VELAMMAL MATRIC HR.SEC SCHOOL-SURAPET
DEPARTMENT OF CHEMISTRY

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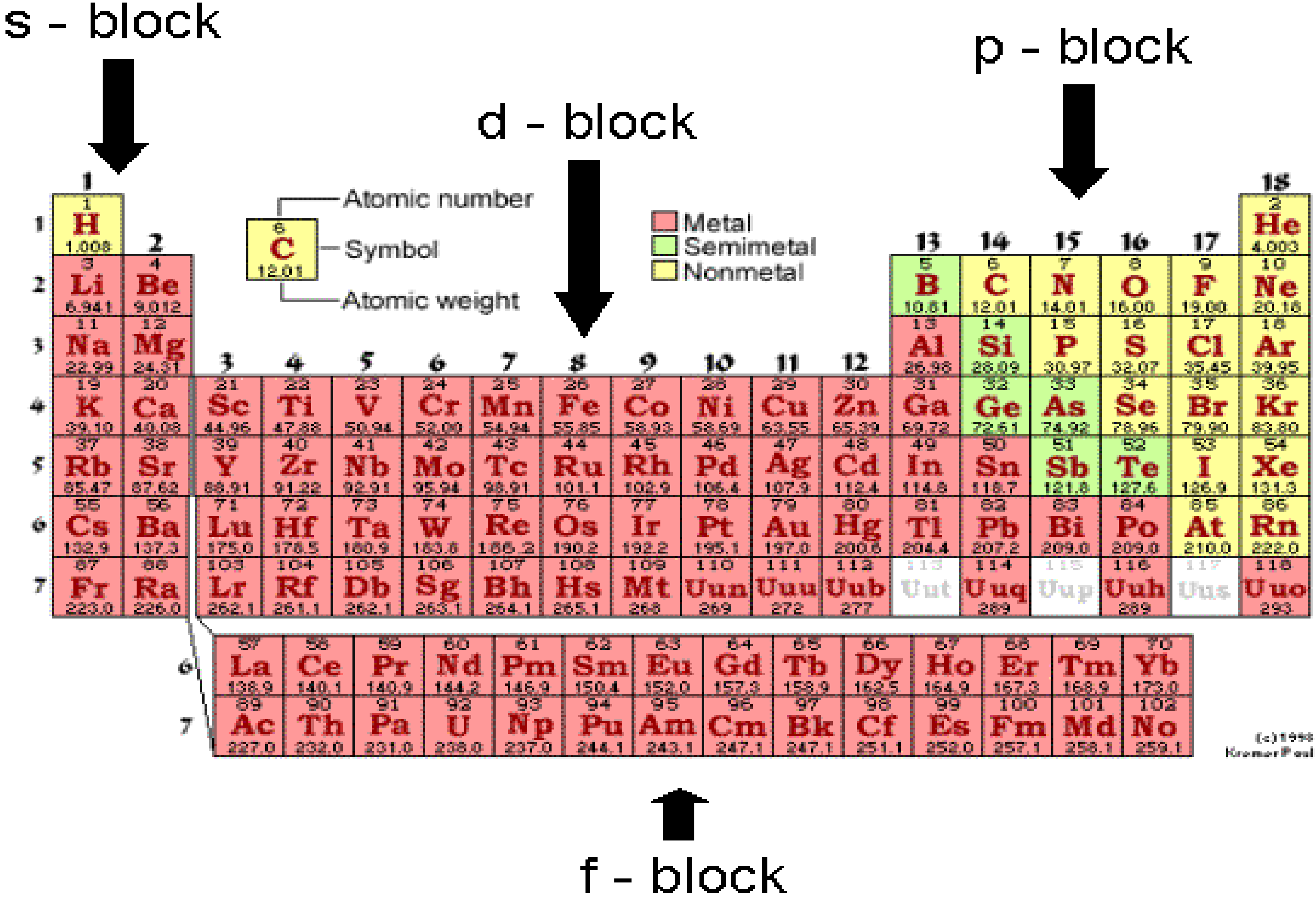
Position of p-block in periodic table



s - block

d - block

p - block

f - block

Atomic number / Symbol / Atomic weight: 6 C 12.01

🟥 Metal
🟩 Semimetal
🟨 Nonmetal

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	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	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	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 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268	110 Uun 269	111 Uuu 272	112 Uub 277	113 Uut	114 Uuq 289	115 Uup	116 Uuh 289	117 Uus	118 Uuo 293

6	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	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
7	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1

What are p-block elements?

- p-block elements are the elements in which the last electron enters ‘np’ orbital .

- which include six groups of elements i.e. group 13 to 18

- Group 13 - Boron family (Icosagens)
- Group 14 - Carbon family (Tetragens)
- Group 15 - Nitrogen family (pnicogens)
- Group 16 - Oxygen family (chalcogens)
- Group 17 - Halogens
- Group 18 - Noble gases (Inert gas or rare gas)

GENERAL TRENDS IN PROPERTIES OF P-BLOCK ELEMENTS

1.Electronic configuration and oxidation state

2. Metallic nature

3.Ionisation Enthalpy

4. Electronegativity

5. Anomalous properties of the first elements.

1.Electronic configuration and oxidation state

- The p-block elements have a general electronic configuration of $ns^2\ np^{1-6}$.
- The elements of each group have similar outer shell electronic configuration and differ only in the value of n (principal quantum number).
- The elements of this block show variable oxidation state and their highest oxidation state (group oxidation state) is equal to the total number of valance electrons present in them.
- Unlike s-block elements which show only positive oxidation state, some of the p-block elements show negative oxidation states also
- The halogens have a strong tendency to gain an electron to give a stable halide ion with completely filled electronic configuration and hence -1 oxidation state is more common in halogens. Similarly, the other elements belonging to pnictogen and chalcogen groups also show negative oxidation states.

Table 2.1 General electronic configurations and oxidation states of p-block elements

Group No.	**13**	**14**	**15**	**16**	**17**	**18**
Group Name	Icosagens	Tetragens	Pnictogens	Chalcogens	Halogens	Inert gases
General outer electronic configuration	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$
Highest oxidation state (Group oxidation state)	+3	+4	+5	+6	+7	+8
Other observed oxidation states	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3, +1, -1	+6. +4, +2

2. Metallic nature

- The tendency of an element to form a cation by loosing electrons is known as electropositive or metallic character.
- This character depends on the ionisation energy.
- Generally on descending a group the ionisation energy decreases and hence the metallic character increases.
- In p-block, the elements present in ***lower left part are metals*** while the elements in the ***upper right part are non metals.***

Group 13 :

Nonmetal : Nil.

Metal : Aluminium (Al), Gallium(Ga),Indium(In),Thallium(Tl).

Metalloid: Boron (B).

Radioactive : Nihonium(Nh).

Group 14:

Nonmetal : Carbon (C)

Metal : Tin (Sn), Lead(Pb).

Metalloid: Silicon(Si), Germanium(Ge)

Radioactive : Flerovium (Fl).

Group 15

Nonmetal : Nitrogen (N), Phosphorous(P)

Metal : Bismuth(Bi)

Metalloid: Arsenic(As), Antimony(Sb)

Radioactive : Moscovium (Mc)

Group 16:

Nonmetal : Oxygen(O), Sulphur(S), Selenium(Se).

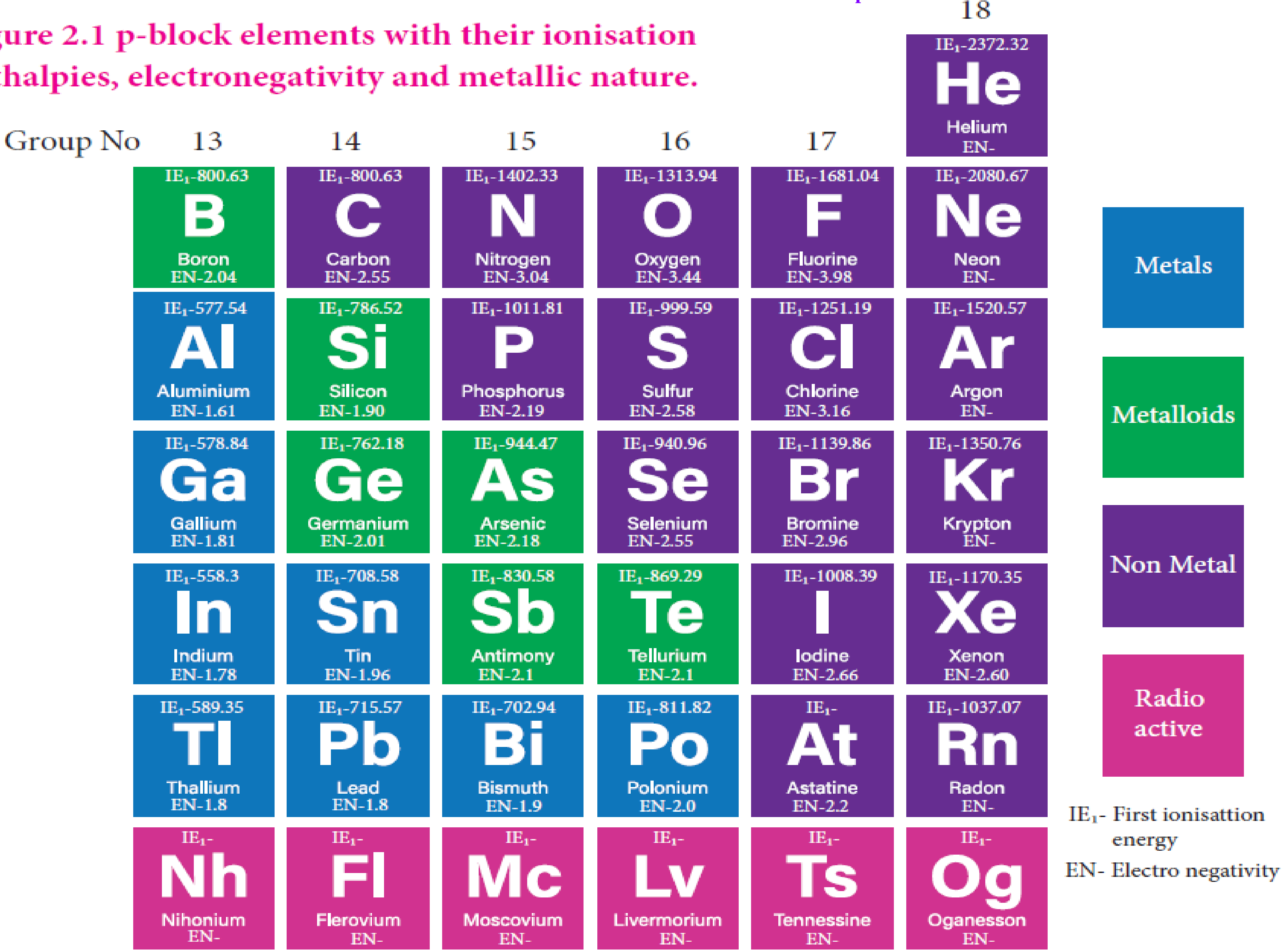
Metal : Polonium(Po)

Metalloid: Tellurium (Te)

Radioactive : Livermorium(Lv)

Group 17 : Nonmetal :F,Cl,Br,I ,At Radioactive: Tennessine(TS).

Group 18 : Noble gases are nonmetals.



Group No	13	14	15	16	17	18
						IE_1-2372.32 He Helium EN-
	IE_1-800.63 B Boron EN-2.04	IE_1-800.63 C Carbon EN-2.55	IE_1-1402.33 N Nitrogen EN-3.04	IE_1-1313.94 O Oxygen EN-3.44	IE_1-1681.04 F Fluorine EN-3.98	IE_1-2080.67 Ne Neon EN-
	IE_1-577.54 Al Aluminium EN-1.61	IE_1-786.52 Si Silicon EN-1.90	IE_1-1011.81 P Phosphorus EN-2.19	IE_1-999.59 S Sulfur EN-2.58	IE_1-1251.19 Cl Chlorine EN-3.16	IE_1-1520.57 Ar Argon EN-
	IE_1-578.84 Ga Gallium EN-1.81	IE_1-762.18 Ge Germanium EN-2.01	IE_1-944.47 As Arsenic EN-2.18	IE_1-940.96 Se Selenium EN-2.55	IE_1-1139.86 Br Bromine EN-2.96	IE_1-1350.76 Kr Krypton EN-
	IE_1-558.3 In Indium EN-1.78	IE_1-708.58 Sn Tin EN-1.96	IE_1-830.58 Sb Antimony EN-2.1	IE_1-869.29 Te Tellurium EN-2.1	IE_1-1008.39 I Iodine EN-2.66	IE_1-1170.35 Xe Xenon EN-2.60
	IE_1-589.35 Tl Thallium EN-1.8	IE_1-715.57 Pb Lead EN-1.8	IE_1-702.94 Bi Bismuth EN-1.9	IE_1-811.82 Po Polonium EN-2.0	IE_1- At Astatine EN-2.2	IE_1-1037.07 Rn Radon EN-
	IE_1- Nh Nihonium EN-	IE_1- Fl Flerovium EN-	IE_1- Mc Moscovium EN-	IE_1- Lv Livermorium EN-	IE_1- Ts Tennessine EN-	IE_1- Og Oganesson EN-

🟦 Metals

🟩 Metalloids

🟪 Non Metal

🟥 Radio active

IE_1- First ionisattion energy

EN- Electro negativity

Figure 2.1 p-block elements with their ionisation enthalpies, electronegativity and metallic nature.

3.Ionisation Enthalpy:

- We have already learnt that as we move down a group, generally there is a steady decrease in ionisation enthalpy of elements due to increase in their atomic radius.
- In p-block elements, there are some minor deviations to this general trend.
- **In group 13, from boron to aluminium the ionisation enthalpy decreases as expected. But from aluminium to thallium there is only a marginal difference. This is due to the presence of inner d and f-electrons which has poor shielding effect compared to s and p-electrons. As a result, the effective nuclear charge on the valance electrons increases.**
- A similar trend is also observed in group 14.
- The remaining groups (15 to 18) follow the general trend. In these groups, the ionisation enthalpy decreases, as we move down the group. Here, poor shielding effect of d- and f-electrons are overcome by the increased shielding effect of the additional p-electrons.
- The ionisation enthalpy of elements in successive groups is higher than the corresponding elements of the previous group as expected.

4. Electronegativity

- As we move down the 13 group, the electronegativity first decreases from boron to aluminium and then marginally increases.

- Similar trend is observed, as move from first element to the next element in other groups, and thereafter, there is no appreciable change in electronegativity values.

- This observed trend can be correlated with their atomic radius.

5. Anomalous properties of the first elements.

In p-block elements, the first member of each group differs from the other elements of the corresponding group. The following factors are responsible for this anomalous behaviour.

1. Small size of the first member
2. High ionisation enthalpy and high electronegativity
3. Absence of d orbitals in their valance shell

INERT PAIR EFFECT:

Heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect.

Let us consider **group 13 elements**. As we move from boron to heavier elements, there is an increasing tendency to have +1 oxidation state, rather than the group oxidation state, +3. For example Al^{+3} is more stable than Al^{+1} while Tl^{+1} is more stable than Tl^{+3}. Aluminium(III)chloride is stable whereas thallium(III)chloride is highly unstable and disproportionates to thallium(I) chloride and chlorine gas. This shows that in thallium the stable lower oxidation state corresponds to the loss of np electrons only and not ns electrons.

