Welcome to

Aakash + BYJU'S LIVE

P-Block Elements

p-block

P-Block Elements

Introduction

Group 13 to 18 of the periodic table constitute the **p–block.**

p–block contains metals, **metalloids,** as well as, **non–metals.**

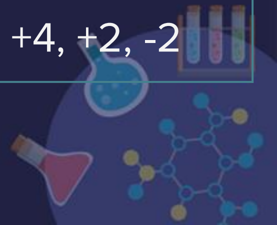
Highest **oxidation state** of p–block elements is equal to the **[Group number - 10].**

Electronic configuration

[Noble gas] $ns^2\ np^{1-6}$ (Except He: $1s^2$)

Group	13	14
Outer electronic configuration	ns^2np^1	ns^2np^2
Elements	B	C
	Al	Si
	Ga	Ge
	In	Sn
	Tl	Pb
Group O.S.	+3	+4
Other O.S.	+1	+2, -4

Group	15	16
Outer electronic configuration	ns^2np^3	ns^2np^4
Elements	N	O
	P	S
	As	Se
	Sb	Te
	Bi	Po
Group O.S.	+5	+6
Other O.S.	+3, -3	+4, +2, -2



Group	17	18
Outer electronic configuration	ns^2np^5	ns^2np^6 (Except He: $1s^2$)
		He
Elements	F	Ne
	Cl	Ar
	Br	Kr
	I	Xe
	At	Rn
Group O.S.	+7	+8
Other O.S.	+5, +3, +1, -1	+6, +4, +2

Introduction

The **first member** of each group from **13 to 17** of the p–block elements **differ** in many respects from the **other members** of their respective groups because of:

- **Small size**
- **High electronegativity**
- **Absence of d–orbitals**

The first member of a group has a greater ability to form **pπ–pπ** multiple bonds to itself and to the element of the **second row.**

Examples

$C=C$, $C\equiv C$, $N\equiv N$
$C=O$, $C=N$, $C\equiv N$, $N=O$

Group 13 (p-block)

- Boron (B)
- Aluminium (Al)
- Gallium (Ga)
- Indium (In)
- Thallium (Tl)

Occurrence

Element	Abundance	Source
B (Boron)	9 ppm (Rare element)	Borax: $Na_2[B_4O_5(OH)_4].8H_2O$ Colemnite: $Ca_2B_6O_{11}.5H_2O$ Kernite: $Na_2[B_4O_5(OH)_4].2H_2O$ Boric acid: H_3BO_3

Occurrence

Element	Abundance	Source
Al (Aluminium)	83000 ppm (Most abundant metal, 3rd most abundant element)	Bauxite: $Al_2O_3.H_2O$-$Al_2O_3.3H_2O$ Aluminosilicate rocks (feldspars, mica) Cryolite: Na_3AlF_6
Ga (Gallium)	19 ppm	Ores of Al, Zn, Ge
In (Indium)	0.24 ppm	ZnS & PbS ores
Tl (Thallium)	0.5 ppm	ZnS & PbS ores

Preparation of Boron

1. From Borax

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

$$B_2O_3 + 3Mg/Na \xrightarrow{\text{High temp.}} 2B + 3MgO/Na_2O$$

1. From BX_3

$$2BX_3 + 3H_2 \xrightarrow[\text{or Tantalum}]{\text{Red hot W}} 2B\ (\text{crystalline}) + 6HX$$

$X = Cl, Br$

99.9% pure

Properties

1 Electronic configuration (**[Noble gas] ns^2np^1**)

B	[He] $2s^2$ $2p^1$
Al	[Ne] $3s^2$ $3p^1$
Ga	[Ar] $3d^{10}$ $4s^2$ $4p^1$
In	[Kr] $4d^{10}$ $5s^2$ $5p^1$
Tl	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^1$

Properties

2 Covalent radius

B < Ga < Al < In < Tl

Exception

Covalent radius of Ga < Covalent radius of Al

Poor shielding of d-electrons

Properties

3 Electronegativity

Group 13	B	Al	Ga	In	Tl
E.N. (Pauling Scale)	2	1.5	1.6	1.7	1.8

4 Ionisation enthalpy

In < Al < **Ga** < **Tl** < B

Ga → Poor shielding of d electrons

Tl → Poor shielding of f electrons

Ionisation Enthalpy

The sum of the first three **ionisation enthalpies** for each of the elements is **very high.**

I.E.$_1$ < I.E.$_2$ < I.E.$_3$

Physical Properties

1. B is a **non-metal**.
2. B is an extremely **hard** and **black coloured** solid.
3. B exists in many **allotropic** forms.
4. B has an unusually **high M.P.** due to very strong **crystalline lattice.**
5. Rest of the members are **soft metals** with **low M.P.** and **high electrical conductivity.**
6. Density of the elements **increases** down the group.

Chemical Properties

Covalent Character

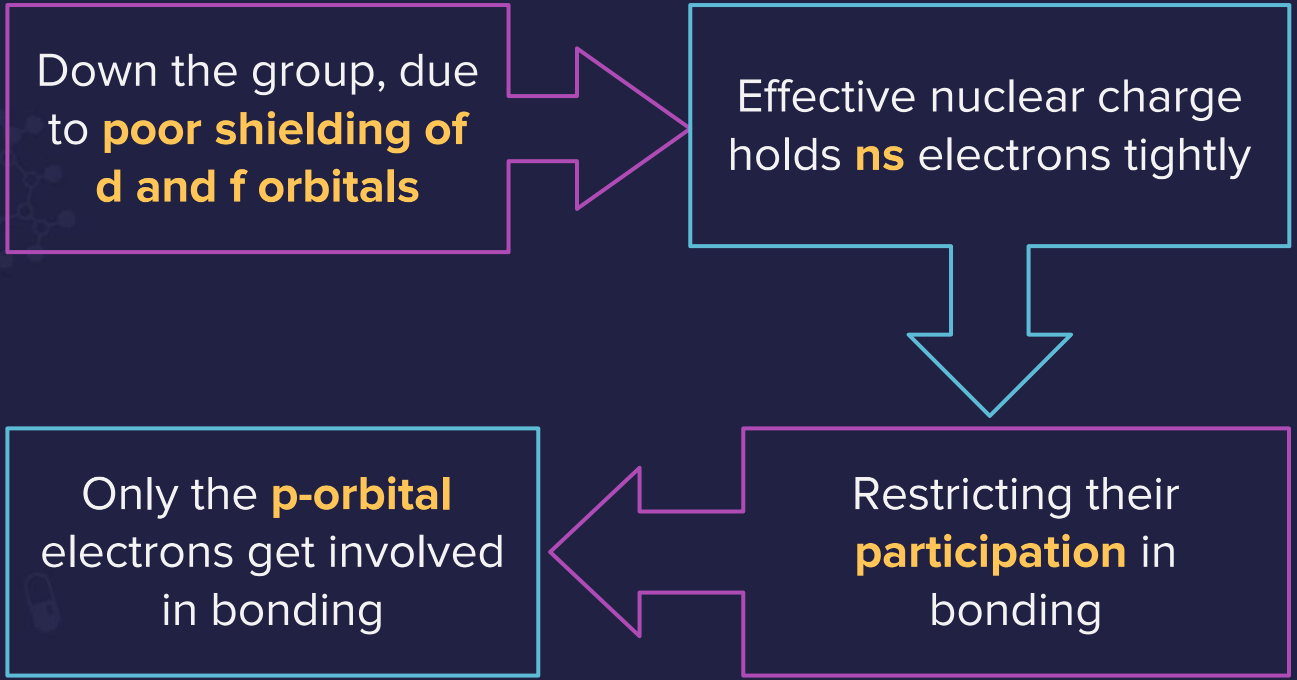
Due to the small size of B, the sum of its first three **I.E.** is **very high.**

This prevents it from forming **+3 ions** and compels it to form only **covalent compounds.**

Other elements normally form **covalent compounds when anhydrous** such as $AlCl_3$.

However, Al, Ga, In, & Tl form **metal ions in solution.**

Oxidation State



Down the group, due to **poor shielding of d and f orbitals**

Effective nuclear charge holds **ns** electrons tightly

Restricting their **participation** in bonding

Only the **p-orbital** electrons get involved in bonding

Oxidation State

In thallium, +1 oxidation state is **predominant,** whereas the +3 oxidation state is **highly oxidising**.

The compounds in **+1** oxidation state are **more ionic** than those in **+3** oxidation state.

Inert Pair Effect

Reluctance of **s-subshell electrons** to participate in chemical bonding.

In Ga, In, and Tl, both **+1** and **+3** oxidations states are observed.

Down the group, the relative stability of **+1** oxidation state progressively **increases.**

Inert Pair Effect

Stability of oxidation state

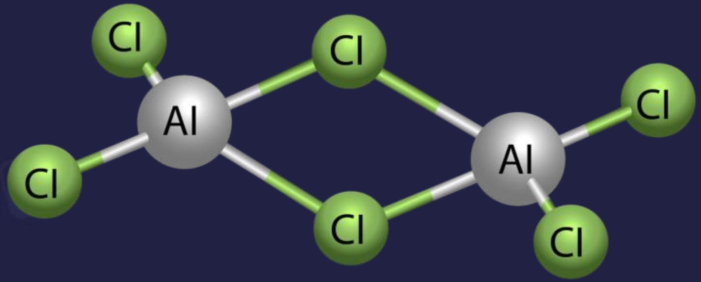
+1 Ga < In < Tl

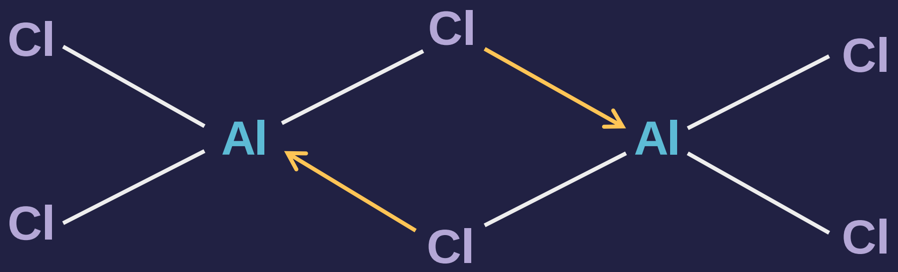
+3 Al > Ga > In > Tl

Halides

Electron deficient molecules tend to **accept** a pair of electrons to achieve stable electronic configuration and thus, behave as **Lewis acids.**

$AlCl_3$ achieves stability by forming a **dimer**.





Halides

Trihalides of all these elements being **covalent** in nature are **hydrolysed in water**.

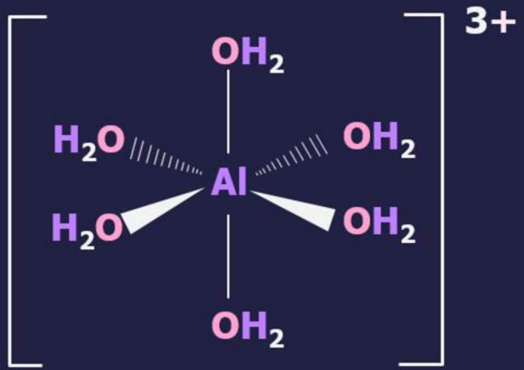
Species like tetrahedral **$[M(OH)_4]^-$** & octahedral **$[M(H_2O)_6]^{3+}$** (except in boron) exist in aqueous medium.

Due to the absence of d orbitals in boron, its maximum covalency **is 4.**

In Al & other elements, d-orbitals are available and hence, the maximum covalency can be expected **beyond 4.**

Halides

$AlCl_3$ undergoes hydrolysis in an acidified aqueous solution to form octahedral **$[Al(H_2O)_6]^{3+}$** ion.



Here covalency of Al is 6

Chemical Reactions

a Reaction with air

Amorphous boron and other group 13 elements reacts with O_2 on heating.

$$4E\,(s) + 3O_2\,(g) \xrightarrow{\Delta} 2E_2O_3\,(s)$$

(Where, E = Group 13 elements)

Boron is **unreactive** in crystalline form. Al forms a very thin oxide layer on its surface.

