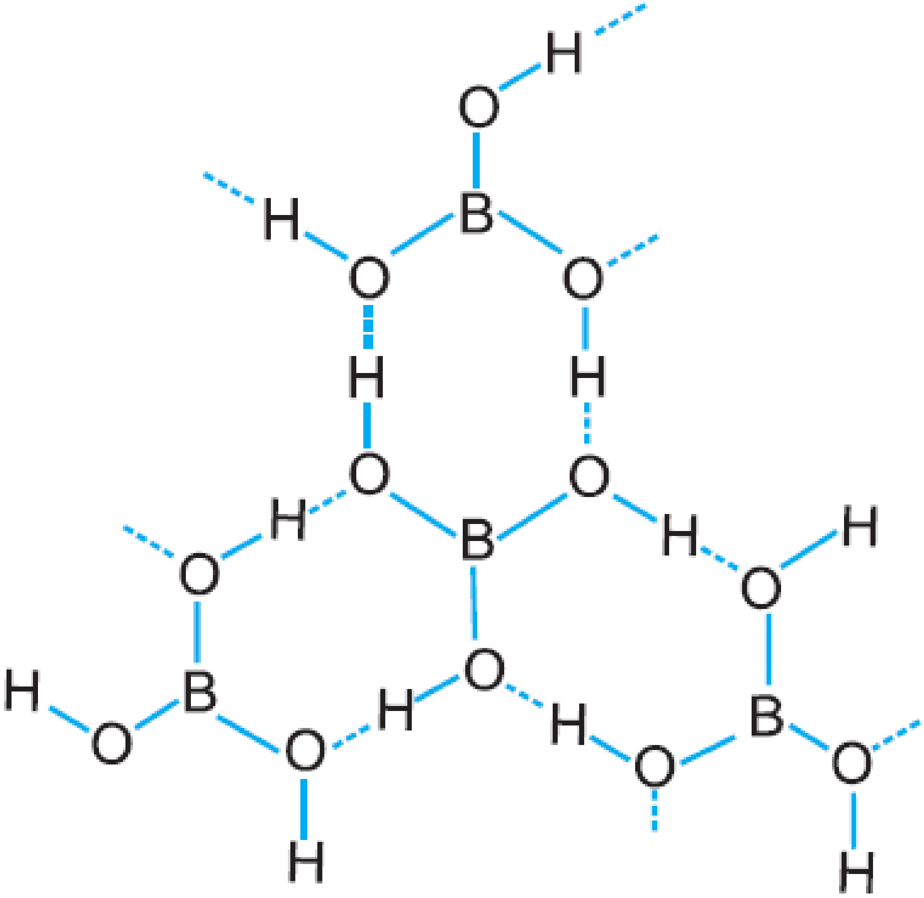
Preparation

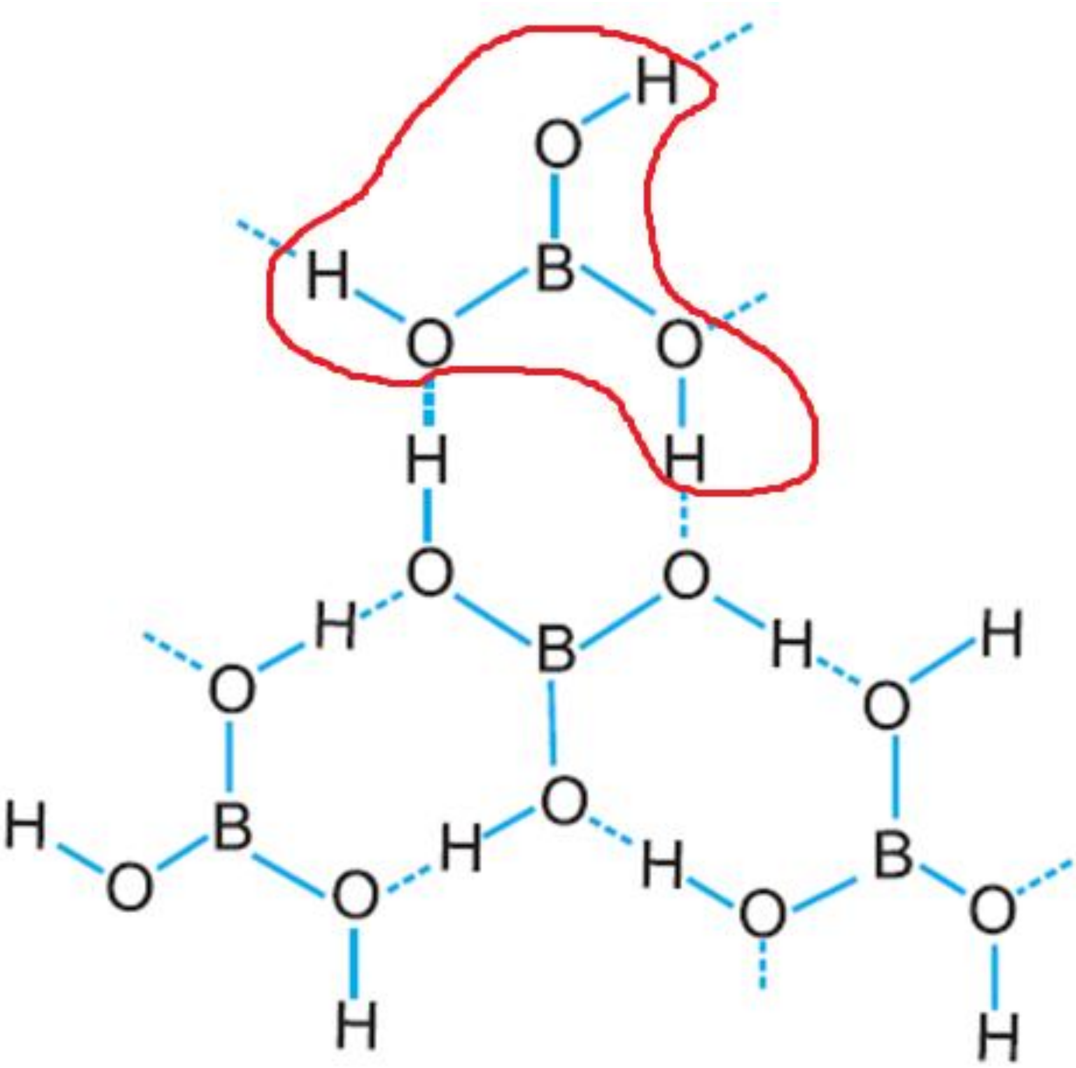
- It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

Boricacid.swf

ORTHOBORIC ACID (STRUCTURE)

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ORTHOBORIC ACID (PROPERTIES)

- Boric acid is a weak monobasic acid.
- It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion:

$$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$$

- On heating, orthoboric acid above 370K forms metaboric acid, HBO_2
- which on further heating yields boric oxide, B_2O_3.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$

The *p*-Block Elements

- Why is boric acid considered as a weak acid?

Answer

- Because it is not able to release H^+ ions on its own.
- It receives OH^- ions from water molecule to complete its octet and in turn releases H^+ ions.

DIBORANE B_2H_6

- The simplest boron hydride known, is diborane.
- It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$$4BF_3 + 3\ LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

laboratory method

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Industrial method

$$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$$

PROPERTIES

1. Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
2. Diborane catches fire spontaneously upon exposure to air.
3. It burns in oxygen releasing an enormous amount of energy.

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O; \quad \Delta_c H^{\ominus} = -1976 \text{ kJ mol}^{-1}$$

PROPERTIES

- Most of the higher boranes are also spontaneously flammable in air.
- Boranes are readily hydrolysed by water to give boric acid.