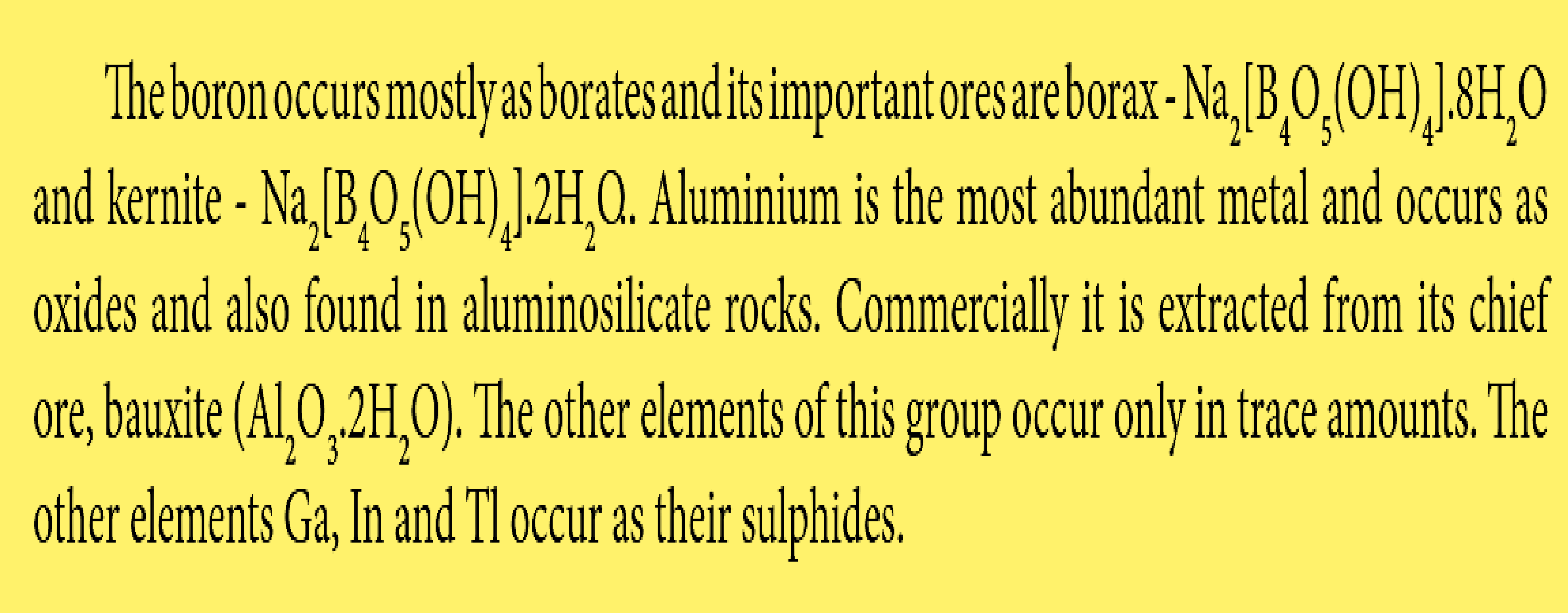
Allotropism in p-block elements:

Some elements exist in more than one crystalline or molecular forms in the same physical state.

For example, carbon exists as diamond and graphite. This phenomenon is called allotropism (in greek '*allos*' means another and '*trope*' means change) and the different forms of an element are called allotropes. Many p-block elements show allotropism and some of the common allotropes are listed in the table.

Element	Most common allotropes
Boron	Amorphous boron, α-rhombohedral boron, β-rhombohedral boron, γ-orthorhombic boron, α-tetragonal boron, β-tetragonal boron
Carbon	Diamond, Graphite, Graphene, Fullerenes, Carbon nanotubes
Silicon	Amourphous silicon, crystalline silicon
Germanium	α-germanium, β-germanium
Tin	Grey tin, white tin, rhombic tin, sigma tin
Phosphorous	White phosphorous, Red phosphorous, Scarlet phosphorous, Violet phosphorous, Black phosphorous.
Arsenic	Yellow arsenic, gray arsenic & Black arsenic
Anitmony	Blue-white antimony, Yellow, Black
Oxygen	Dioxygen, ozone
Sulphur	Rhombus sulphur, monoclinic sulphur
Selenium	Red selenium, Gray selenium, Black selenium, Monoclinic selenium,
Tellurium	Amourphous & Crystalline

Group 13 elements: The boron family



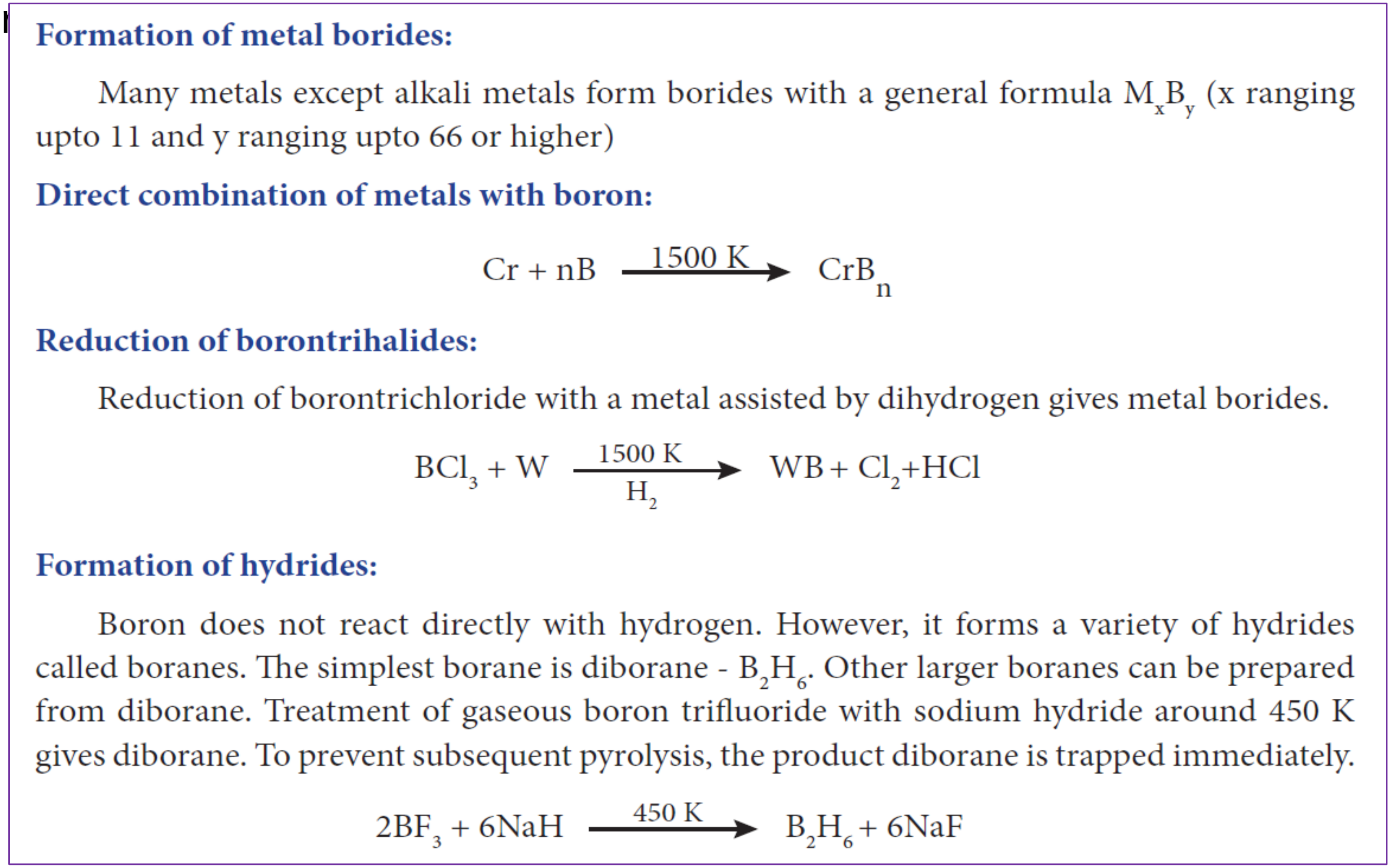
The boron occurs mostly as borates and its important ores are borax - $Na_2[B_4O_5(OH)_4].8H_2O$ and kernite - $Na_2[B_4O_5(OH)_4].2H_2O$. Aluminium is the most abundant metal and occurs as oxides and also found in aluminosilicate rocks. Commercially it is extracted from its chief ore, bauxite ($Al_2O_3.2H_2O$). The other elements of this group occur only in trace amounts. The other elements Ga, In and Tl occur as their sulphides.

Property	Boron	Aluminum	Gallium	Indium	Thallium
Physical state at 293 K	Solid	Solid	Solid	Solid	Solid
Atomic Number	5	13	31	49	81
Isotopes	^{11}B	^{27}Al	^{69}Ga	^{115}In	^{205}Tl

Property	Boron	Aluminum	Gallium	Indium	Thallium
Atomic Mass ($g.mol^{-1}$ at 293 K)	10.81	26.98	69.72	114.81	204.38
Electronic configuration	$[He]2s^2\ 2p^1$	$[Ne]3s^2\ 3p^1$	$[Ar]3d^{10}\ 4s^2\ 4p^1$	$[Kr]4d^{10}\ 5s^2\ 5p^1$	$[Kr]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$
Atomic radius (Å)	1.92	1.84	1.87	1.93	1.96
Density ($g.cm^{-3}$ at 293 K)	2.34	2.70	5.91	7.31	11.80
Melting point (K)	2350	933	302.76	429	577
Boiling point (K)	4273	2792	2502	2300	1746

CHEMICAL PROPERTIES OF BORON:

Boron is the only nonmetal in this group and is less reactive. However, it shows reactivity at higher temperatures. Many of its compounds are electron deficient and has unusual type of covalent bonding which is due to its small size, high ionisation energy and similarity in electronegativity with carbon and hydr



Formation of metal borides:

Many metals except alkali metals form borides with a general formula M_xB_y (x ranging upto 11 and y ranging upto 66 or higher)

Direct combination of metals with boron:

$$Cr + nB \xrightarrow{1500\ K} CrB_n$$

Reduction of borontrihalides:

Reduction of borontrichloride with a metal assisted by dihydrogen gives metal borides.

$$BCl_3 + W \xrightarrow[H_2]{1500\ K} WB + Cl_2 + HCl$$

Formation of hydrides:

Boron does not react directly with hydrogen. However, it forms a variety of hydrides called boranes. The simplest borane is diborane - B_2H_6. Other larger boranes can be prepared from diborane. Treatment of gaseous boron trifluoride with sodium hydride around 450 K gives diborane. To prevent subsequent pyrolysis, the product diborane is trapped immediately.

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

Formation of boron trihalides:

Boron combines with halogen to form boron trihalides at high temperatures.

$$2B + 3X_2 \xrightarrow{\Delta} 2BX_3$$

Formation of boron nitride:

Boron burns with dinitrogen at high temperatures to form boron nitride.

$$2B + N_2 \xrightarrow{\Delta} 2BN$$

Formation of oxides:

When boron is heated with oxygen around 900 K, it forms its oxide.

$$4B + 3O_2 \xrightarrow{900\ K} 2B_2O_3$$

Reaction with acids and alkali:

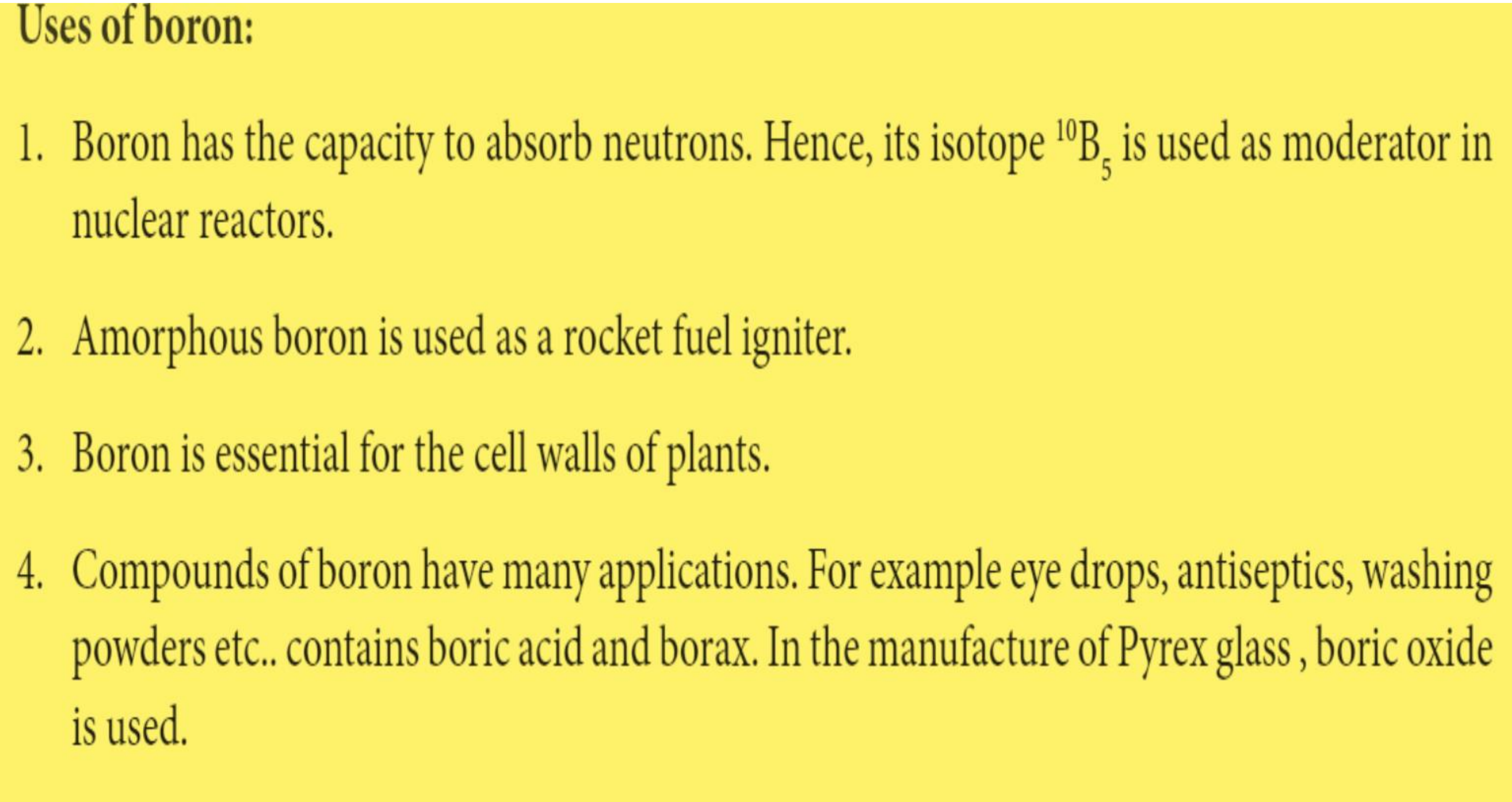
Halo acids have no reaction with boron. However, boron reacts with oxidising acids such as sulphuric acid and nitric acids and forms boric acid.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

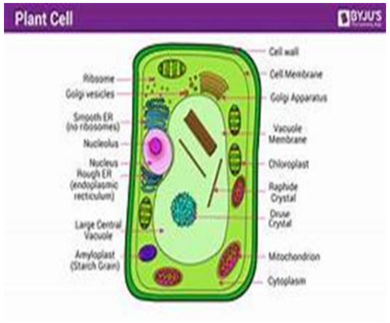
Boron reacts with fused sodium hydroxide and forms sodium borate.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$



Uses of boron:

1. Boron has the capacity to absorb neutrons. Hence, its isotope $^{10}B_5$ is used as moderator in nuclear reactors.
2. Amorphous boron is used as a rocket fuel igniter.
3. Boron is essential for the cell walls of plants.
4. Compounds of boron have many applications. For example eye drops, antiseptics, washing powders etc.. contains boric acid and borax. In the manufacture of Pyrex glass , boric oxide is used.



BORAX

Preparation:

Borax is a sodium salt of tetraboric acid. It is obtained from colemanite ore by boiling its solution with sodium carbonate.

$$2Ca_2B_6O_{11} + 2NaCO_3 + H_2O \xrightarrow{\Delta} 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

Properties

Borax is basic in nature and its solution in hot-water is alkaline as it dissociates into boric acid and sodium hydroxide.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

On heating it forms a transparent borax beads.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

Borax reacts with acids to form sparingly soluble boric acid.

$$Na_2B_4O_7 + 2HCl + 7H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + 2Na_2SO_4$$

When treated with ammonium chloride it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 2H_2O$$

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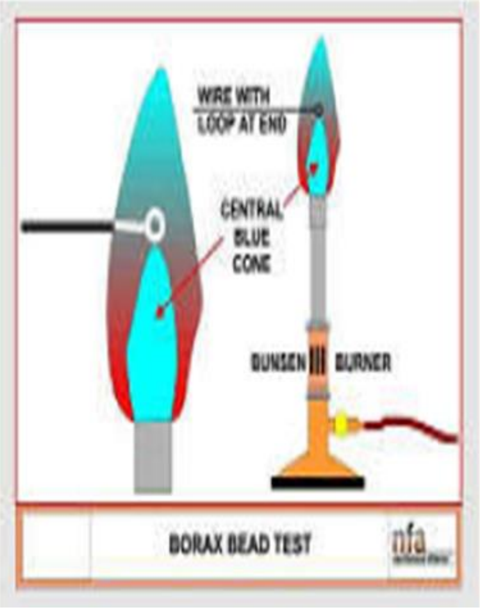
$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 2H_2O$$

Uses of Borax:

1. Borax is used for the identification of coloured metal ions
2. In the manufacture optical and borosilicate glass, enamels and glazes for pottery
3. It is also used as a flux in metallurgy and also acts as a good preservative



BORIC ACID H_3BO_3 or $B(OH)_3$

- PREPARATION:

Boric acid can be extracted from borax and colemanite.