Reaction with Air

The nature of the oxides varies down the group

B_2O_3

Acidic

Al_2O_3 & Ga_2O_3

Amphoteric

In_2O_3 & Tl_2O_3

Basic

Al & amorphous B react with dinitrogen at high temperatures to form **nitrides.**

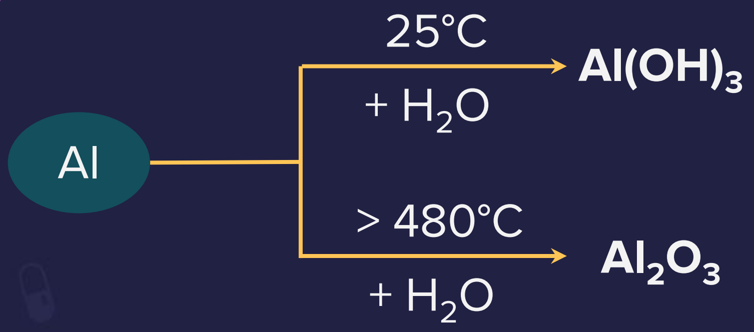
$$2E\ (s) + N_2\ (g) \xrightarrow{\Delta} 2EN\ (s)$$

(Where, E = Al, B)

b

Reaction with water

Boron **Does not** react with water



Ga

In

Not attacked by cold & hot water unless oxygen is present

Tl

Oxidises in moist air & decomposes steam at red heat

c Reaction with acids

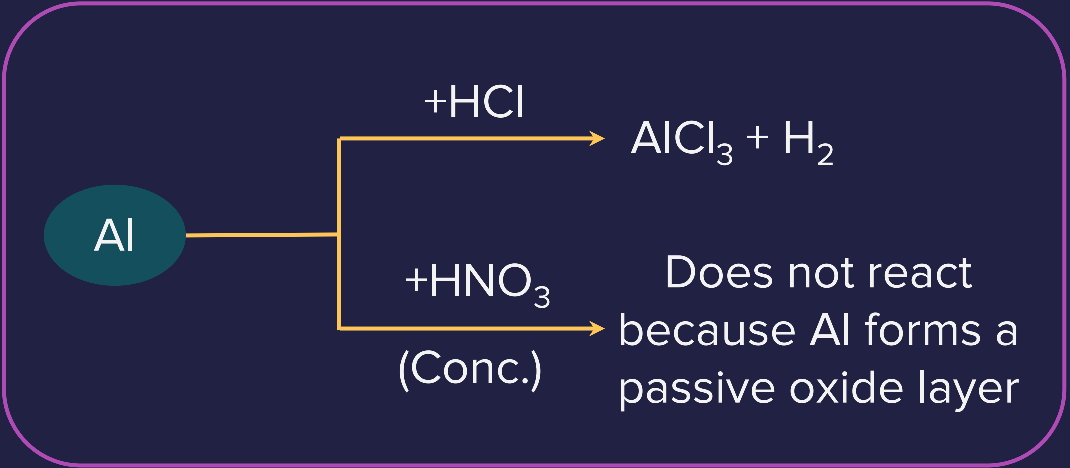
$$B \xrightarrow[\text{(Hot \& Conc.)}]{+H_2SO_4} H_3BO_3 + SO_2$$

$$B \xrightarrow[\text{(Hot \& Conc.)}]{+HNO_3} H_3BO_3 + NO_2$$

(Boron reacts with only oxidising acids)

Conc. H_2SO_4 is an oxidizing acid whereas **dil. H_2SO_4** is non-oxidizing acid. So, boron reacts with conc. acid only.

Reaction with Acids



Al $\xrightarrow{+HCl}$ $AlCl_3 + H_2$

Al $\xrightarrow[\text{(Conc.)}]{+HNO_3}$ Does not react because Al forms a passive oxide layer

Ga

In

Tl

Can also react with dilute mineral acids.

d Reaction with alkali

B

$$2B + NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$2B + 6NaOH \xrightarrow{\text{fused}} 2Na_3BO_3 + 3H_2$$

Al

$$Al \xrightarrow{NaOH + H_2O} NaAlO_2.2H_2O + H_2 \text{ or } Na^+[Al(OH)_4]^-$$

$$Al \xrightarrow{NaOH} Na_3AlO_3 + H_2$$

Al, Ga } Readily dissolves in alkalies

In, Tl } Do not react with alkali

e

Reaction with halogens

$$2E + 3X_2 \longrightarrow 2EX_3$$

(X = F, Cl Br, I)

BX_3	Covalent (BI_3 cannot be formed directly)
AlF_3	Ionic
GaF_3	Ionic
InF_3	Ionic
TlI_3	Exist as $Tl^+I_3^-$ & TlI also forms

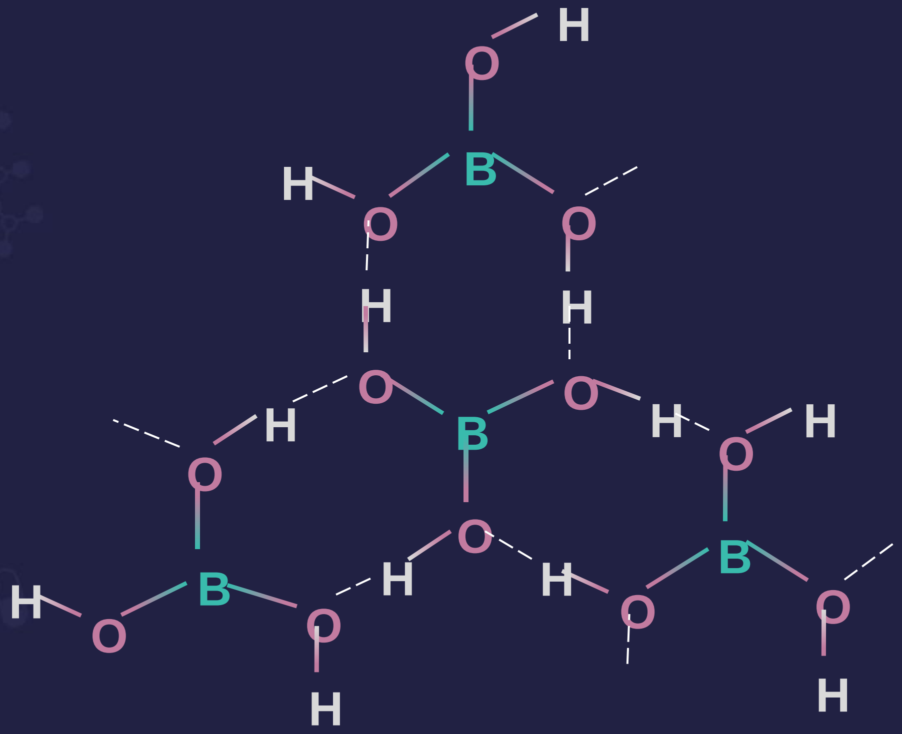
Compounds of Boron

Orthoboric Acid: Preparation

It is precipitated by treating a concentrated solution of **borax** with sulphuric acid.

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

Orthoboric Acid: Structure



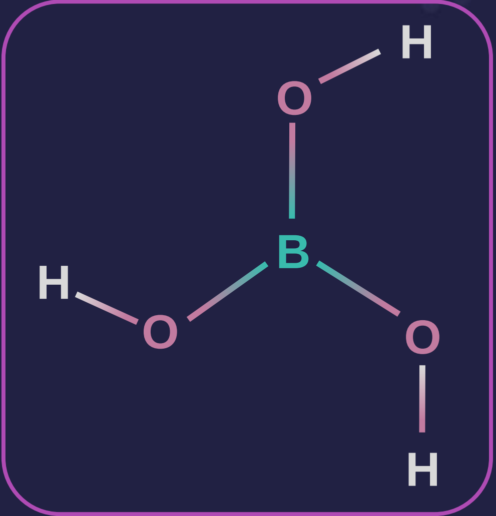
In **solid state**, the $B(OH)_3$ units are **H-bonded** into 2-D sheets with almost **hexagonal** symmetry.

Orthoboric Acid: Properties

1. **White crystalline** solid with a soapy touch.

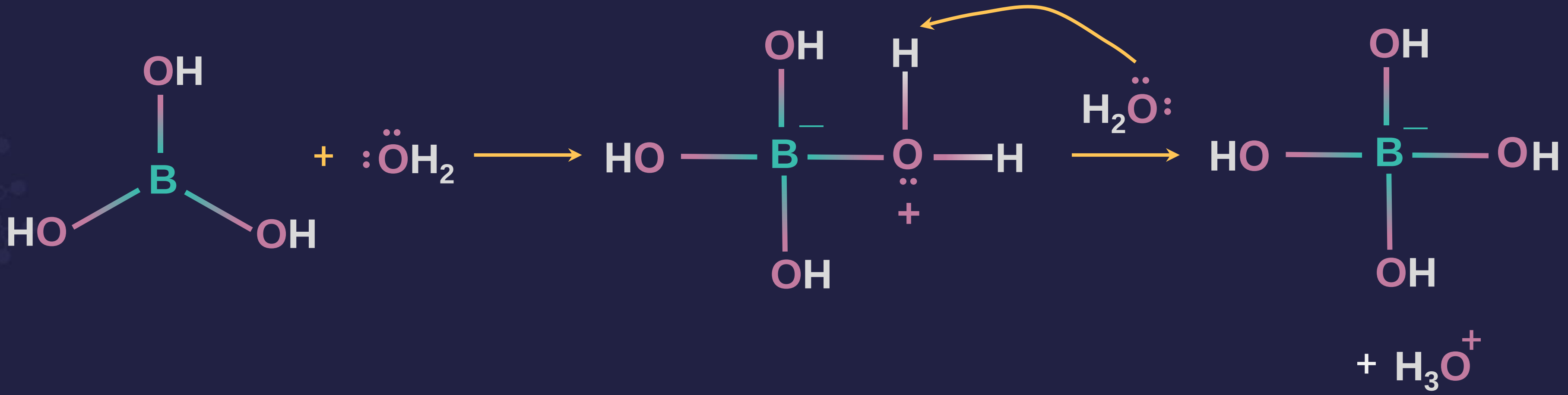
2. **Less soluble in cold water** but **more soluble in hot water**.

3. Boric acid is a **weak monobasic** acid



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

Properties



It is **not a protonic acid,** but it acts as a **Lewis acid** by accepting electrons from a hydroxyl ion.

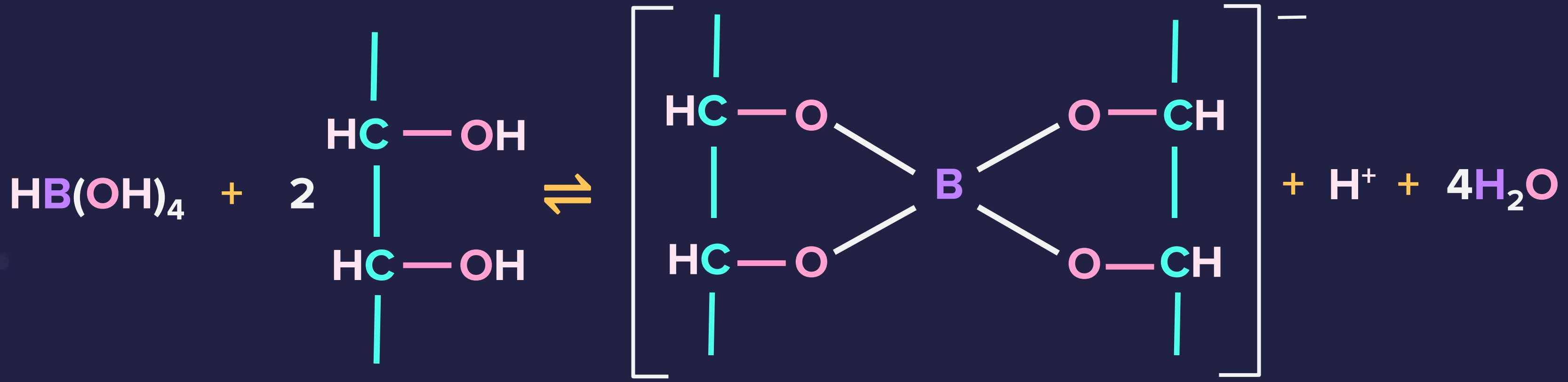
Properties

cis-diol is added to enhance the acid properties. The cis-diol forms a very stable complex with the $[B(OH)_4]^-$, thus removing it from the solution.

The reaction is **reversible** and thus, the removal of one of the products shifts the equilibrium in the forward direction.

In effect, it acts as a **strong acid** in the presence of the cis-diol.

Properties



4

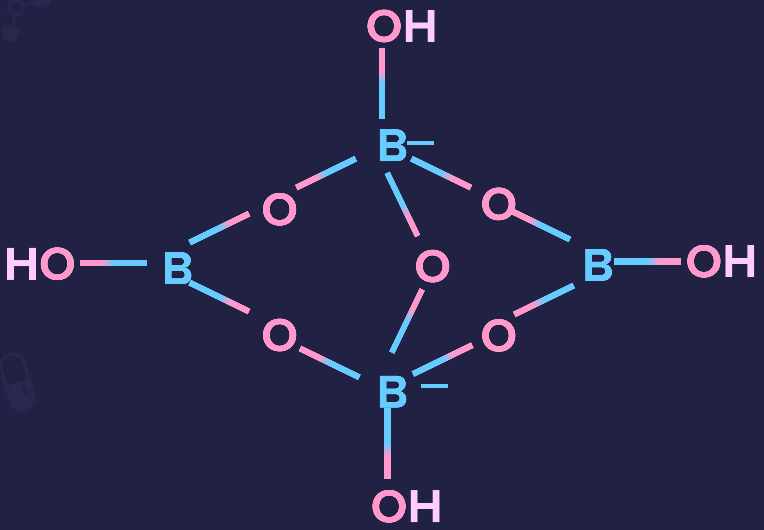
When heated, it first forms **metaboric acid (HBO_2)** and then boron trioxide

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ C} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Borax ($Na_2B_4O_7.10H_2O$) : Preparation

By the action of **Na_2CO_3** on **H_3BO_3**

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$



It contains the **tetranuclear** units **$[B_4O_5(OH)_4]^{2-}$** and the correct formula is **$Na_2[B_4O_5(OH)_4].8H_2O$.**

Properties

1 Borax is a **white powder which is more soluble** in hot water.

2 Its aqueous solution is **alkaline.**

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

3 Effect of **heating**

When **borax powder** is heated, it first swells due to the **loss of water** in the form of **steam** but, at **740°C,** it gets converted into colourless transparent **borax bead**.