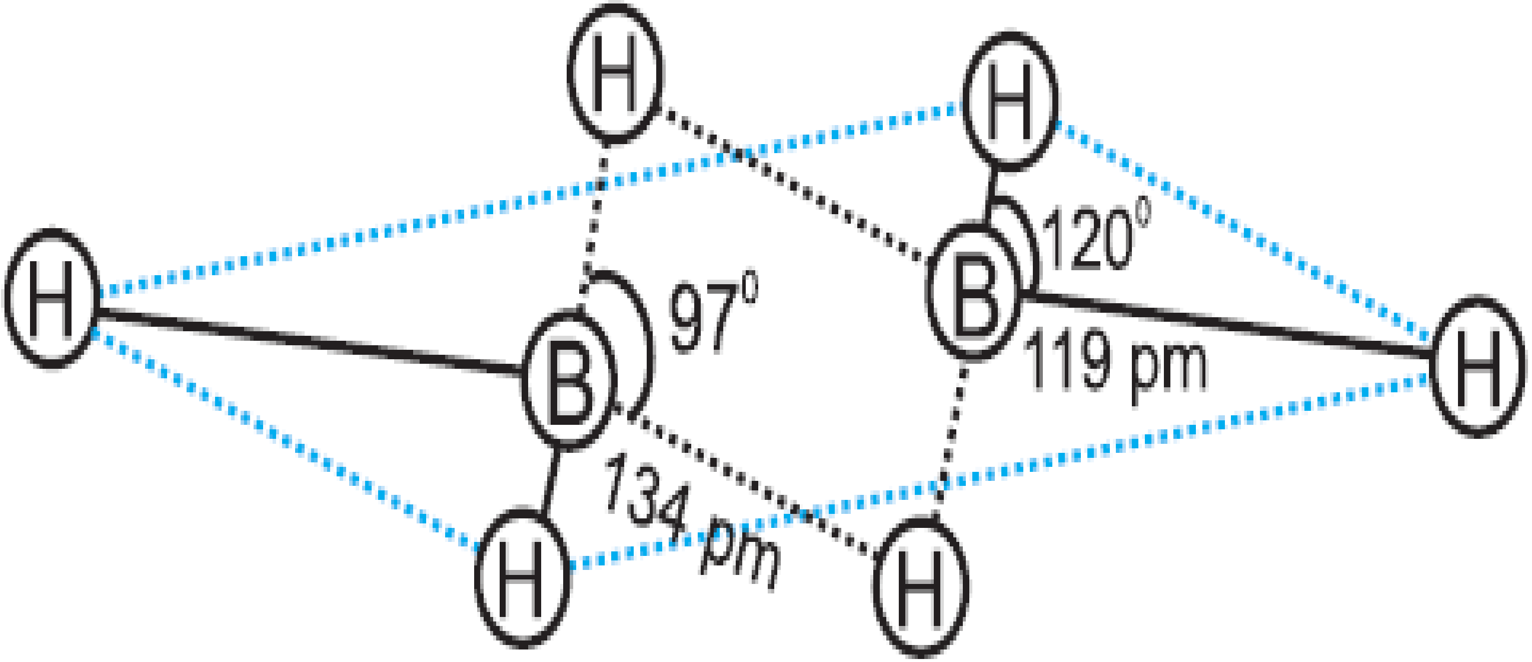
$$B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$$

- Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $BH_3 \cdot L$

$$B_2H_6 + 2NMe_3 \rightarrow 2BH_3.NMe_3$$

$$B_2H_6 + 2\ CO \rightarrow 2BH_3.CO$$

STRUCTURE OF DIBORANE



diborane.swf

STRUCTURE OF DIBORANE

- The four terminal hydrogen atoms and the two boron atoms lie in one plane.

- Above and below this plane, there are two bridging hydrogen atoms.

- The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are different and can be described in terms of three centre–two electron bonds

ANOMALOUS BEHAVIOUR OF BORON

- Because of extremely small size of its atom and high electronegativity, boron differs in its properties from other elements of the group.

ANOMALOUS PROPERTIES OF BORON

1. Boron is a non-metal whereas aluminium is a metal.
2. Boron is a bad conductor of electricity whereas aluminium is a good conductor.
3. Boron exists in two forms-crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.
4. The melting point and boiling point of boron are much higher than those of aluminium.

ANOMALOUS PROPERTIES OF BORON

5. Boron forms only covalent compounds whereas aluminium forms even some ionic compounds.
6. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.
7. The trihalides of boron (BX_3) exist as monomers. On the other hand, aluminium halides exist as dimers (Al_2X_6).
8. The hydrides of boron are quite stable while those of aluminium are unstable.

USES OF BORON

- Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- The boron-10 (10B) isotope has high ability to absorb neutrons and, therefore,metal borides are used in nuclear industry as protective shields and control rods.
- The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass.
- Borax is also used as a flux for soldering metals

ALUMINIUM

- Aluminium is a bright silvery-white metal,with high tensile strength.
- It has a high electrical and thermal conductivity.
- On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- Aluminium is used extensively in industry and every day life. It forms alloys with Cu, Mn, Mg, Si and Zn.

ALUMINIUM

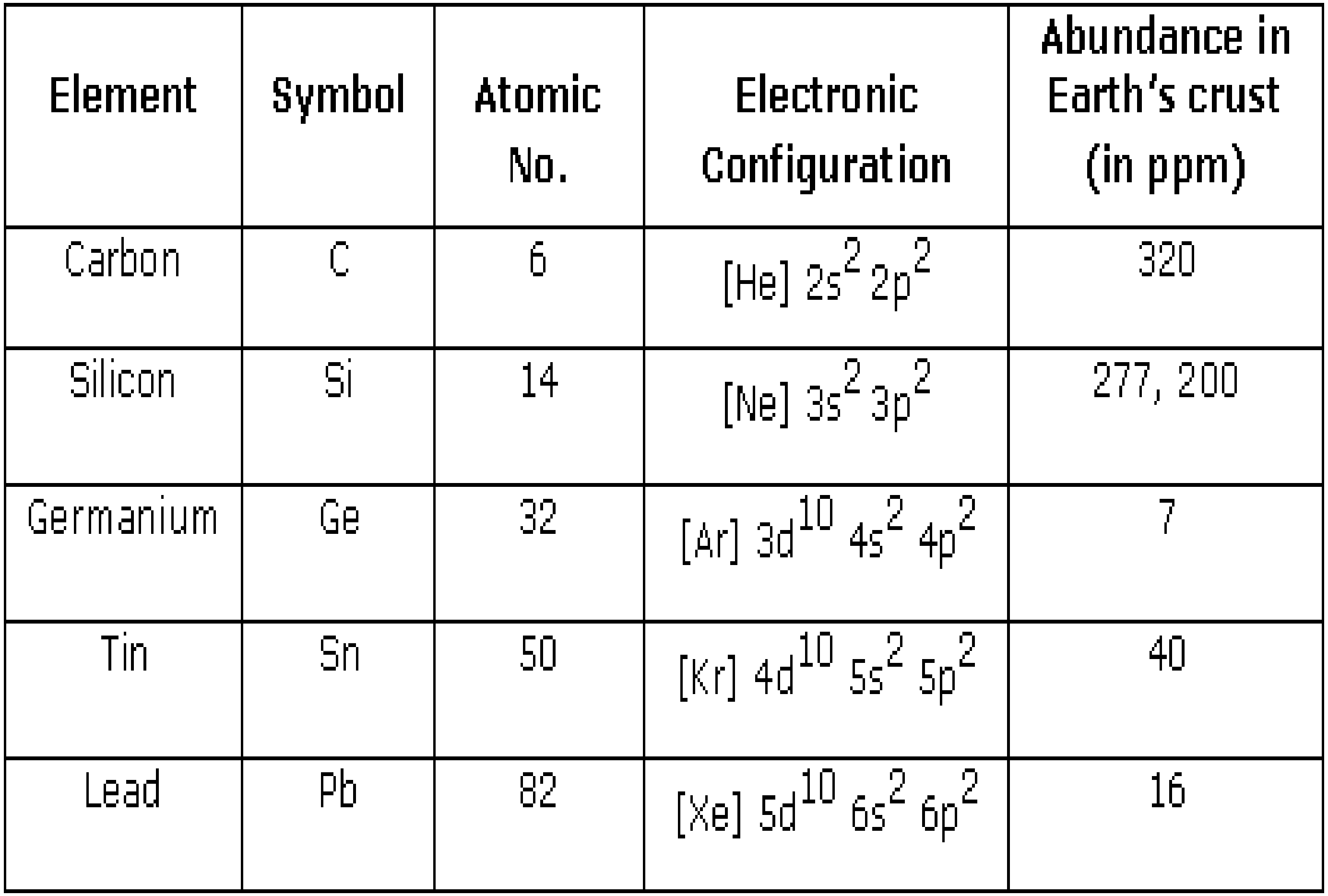
- Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.

- The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

GROUP 14 ELEMENTS: THE CARBON FAMILY

- Carbon (C),
- silicon (Si),
- germanium (Ge),
- tin (Sn) and
- lead (Pb).
- This group is known as carbon family
- The elements of group 14 have four electrons in the outermost orbitals.
- The general electronic configuration may be written as ns^2np^2

ELECTRONIC CONFIGURATIONS

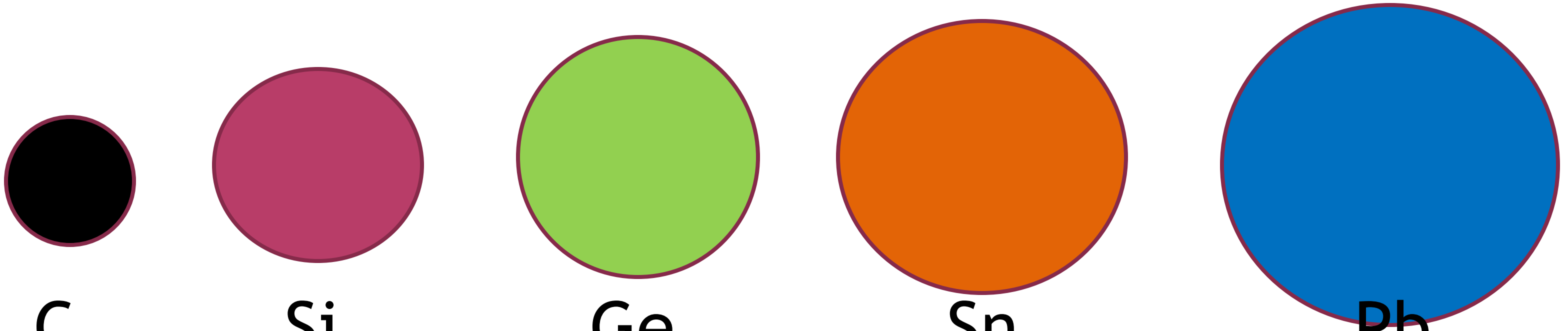


Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's crust (in ppm)
Carbon	C	6	[He] $2s^2\ 2p^2$	320
Silicon	Si	14	[Ne] $3s^2\ 3p^2$	277, 200
Germanium	Ge	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$	7
Tin	Sn	50	[Kr] $4d^{10}\ 5s^2\ 5p^2$	40
Lead	Pb	82	[Xe] $5d^{10}\ 6s^2\ 6p^2$	16

COVALENT RADIUS

- There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed.