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

Borax Boric acid

$$Ca_2B_6O_{11} + 11\,H_2SO_4 + So_2 \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Colemanite

Properties:

- Boric acid is a colourless transparent crystal. It is a very weak monobasic acid and, it accepts hydroxyl ion rather than donating proton.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

- It reacts with sodium hydroxide to form sodium metaborate and sodium tetraborate.

$$NaOH + H_3BO_3 \longrightarrow NaBO_2 + 2H_2O$$

$$2NaOH + 4H_3BO_3 \longrightarrow Na_2B_4O_7 + 7H_2O$$

Action of Heat:

- Boric acid when heated at 373 K gives metaboric aid and at 413 K, it gives tetraboric acid. When heated at red hot, it gives boric anhydride which is a glassy mass.

$$4H_3BO_3 \xrightarrow{373\ K} 4HBO_2 + H_2O$$

$$4HBO_2 \xrightarrow{413\ K} H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$

Acton of amonia :

- Fusion of urea with B(OH)₃, in an atmosphere of ammonia at 800 - 1200 K gives boron nitride.

$$B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$$

- When boric acid or borate salt is heated with ethyl alcohol in presence of conc. sulphuric acid, an ester, trialkylborate is formed. The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$4H_3BO_3 + 3C_2H_5OH \xrightarrow[H_2SO_4]{Conc.} B(OC_2H_5)_3 + 3H_2O$$

Formation of boron trifluoride:

- Boric acid reacts with calcium fluoride in presence of conc. sulphuric acid and gives boron trifluo

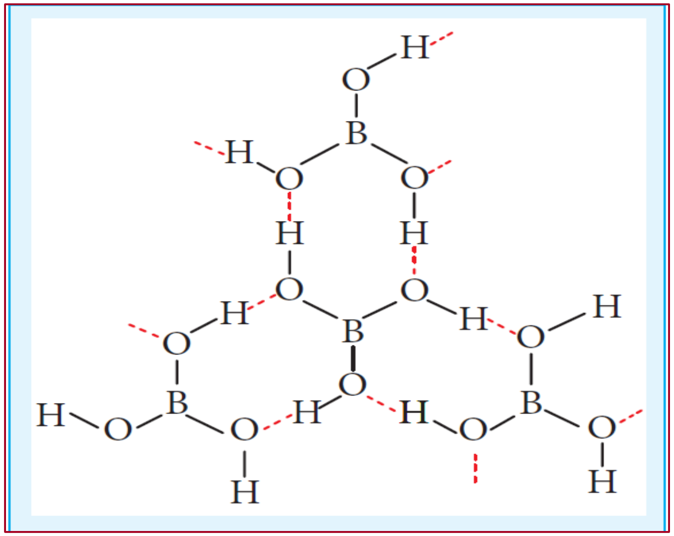
$$CaF_2 + 3H_2SO_4 + 2\,B(OH)_3 \longrightarrow 3CaSO_4 + 2BF_3 + 6H_2O$$

Borax when heated with soda ash it gives borax

$$Na_2CO_3 + 4B(OH)_3 \longrightarrow Na_2B_4O_7 + CO_2 + 6H_2O$$

Structure of Boric acid:

- Boric acid has a two dimensional layered structure.
- It consists of $[BO_3]^{3-}$ unit and these are linked to each other by hydrogen bonds.



Uses of boric acid:

1. Boric acid is used in the manufacture of pottery glazes, glass, enamels and pigments.

2. It is used as an antiseptic and as an eye lotion.

3. It is also used as a food preservative.

BORANES

Boranes are synthetic hydrides of boron with general formula B_xH_y.

Cluster type	Formula	Example	IUPAC Name
closo-	$B_nH_n^{2-}$	$CaB_{12}H_{12}^{2-}$	**Caesium dodecaborate**
nido-	B_nH_{n+4}	B_2H_6	**Diborane(6)**
		B_5H_9	**Pentaborane(9)**
		$B_{10}H_{14}$	**decaborane(14)**
arachno-	B_nH_{n+6}	B_4H_{10}	**tetraborane(10)**
		B_5H_{11}	**pentaborane(11)**

DIBORANE (B_2H_6)

Preparation:

- Diborane can be prepared by the action of metal hydride with boron. This method is used for the industrial production.

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

- Diborane can also be obtained in small quantities by the reaction of iodine with sodium borohydride in diglyme.

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

On heating magnesium boride with HCl a mixture of volatile boranes are obtained.

$$2Mg_3B_2 + 12HCl \longrightarrow 6MgCl_2 + B_4H_{10} + H_2$$

$$B_4H_{10} + H_2 \longrightarrow 2B_2H_6$$

Properties:

- Boranes are colourless diamagnetic compounds with low thermal stability.

- Diborane is a gas at room temperature with sweet smell and it is extremely toxic.
  It is also highly reactive.

- At high temperatures it forms higher boranes liberating hydrogen.

$$5B_2H_6 \xrightarrow[\text{U - tube}]{388\ \text{K}} 2B_5H_{11} + 4H_2$$

$$2B_2H_6 \xrightarrow{198\ -\ 373\ \text{K}} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow[\text{sealed tube}]{373\ \text{K}} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow{473\ -\ 523\ \text{K}} 2B_5H_9 + 6H_2$$

$$10B_2H_6 \xrightarrow{523\ \text{K}} 2B_5H_9 + 2B_5H_{10} + 11H_2$$

$$B_2H_6 \xrightarrow{\text{Red hot}} 2B + 3H_2$$

- Diboranes reacts with water and alkali to give boric acid and metaborates resp

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

$$B_2H_6 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 6H_2$$

Action of air:

- At room temperature pure diborane does not react with air or oxygen but in impure form it gives B_2O_3 along with large amount of heat.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \quad \Delta H = -2165 \text{ KJ mol}^{-1}$$

- Diborane reacts with methyl alcohol to give trimethyl Borate.

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

Hydroboration:

- Diborane adds on to alkenes and alkynes in ether solvent at room temperature.
- This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti Markovnikov addition.

$$B_2H_6 + 3RCH_2{=}CH_2R \longrightarrow B(CH_2\text{-}CH_2R)_3 + 6H_2$$

Reaction with ionic hydrides

- When treated with metal hydrides it forms metal borohydrides

$$B_2H_6 + 2LiH \xrightarrow{\text{Ether}} 2LiBH_4$$

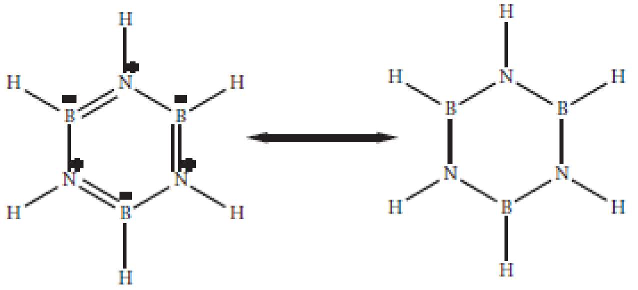
$$B_2H_6 + 2NaH \xrightarrow{\text{Diglyme}} 2NaBH_4$$

Reaction with ammonia:

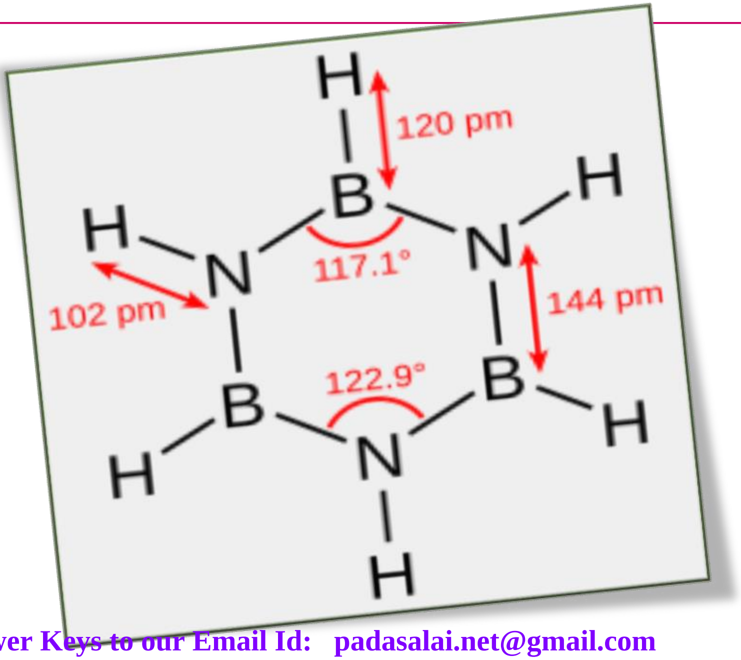
- When treated with excess ammonia at low temperatures diborane gives diboranediammonate. On heating at higher temperatures it gives borazole.

$$3B_2H_6 + 6NH_3 \xrightarrow{-153\ K} 3B_2H_6.2NH_3 \text{ (or) } 3[BH_2(NH_3)_2]^+[BH_4]^-$$

$$3B_2H_6+2NH_3 \xrightarrow[\text{Clossed vessel}]{\text{High temp}}$$



$2B_3N_3H_6$ (Borazole or Borazine - Inorganic benzene)



Structure of diborane:

In diborane two BH_2 units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds.

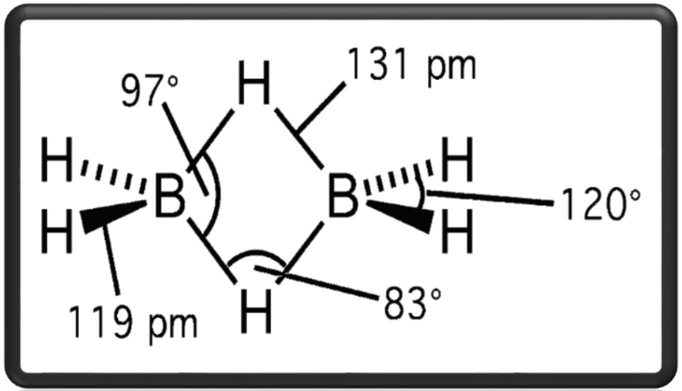
However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds.

The four terminal B-H bonds are normal covalent bonds (two centre - two electron bond or 2c-2e bond).

The remaining four electrons have to used for the bridged bonds. i.e. two three centred B-H-B bonds utilise two electrons each.

Hence, these bonds are three centre- two electron bonds. The bridging hydrogen atoms are in a plane.

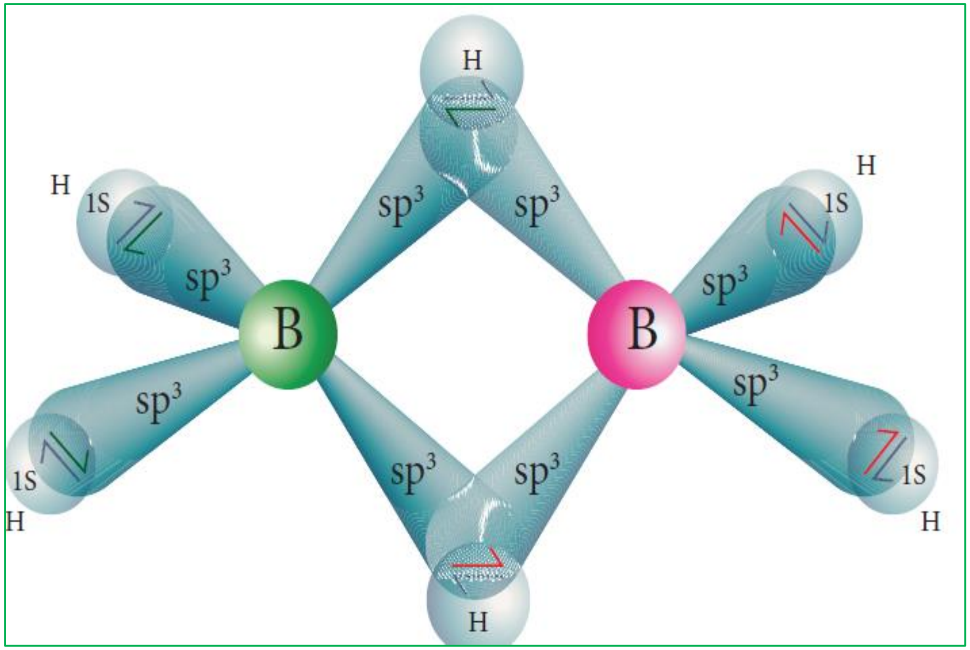
In diborne, the boron is sp^3 hybridised.



Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty.

Two of the half filled hybridised orbitals of each boron overlap with the two hydrogens to form four terminal 2c-2e bonds, leaving one empty and one half filled hybridised orbitals on each boron.

The Three centre - two electron bonds), B-H-B bond formation involves overlapping the half filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half filled 1s orbital of hydrogen

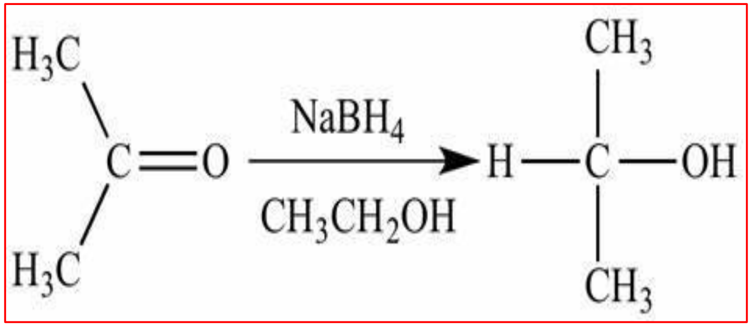


Uses of diborane:

1. Diborane is used as a high energy fuel for propellant

2. It is used as a reducing agent in organic chemistry

3. It is used in welding torches



BORON TRIFLUORIDE (BF$_3$)

Preparation:

Boron trifuloride is obtained by the treatment of calcium fluoride with boron trioxide in presence of conc.

$$\boxed{B_2O_3 + 3CaF_2 + 3H_2SO_4 \xrightarrow{\Delta} 2BH_3 + 3CaSO_4 + 3H_2O}$$

It can also be obtained by treating boron trioxide with carbon and fluorine.

$$\boxed{B_2O_3 + 3C + 3F_2 \longrightarrow 2BF_3 + 3CO}$$

In the laboratory pure BF$_3$ is prepared by the thermal decomposition of benzene diazonium tetrafluoro borate.

$$\boxed{PhN_2BF_4 \xrightarrow{\Delta} BF_3 + PhF + N_2}$$

Properties:

Boron trifluoride has a planar geometry. It is an electron deficient compound and accepts electron pairs to form coordinate covalent bonds. They form complex of the type $[BX_4]^-$.

$$BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$$

$$BF_3 + H_2O \longrightarrow F_3B \leftarrow OH_2$$

On hydrolysis, boric acid is obtained. This then gets converted into fluoro boric acid.

$$4BF_3 + 12H_2O \longrightarrow 4H_3BO_3 + 12HF$$

$$3H_3BO_3 + 12HF \longrightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$

$$4BF_3 + 9H_2O \longrightarrow 4H_3BO_3 + 3H^+ + 3[BF_4]^-$$

Uses of Boron trifluoride:

1. Boron trifluoride is used for preparing HBF_4, a catalyst in organic chemistry

2. It is also used as a fluorinating reagent.

Preparation:

When aluminium metal or aluminium hydroxide is treated with hydrochloric acid, aluminium trichloride is formed. The reaction mixture is evaporated to obtain hydrated aluminium chloride

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

McAfee Process:

Aluminium chloride is obtained by heating a mixture of alumina and coke in a current of chlorine.

$$\boxed{Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO_2}$$

On industrial scale it is prepared by chlorinating aluminium around 1000 K

$$\boxed{2Al + 3Cl_2 \xrightarrow{1000\ K} 2AlCl_3}$$

PROPERTIES:

Anhydrous aluminium chloride is a colourless, hygroscopic substance.

- An aqueous solution of aluminium chloride is acidic in nature. It also produces hydrogen chloride fumes in moist air.

$$\boxed{AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl}$$

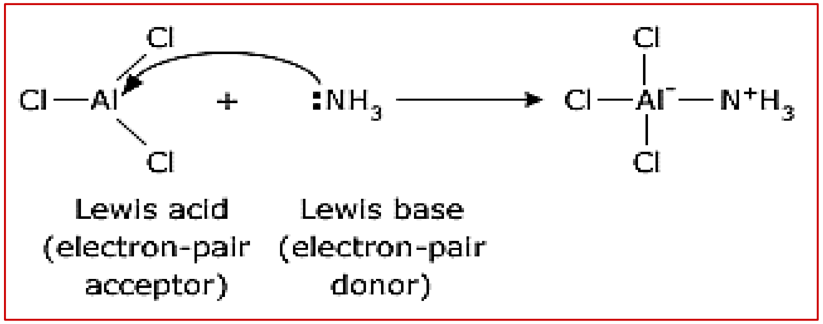
- With ammonium hydroxide it forms aluminium hydroxide.

$$\boxed{AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl}$$

- With excess of sodium hydroxide it produces metal aluminate

$$\boxed{AlCl_3 + 4NaOH \longrightarrow NaAlO_2 + 2H_2O + 3NaCl}$$

- It behaves like a Lewis acid and forms addition compounds with ammonia, phosphine and carbonylchloride etc... Eg. $AlCl_3.6NH_3$.