Properties

3 Effect of **heating**

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O \uparrow$$

$$Na_2B_4O_7 \xrightarrow{740^\circ C} \underset{\textbf{Sodium metaborate}}{2NaBO_2} + B_2O_3$$

Sodium metaborate

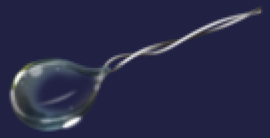
Borax-bead Test

Borax reacts with certain metal salts such as **Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}** etc., to form **coloured metaborates**.

Borax-bead Test

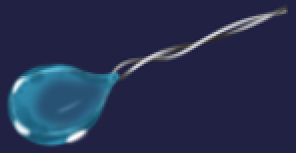
The colour of the **metaborates** can be used to identify the **metallic ions** (cations) in salts.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740^{\circ}C} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy mass}}$$



$B_2O_3 + NaBO_2$

$$CuO + B_2O_3 \longrightarrow \underset{\text{Blue bead}}{Cu(BO_2)_2}$$



$Cu(BO_2)_2$

Diborane (B_2H_6)

Binary compounds of **boron** with **Hydrogen** are called **boron hydrides or boranes.**

The simplest boron hydride known is **diborane.**

Diborane: Preparation

1

By treating **boron trifluoride** with **$LiAlH_4$** in diethyl ether

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3Li[AlF_4]$$

2

Laboratory method for the preparation of diborane

$$2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$$

3

By the reaction of **BF_3** with **NaH** on industrial scale

$$2BF_3 + 6NaH \xrightarrow{453\text{ K}} B_2H_6 + 6NaF$$

Diborane: Preparation

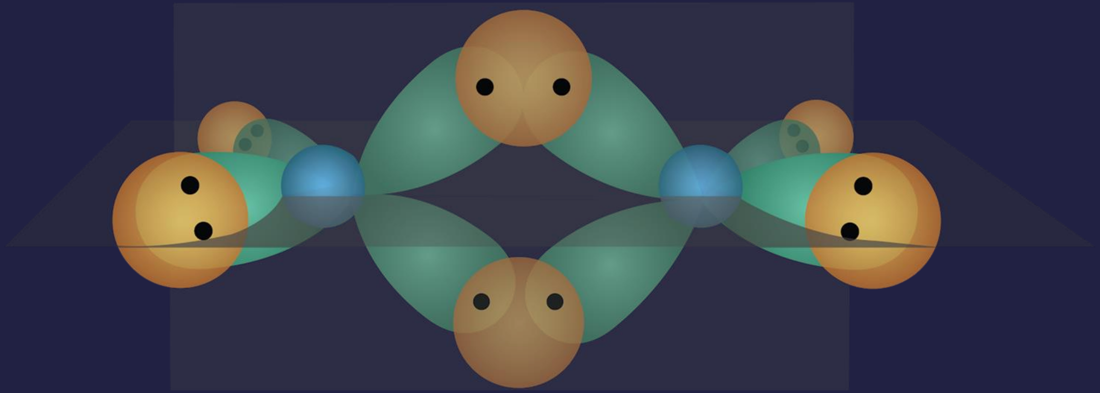
4

By the reaction of **BCl_3**
with **excess H_2**

$$2BCl_3 + 6H_2\,(\text{excess}) \xrightarrow[\text{discharge}]{\text{Electric}} B_2H_6 + 6HCl$$

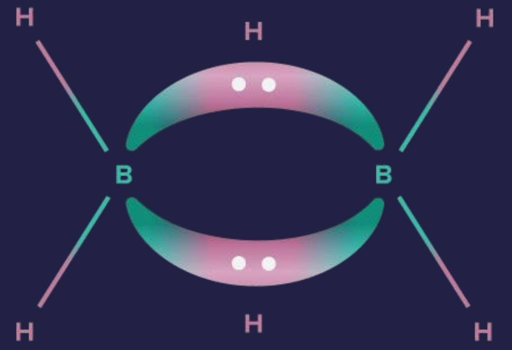
Diborane (B_2H_6): Structure

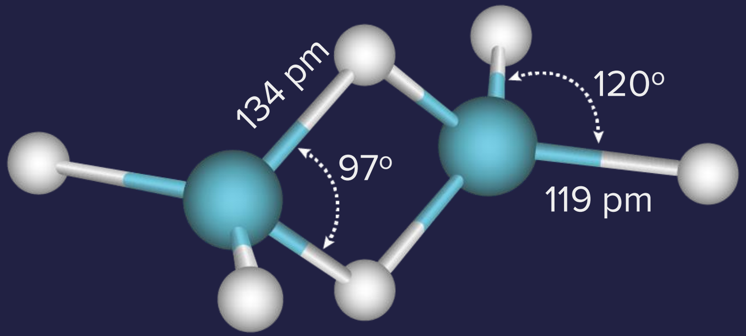
The **four terminal H** atoms and the **two boron** atoms lie in one plane. Above and below this plane, there are two bridging H atoms.



Diborane (B_2H_6): Structure

The **four terminal B-H** bonds are regular **two centre-two electron** bonds while the **two bridge (B-H-B)** bonds are **three centre-two electron** bonds.





Properties

1. B_2H_6 is a **colourless gas** and a highly reactive gas with boiling point **183 K.**

2. Diborane **catches fire spontaneously** upon exposure to air.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

$$\Delta H = -2160 \text{ kJ mol}^{-1}$$

3. Reacts with water to give **boric acid**

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

Properties

4 Diborane is also hydrolysed by **weaker acids** (e.g. alcohols) or **aqueous alkali**

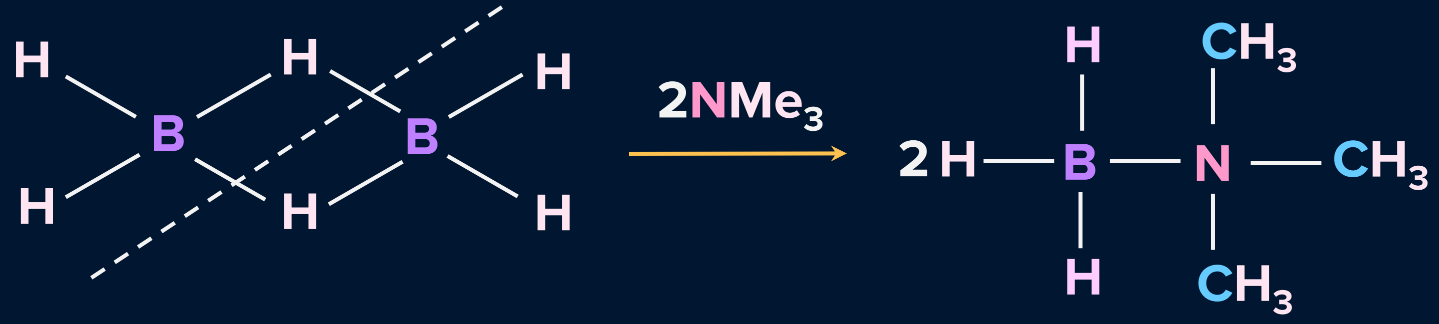
$$B_2H_6 + 6ROH \longrightarrow 2B(OR)_3 + 6H_2$$

5 **Large amines** such as $(CH_3)_3N$, pyridine and CO give **symmetrical cleavage** of diborane.

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

$$B_2H_6 + 2CO \xrightarrow{200^\circ C,\ 20\ atm} 2BH_3.CO$$

Symmetrical Cleavage



$$B_2H_6 \xrightarrow{2NMe_3} 2\,H_3B\text{—}N(CH_3)_3$$

Properties

6

Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give **unsymmetrical cleavage** of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [BH_4]^-$$

7

Reduction of diborane can be accomplished with **Na**

$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$

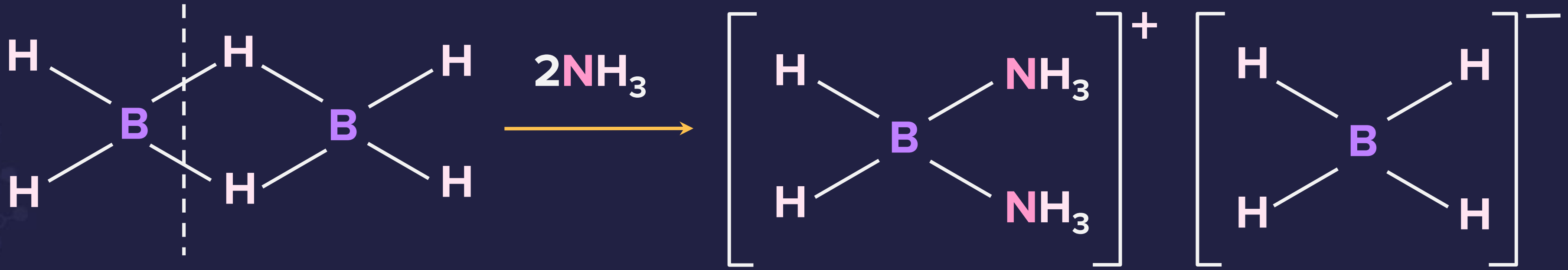
Properties

8

Li and Na hydrides react with **B_2H6 in diethyl ether** to give borohydrides.

$$B_2H_6 + 2MH \xrightarrow{\text{Diethyl ether}} 2M^+ + [BH_4]^-$$

Asymmetrical Cleavage



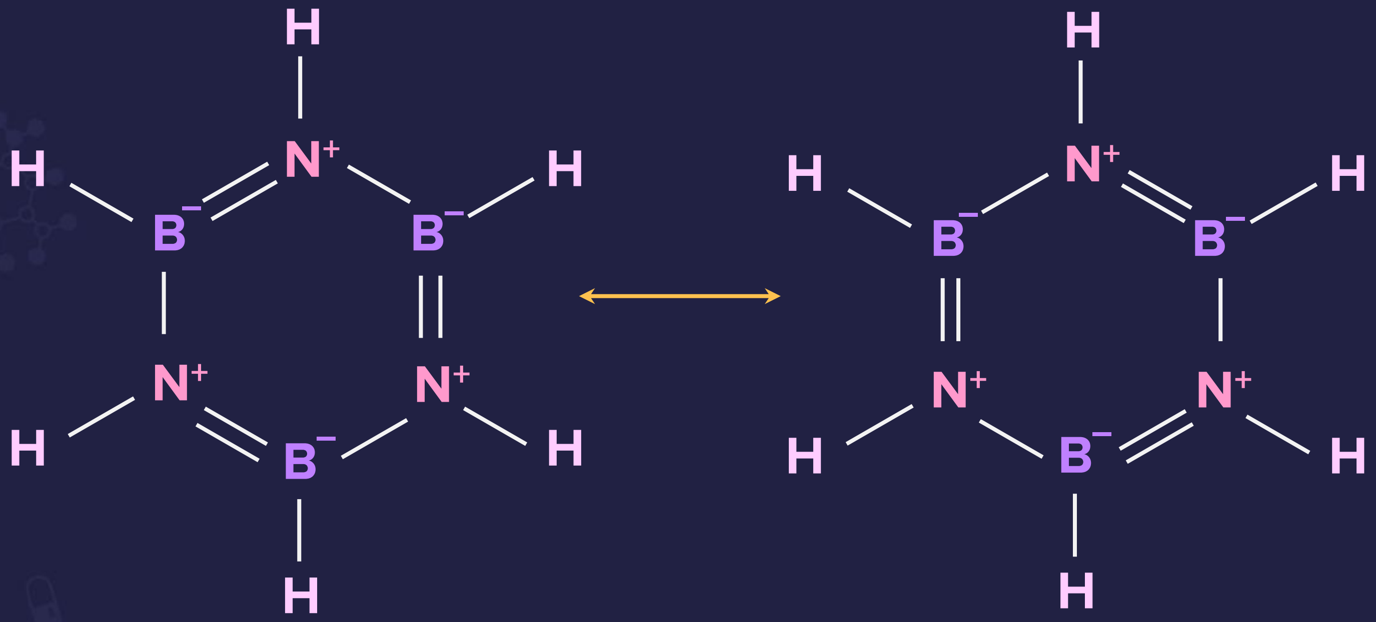
Inorganic Benzene

Preparation

$$\begin{tikzcd} 3B_2H_6 + 6NH_3 \arrow[r] & 3[H_2B(NH_3)_2]^+ [BH_4]^- \arrow[d, "\Delta"] \\ & 2B_3N_3H_6 + 12H_2 \end{tikzcd}$$