- This is due to the presence of completely filled *d and f* orbitals in heavier members.



- C Si Ge Sn Pb

IONIZATION ENTHALPY

- The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13.

- In general the ionisation enthalpy decreases down the group.

ELECTRONEGATIVITY

- Due to small size, the elements of this group are slightly more electronegative than group 13 elements.
- The electronegativity values for elements from Si to Pb are almost the same.

PHYSICAL PROPERTIES

- All group 14 members are solids.
- Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points.
- Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

PHYSICAL PROPERTIES

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	**77**	**118**	**122**	**140**	**146**
Ionic radius (pm)	**-**	**40**	**53**	**69**	**78**
M^{4+} M^{2+}	**-**	**-**	**73**	**118**	**119**
Ionisation energy IE_1(k.J mol^{-1})	**1086**	**756**	**761**	**708**	**715**
IE_2	**2352**	**1577**	**1537**	**1411**	**1450**
IE_3	**4620**	**3228**	**3300**	**2942**	**3081**
IE_4	**6220**	**4354**	**4409**	**3929**	**4082**
Electro negativity	**2.5**	**1.8**	**1.8**	**1.8**	**1.9**
Melting point (K)	**4373**	**1693**	**1218**	**505**	**600**
Boiling point (K)	**-**	**3550**	**3123**	**2896**	**2024**

CHEMICAL PROPERTIES

(i) Reactivity towards oxygen

- All members when heated in oxygen form oxides.

- There are mainly two types of oxides, *i.e.*, *monoxide and dioxide of formula MO and* MO_2 respectively.

- SiO only exists at high temperature.

CHEMICAL PROPERTIES

(i) Reactivity towards oxygen

- Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states.

- The dioxides CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature.

- Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

(ii) Reactivity towards water

- Carbon, silicon and germanium are not affected by water.
- Tin decomposes steam to form dioxide and dihydrogen gas.

$$\mathbf{Sn + 2H_2O \longrightarrow SnO_2 + 2H_2}$$

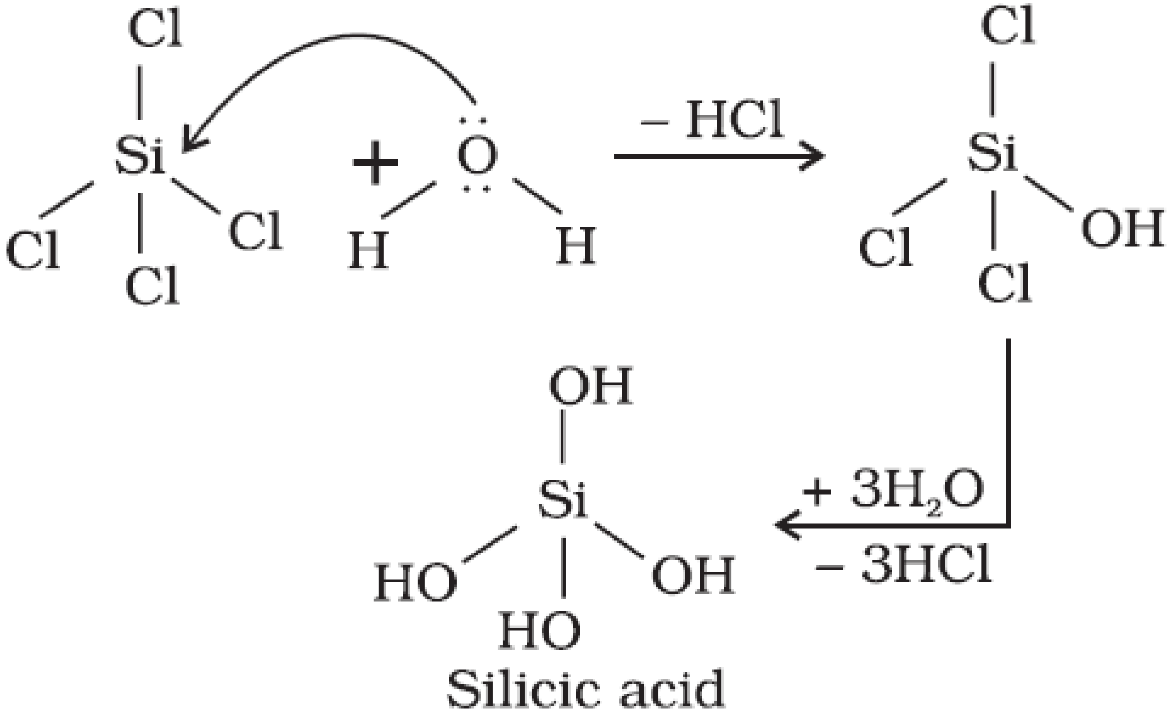
- Lead is unaffected by water, probably because of a protective oxide film formation.

(iii) Reactivity towards halogen

- These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I).
- Except carbon, all other members react directly with halogen under suitable condition to make halides.
- Most of the MX_4 are covalent in nature.
- Heavier members Ge to Pb are able to make halides of formula MX_2 .
- Stability of dihalides increases down the group.
- Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more than PbX_4.

HYDROLYSIS

- Except CCl_4, other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d orbital*



ANOMALOUS BEHAVIOUR OF CARBON

- Why Carbon shows ANOMALOUS BEHAVIOUR ?

1. It is due to its smaller size,
2. Higher electronegativity,
3. higher ionisation enthalpy
4. and unavailability of *d orbitals*.

- In carbon, only *s and p orbitals are* available for bonding and, therefore, it can accommodate only four pairs of electrons around it.
- This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of *d orbitals*.

Pπ- Pπ BONDS

- Carbon also has unique ability to form *pπ- pπ multiple bonds with itself and with other* atoms of small size and high electronegativity.
- Few examples of multiple bonding are:

$C{=}C$, $C \equiv C$, $C = O$, $C = S$, and $C \equiv N$.

- Heavier elements do not form *pπ- pπ bonds because their atomic* orbitals are too large and diffuse to have effective overlapping.

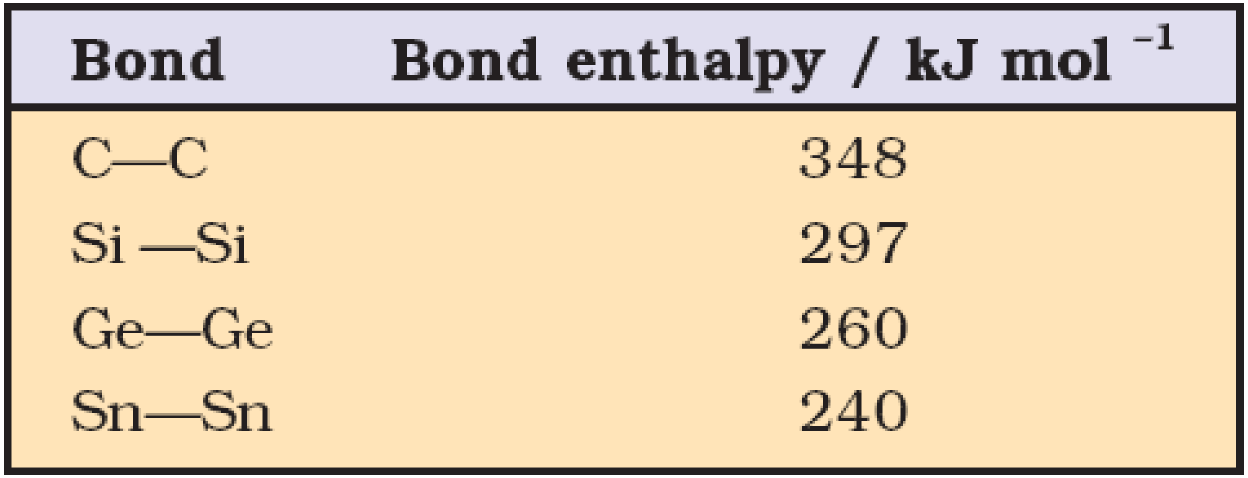
CATENATION

- Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings.
- This property is called **catenation**.
- **This is because C—C bonds are** very strong.
- Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases.
- This can be clearly seen from bond enthalpies values.