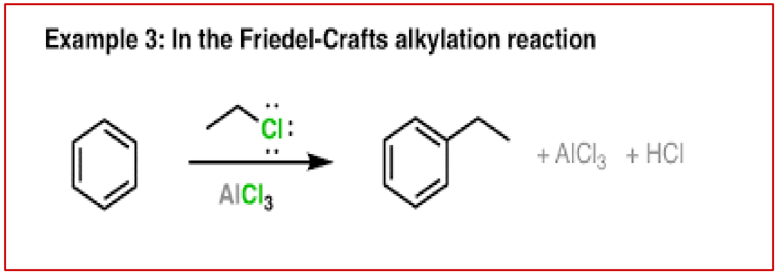


Uses of aluminium chloride:

1. Anhydrous aluminium chloride is used as a catalyst in Friedels Crafts reactions

2. It is used for the manufacture of petrol by cracking the mineral oils.

3. It is used as a catalyst in the manufacture on dyes, drugs and perfumes.


Example 3: In the Friedel-Crafts alkylation reaction

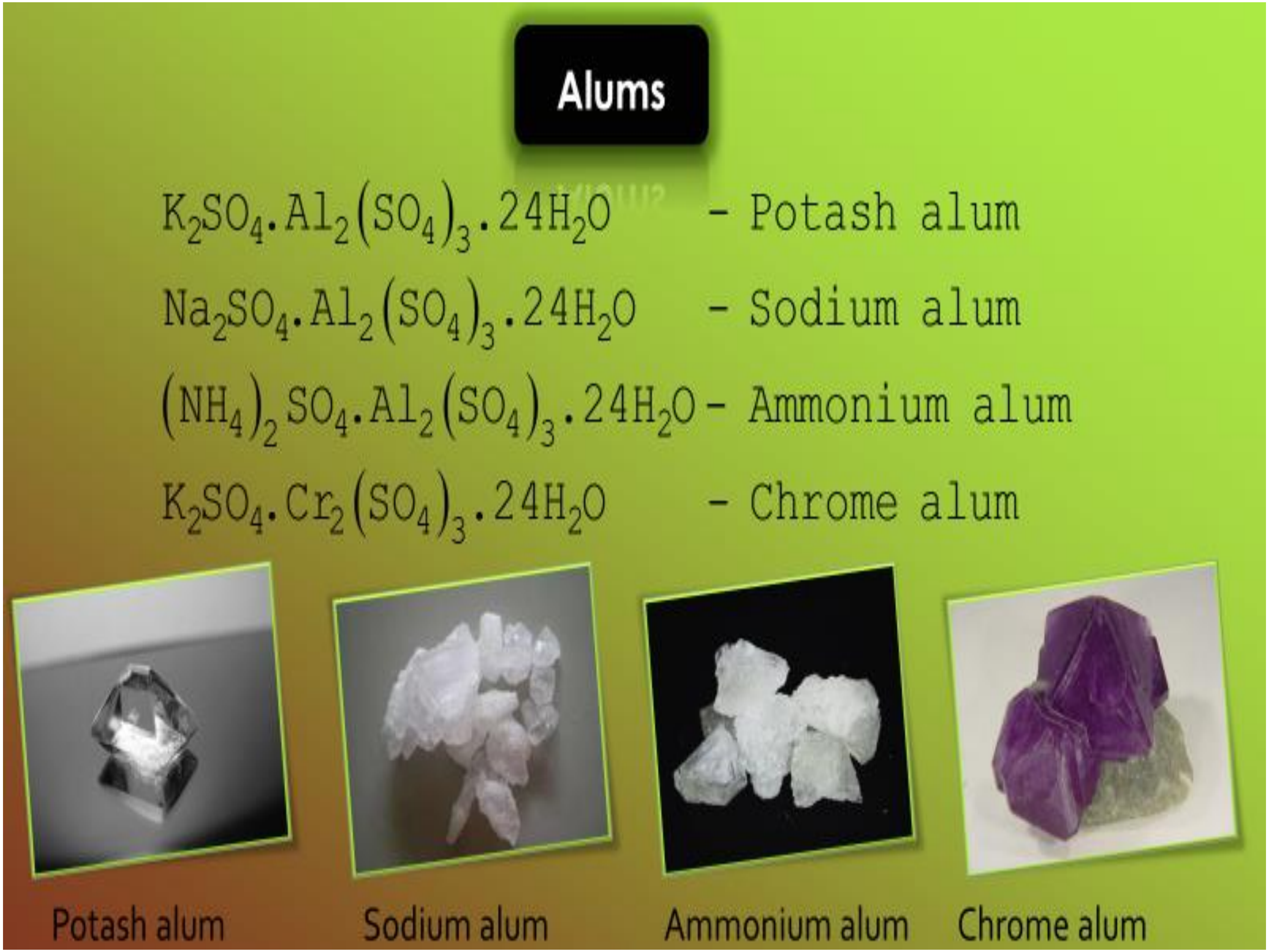
ALUMS

- The name alum is given to the double salt of potassium aluminium sulphate

  $[K_2SO_4.\ Al_2(SO_4)_3.24.H_2O]$.

- Now a days it is used for all the double salts with $M'_2SO_4.M''_2(SO_4)_3.24H_2O$
- Where M' is univalent metal ion or [NH4]+

  M" is trivalent metal ion Al^{3+}



Alums

$K_2SO_4.Al_2(SO_4)_3.24H_2O$ - Potash alum

$Na_2SO_4.Al_2(SO_4)_3.24H_2O$ - Sodium alum

$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$ - Ammonium alum

$K_2SO_4.Cr_2(SO_4)_3.24H_2O$ - Chrome alum

PREPARATION:

- The alunite the alum stone is the naturally occurring form and it is **$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.**

- When alum stone is treated with excess of **sulphuric acid, the aluminium hydroxide is converted to aluminium sulphate**.

- A calculated quality of **potassium sulphate** is added and the solution is crystallised to generate potash alum. It is purified by recrystallisation.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + Al_2(SO_4)_3 + 12\,H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24\,H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24\,H_2O$$

PROPERTIES

- Potash alum is a white crystalline solid it is soluble in water and insoluble in alcohol.

- **The aqueous solution is acidic** due to the hydrolysis of aluminium sulphate.

- Potash alum melts at 365 K on heating. At 475 K loses water of hydration and swells up. The swollen mass is known as **burnt alum.**
- Heating to red hot it decomposes into potassium sulphate, alumina and sulphur trioxide.

$$K_2SO_4.Al_2(SO_4)_3.24\,H_2O \xrightarrow{500\text{ K}} K_2SO_4.Al_2(SO_4)_3 + 24\,H_2O$$

$$K_2SO_4.Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} K_2SO_4 + Al_2O_3 + 3SO_3$$

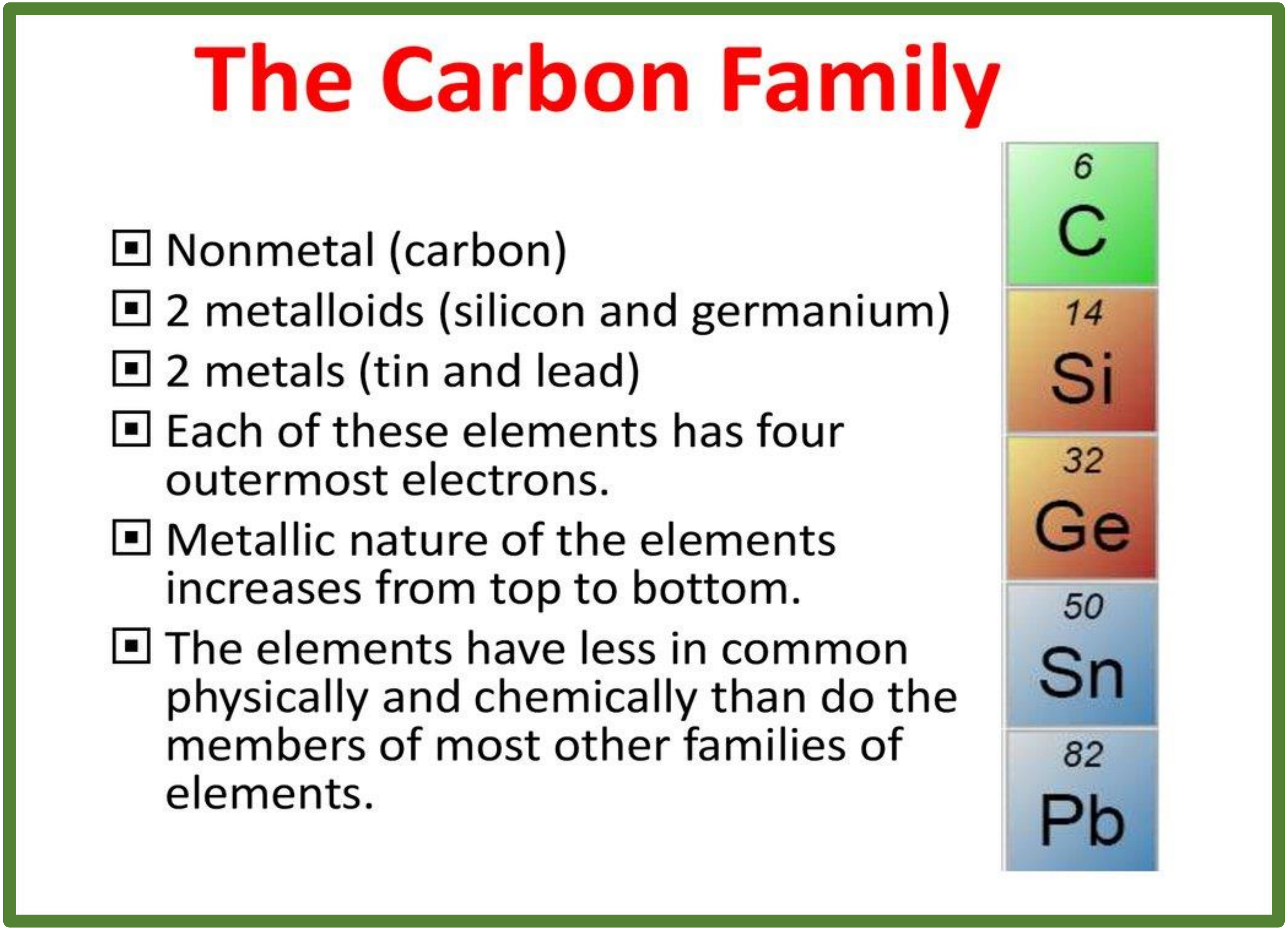
Potash alum forms aluminium hydroxide when treated with ammonium hydroxide.

$$K_2SO_4.Al_2(SO_4)_3.24\,H_2O + 6NH_4OH \longrightarrow K_2SO_4 + 3(NH_4)_2SO_4 + 24\,H_2O + 3Al(OH)_3$$

USES OF ALUM:

1. It is used for **purification of water**
2. It is also used for **water proofing and textiles**
3. It is used in **dyeing, paper** and **leather tanning industries**
4. It is employed as a **styptic agent to arrest bleeding.**

Group 14 (Carbon group) elements:

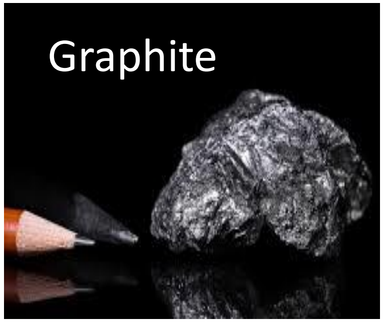


The Carbon Family

- Nonmetal (carbon)
- 2 metalloids (silicon and germanium)
- 2 metals (tin and lead)
- Each of these elements has four outermost electrons.
- Metallic nature of the elements increases from top to bottom.
- The elements have less in common physically and chemically than do the members of most other families of elements.

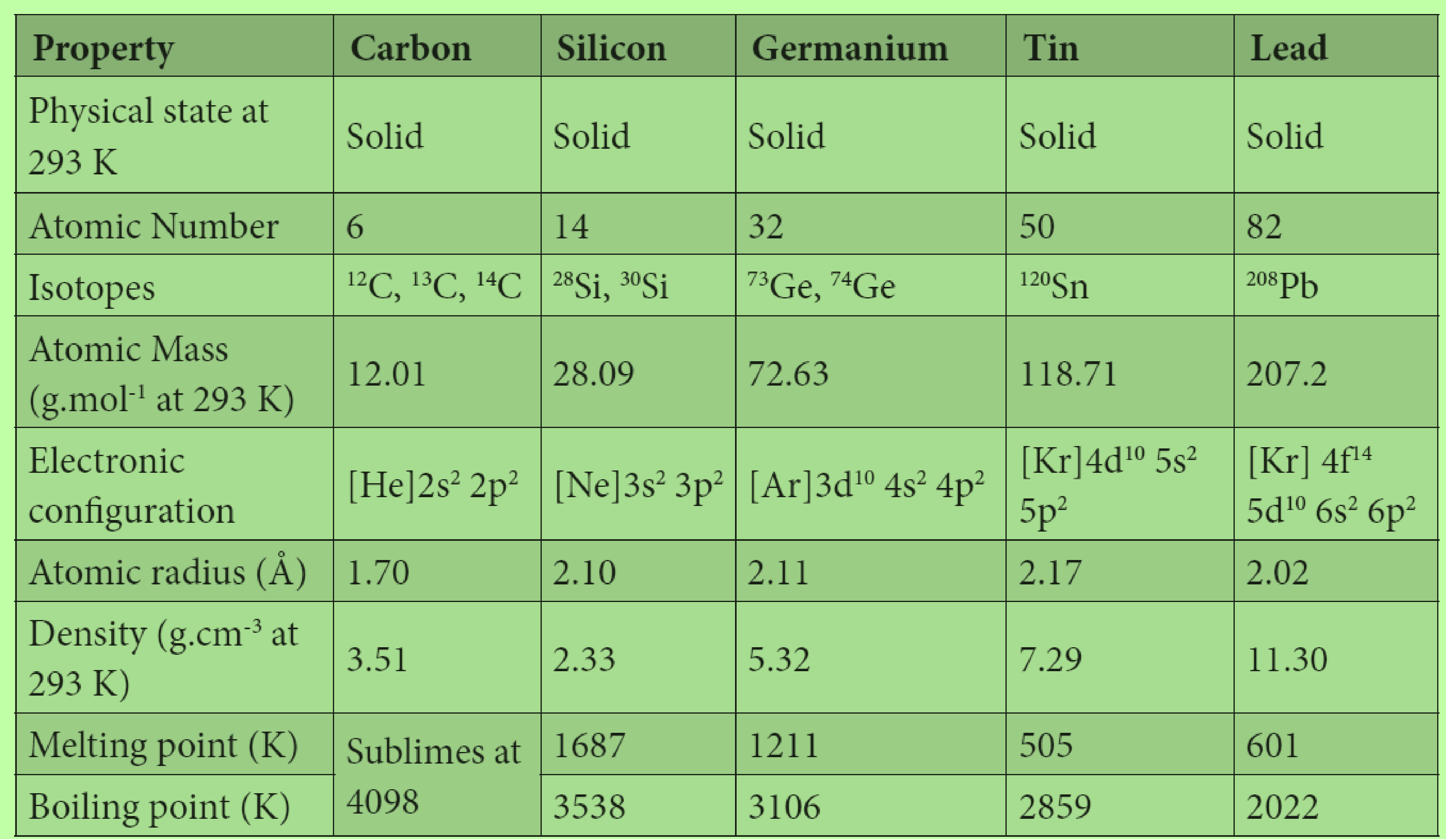
OCCURRENCE:

- **Carbon is found in the native form as** Graphite. Coal, crude oil and carbonate rocks such as calcite, magnesite etc...contains large quantities of carbon in its combined form with other elements.



- **Silicon occurs as** silica (sand and quartz crystal). Silicate minerals and clay are other important sources for silicon.