Inorganic benzene

Inorganic Benzene/Borazine

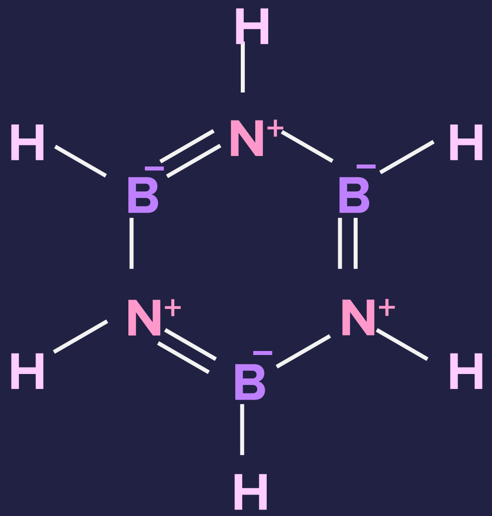


Borazine vs Benzene

Borazine

More reactive

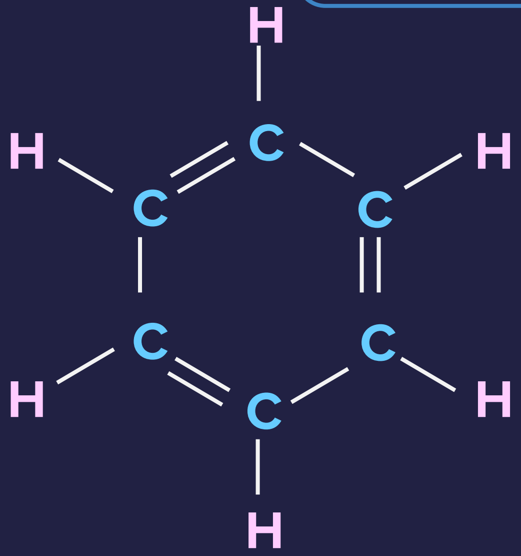
Undergoes addition reactions



Benzene

Less reactive

No addition reactions



Borazine

If heated with water,
$B_3N_3H_6$ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$

Note

$$B_2H_6 + NH_3 \xrightarrow[\text{Low T}]{\text{Excess } NH_3} B_2H_6.2NH_3 \text{ or } [H_2B(NH_3)_2]^+[BH_4]^-$$

$$B_2H_6 + NH_3 \xrightarrow[\text{Higher T } (200^{0}C)]{\text{Ratio } 2NH_3 : 1B_2H_6} B_3N_3H_6$$

$$B_2H_6 + NH_3 \xrightarrow[\text{Higher T } (>200^{0}C)]{\text{Excess } NH_3} (BN)_X \text{ Boron nitride}$$

Uses of Boron

Construction of high impact-resistant steel

Controlling atomic reactions

Boron carbide is used as an abrasive

Uses of Boron


Reactor rods in nuclear reactions


Boron carbide abrasive


High-resistance stainless steel

Compounds of Aluminium

Aluminium Oxide (Al_2O_3): Preparation & Properties

Preparation

Pure Al_2O_3 is obtained by **igniting $Al_2(SO_4)_3$ or $Al(OH)_3$**

$$Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3 \uparrow$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O \uparrow$$

Properties

1. It is a **white amorphous powder**.
2. **Insoluble in water** but **soluble in acids,** as well as **alkalies (amphoteric).**

Aluminium Chloride ($AlCl_3.6H_2O$):Preparation

By **dissolving** aluminium, Al_2O_3, or $Al(OH)_3$ in **dilute HCl**.

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

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

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

Properties

1 It is a **colourless crystalline solid.**

2 **Soluble** in water

3 Action of heat

$$2AlCl_3.6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl \uparrow + 3H_2O$$

4 Action of moisture on anhydrous $AlCl_3$

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

Uses of Aluminium

Manufacture of utensils

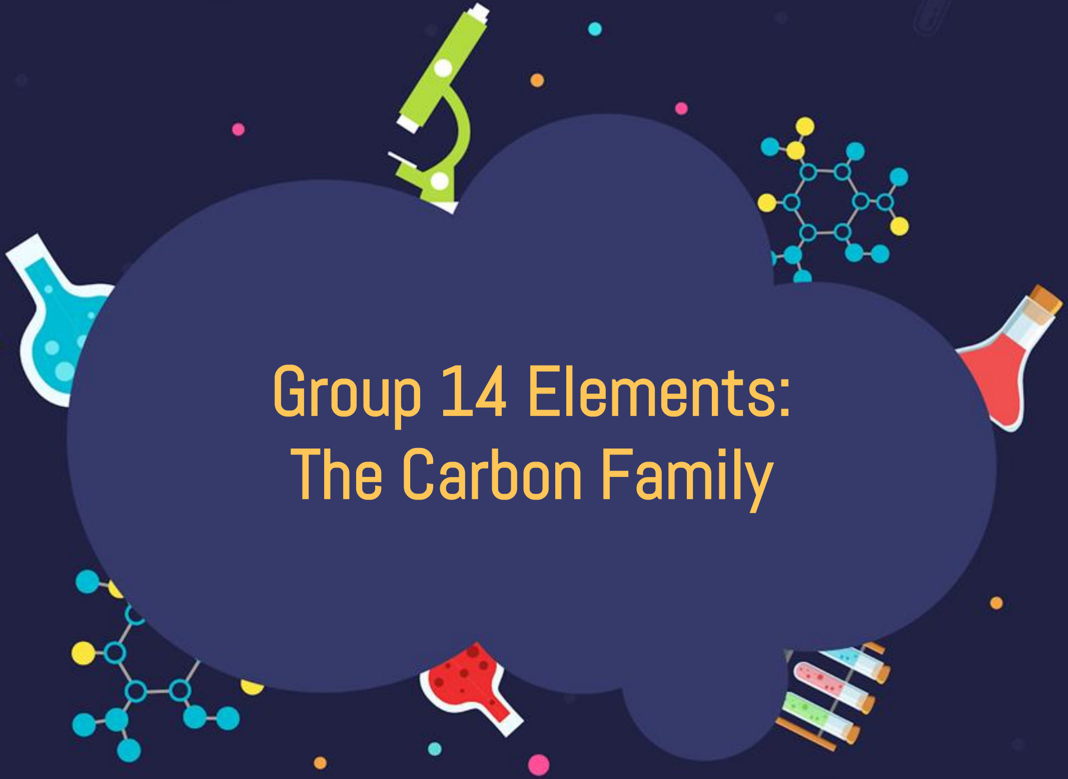
Plating steel objects

Manufacture cables

Making precision instruments

Making motorboats, car

Constituent of portland cement



Group 14 Elements: The Carbon Family

Group 14

- Carbon (C)
- Silicon (Si)
- Germanium (Ge)
- Tin (Sn)
- Lead (Pb)

Group 14: Occurance

Element	Abundance	Source
C (Carbon)	180 ppm	Coal, natural gas, oil (hydrocarbon), natural graphite, natural diamond, Calcite ($CaCO_3$), Magnesite ($MgCO_3$), Dolomite ($MgCO_3.CaCO_3$)

Carbon has three **isotopes**

^{12}C

^{13}C

^{14}C → Radioactive isotope

Group 14: Occurance

Element	Abundance	Source
Si (Silicon)	272000 ppm	Silica (sand & quartz) SiO_2, Silicate minerals
Ge (Germanium)	1.5 ppm	Silver & Zinc ores, coal
Sn (Tin)	2.1 ppm	Cassiterite (SnO_2)
Pb (Lead)	13 ppm	Galena (PbS)

Physical Properties

Melting points and boiling points of group **13** elements < **Melting points and boiling points** of group **14** elements

All group 14 members are **solids**.

Carbon is a **non-metal**.

Si & Ge are metalloid.

Sn and Pb are metals.

Atomic Properties

1 Electronic configuration (**[Noble gas] ns^2np^2**)

C	[He] $2s^2\ 2p^2$
Si	[Ne] $3s^2\ 3p^2$
Ge	[Ar] $3d^{10}\ 4s^2\ 4p^2$
Sn	[Kr] $4d^{10}\ 5s^2\ 5p^2$
Pb	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

Atomic Properties

2 Covalent radii

Covalent radius **increases** down the group.

C < **Si** < **Ge** < **Sn** < **Pb**

Considerable increase in covalent radius from **C to Si**, followed by a small increase from **Si to Pb.**

Due to the presence of **completely filled d and f orbitals** in heavier members.

Atomic Properties

3 Ionisation enthalpy

In general, ionisation enthalpy **decreases** down the group.

I.E._1 of group 13 < I.E._1 of group 14

C > **Si** > **Ge** > **Sn** < **Pb**

⇧

Poor shielding of f electrons

Atomic Properties

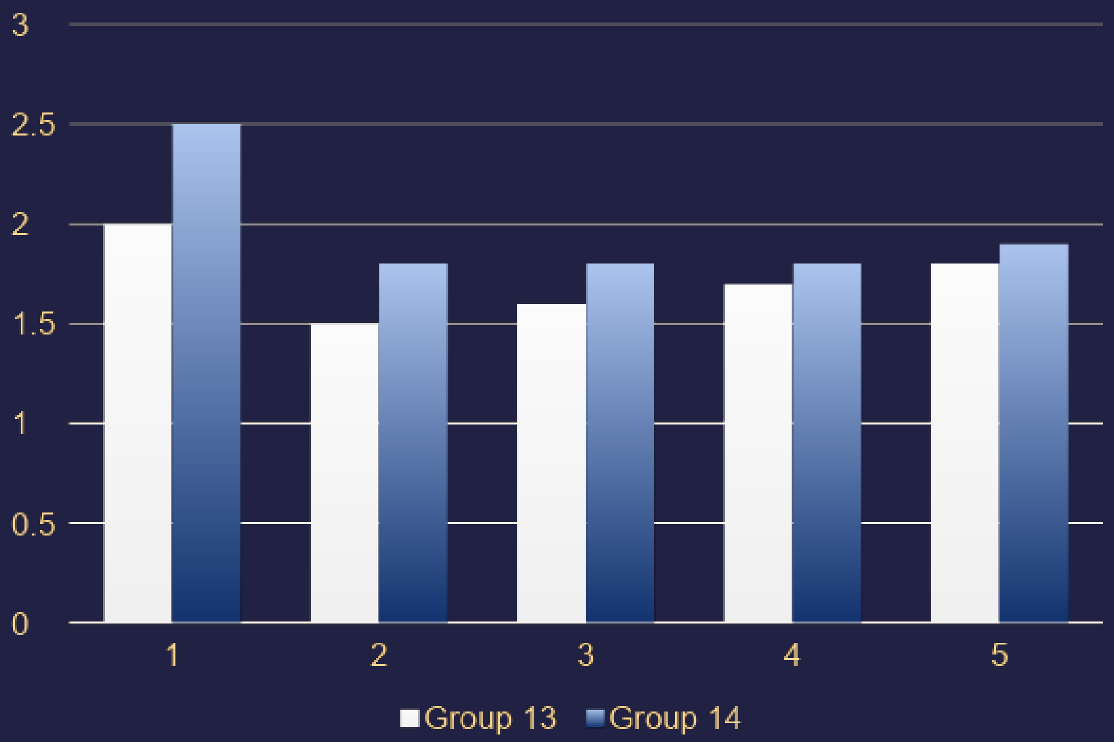
4 Metallic character

C	Si	Ge	Sn	Pb
Non-metal	Metalloid	Metalloid	Metal	Metal

5 Electronegativity (Pauling Scale)

C	Si	Ge	Sn	Pb
2.5	1.8	1.8	1.8	1.9

Electronegativity of group 13 elements < Electronegativity of group 14 elements



Chemical Properties: Covalency

Being **electron precise** molecules, the elements are not expected to accept or donate electrons. Carbon cannot exceed its **covalency** of **4**.

Other elements of the group can do so because of the **presence of d orbitals** in them.

Chemical Properties: Oxidation State

The elements have **four electrons** in their outermost shell.

Since the sum of the **first four ionisation enthalpies** is very high, the compounds in **+4** oxidation state are generally **covalent** in nature.

The common oxidation states exhibited by these elements are **+4 and +2**. **Carbon** also exhibits **negative** oxidation states.

Inert Pair Effect

Down the group, due to **poor shielding of d and f orbitals**

Effective nuclear charge holds **ns** electrons tightly

Restricting their **participation** in bonding

Only the electrons in **p-orbital** get involved in bonding

For **Ge**, **Sn,** and **Pb**, both **+2** and **+4** oxidation states are observed.

Down the group, the relative stability of **+2** oxidation state progressively **increases.**

Inert Pair Effect

Stability of Oxidation state

+2 Ge **<** Sn **<** Pb

+4 Ge **>** Sn **>** Pb

C & Si mostly show **+4 oxidation state**.

Tin forms compounds in both oxidation states. Tin in **+2 state** is a **reducing agent**.

Lead compounds in **+2 state** are stable and in **+4 state** are strong **oxidising agents**.

Chemical Reactions

a Reaction with oxygen

All members when heated in oxygen form **oxides.**

Monoxide
MO

Dioxide
MO_2

$$E + O_2 \xrightarrow{\Delta} EO_2$$

dioxide

$$E + \frac{1}{2}O_2 \xrightarrow{\Delta} EO$$

mono oxide

(E = Group 14 element)

Reaction with Oxygen

Acidity of **oxides** in **lower** oxidation states

<

Acidity of **oxides** in **higher** oxidation states

CO_2	Acidic
SiO_2	Acidic
GeO_2	Acidic
SnO_2	Amphoteric
PbO_2	Amphoteric

CO	Neutral
SiO	Unstable
GeO	Acidic
SnO	Amphoteric
PbO	Amphoteric

Note

$$2C\,(s) + O_2\,(g) + 4N_2\,(g) \xrightarrow{1273\text{ K}} \underbrace{2CO\,(g) + 4N_2\,(g)}_{\text{Producer gas}}$$

b Reaction with water

$$C\ (s) + H_2O\ (steam) \xrightarrow[\text{heat}]{\text{red}} CO\ (g) + H_2\ (g)$$

$$E\ (s) + 2H_2O\ (steam) \xrightarrow[\text{heat}]{\text{red}} EO_2\ (g) + 2H_2\ (g)$$

E = Si, Ge, Sn

Pb is unaffected by water, probably because of the protective oxide layer.