CATENATION

- The order of catenation is

  C > > Si >Ge ≈ Sn.
- Lead does not show catenation.



Bond	Bond enthalpy / kJ mol^{-1}
C—C	348
Si —Si	297
Ge—Ge	260
Sn—Sn	240

- Due to property of catenation and pπ– pπ bond formation, carbon is able to show allotropic forms.

ALLOTROPES OF CARBON

- Carbon exhibits many allotropic forms; both crystalline as well as amorphous.
- Diamond and graphite are two well-known crystalline forms of carbon.
- In 1985, third form of carbon known as **fullerenes was discovered by** H.W.Kroto, E.Smalley and R.F.Curl.
- For this discovery they were awarded the Nobel Prize in 1996.

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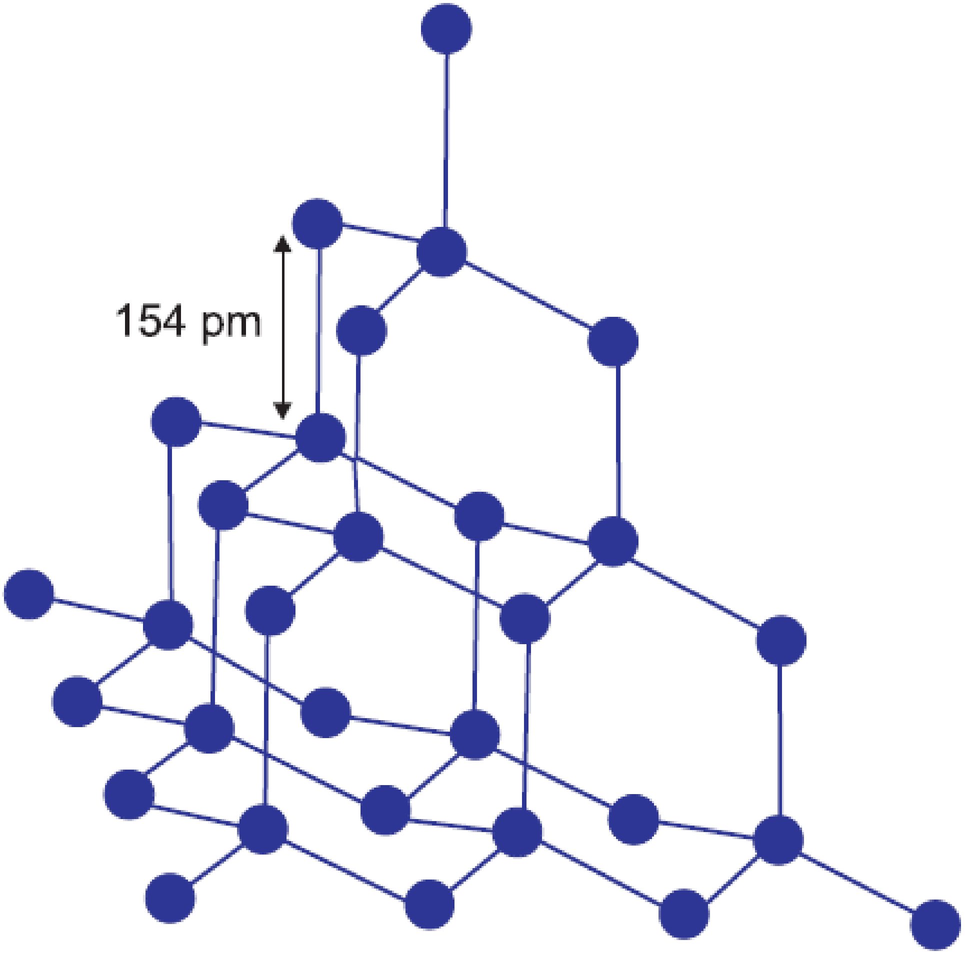
Diamond



Diamond

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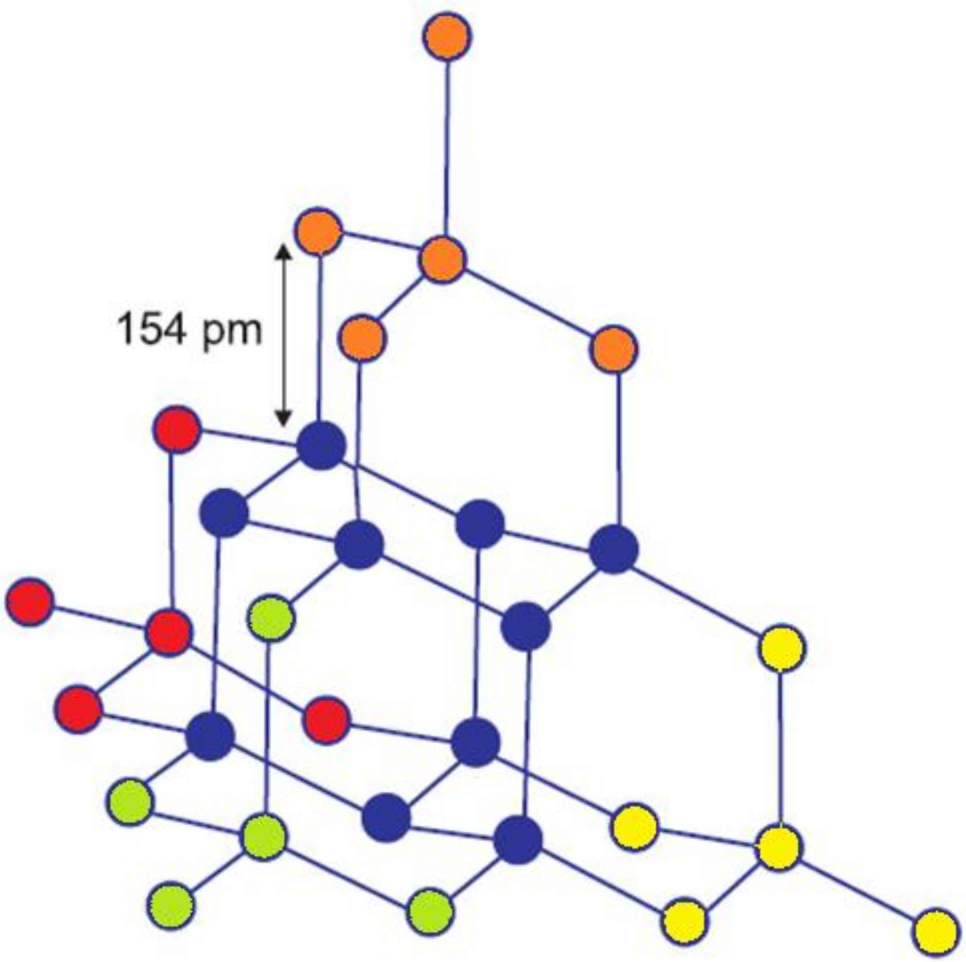


Diamond

- It has a crystalline lattice.

- In diamond each carbon atom undergoes sp^3 *hybridisation and* linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.

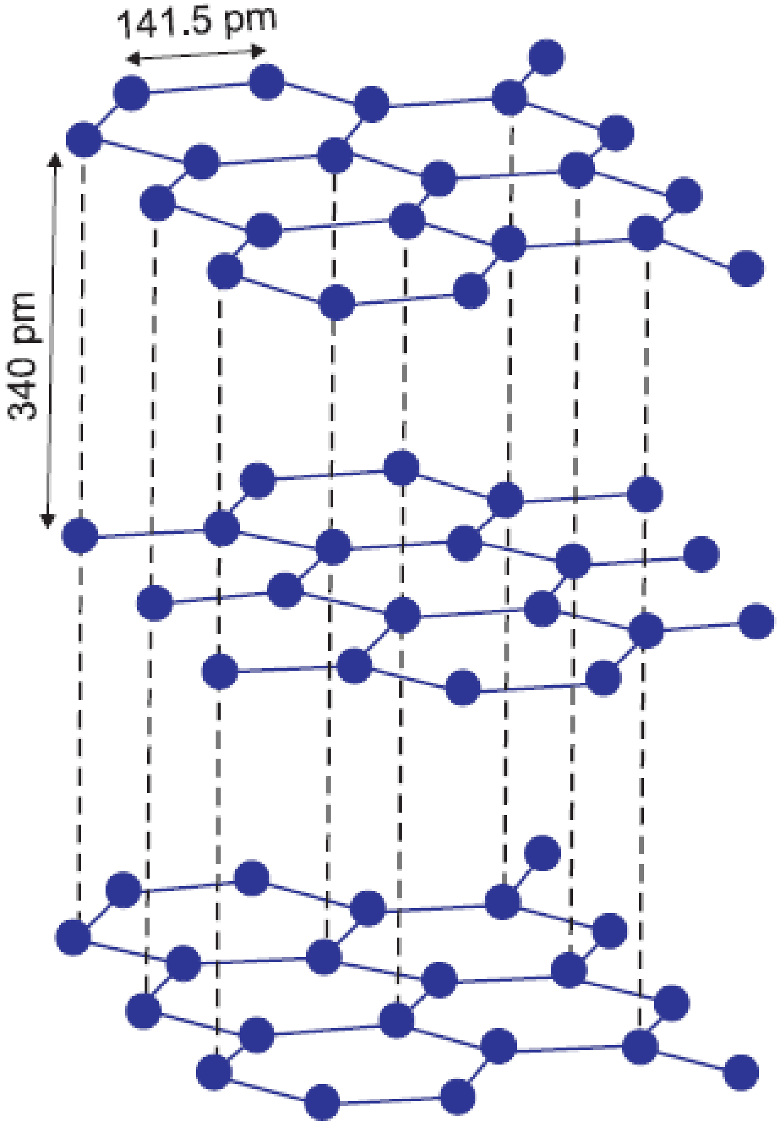
- The C–C bond length is 154 pm.