PHYSICAL PROPERTIES:



Property	Carbon	Silicon	Germanium	Tin	Lead
Physical state at 293 K	Solid	Solid	Solid	Solid	Solid
Atomic Number	6	14	32	50	82
Isotopes	^{12}C, ^{13}C, ^{14}C	^{28}Si, ^{30}Si	^{73}Ge, ^{74}Ge	^{120}Sn	^{208}Pb
Atomic Mass (g.mol^{-1} at 293 K)	12.01	28.09	72.63	118.71	207.2
Electronic configuration	[He]$2s^2$ $2p^2$	[Ne]$3s^2$ $3p^2$	[Ar]$3d^{10}$ $4s^2$ $4p^2$	[Kr]$4d^{10}$ $5s^2$ $5p^2$	[Kr] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$
Atomic radius (Å)	1.70	2.10	2.11	2.17	2.02
Density (g.cm^{-3} at 293 K)	3.51	2.33	5.32	7.29	11.30
Melting point (K)	Sublimes at 4098	1687	1211	505	601
Boiling point (K)		3538	3106	2859	2022

TENDENCY FOR CATENATION

Catenation is an ability of an element to form chain of atoms.

The following conditions are necessary for catenation.

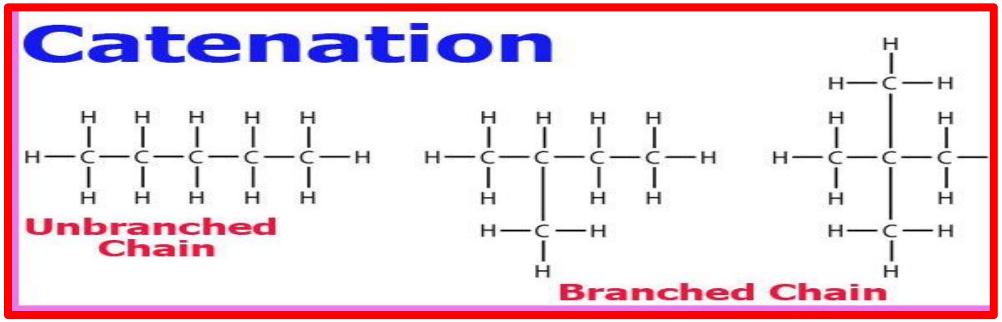
(i) the valency of element is greater than or equal to two,

(ii) element should have an ability to bond with itself

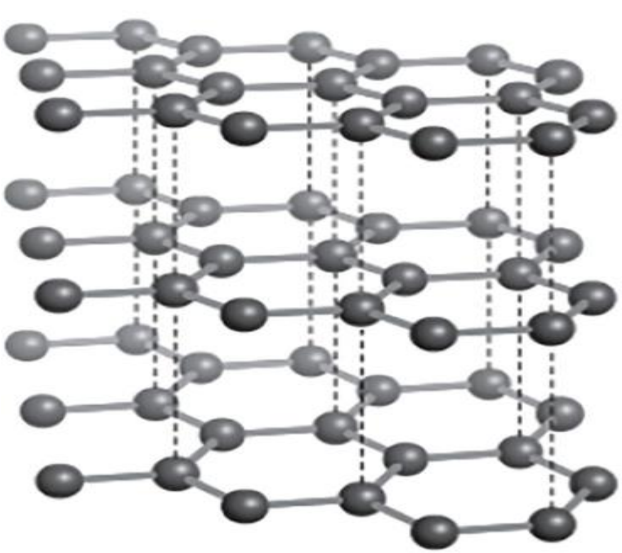
(iii) the self bond must be as strong as its bond with other elements

(iv) kinetic inertness of catenated compound towards other molecules.

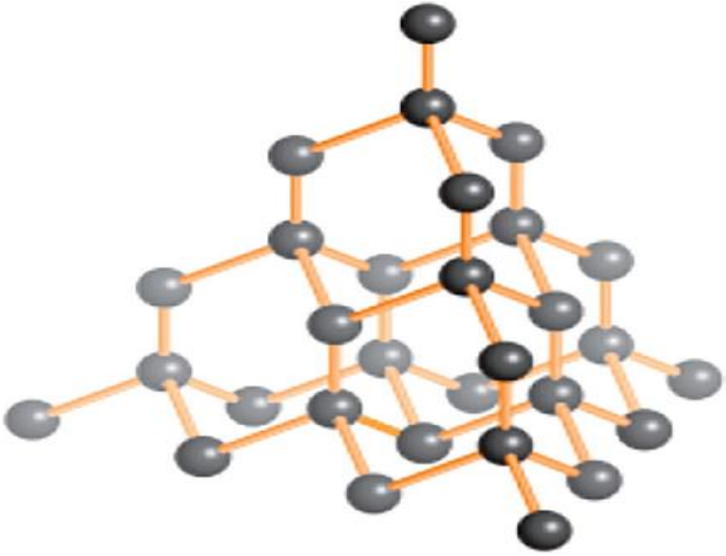
Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.



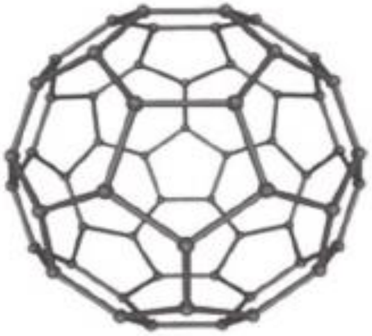
ALLOTROPES OF CARBON



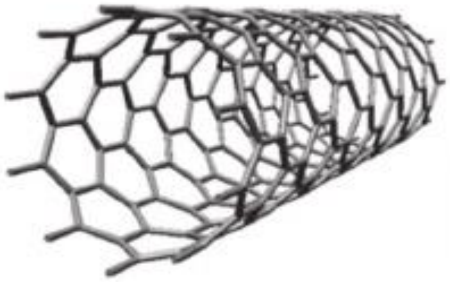
Graphite



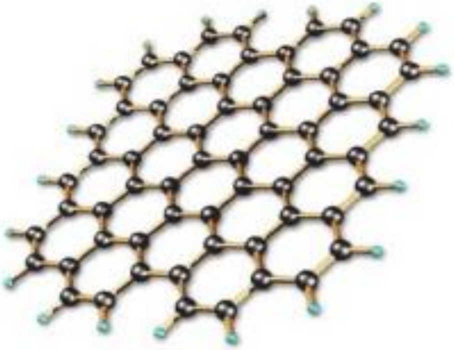
Diamond



fullerene



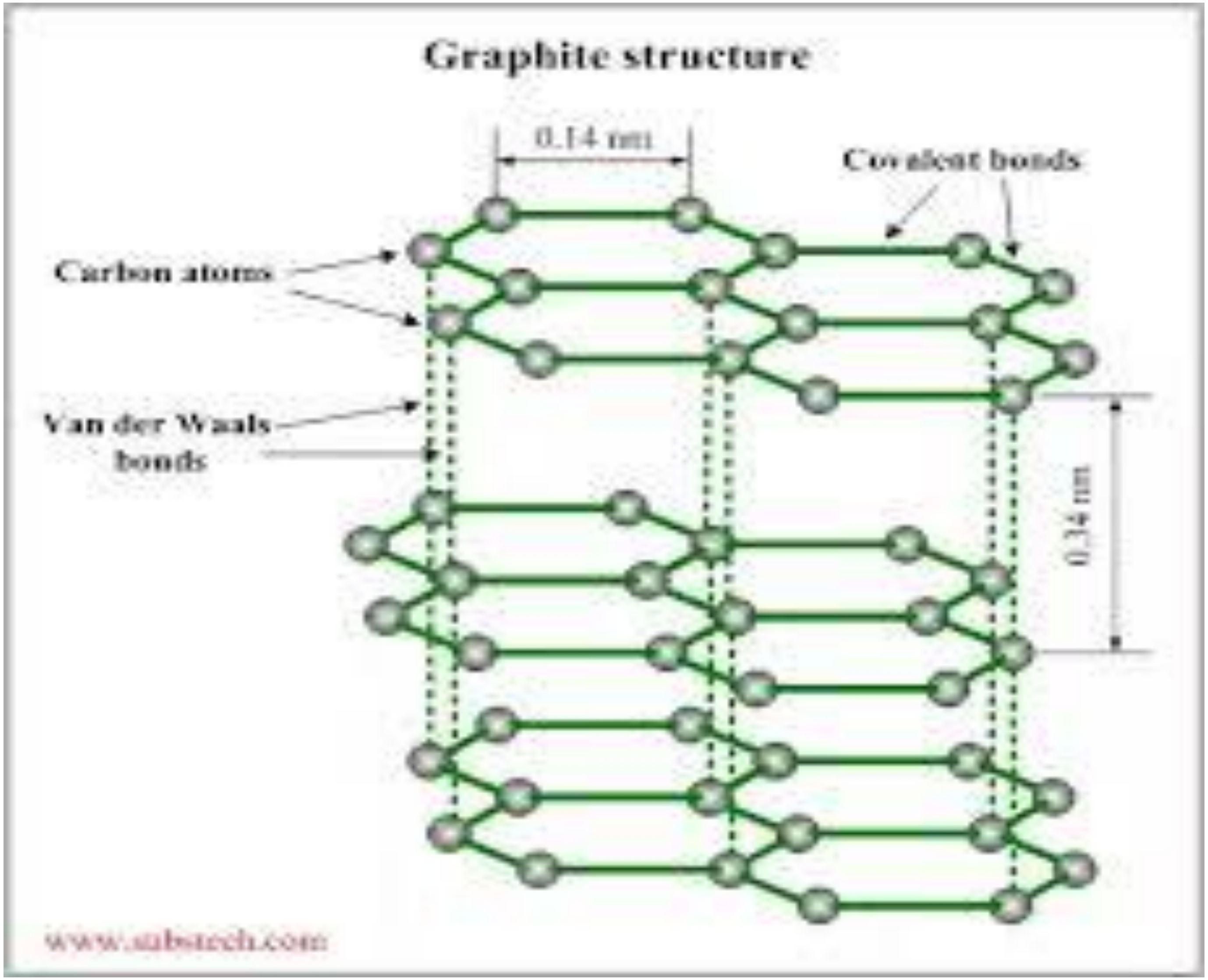
nanotube



graphene

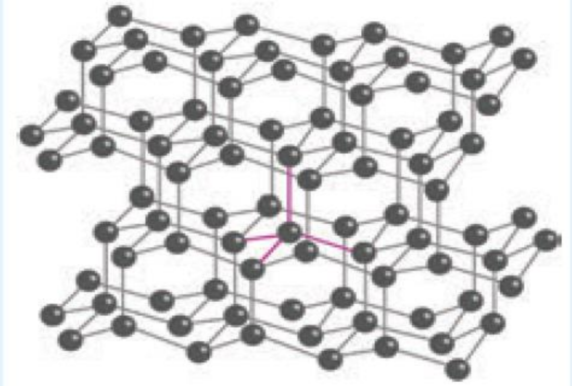
GRAPHITE

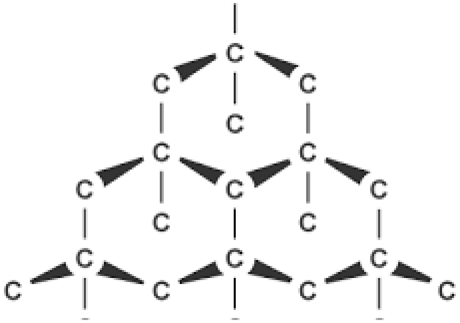
- The **most stable allotropic form of carbon at normal temperature and pressure.**
- It is **soft and conducts electricity.**
- It is composed of flat two dimensional sheets of carbon atoms.
- Each sheet is a hexagonal net of sp^2 hybridised carbon atoms with a C-C bond length of 1.41 Å which is close to the C-C bond distance in benzene (1.40 Å).
- Each carbon atom forms three σ bonds with three neighbouring carbon atoms using three of its valence electrons and the fourth electron present in the unhybridised p orbital forms a π-bond.
- These **π electrons are delocalised** over the entire sheet which is responsible for its electrical conductivity.
- The successive **carbon sheets are held together by weak van der Waals forces.**
- The distance between successive sheet is **3.40 Å**. It is used as a lubricant either on its own or as a graphited oil


Graphite structure
0.14 nm
Covalent bonds
Carbon atoms
Van der Waals bonds
0.34 nm
www.substech.com

DIAMOND

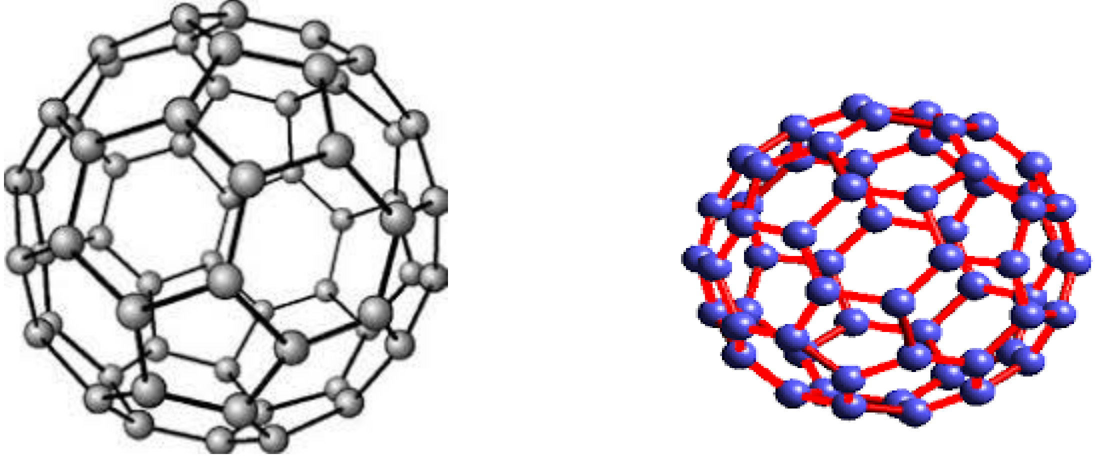
- Diamond is **very hard.**
- The carbon atoms in diamond are **sp^3 hybridised** and bonded to four neighbouring carbon atoms by σ bonds with a **C-C bond length of 1.54 Å.**
- This results in a tetrahedral arrangement around each carbon atom that extends to the entire lattice.
- **Since all four valance electrons of carbon are involved in bonding there is no free electrons for conductivity.**
- Being the hardest element, it used for sharpening hardtools, cutting glasses, making bores and rock drilling.





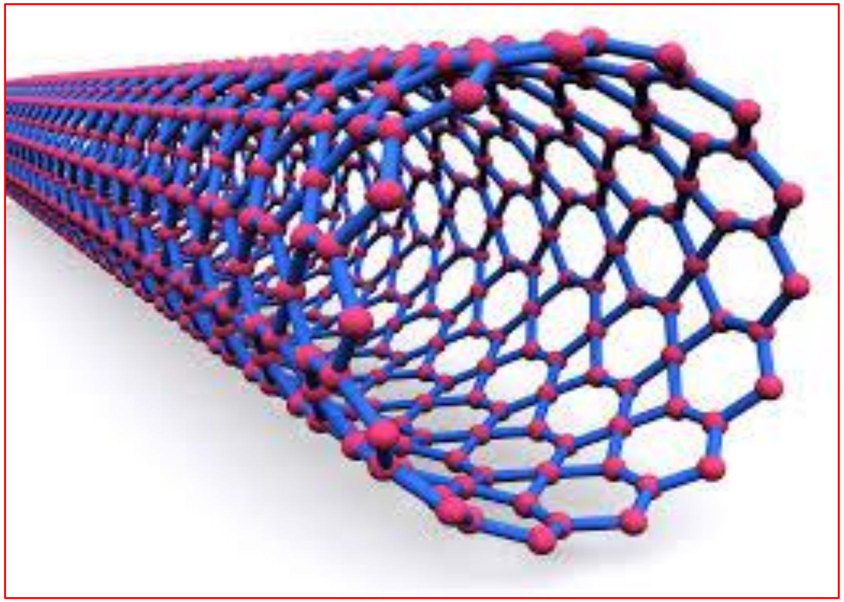
FULLERENES

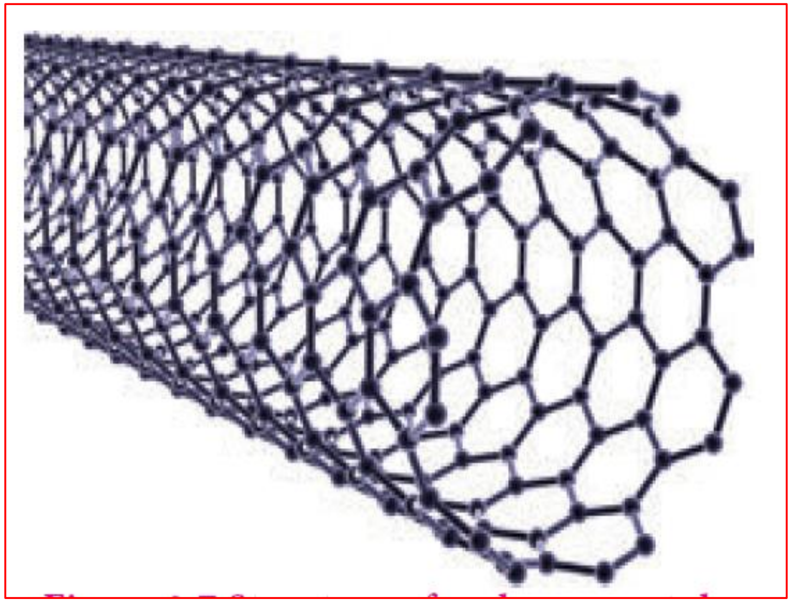
- Fullerenes are **newly synthesised allotropes of carbon.**
- Unlike graphite and diamond, these allotropes are **discrete molecules** such as C_{32}, C_{50}, C_{60}, C_{70}, C_{76} etc..
- These molecules have **cage like structures** as shown in the figure.
- The C_{60} molecules have a **soccer ball like structure and is called buckminster fullerene or buckyballs.**
- It has a fused ring structure consists of 20 six membered rings and 12 five membered rings.
- Each carbon atom is sp^2 hybridised and forms thee σ bonds & a delocalised π bond giving aromatic character to these molecules.
- The **C-C bond distance is 1.44 Å and C=C distance 1.38 Å.**