C, Si, Ge - Not attacked by cold water

c Reaction with halogens

$$E + 2X_2 \longrightarrow EX_4$$

X = F, Cl, Br, I

All members form MX_4; Ge & Pb form MX_2

PbI_4 does not exist

Down the group → Stability of EX_4 ↓

Down the group → Stability of EX_2 ↑

Stability

$GeX_4 > GeX_2$

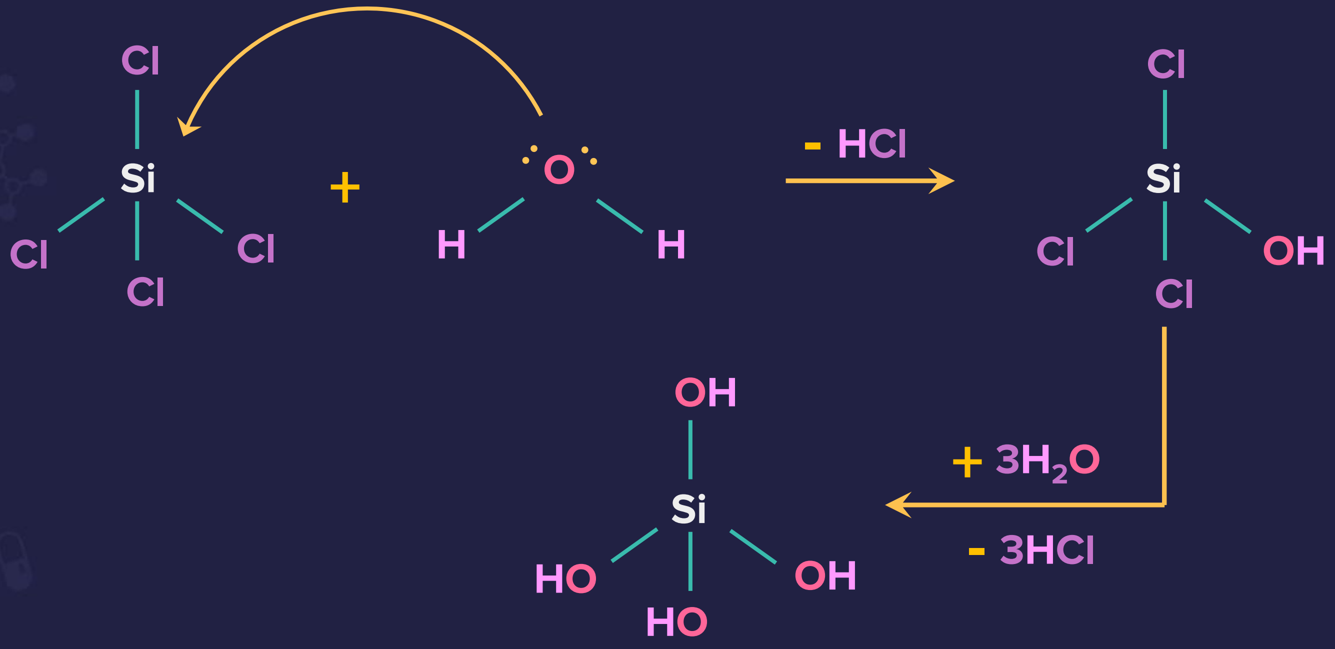
$PbX_2 > PbX_4$

Hydrolysis of Halides

CCl_4 is kinetically **inert** towards hydrolysis, but **$SiCl_4$** is **readily hydrolysed** by water.

Availability of **3d orbitals on Si**

Hydrolysis of $SiCl_4$



Anomalous Behaviour of Carbon

Like the first members of the other groups, **carbon also differs** from rest of the members of its group.
It is due to:

1. Smaller **size**
2. **Higher ionisation enthalpy**
3. Higher **electronegativity**
4. **Unavailability of d orbitals**

Anomalous Behaviour of Carbon

Carbon can accommodate only four pairs of electrons around it. This would **limit the maximum covalency of carbon to four.**

Whereas, other members can **expand their covalency** due to the presence of **d orbitals.**

Carbon forms **pπ-pπ** multiple bonds with **itself** and with **other atoms** of **small size** and **high electronegativity.**

C = C

C ≡ C

C = S

C ≡ N

Heavier elements do **NOT** form **pπ-pπ** bonds.

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.**

Catenation

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

Down the group → Size ↑ → Tendency to show **catenation** ↓

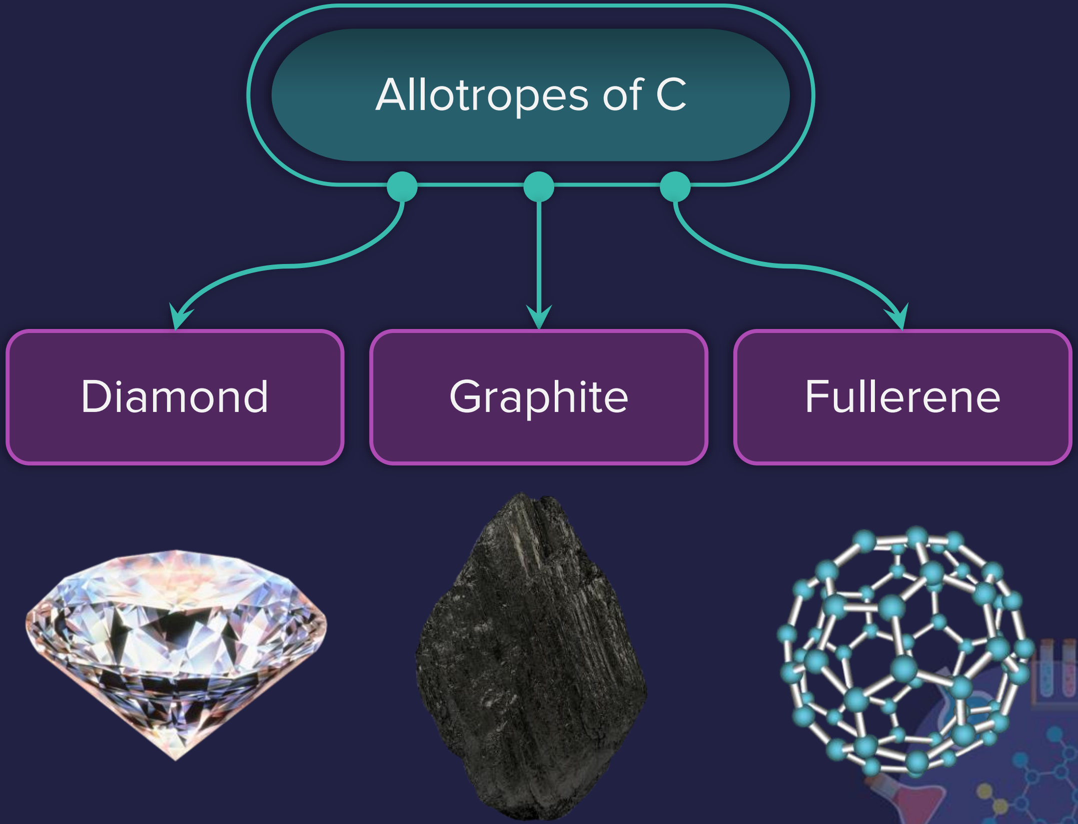
Order of **catenation**

C $>>$ **Si** $>$ **Ge** $\approx$ **Sn**

Lead does not show **catenation.**

Catenation

Due to the property of **catenation** and **pπ-pπ** bonds formation, **carbon** is able to show **allotropic** forms.



Allotropes of C

Diamond

Graphite

Fullerene

Diamond: Preparation

1. **Natural diamond** can be extracted from mines.

2. $$\text{Graphite} \xrightarrow[50000\text{–}60000\ \text{atm}]{1600^\circ\text{C}} \text{Synthetic diamond}$$

Diamond

1. It has a **crystalline** lattice in which each carbon atom is **sp^3 hybridised.**

2. Each C is linked to **four** other carbons and the C-C bond length is **154 pm.**

3. The structure extends in **space** and produces a **rigid 3D network** of carbon atoms.

Diamond

It is very difficult to **break** extended covalent bonding, which makes diamond one of the **hardest substances** on the earth.

Diamond has the **highest known thermal conductivity** because its structure distributes thermal motion in three dimensions efficiently.

Diamond is an excellent **electrical insulator.**

The measurement of thermal conductivity is used to **identify fake diamonds.**

Because of diamond’s durability, clarity, and high refractive index, it is one of the **most expensive gemstones.**

Uses of Diamond

01

Abrasive for sharpening hard tools

02

As a gem

03

Manufacture of **tungsten filaments** for electric light bulbs

Graphite: Preparation and Properties

$$3C + SiO_2 \xrightarrow{\Delta} SiC + 2CO \xrightarrow{2500^\circ C} C\ (\text{graphite}) + Si\ (\text{gas})$$

1. Graphite has a **layered structure** held by **van der Waals forces,** and the **distance** between two layers is **340 pm.**
2. Each layer is composed of **planar hexagonal rings** of sp^2 hybridised C atoms.
3. Each C atom in the **hexagonal ring** makes three **sigma bonds** with three **neighbouring** C **atoms,** and the fourth electron forms a **π** bond.

Graphite

Graphite **cleaves** easily between the layers. Hence, it is very **soft** and **slippery**.

Graphite is used as a **dry lubricant** in machines running at **high temperatures**, where oil cannot be used as a lubricant.

Electrons are **mobile** and delocalised over the whole sheet. Therefore, graphite **conducts electricity** along the sheet.

Graphite vs Diamond

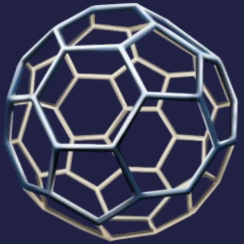
Electrical conductivity of graphite	>	Electrical conductivity of diamond
Thermal conductivity of graphite	<	Thermal conductivity of diamond

Graphite is **thermodynamically more stable** and **reactive** than diamond.

Fullerenes: Preparation and Properties

Heating graphite in an electrical arc in the presence of inert gases such as helium or argon **can result in the formation of fullerene.**

Fullerenes are the only **pure form** of carbon because they have a smooth structure **without** ‘**dangling**’ bonds.



Fullerenes are **cage**-like molecules.
C_{60} molecule has a shape like a **soccer** ball and is known as **Buckminsterfullerene**.

Buckminsterfullerene (C_{60})

1. It contains **20** six-membered rings and **12** five-membered rings.

2. A six-membered ring is **fused** with six or five-membered rings.

3. **Five**-membered rings are fused **only with six-**membered rings.

4. All the carbon atoms are **sp^2 hybridised**.

5. C_{60} exhibits a **small degree of aromatic character**. Its reactions tend to reflect the presence of localised double and single C-C bonds.

Note

Graphite is thermodynamically the **most stable allotrope** of carbon. Hence, $\Delta_f H^o$ of graphite is taken as **zero**.

$\Delta_f H^o$ (Diamond) > 0

$\Delta_f H^o$ (Fullerene, C_{60}) > 0

Other Forms of Elemental Carbon

1. **Carbon black**
2. **Coke**
3. **Charcoal**

Other Forms of Elemental Carbon

Carbon black is obtained
by burning hydrocarbons
in a limited supply of **air.**

Charcoal and **coke** are obtained
by heating wood and coal,
respectively, at high temperatures
in the **absence of air**.

Uses of Carbon

Graphite is used as **electrodes** in batteries & industrial electrolysis.

Activated charcoal adsorbs poisonous gases.

Coke is used as a **fuel** and as a **reducing agent** in metallurgy.

Diamond is a precious stone and used in **jewellery**.

Oxides of Carbon

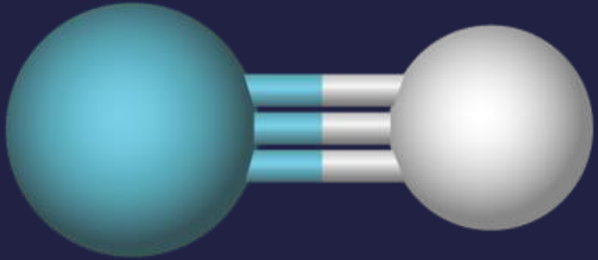
Carbon Monoxide: Preparation

1 Direct **oxidation** of **C** in **limited supply of oxygen** or air

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

2 Pure CO is obtained by dehydrating **methanoic acid** with concentrated **H_2SO_4** at 373 K.

$$HCOOH\ (l) \xrightarrow[\text{Conc. } H_2SO_4]{373\text{ K}} CO\ (g) + H_2O\ (l)$$



Preparation

3 If **oxalic acid** is dehydrated in the same way, **CO_2** is formed as well.

4 By the passage of **steam** over hot coke (on commercial scale)

$$H_2C_2O_4 \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4,\ \Delta} CO + CO_2$$

$$C\ (s) + H_2O\ (g) \xrightarrow{473\text{-}1273\ K} \underbrace{CO\ (g) + H_2\ (g)}_{\textbf{Water or synthesis gas}}$$

Preparation

5 If **air** is used instead of steam, a mixture of **CO and N_2** is produced.

$$2C\,(s) + O_2\,(g) + 4N_2\,(g) \xrightarrow{1273\ \text{K}} \underbrace{2CO\,(g) + 4N_2\,(g)}_{\textbf{Producer gas}}$$

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

CO in water gas or producer gas can undergo further combustion, forming **CO_2** with the **liberation of heat**.