- The structure extends in space and produces a rigid three dimensional network of carbon atoms.

Diamond

- In this structure directional covalent bonds are present throughout the lattice.
- It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.
- It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

Graphite



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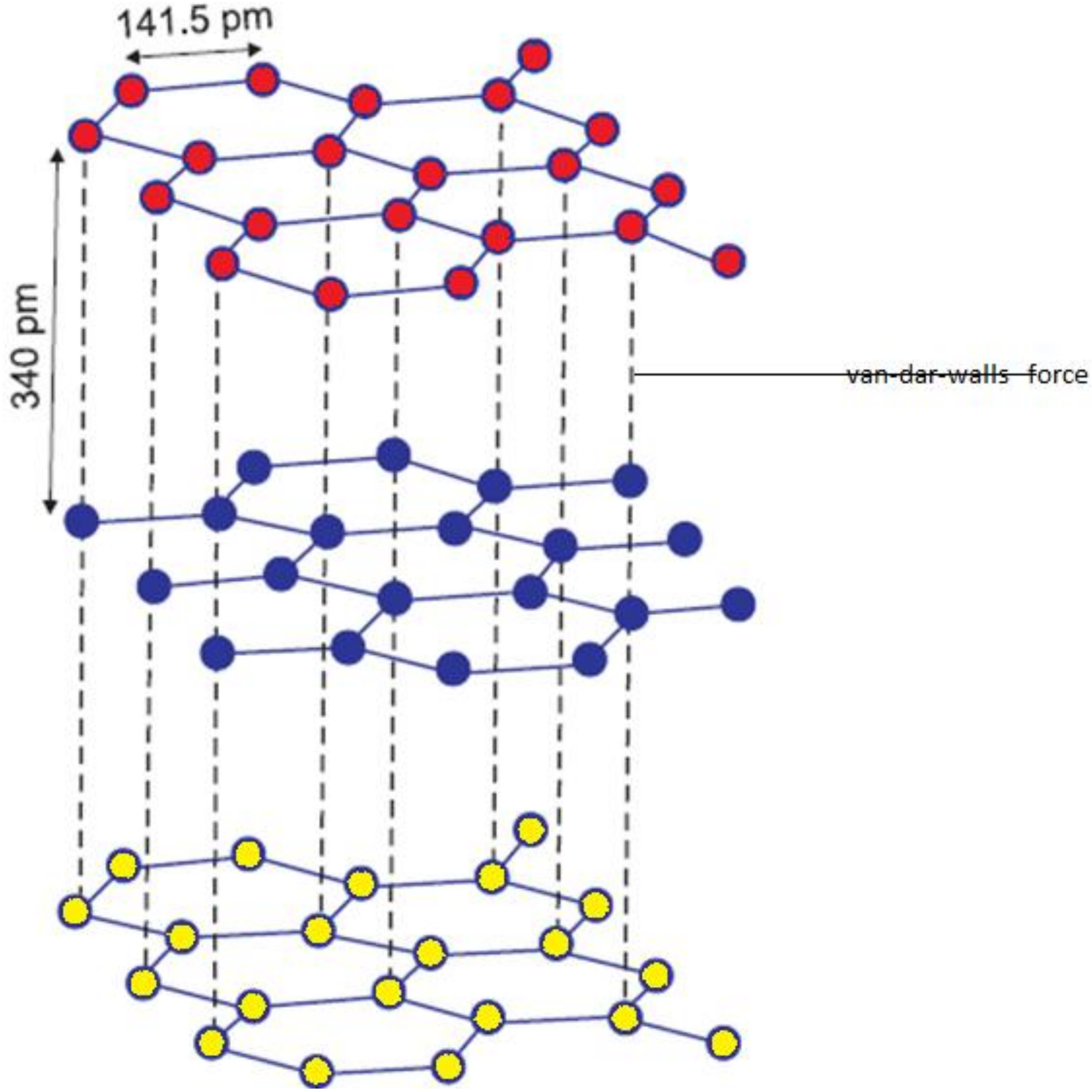
Graphite



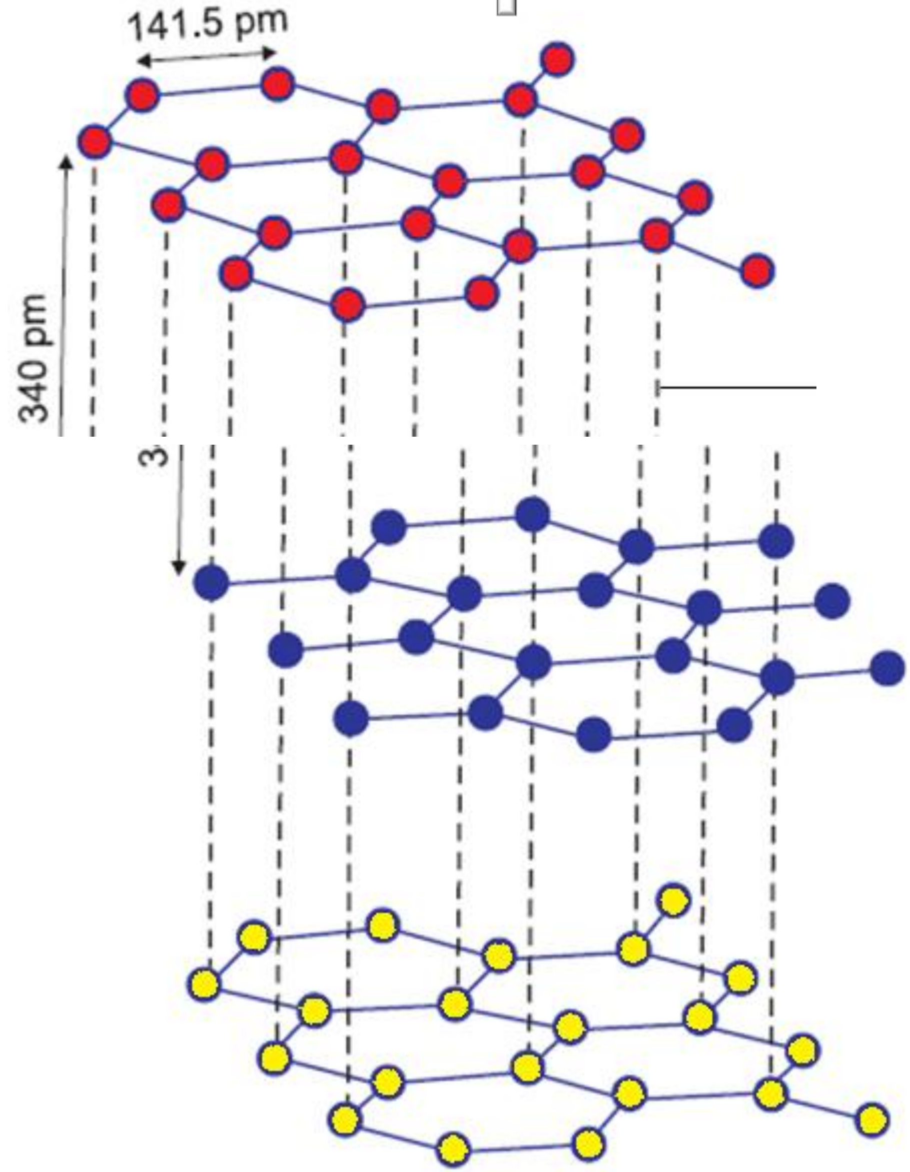
Graphite

- Graphite has layered structure.
- Layers are held by van der Waals forces and distance between two layers is 340 pm.
- Each layer is composed of planar hexagonal rings of carbon atoms.
- C—C bond length within the layer is 141.5 pm.
- Each carbon atom in hexagonal ring undergoes *sp*^{2} *hybridisation* and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet.

Graphite

- Electrons are mobile and, therefore, graphite conducts electricity along the sheet.
- Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.
- For this reason graphite is used as a dry
- lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Graphite



FULLERENES

- Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.
- The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.
- Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.
- Fullerenes are cage like molecules.