CARBON NANOTUBES

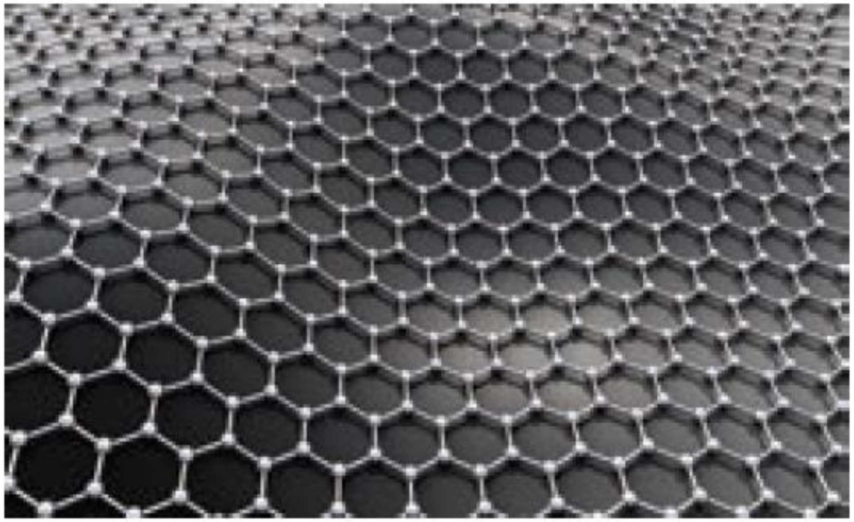
- Carbon nanotubes, another recently discovered allotropes, have **graphite like tubes with fullerene ends.**
- Along the axis, these nanotubes are **stronger than steel and conduct electricity.**
- These have many applications in nanoscale electronics, catalysis, polymers and medicine.

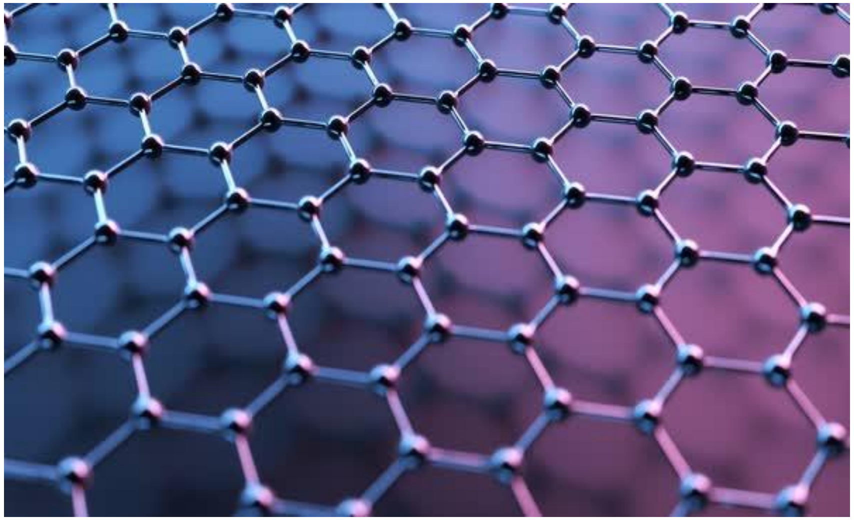




GRAPHENE

- Another **allotrophic form of carbon is graphene.**
- It has a **single planar sheet of sp^2 hybridised** carbon atoms that are densely packed in a **honeycomb crystal lattice.**





CARBON MONOXIDE (CO)

Preparation:

- Carbon monoxide can be prepared by the reaction of carbon with limited amount of oxygen.

$$2C + O_2 \longrightarrow 2CO$$

- On industrial scale carbon monoxide is produced by the reaction of carbon with air.The carbon monoxide formed will contain nitrogen gas also and **the mixture of nitrogen and carbon monoxide is called producer gas.**

$$2C + O_2/N_2\ (\text{air}) \longrightarrow \underset{\text{Producers Gas}}{2CO + N_2}$$

- The producer gas is then passed through a solution of copper(I)chloride under pressure which results in the formation of $CuCl(CO).2H_2O$.
- At reduced pressures this solution releases the pure carbon monoxide.
- **Pure carbon monoxide** is prepared by warming **methanoic acid** (HCOOH) with **concentrated sulphuric acid** which acts as a **dehydrating agent**.

$$HCOOH + H_2SO_4 \longrightarrow CO + H_2O + H_2SO_4$$

PROPERTIES OF CARBON MONOXIDE :

It is a **colourless, odourless**, and **poisonous gas**. It is slightly soluble in water.

It burns in air with a blue flame forming carbon dioxide.

$$2CO + O_2 \longrightarrow 2CO_2$$

When carbon monoxide is treated with chlorine in presence of light or charcoal, it forms a poisonous gas carbonyl chloride, which is also known as phosgene. It is used in the synthesis of isocynates.

$$CO + Cl_2 \longrightarrow COCl_2$$

Carbon monoxide acts as a strong reducing agent.

$$CO + Fe_2O_3 \longrightarrow 2Fe + 3CO_2$$

Under high temperature and pressure a mixture of carbon monoxide and hydrogen (synthetic gas or syn gas) gives methanol.

$$CO + 2H_2 \longrightarrow CH_3OH$$

In oxo process, ethene is mixed with carbon monoxide and hydrogen gas to produce propanal.

$$CO + C_2H_4 + H_2 \longrightarrow CH_3CH_2CHO$$

Fischer Tropsch synthesis:

The reaction of carbon monoxide with hydrogen at a pressure of less than 50 atm using metal catalysts at 500 - 700 K yields saturated and unsaturated hydrocarbons.

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{(2n+2)} + nH_2O$$

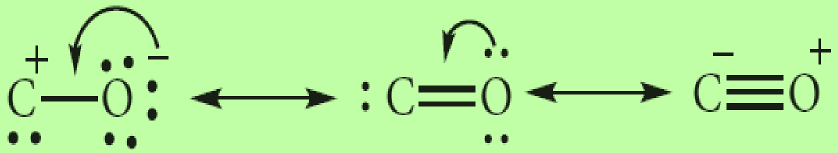
$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

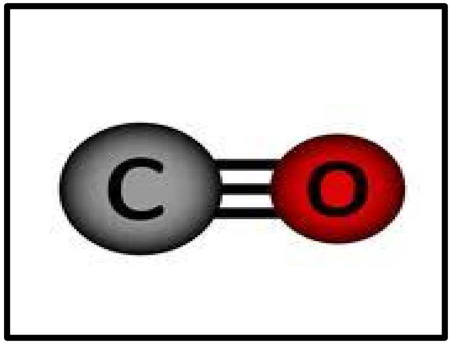
Carbon monoxide forms numerous complex compounds with transition metals in which the transition meal is in zero oxidation state. These compounds are obtained by heating the metal with carbon monoxide.

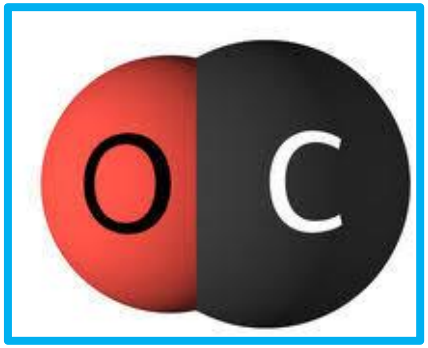
Eg. Nickel tetracarbonyl [$Ni(CO)_4$], Iron pentacarbonyl [$Fe(CO)_5$], Chromium hexacarbonyl [$Cr(CO)_6$].

Structure:

It has a linear structure. In carbon monoxide, three electron pairs are shared between carbon and oxygen. The bonding can be explained using molecular orbital theory as discussed in XI standard. The C-O bond distance is 1.128Å. The structure can be considered as the resonance hybrid of the following two canonical forms.

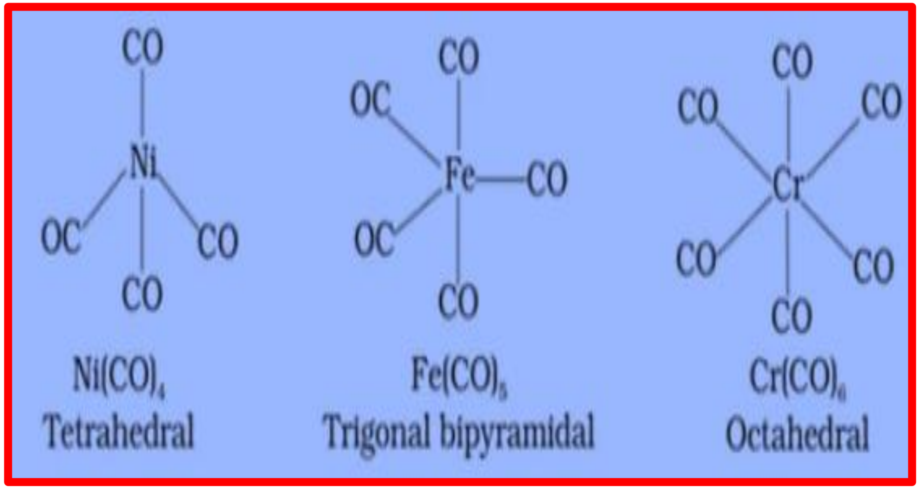






USES OF CARBON MONOXIDE

1. Equimolar mixture of hydrogen and carbon monoxide - water gas and the mixture of carbon monoxide and nitrogen - producer gas are important industrial fuels
2. Carbon monoxide is a good reducing agent and can reduce many metal oxides to metals.
3. Carbon monoixde is an important ligand and forms carbonyl compound with transition metals



Carbon dioxide

Carbon dioxide occurs in nature in free state as well as in the combined state.

It is a constituent of air (0.03%).

It occurs in rock as calcium carbonate and magnesium carbonate.

Production

On industrial scale it is produced by burning coke in excess of air.

$$2CO + O_2 \longrightarrow 2CO_2 \quad \Delta H = 394\ \text{kJ mol}^{-1}$$

Calcination of lime produces carbon dioxide as by product.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Carbon dioxide is prepared in laboratory by the action of dilute hydrochloric acid on metal carbonates.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Properties

It is a colourless, nonflammable gas and is heavier than air. Its critical temperature is 31^{0} C and can be readily liquefied.

Carbon dioxide is a very stable compound. Even at 3100 K only 76 % decomposes to form carbon monoxide and oxygen. At still higher temperature it decomposes into carbon and oxygen.

$$CO_2 \overset{3100\ K}{\rightleftharpoons} CO + \frac{1}{2}O_2$$

$$CO_2 \overset{\text{high temperature}}{\rightleftharpoons} C + O_2$$

Reducing behaviour:

At elevated temperatures, it acts as a strong reducing agent. For example,

$$CO_2 + Mg \longrightarrow 2MgO + C$$

Water gas equilibrium:

The equilibrium involved in the reaction between carbon dioxide and hydrogen, has many industrial applications and is called water gas equilibrium.

$$CO_2 + H_2 \rightleftharpoons \underbrace{CO + H_2O}_{\text{Water gas}}$$

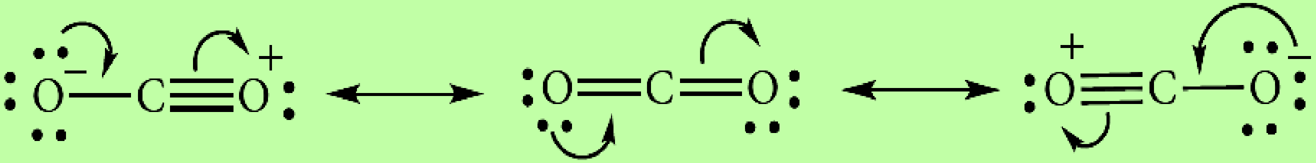
Acidic behaviour:

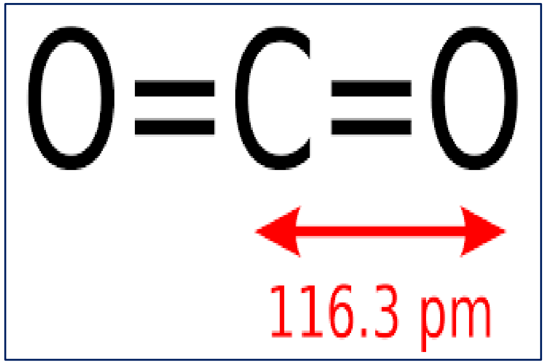
The aqueous solution of carbon dioxide is slightly acidic as it forms carbonic acid.

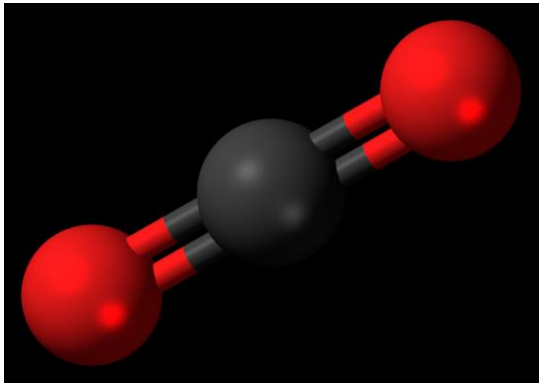
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^{+} + HCO_3^{-}$$

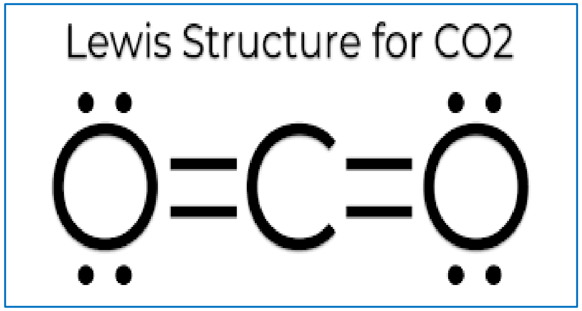
Structure of carbon dioxide

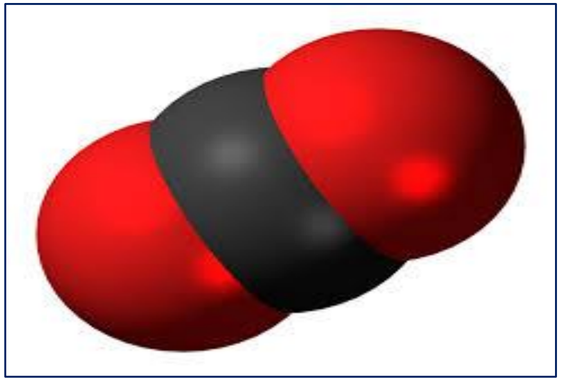
Carbon dioxide has a liner structure with equal bond distance for the both C-O bonds. In this molecule there is one C-O sigma bond. In addition there is 3c-4e bond covering all the three atoms.