Properties

1 CO is **colourless**, **odourless**, and is **sparingly soluble in water**.

2 It is a powerful **reducing agent**.

The reducing property of CO is used in the **extraction of many metals** from their **oxide ores**.

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

$$NiO\,(s) + CO\,(g) \xrightarrow{\Delta} Ni\,(s) + CO_2\,(g)$$

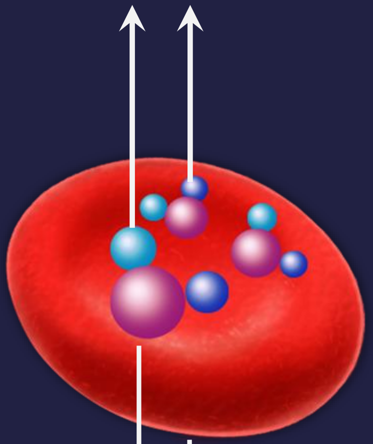
Properties

3 The molecule contains **one σ** and **two π** bonds between carbon and oxygen.

4 Due to the presence of a lone pair on C, CO acts as a **donor** and reacts with certain metals when heated to form **metal carbonyls**.

5 **CO is toxic** because it forms a complex with haemoglobin in the blood, which is more stable than oxy-haemoglobin.

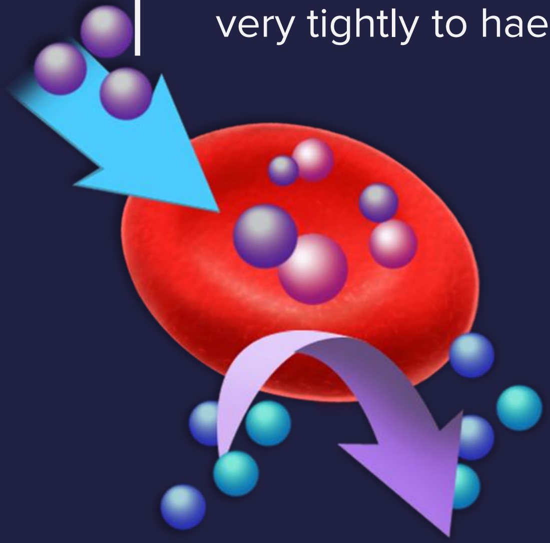
This complex causes **oxygen deficiency** by preventing the haemoglobin in the RBCs from carrying oxygen throughout the body, leading to unconsciousness and then **death.**



Haemoglobin carries oxygen and carbon dioxide.

Haemoglobin

Red blood cell

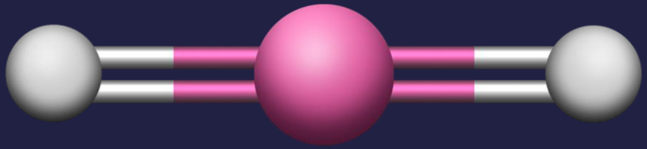


Carbon monoxide binds very tightly to haemoglobin.

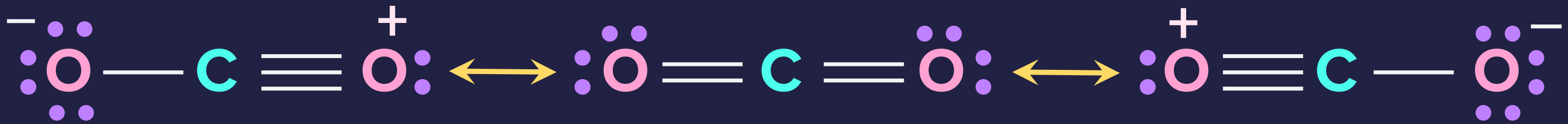
Oxygen and carbon dioxide can no longer be carried.

Carbon Dioxide

It has a linear shape [with both **C-O** bonds of equal length (**115 pm**)] with **no net dipole moment.**



Resonance structures of CO_2



$${}^{-}\!:\ddot{\underset{..}{O}}-C\equiv\ddot{O}^{+}: \longleftrightarrow :\ddot{O}=C=\ddot{O}: \longleftrightarrow :{}^{+}O\equiv C-\ddot{\underset{..}{O}}:^{-}$$

Carbondioxide: Preparation

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

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

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

2 In a **laboratory**, it is prepared by the action of **dilute HCl** on **$CaCO_3$.**

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

Preparation

3

Industrially, produced as a **by-product** during the manufacture of **CaO**.

$$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)$$

Properties

1. CO_2 is a **colourless** and **odourless gas**.

2. CO_2 has **low solubility in water** and forms **carbonic acid** on reacting with water.

3. H_2CO_3 is a **weak dibasic acid** and ionises in **two steps** as follows:

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)$$

Properties

4. **H_2CO_3/HCO_3^-** buffer system helps to maintain the pH of blood between **7.26 and 7.42.**

5. CO_2 readily reacts with **alkalis to form the corresponding carbonate.** If CO_2 is in excess, it forms the corresponding hydrogen carbonate. This is the basis of the **limewater test** for CO_2 gas.

$$Ca(OH)_2\,(aq) + CO_2\,(g) \longrightarrow CaCO_3\,(s) + H_2O\,(\mathit{l})$$

$$CaCO_3\,(s) + H_2O\,(\mathit{l}) + CO_2\,(g) \longrightarrow Ca(HCO_3)_2\,(aq)$$

Properties

6 Removal from atmosphere by **photosynthesis**

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

It is the process by which **green plants** convert atmospheric CO_2 into carbohydrates such as **glucose**.

Greenhouse Effect

Unlike CO, CO_2 is **not poisonous,** but the increase in **combustion of fossil fuels** and **decomposition of limestone for cement manufacture** seem to increase the CO_2 content in the atmosphere.

This may lead to an **increase in the greenhouse effect** and thus raise the temperature of the atmosphere.

Some other **greenhouse gases** are:
Methane, water vapour, nitrous oxide, CFCs and ozone.

Uses of CO_2

Carbonate soft drinks

Refrigerant for frozen foods

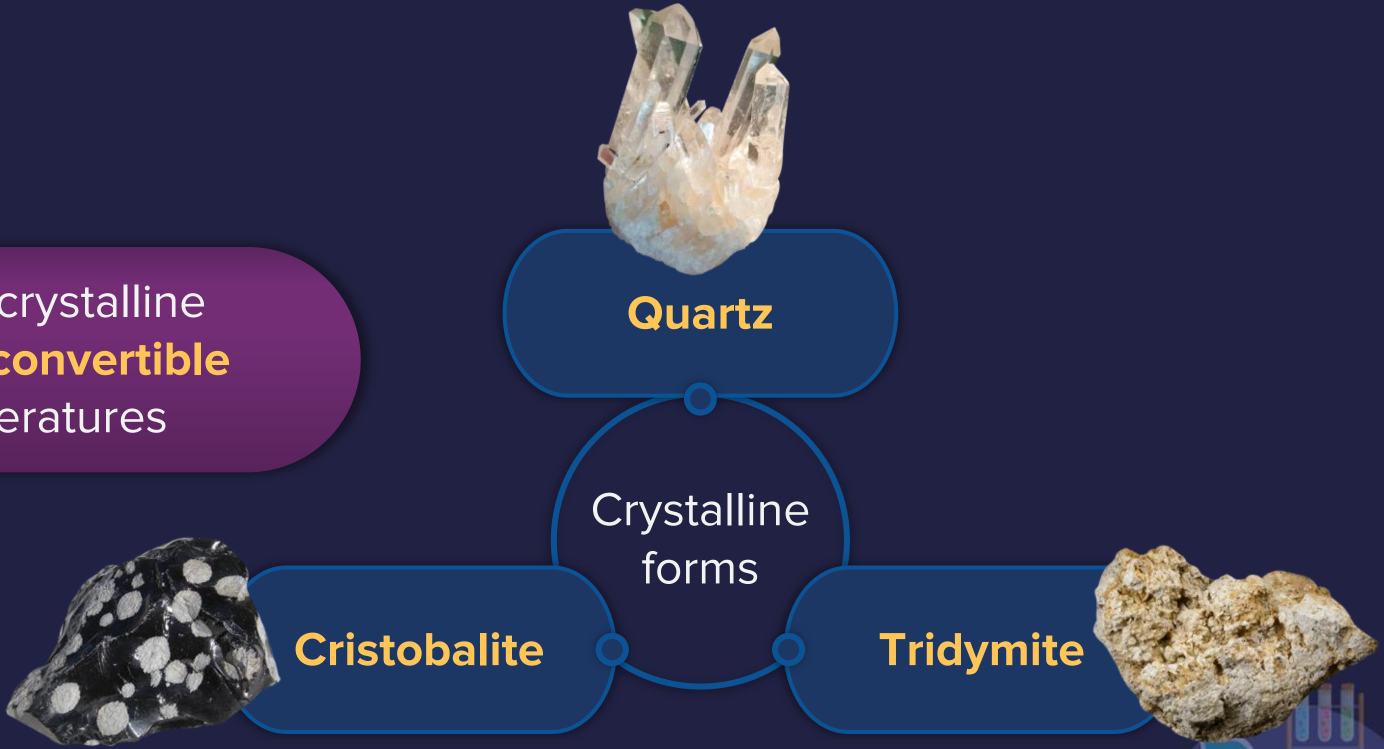
Fire extinguisher

Manufacture urea

Silicon Dioxide

Commonly known as **silica**

Occurs in several crystalline forms that are **interconvertible** at suitable temperatures



Crystalline forms

Quartz

Cristobalite

Tridymite

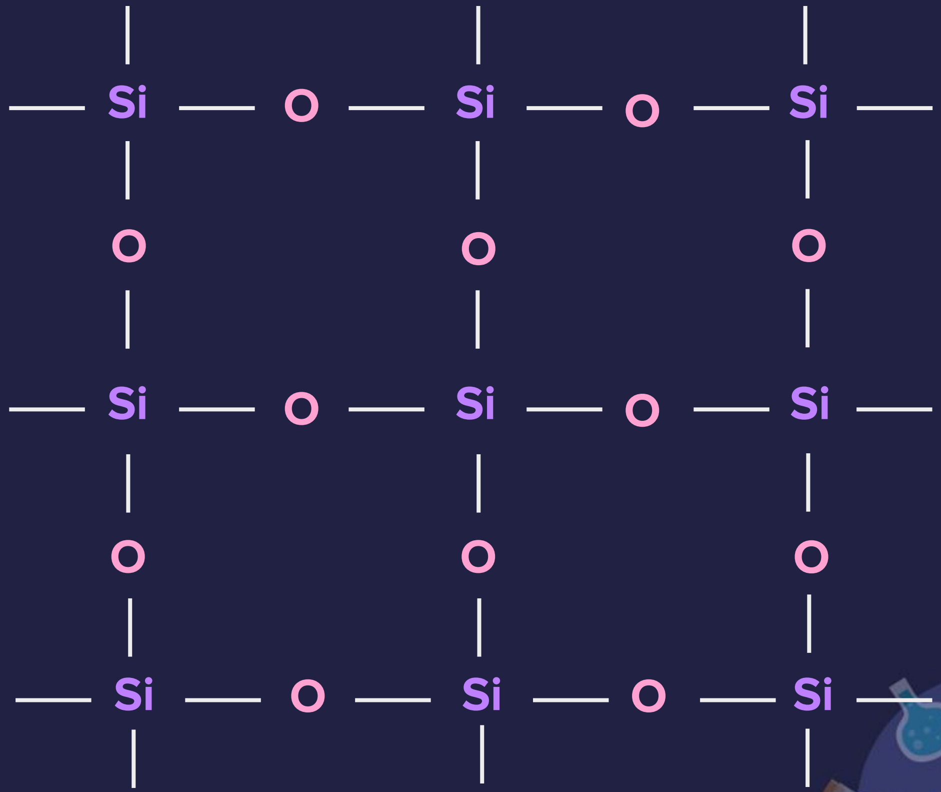
Structure of SiO_2

Covalent 3D network solid

Each Si-atom is covalently bonded to O-atoms in a **tetrahedral manner**

Each **O-** tom in turn is **covalently** bonded to another Si-atom

Eight-membered rings are formed with alternate Si and O-atoms



Properties

a

Si–O bond enthalpy is very high. That's why silica in its normal form is almost **non-reactive.**

However, it is attacked by **HF** and **NaOH.**

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

b

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

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

Uses of SiO_2

1 **Quartz** is extensively used as a **piezoelectric material.**

- **Extremely accurate clocks**
- **Modern radio**
- **Television broadcasting**
- **Mobile radio communications**

2 **Silica gel** is used as a **drying agent** and as a support for **chromatographic materials** and **catalysts**.