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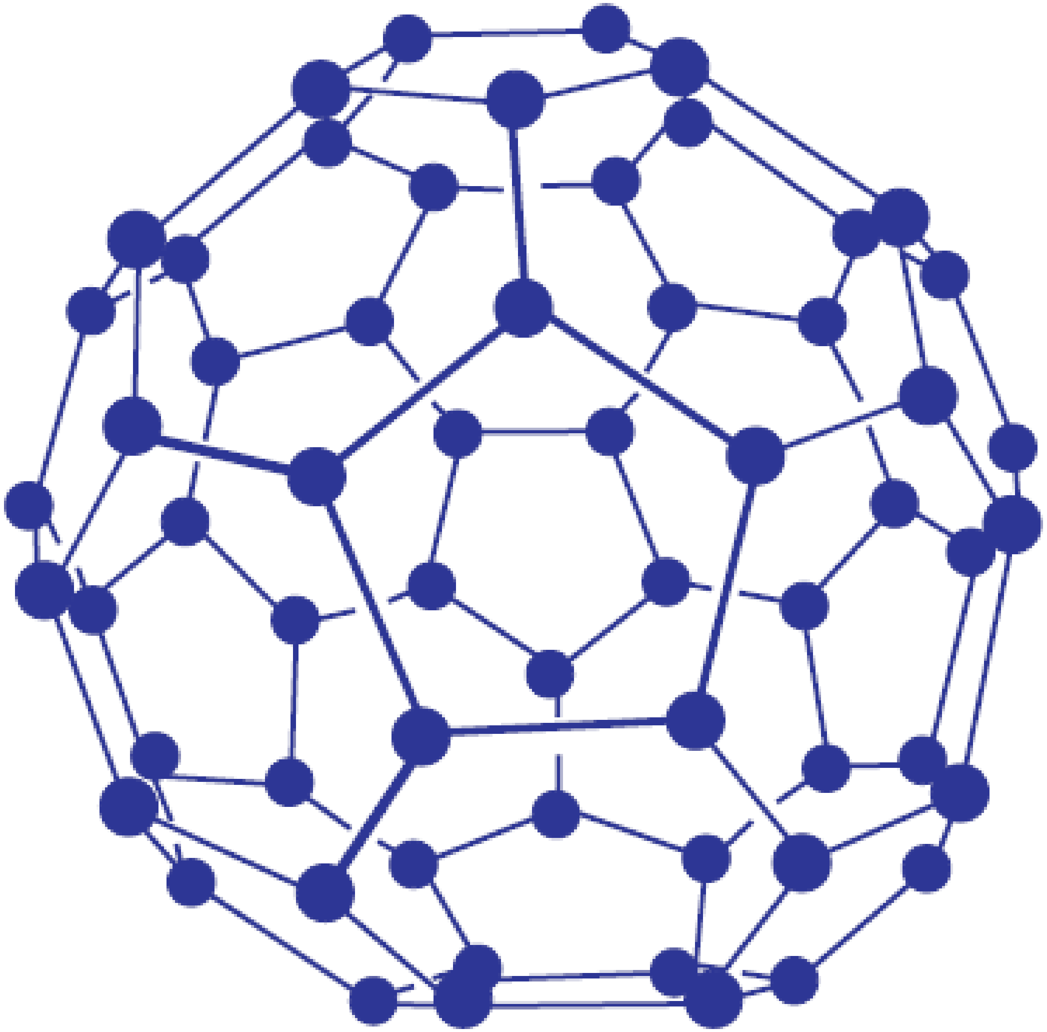
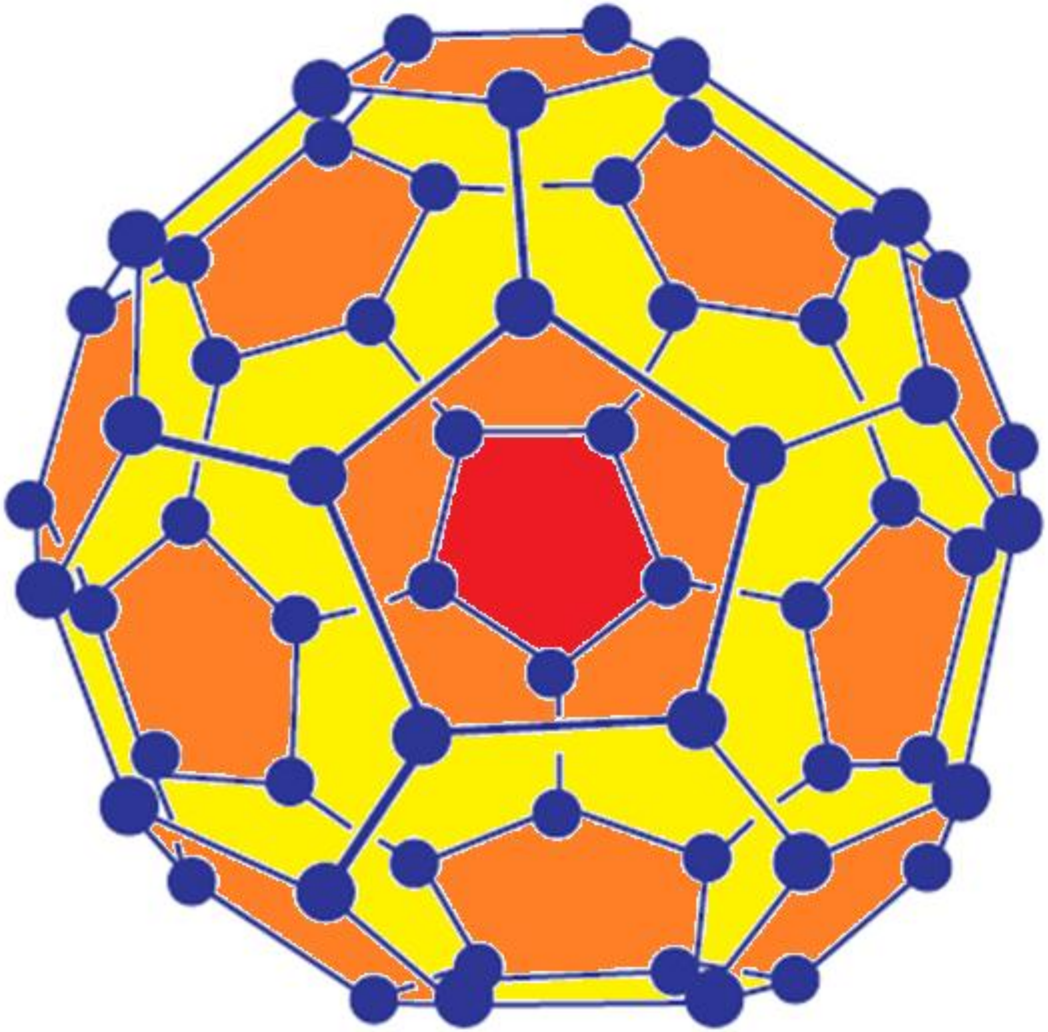
FULLERENES



FULLERENES



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FULLERENES

- C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene**
- It contains twenty six- membered rings and
- twelve five membered rings.
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- All the carbon atoms are equal and they undergo sp^2 *hybridisation*.
- Each carbon atom forms three sigma bonds with other three carbon atoms.

FULLERENES---- *BUCKY BALLS*

- The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule.
- This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively.

- Spherical fullerenes are also called *bucky balls*

OTHER FORMS OF CARBON

- Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.
- Carbon black is obtained by burning hydrocarbons in a limited supply of air.
- Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

USES OF CARBON

- The composites of carbon are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- Crucibles made from graphite are inert to dilute acids and alkalies.
- Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water

USES OF CARBON

- Also used in water filters to remove organic contaminators and in air conditioning system to control odour.
- Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- Coke is used as a fuel and largely as a reducing agent in metallurgy.
- Diamond is a precious stone and used in jewellery.
- It is measured in carats (1 carat = 200 mg).

IMPORTANT COMPOUNDS OF CARBON

1. **Carbon Monoxide**
2. **Carbon Dioxide**

Carbon Monoxide

- Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

On small scale

- pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

$$\mathrm{HCOOH} \xrightarrow[\text{conc.}\,H_2SO_4]{373\mathrm{K}} H_2O + CO$$

On commercial scale

- it is prepared by the passage of steam over hot coke.

$$\underset{}{C(s) + H_2O(g)} \xrightarrow{473\text{–}1273\mathrm{K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

- The mixture of CO and H_2 thus produced is known as **water gas** or **synthesis gas**.

- When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas.**

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} 2CO(g) + 4N_2(g)$$

Producer gas

- Water gas and producer gas are very important industrial fuels.

- Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

PROPERTIES

- Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals.
- This property of CO is used in the extraction of many metals from their oxides ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

DANGER OF CO

- The highly poisonous nature of CO arises because of its ability to form a **complex with** haemoglobin,**called** Carboxyhaemoglobin **which** is about 300 times more stable than the oxygen-haemoglobin complex.