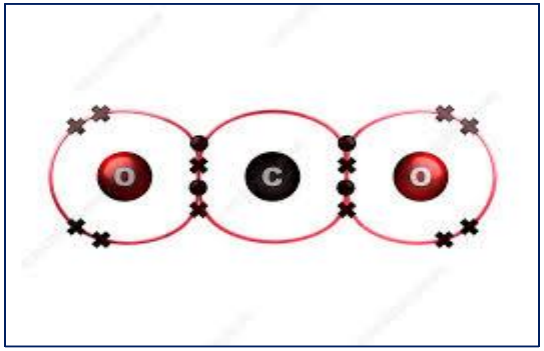












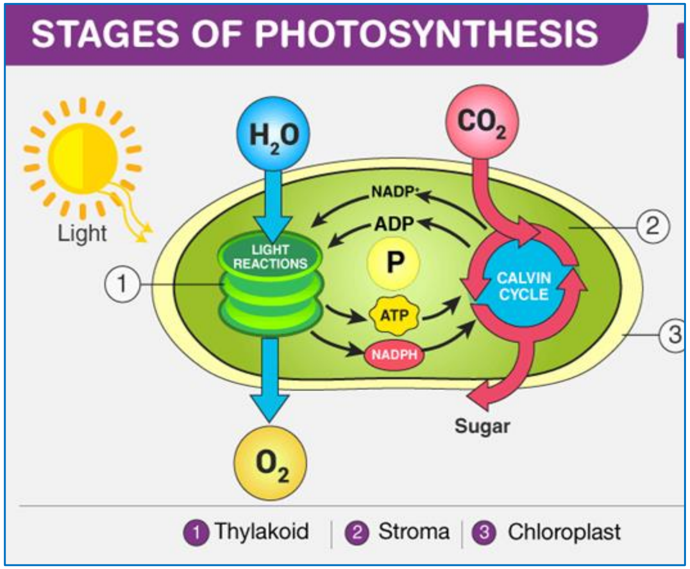
USES OF CARBON DIOXIDE

1. Carbon dioxide is used to produce an **inert atomosphere for chemical processing.**

2. Biologically, it is important for **photosynthesis.**

3. It is also used as **fire extinguisher and as a propellent gas.**

4. It is used in the production of **carbonated beverages** and in the production of **foam.**



Silicon tetrachloride

$SiCl_4$

Preparation:

Silicon tetrachloride can be prepared by passing dry chlorine over an intimate mixture of silica and carbon by heating to 1675 K in a porcelain tube

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

On commercial scale, reaction of silicon with hydrogen chloride gas occurs above 600 K

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$

Properties:

Silicon tetrachloride is a colourless fuming liquid and it freezes at -70 ^{0}C

In moist air, silicon tetrachloride is hydrolysed with water to give silica and hydrochloric acid.

$$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4$$

When silicon tetrachloride is hydrolysed with moist ether, linear perchloro siloxanes are formed $[Cl\text{-}(Si\,Cl_2O)_nSiCl_3$ where n=1-6.

Alcoholysis

The chloride ion in silicon tetrachloride can be substituted by nucleophile such as OH, OR, etc.. using suitable reagents. For example, it forms silicic esters with alcohols.

$$SiCl_4 + C_2H_5OH \longrightarrow \underset{\text{Tetraethoxy silane}}{Si(OC_2H_5)_4} + 2Cl_2$$

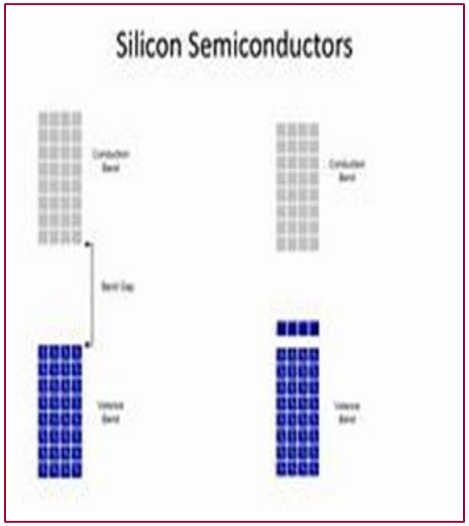
Ammonialysis.

Similarly silicon tetrachloride undergoes ammonialysis to form chlorosilazanes.

$$2SiCl_4 + NH_3 \xrightarrow[\text{Ether}]{330\text{ K}} Cl_3Si\text{-}NH\text{-}SiCl_3$$

Uses:

1. Silicon tetrachloride is used in the production of semiconducting silicon.
2. It is used as a starting material in the synthesis of silica gel, silicic esters, a binder for ceramic materials.



SILCONES

- Silicones or poly siloxanes are **organo silicon polymers with general empirical formula (R_2SiO).**
- Since their **empirical formula is similar to that of ketone (R2CO), they were named "silicones".**
- These silicones may be **linear or cross linked.**
- Because of their very high thermal stability they are called **high –temperature polymers.**

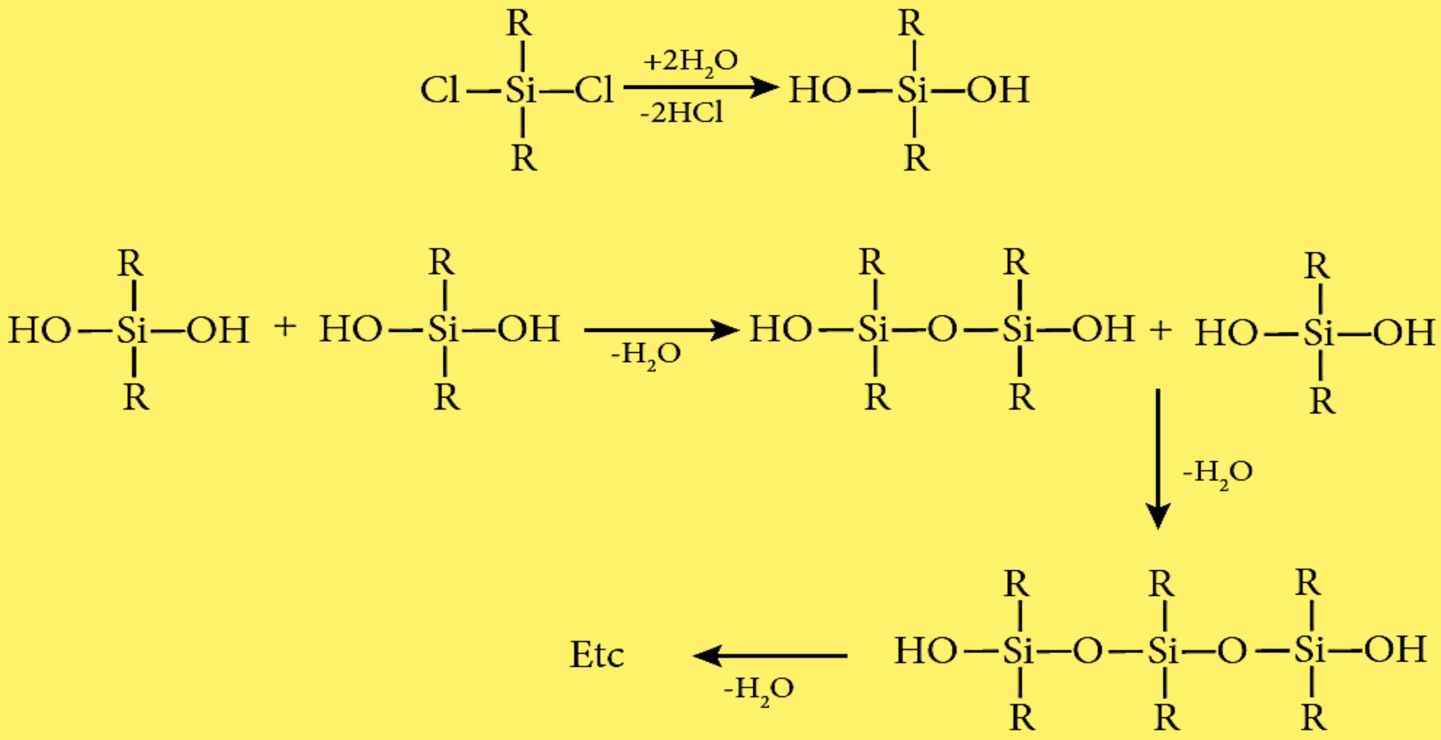


PREPARATION:

Generally silicones are prepared by the **hydrolysis of dialkyldichlorosilanes (R_2SiCl_2) or diaryldichlorosilanes Ar_2SiCl_2,** which are prepared by passing vapours of **RCl or ArCl over silicon at 570 K with copper as a catalyst.**

$$2RCl + Si \xrightarrow{Cu\ /\ 570\ K} R_2SiCl_2$$

The hydrolysis of dialkylchloro silanes R_2SiCl_2 yields to a straight chain polymer which grown from both the sides



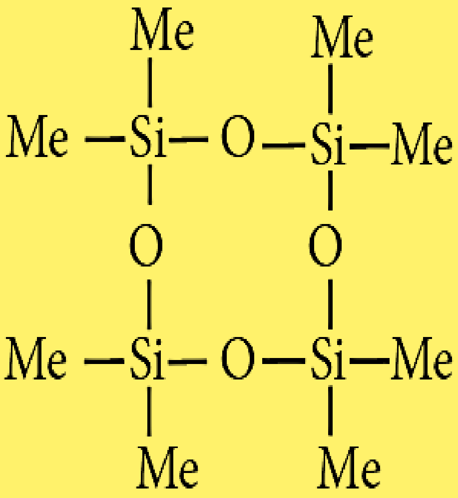
$$Cl-\overset{R}{\underset{R}{Si}}-Cl \xrightarrow[-2HCl]{+2H_2O} HO-\overset{R}{\underset{R}{Si}}-OH$$

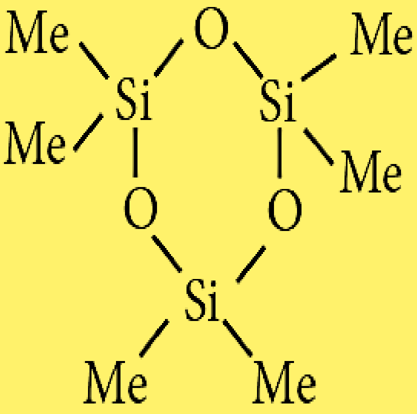
$$HO-\overset{R}{\underset{R}{Si}}-OH + HO-\overset{R}{\underset{R}{Si}}-OH \xrightarrow[-H_2O]{} HO-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH + HO-\overset{R}{\underset{R}{Si}}-OH$$

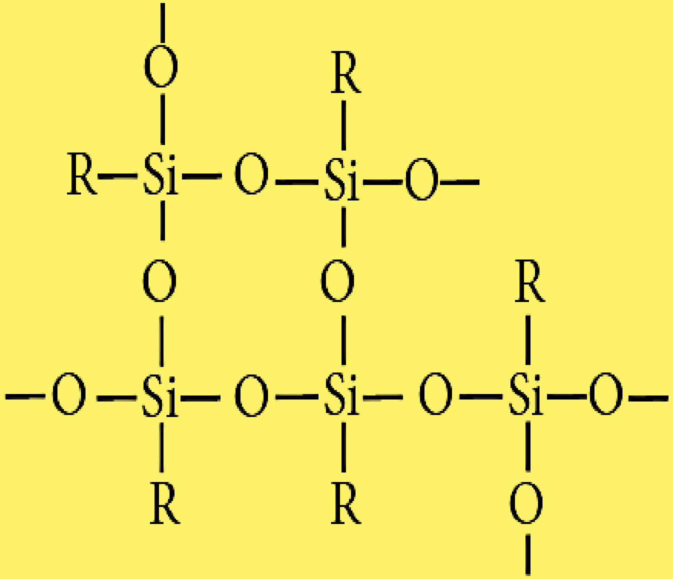
$$\big\downarrow -H_2O$$

$$Etc \xleftarrow[-H_2O]{} HO-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-OH$$

The hydrolysis of monoalkylchloro silanes $RSiCl_3$ yields to a very complex cross linked polymer.. Linear silicones can be converted into cyclic or ring silicones when water molecules is removed from the terminal –OH groups.



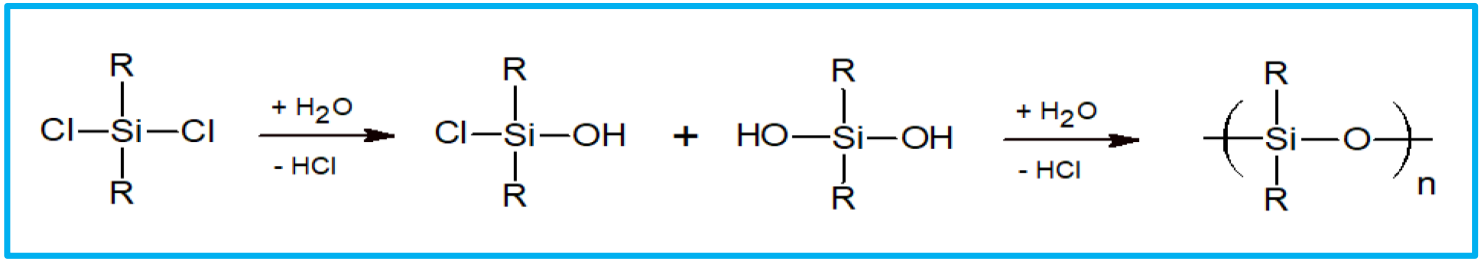




TYPES OF SILICONES:

(i) Liner silicones:

They are obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl silicon chlorides.



a) **Silicone rubbers:**

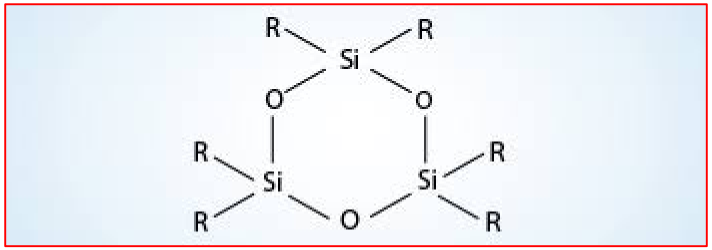
These silicones are bridged together by methylene or similar groups

b) **Silicone resins:**

They are obtained by blending silicones with organic resins such as acrylic esters.

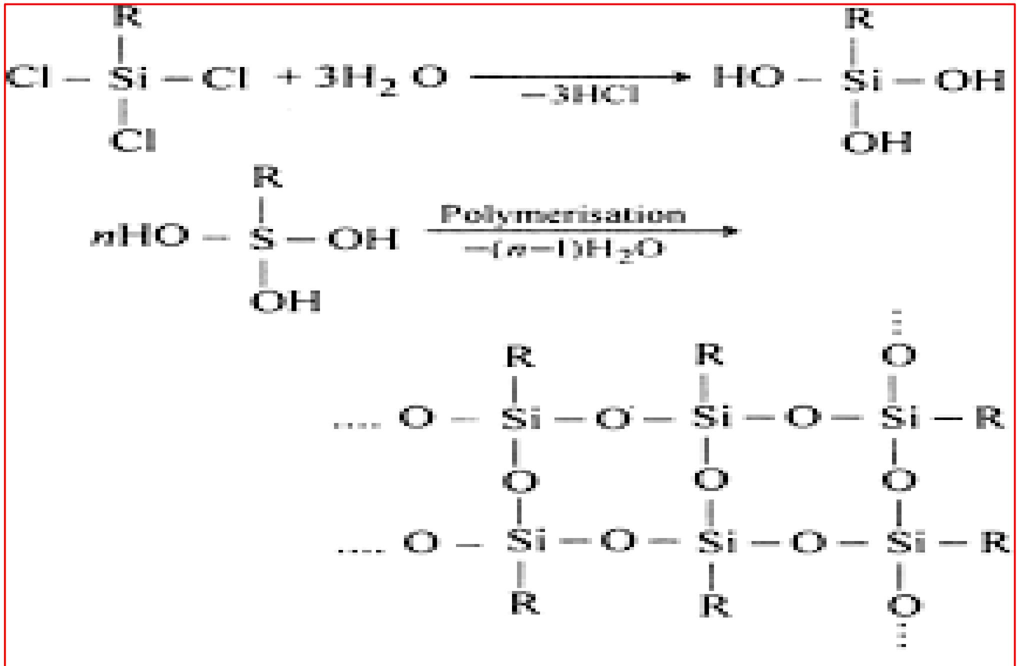
(ii) Cyclic silicones

These are obtained by the hydrolysis of R_2SiCl_2.



(iii) Cross linked silicones

They are obtained by hydrolysis of $RSiCl_3$



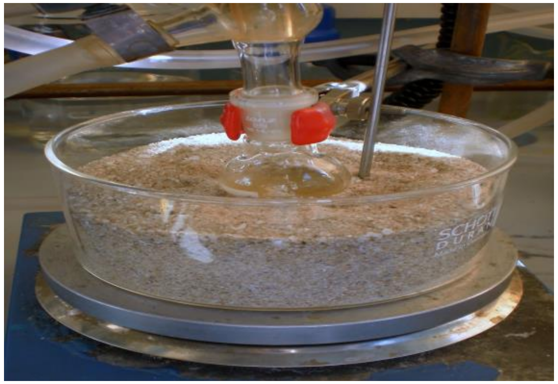
Cross-linked silicon

PROPERTIES

- The extent of cross linking and nature of alkyl group determine the nature of polymer.
- They range from oily liquids to rubber like solids. All silicones are water repellent. This property arises due to the presence of organic side groups that surrounds the silicon which makes the molecule looks like an alkane.
- They are also thermal and electrical insulators.
- Chemically they are inert.
- Lower silicones are oily liquids whereas higher silicones with long chain structure are waxy solids.
- The viscosity of silicon oil remains constant and doesn’t change with temperatureand they don't thicken during winter

Uses:

1. Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc...
2. They are used for making water proofing clothes
3. They are used as insulting material in electrical motor and other appliances
4. They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.