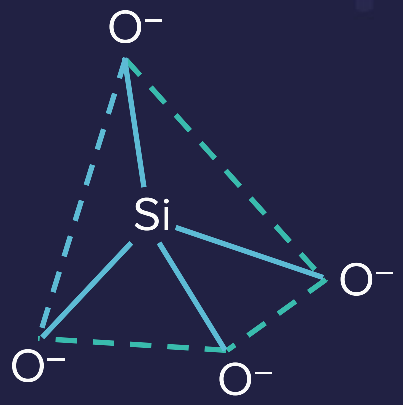
3 **Kieselguhr,** an amorphous form of silica, is used in **filtration plants.**

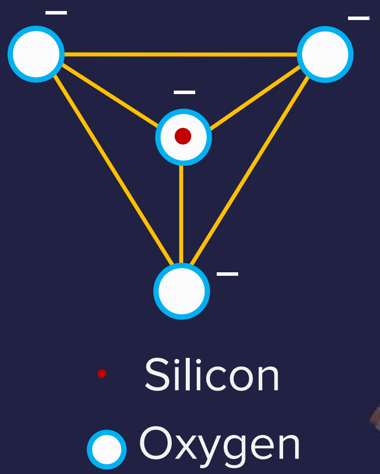
Silicates

Binary compounds of silicon with oxygen are called **silicates,** but they also contain **other metals** in their structures.

Since the electronegativity difference between O and Si is about **1.7,** the Si–O bond can be considered **50% ionic** & **50% covalent.**

SiO_4^{4-} tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.





Properties

a When silicate units are linked together, they form **chains**, **rings**, **sheets,** or 3D structures.

b Negative charge on silicate structures is **neutralised** by positively charged metal ions.

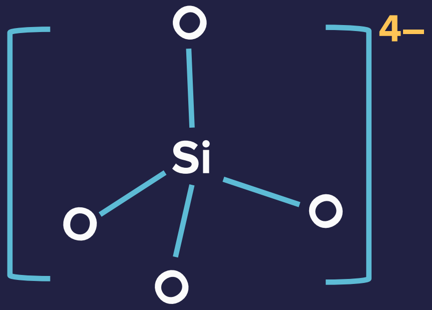
Classification of Silicates

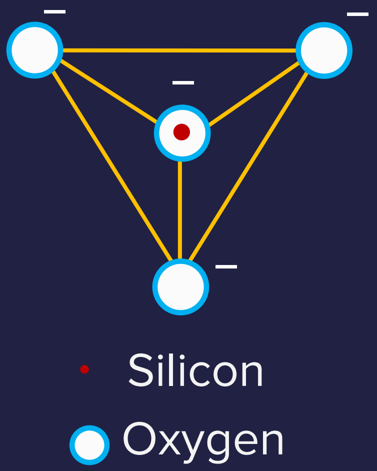
Silicates

- Ortho-silicates
- Pyro-silicates
- Cyclic silicates
- Chain silicates
- 2D Sheet silicates
- 3D Sheet silicates

Ortho-Silicates

These contain discrete $[SiO_4]^{4-}$ units, i.e., there is **no sharing** of corners with one another.



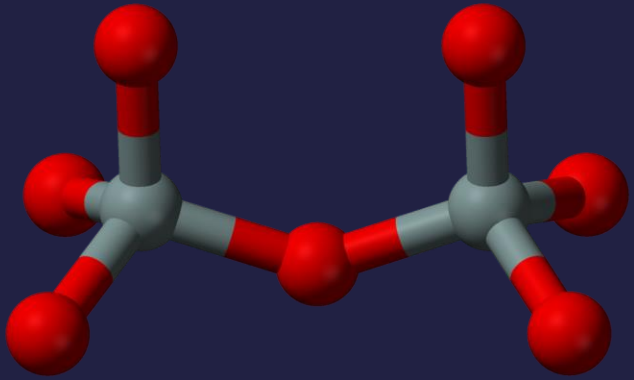


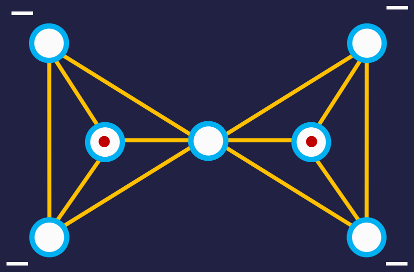
Pyro-Silicates

Two tetrahedral units are joined by sharing an oxygen at **one corner.**

Negative charge is on the O atoms, which is bonded with **one Si atom**.

General formula $[Si_2O_7]^{6-}$

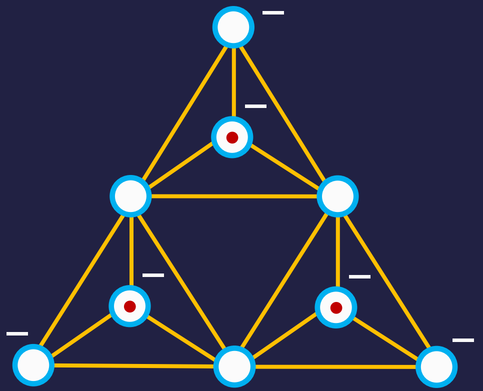




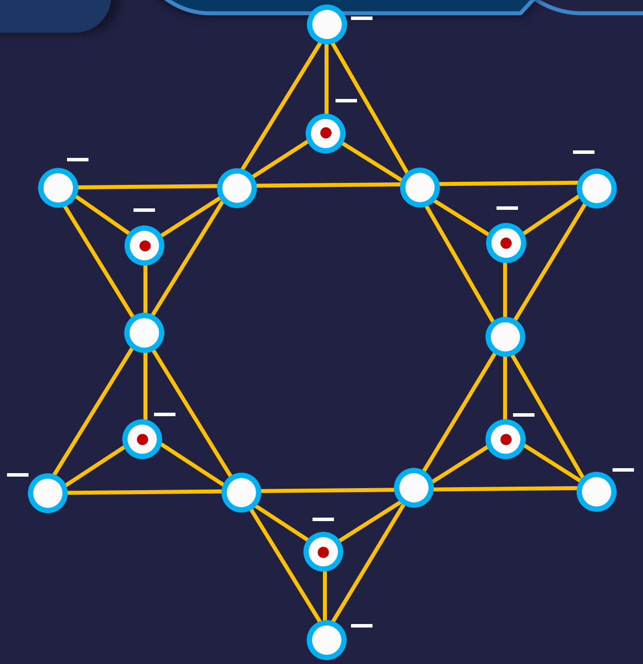
Cyclic-Silicates

Two oxygen atoms per **tetrahedron** are shared to form **closed** rings.

General formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$



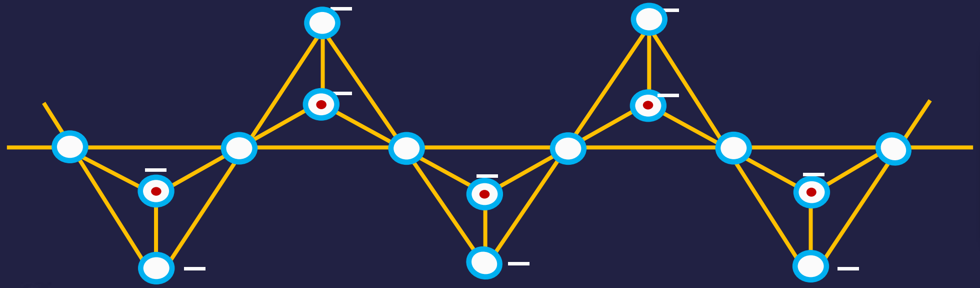
$Si_3O_9^{6-}$



$Si_6O_{18}^{12-}$

Chain Silicates

- Single chain silicates
- Double chain silicates



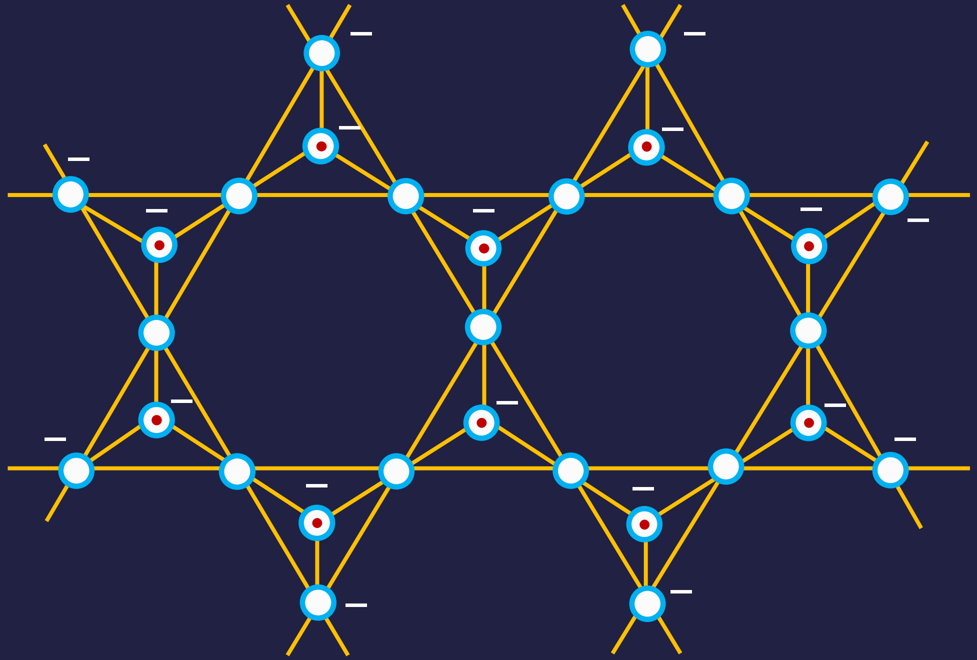
$(SiO_3)_n^{2n-}$

Single Chain

- **Two corners** of each tetrahedron are shared
- A **long chain** of tetrahedron
- General formula is $(SiO_3)_n^{2n-}$

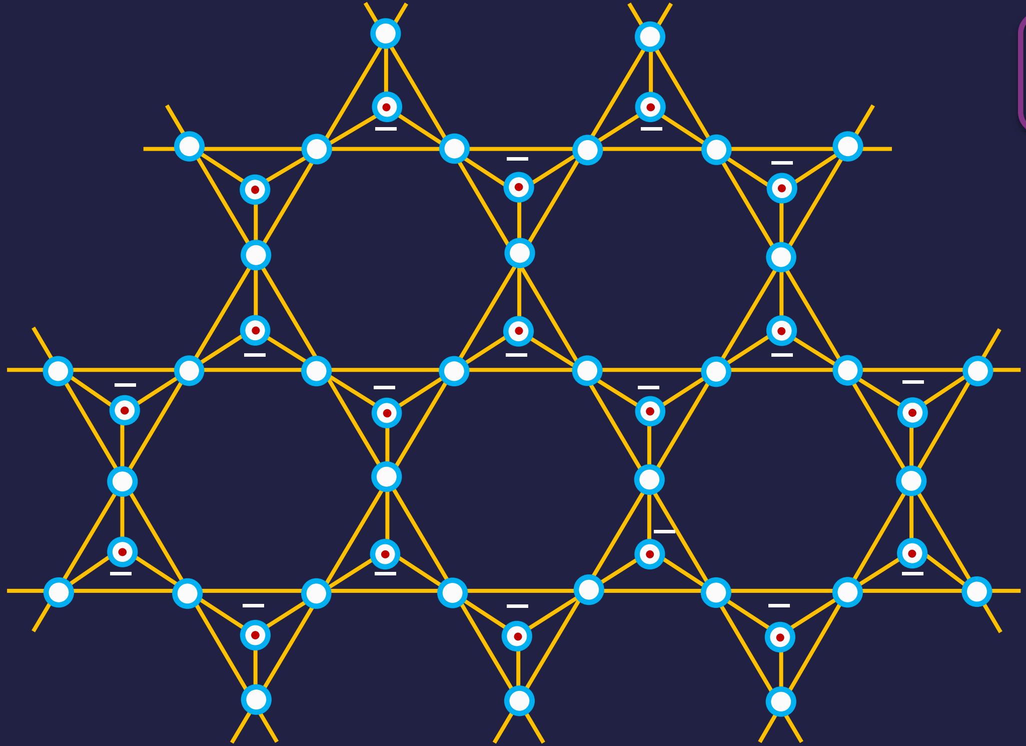
Double Chain

- **Two** single chains are joined together by shared **O atoms.**
- General formula: $(Si_4O_{11})_n^{6n-}$



2D-Sheet

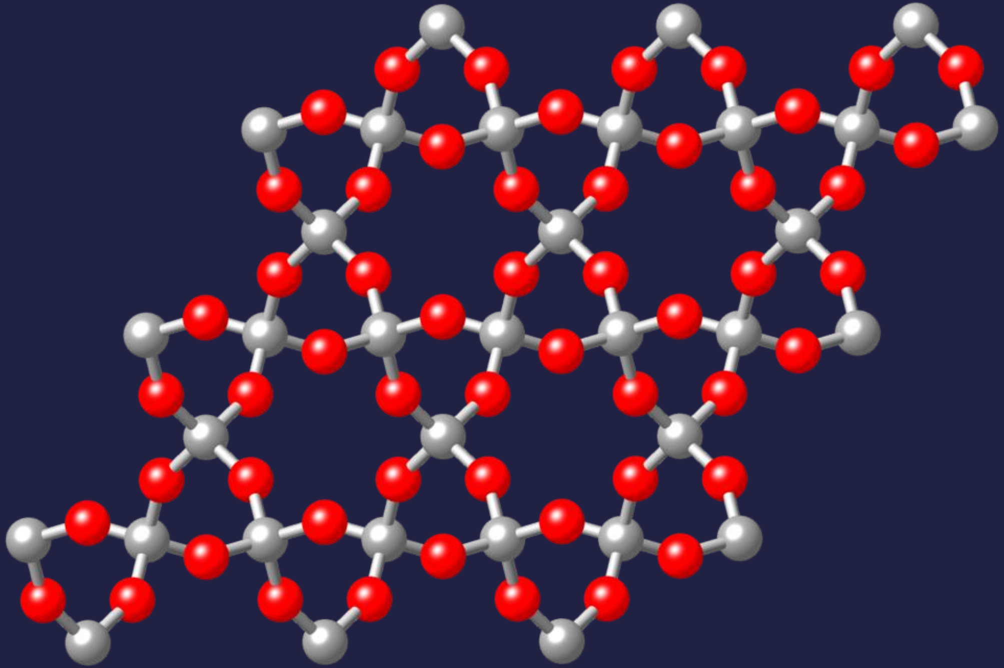
Three oxygen atoms of each tetrahedron are shared with the adjacent **SiO_4^{4-}** tetrahedrons.