- This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

CARBON DIOXIDE

Preparation

- It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

Lab method

$$CaCO_3(s) + 2HCl\,(aq) \rightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O(l)$$

PHOTOSYNTHESIS

- Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as photosynthesis.
- **It is the process** by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. By this process plants make food for themselves as well as for animals and human beings.
- The overall chemical change is as follows

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorphyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

GREEN HOUSE EFFECT

- The increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere.

- This may lead to increase in **green house effect and** thus, raise the temperature of the atmosphere which might have serious consequences.

vc1.swf

The *p*-Block Elements

USES OF CARBON DIOXIDE

- Dry ice is used as a refrigerant for ice-cream and frozen food.
- Gaseous CO_2 is extensively used to carbonate soft drinks.
- Being heavy and non-supporter of combustion it is used as fire extinguisher.
- A substantial amount of CO_2 is used to manufacture urea.

IMPORTANT COMPOUNDS OF SILICON

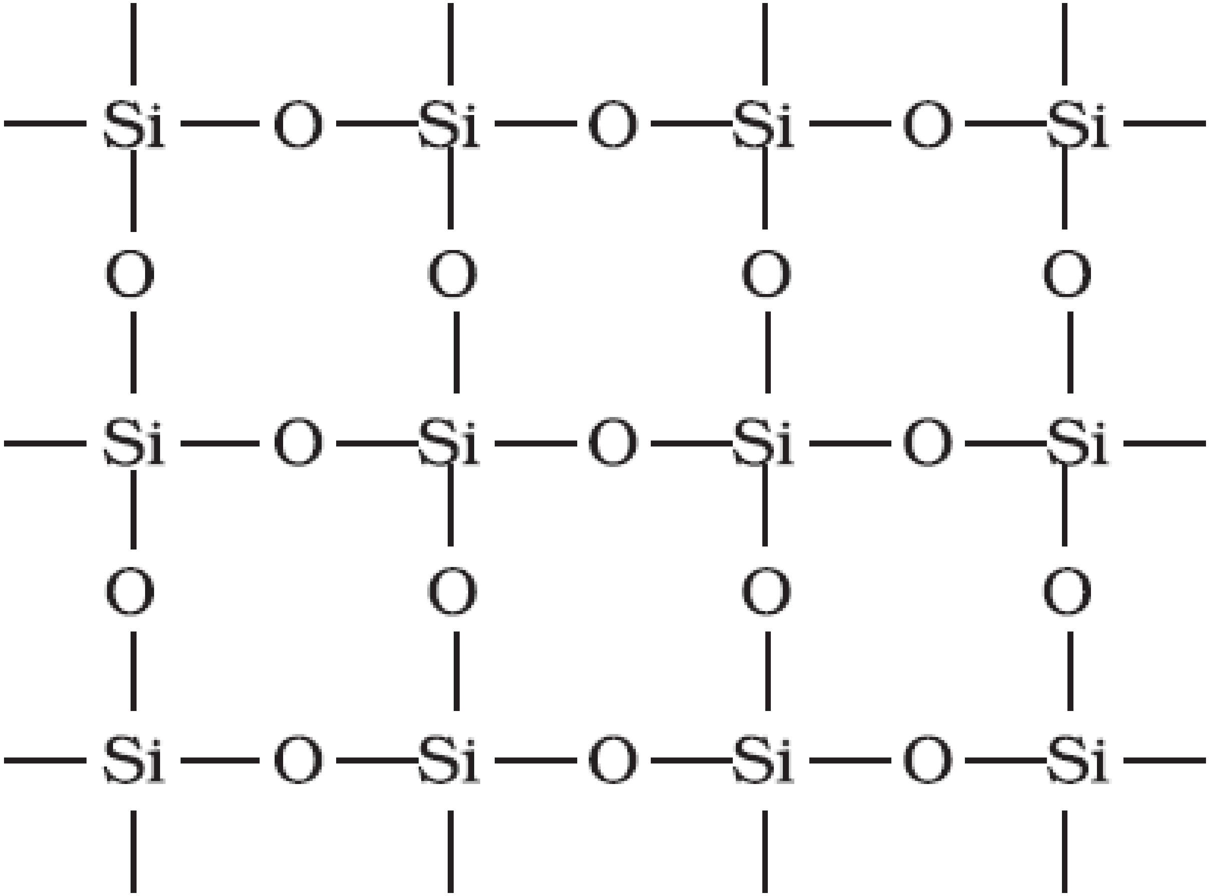
1. Silicon Dioxide, SiO_2
2. Silicones
3. Silicates
4. Zeolites

SILICON DIOXIDE, SIO_2

- 95% of the earth's crust is made up of silica and silicates.
- Silicon dioxide, commonly known as silica, occurs in several crystallographic forms.
- Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature.
- Silicon dioxide is a covalent, three-dimensional network solid

SILICON DIOXIDE, SIO_2

STRUCTURE



SILICON DIOXIDE, SIO$_2$

PROPERTIES

- Silica in its normal form is almost nonreactive because of very high Si—O bond enthalpy.

- It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures.

- However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

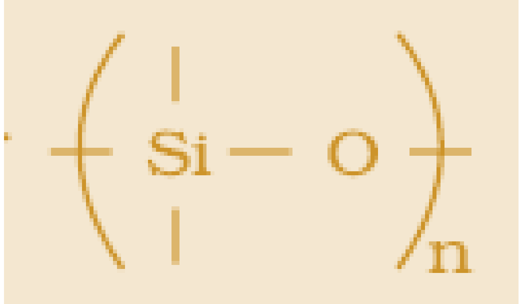
SILICON DIOXIDE, SiO_2

USES

- Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.
- Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
- Kieselghur, an amorphous form of silica is used in filtration plants.

SILICONES

- What are silicones ?
- Simple silicones consist of



chains in which alkyl or phenyl groups occupy the remaining bonding positions on each silicon.

- They are hydrophobic (water repellant) in nature.

SILICONES

Method of preparation

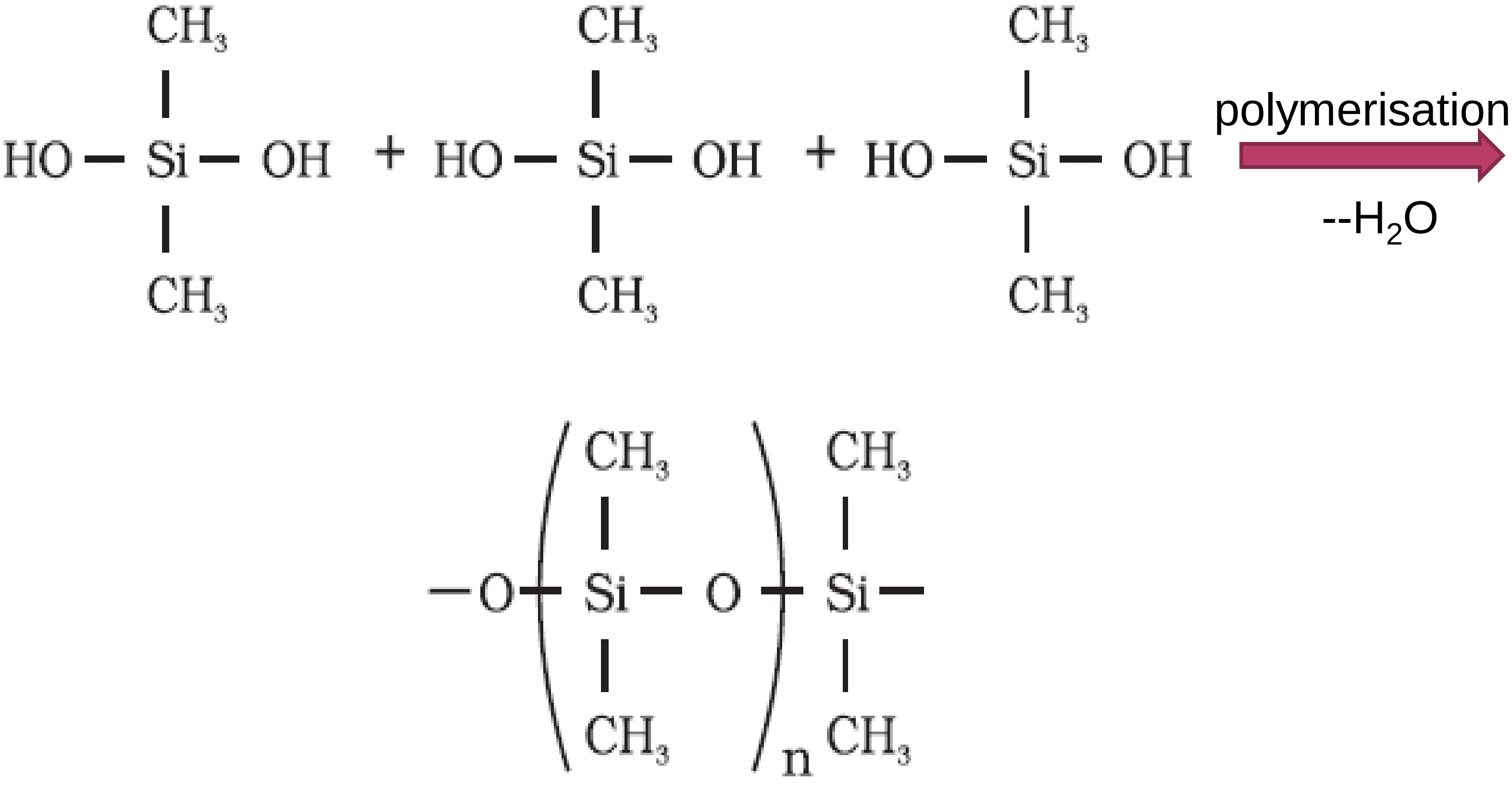
- Hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ followed by condensation polymerisation

$$2CH_3Cl + Si \xrightarrow[570\ K]{Cu\ powder} (CH_3)_2SiCl_2$$

$$(CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$

SILICONES

Method of preparation



$$\mathrm{HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH \xrightarrow[--H_2O]{\text{polymerisation}}}$$