SILICATES

The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linked together in different patterns are called silicates.

Nearly 95 % of the earth crust is composed of silicate minerals and silica.

The glass and ceramic industries are based on the chemistry silicates.

TYPES OF SILICATES

- Silicates are classified into various types based on the way in which the tetrahedral units, $[SiO_4]^{4-}$ are linked together.

1.Ortho silicates (Neso silicates)

2.Pyro silicate (Soro silicates)

3.Cyclic silicates (Ring silicates)

4.Inosilicates

  I)Chain silicates (pyroxenes)

  II)Double chain silicates (amphiboles)

5.Sheet or phyllo silicates

6.Three dimensional silicates (tecto silicates)

Ortho silicates (Neso silicates):

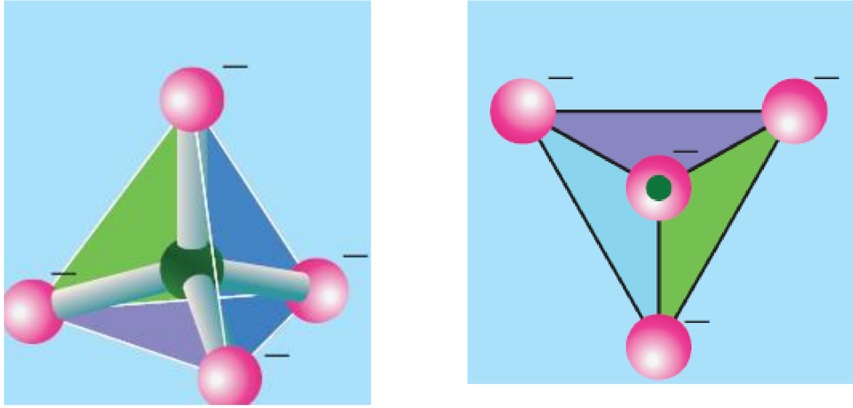
The simplest silicates which contain discrete $[SiO4]^{4-}$ tetrahedral units are called ortho silicates or neso silicates.

Examples :

Phenacite - Be_2SiO_4 (Be^{2+} ions are tetrahedrally surrounded by O^{2-} ions)

Olivine - $(Fe/Mg)_2SiO_4$ (Fe^{2+} and Mg^{2+} cations are octahedrally surrounded by O^{2-} ions)

STRUCTURE OF ORTHO SILICATES



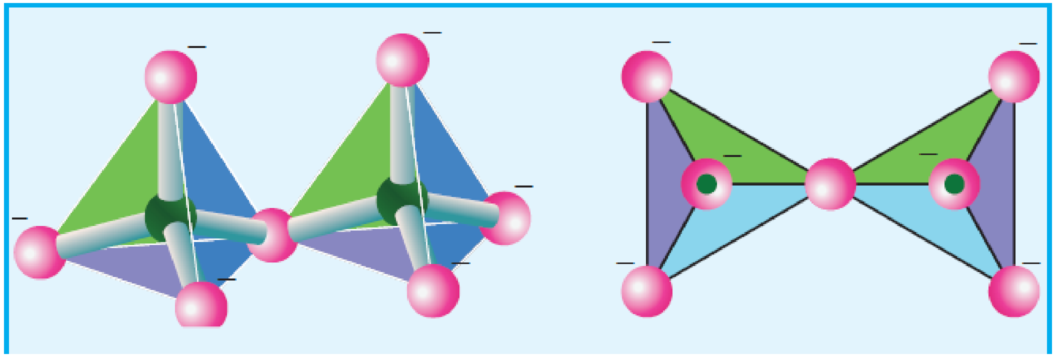
Pyro silicate (Soro silicates)

Silicates which contain **$[Si_2O_7]^{6-}$** ions are called pyro silicates (or) Soro silicates.

They are formed by joining **two $[SiO_4]^{4-}$ tetrahedral units** by sharing one oxygen atom at one corner.(one oxygen is removed while joining).

Example :

Thortveitite - $Sc_2Si_2O_7$



Cyclic silicates (or Ring silicates)

Silicates which contain $(SiO_3)_n^{2n-}$ ions which are formed by linking three or more tetrahedral SiO_4^{4-} units cyclically are called cyclic silicates. Each silicate unit shares two of its oxygen atoms with other units.

Example: Beryl $[Be_3Al_2(SiO_3)_6]$ (an aluminosilicate with each aluminium is surrounded by 6 oxygen atoms octahedrally)

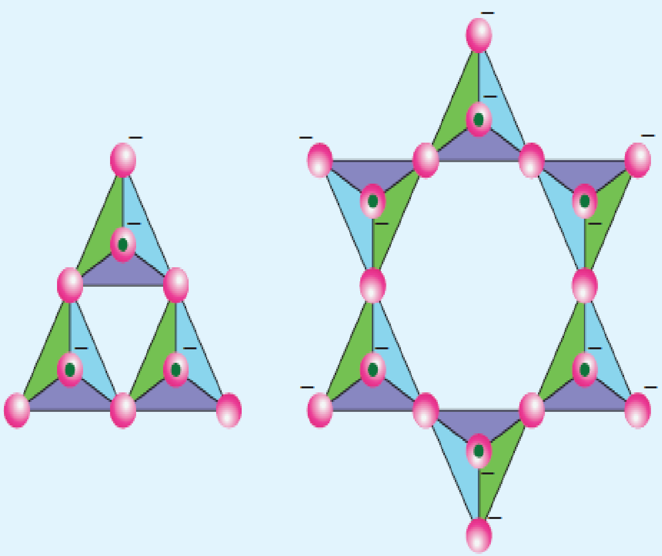


Figure 2.13 Structure of Cyclic silicates

Inosilicates :

Silicates which contain 'n' number of silicate units liked by sharing two or more oxygen atoms are called inosilicates. They are further classified as chain silicates and double chain silicates.

Chain silicates (or pyroxenes): These silicates contain $[(SiO_3)_n]^{2n-}$ ions formed by linking 'n' number of tetrahedral $[SiO_4]^{4-}$ units linearly. Each silicate unit shares two of its oxygen atoms with other units.

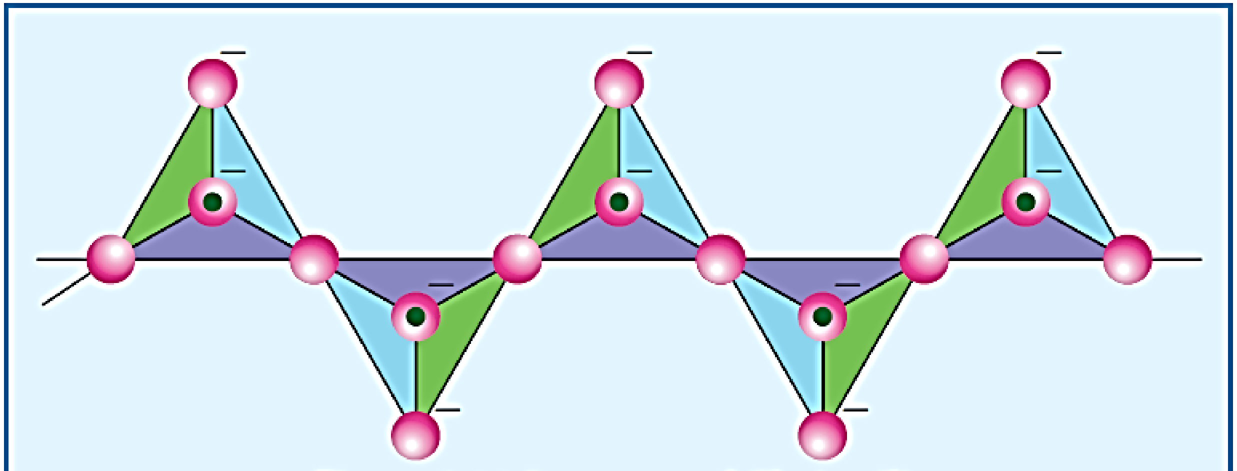


Figure 2.14 Structure of Chain silicates

Example: Spodumene - $LiAl(SiO_3)_2$.

Double chain silicates (or amphiboles): These silicates contains $[Si_4O_{11}]_n^{6n-}$ ions. In these silicates there are two different types of tetrahedra : (i) Those sharing 3 vertices (ii) those sharing only 2 vertices.

Examples:

1) **Asbestos :** These are fibrous and non-combustible silicates. Therefore they are used for thermal insulation material, brake linings, construction material and filters. Asbestos being carcinogenic silicates, their applications are restricted.

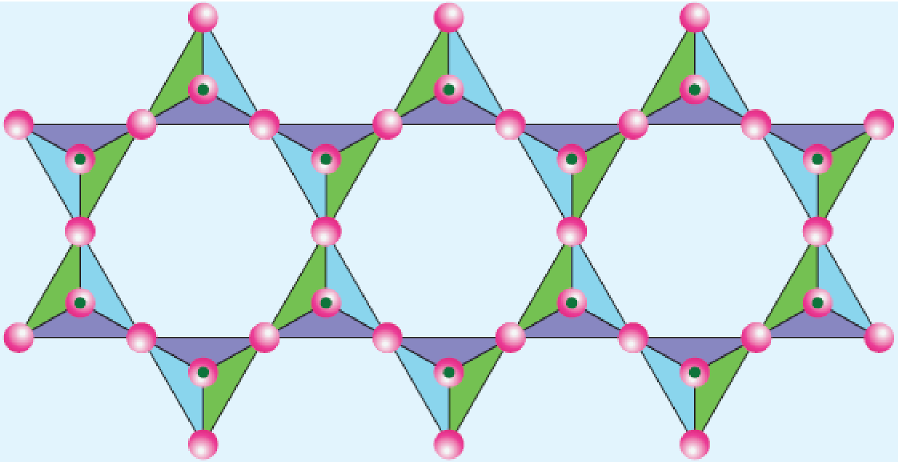
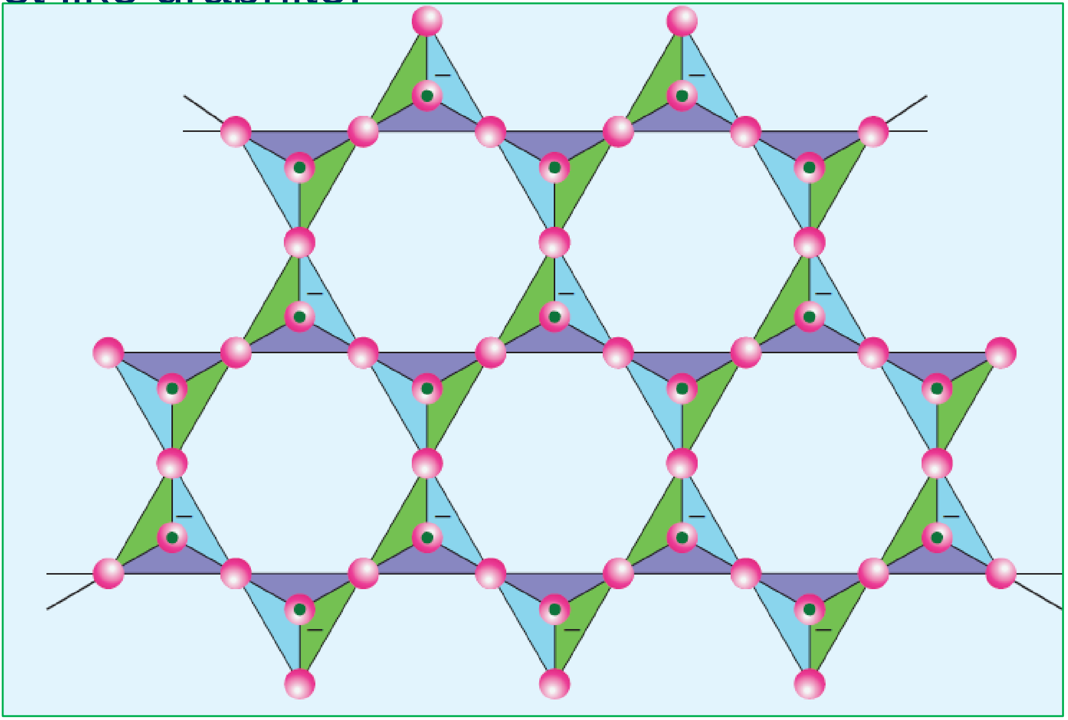


Figure 2.15 Structure of Double chain silicates

Sheet (or) phyllo silicates:

- **Silicates which contain $(Si_2O_5)_n^{2n-}$** are called sheet or phyllo silicates.
- In these, **Each $[SiO_4]^{4-}$ tetrahedron unit shares three oxygen atoms with others and thus by forming two-dimensional sheets.**
- These sheets silicates form layered structures in which silicate sheets are stacked over each other.
- The attractive forces between these layers are very week, hence they can be cleaved easily just like graphite.

E a etc..



Three dimensional silicates (or tecto silicates):

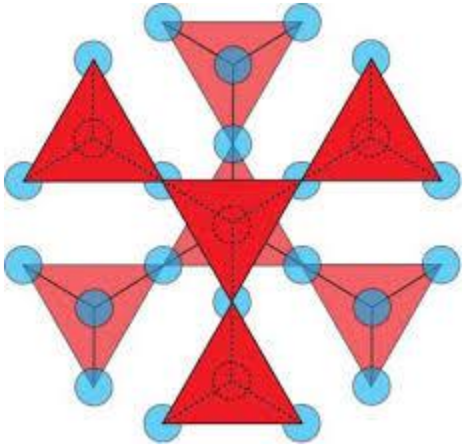
- Silicates in which all the oxygen atoms of $[SiO_4]^{4-}$tetrahedra are shared with other tetrahedra to form three-dimensional network are called three dimensional or tecto silicates.
- They have general formula $\mathbf{(SiO_2)_n}$.

Examples: Quartz

These tecto silicates can be converted into Three dimensional aluminosilicates by replacing $[SiO_4]^{4-}$ units by $[AlO_4]^{5-}$ units. E.g. Feldspar, Zeolites etc.,


Feldspar

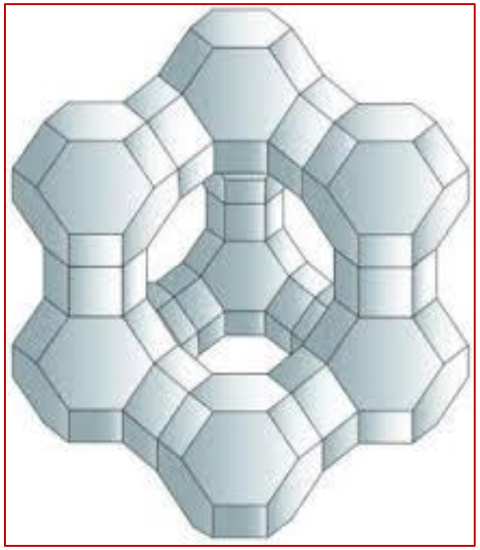
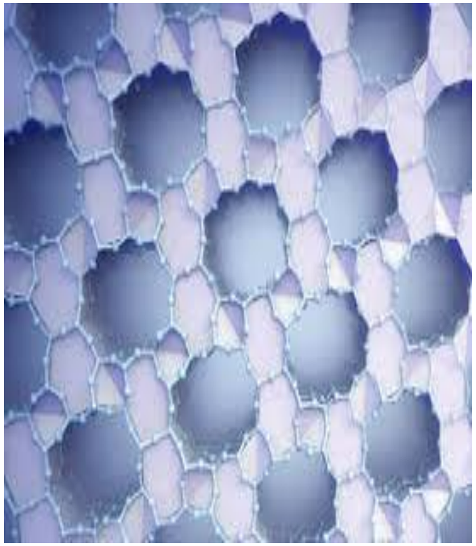

Zeolites



ZEOLITES:

- Zeolites are three-dimensional crystalline solids containing aluminium, silicon, and oxygen in their regular three dimensional framework.

- They are hydrated sodium alumino silicates with general formula $NaO.(Al_2O_3).x(SiO_2).yH_2O$ (x=2 to 10; y=2 to 6).


- Zeolites have **porous structure** in which the **monovalent sodium ions and water molecules are loosely held.**
- The **Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms**.
- Zeolites are **similar to clay minerals but they differ in their crystalline structure.**
- Zeolites have a three dimensional crystalline structure looks like a **honeycomb consisting of a network of interconnected tunnels and cages.**
- Water molecules moves freely in and out of these pores but the zeolite framework remains rigid.
- Another special aspect of this structure is that the pore/channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve.
- We have already discussed in XI standard, the removal of permanent hardness of water using zeolites.

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