General formula: **$(Si_2O_5)_n^{2n-}$**

3D Sheet

Involves all four O-atoms in sharing with the adjacent **SiO_4^{4-} tetrahedral units. Examples:** Quartz, Feldspar, Zeolite.



Silicones

Silicones are **synthetic organosilicon** compounds having repeated **R_2SiO** units held by **Si–O–Si linkages**.

General formula **$(R_2SiO)_n$**

R = Alkyl or Aryl group

Preparation

Silicones are formed by the **hydrolysis** of alkyl or aryl-substituted chlorosilanes and their subsequent **polymerisation**.

Preparation

Step 1 Formation of **silane derivatives**

a) $$RCl + Si \xrightarrow[300^\circ C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$$

b) $$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$

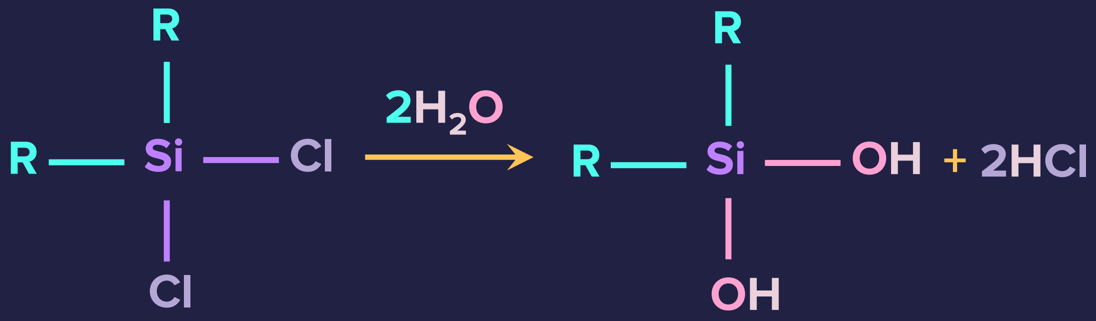
$$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$

$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

Preparation

Step 2

Silane derivatives are **hydrolysed**



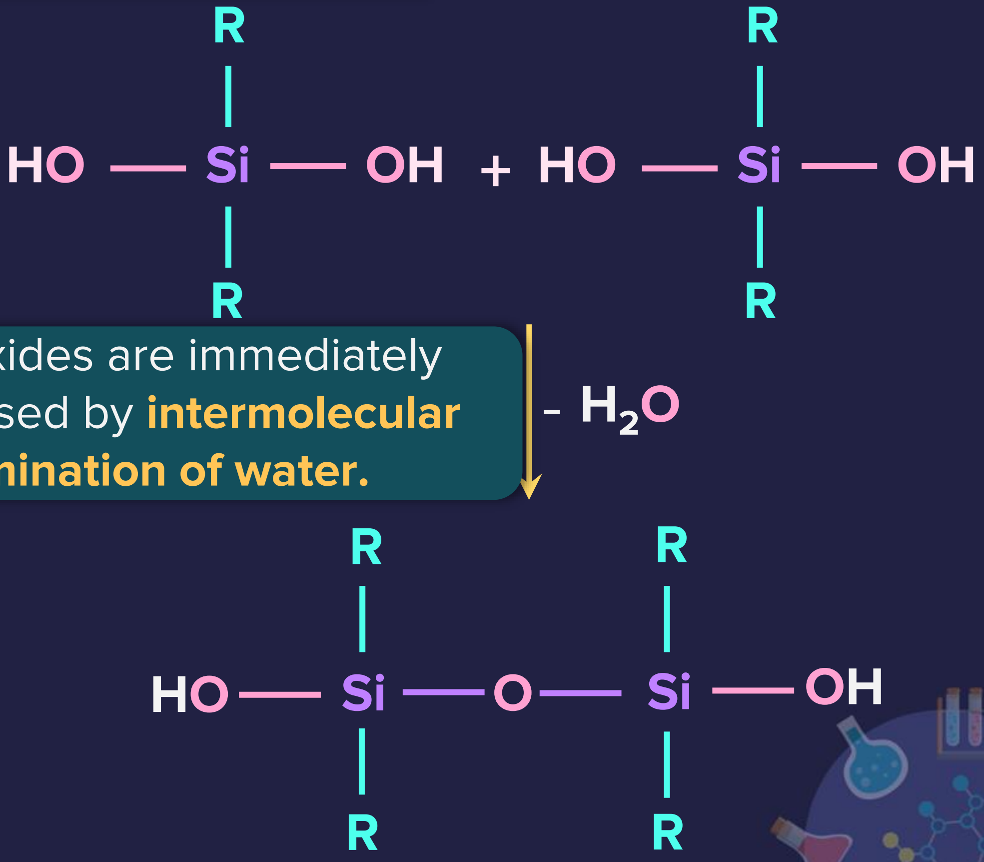
$$R-\underset{Cl}{\overset{R}{Si}}-Cl \xrightarrow{2H_2O} R-\underset{OH}{\overset{R}{Si}}-OH + 2HCl$$

After fractional distillation, the silane derivatives are hydrolysed to form **hydroxides.**

Preparation

Step 3

Intermolecular
elimination of water



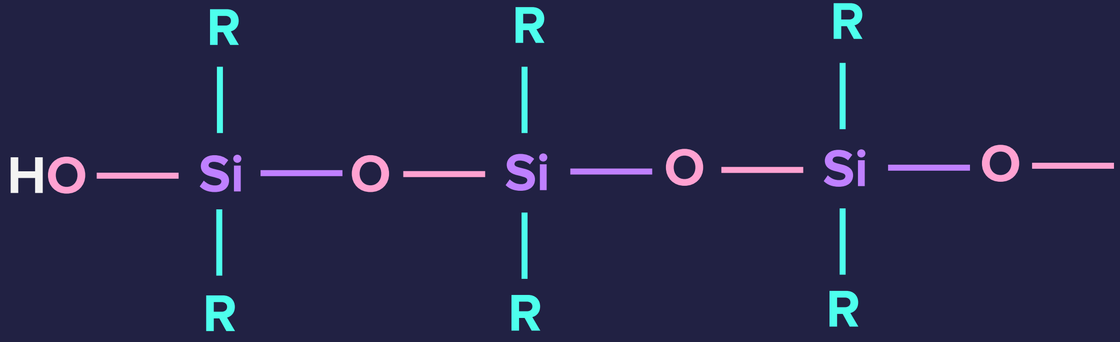
$$\mathrm{HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH \xrightarrow{-\,H_2O} HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH}$$

Hydroxides are immediately condensed by **intermolecular elimination of water.**

Preparation

Step 4 Polymerisation

Several molecules combine to form a **long chain polymer** whose ends will be occupied by **–OH groups.**



$$\mathrm{HO-\underset{R}{\overset{R}{\overset{|}{\underset{|}{Si}}}}-O-\underset{R}{\overset{R}{\overset{|}{\underset{|}{Si}}}}-O-\underset{R}{\overset{R}{\overset{|}{\underset{|}{Si}}}}-O-}$$

Preparation

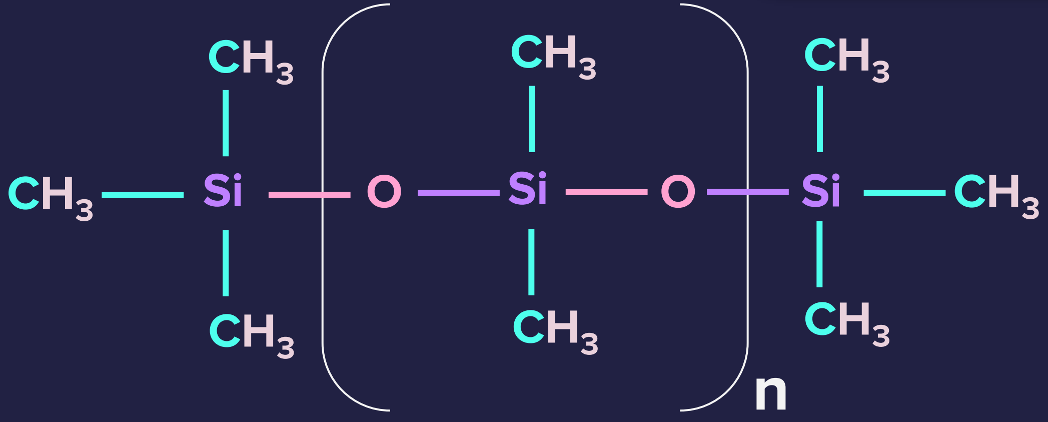
Step 5 Chain termination

The polymer chain is terminated by incorporating a small quantity of the **monochlorosilane derivative** into the hydrolysis mixture.

Silicone: Linear Chain

From the hydrolysis of a mixture of **$(CH_3)_3SiCl$ & $(CH_3)_2SiCl_2$**

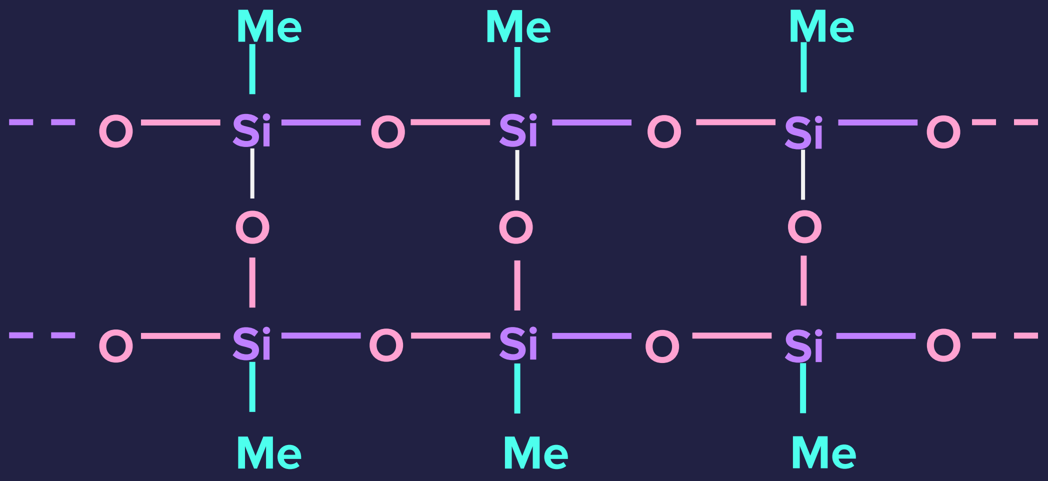
The dichloro derivative will form a **long chain polymer** as usual. However, the growth of the polymer can be blocked at any stage by the hydrolysis product of the mono-chloro derivative.



Silicone: Cross-Linked

From the hydrolysis of the **trichloro derivative**

When a compound like CH_3SiCl_3 undergoes hydrolysis, a **complex cross-linked polymer** is obtained, as the **chain can grow** in **three places**.



Properties

1. The hydrocarbon layer along the silicon-oxygen chain makes silicones **water-repellent**.
2. **Chemically inert**
3. Heat and electrical **insulators**
4. **Thermally stable** and their **viscosity** alters very little with temperature

Preparation of products having physical properties of oil, rubber, and resins.

Insulating wiring (fire resistant)

Uses of Silicones

Hydraulic system of planes (silicone fluid)

Silicone rubber: They retain their elasticity at much lower temperatures.

Zeolites

If **Al** atoms replace a few **Si** atoms in the 3D network of SiO_2, the overall structure known as **aluminosilicate**, acquires a negative charge. Cations such as **Na^+**, **K^+,** or **Ca^{2+}** balance the negative charge.

Used as **catalysts** in various processes

ZSM-5 (a type of zeolite) is used to convert **alcohols directly into gasoline**.