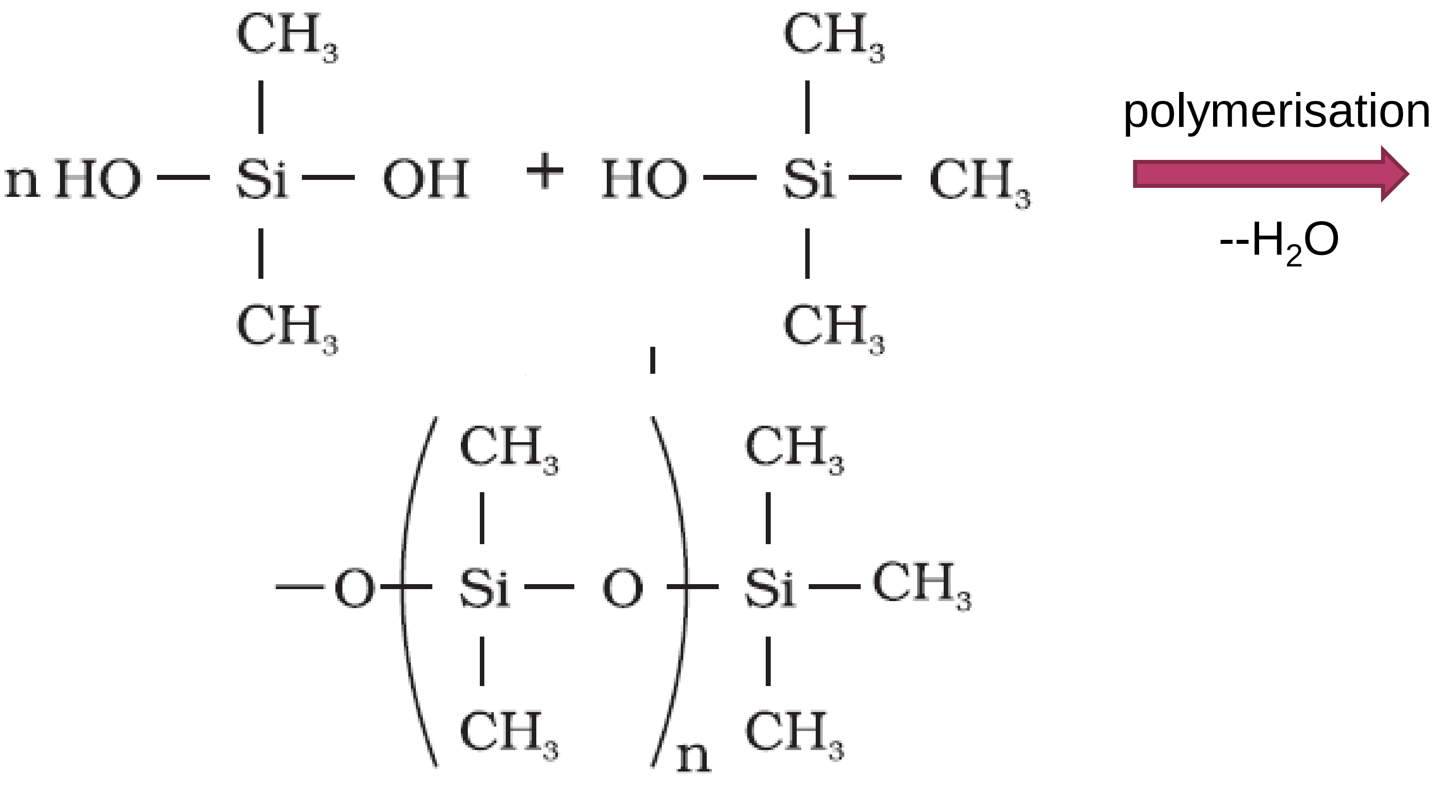
$$\mathrm{-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-}$$

Silicone

SILICONES

Method of preparation

- The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ which blocks the ends as shown below



$$n\,HO-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-OH + HO-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3 \xrightarrow[\text{--}H_2O]{\text{polymerisation}} -O\left(\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O\right)_n\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3$$

Silicone

SILICONES PROPERTIES & USES

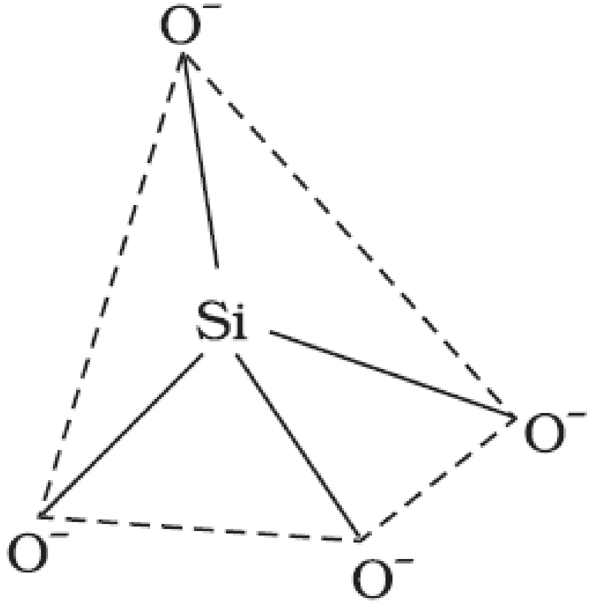
- Silicones being surrounded by non-polar alkyl groups are water repelling in nature.
- They have in general high thermal stability, high dielectric strength and resistance to oxidation and chemicals.

They have wide applications.

- They are used as sealant, greases,electrical insulators and for water proofing of fabrics.
- Being biocompatible they are also used in surgical and cosmetic plants.

SILICATES

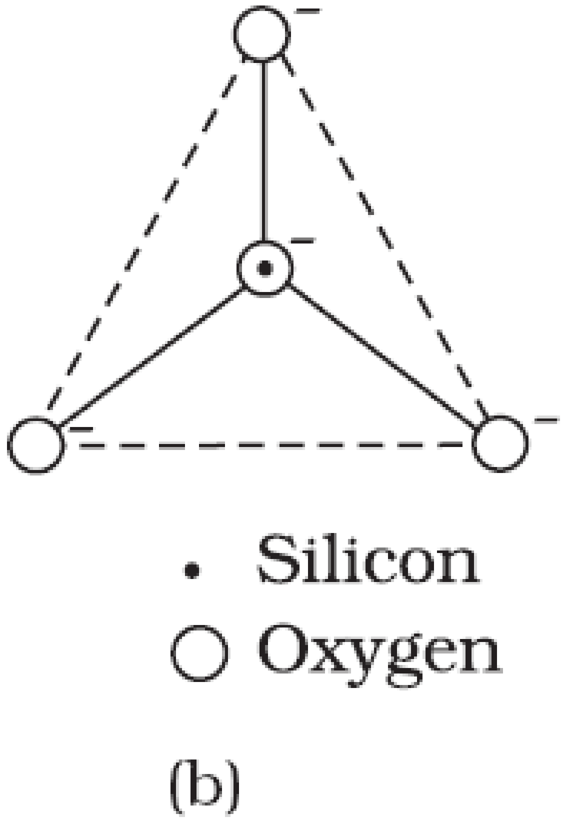
- A large number of silicates minerals exist in nature.
- Some of the examples are feldspar, zeolites, mica and asbestos.
- The basic structural unit of silicates is SiO_4^{4-}



(a)

(a) Tetrahedral structure of SiO_4^{4-}

SILICATES



(b) Representation of SiO_4^{4-} *unit*

- Two important man-made silicates are glass and cement.

ZEOLITES

- If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate,acquires a negative charge.

- Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge.

- Examples are feldspar and zeolites.

ZEOLITES USES

- Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation,
- e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline.
- Hydrated zeolites are used as ion exchangers in softening of "hard" water.

Thank you

All the best in final Exams