$$2BCl_3 + 6H_2 \xrightarrow[\text{electric discharge}]{\text{silent}} B_2H_6 + 6HCl$$

- **From boron trifluoride :**

$$8BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4$$

- **Properties**

$$B_2H_6 \xrightarrow[\text{ether}]{LiH} LiBH_4$$
$$B_2H_6 \xrightarrow{2Na} B_2H_6\cdot Na_2$$
$$B_2H_6 \xrightarrow{\text{red heat}} 2B + H_2$$
$$B_2H_6 \xrightarrow{+O_2} B_2O_3 + H_2O + \text{heat}$$
$$B_2H_6 \xrightarrow[\text{low temp.}]{NH_3} B_2H_6\cdot 2NH_3$$
$$B_2H_6 \xrightarrow[200°C]{NH_3} \underset{\text{Borazole}}{B_3N_3H_6}$$
$$B_2H_6 \xrightarrow{H_2O} H_2 + H_3BO_3$$
$$B_2H_6 \xrightarrow{\text{aq. KOH}} H_2 + KBO_2$$
$$B_2H_6 \xrightarrow{Cl_2} BCl_3$$
$$B_2H_6 \xrightarrow{HCl} \underset{\text{Chlorodiborane}}{B_2H_5Cl}$$

- **Uses :** The important uses of diborane are
  - as a catalyst in polymerisation reactions
  - as a reducing agent in organic reactions
  - for making high energy fuels and propellants
  - for preparing hydrocarbons, alcohols, ketones and acids through hydroboration method.

ALUMINIUM

- Aluminium is the third most abundant element found in earth's crust (after oxygen and silicon). It does not occur in free state in nature.
- Aluminium is a light silvery white metal with high tensile strength, high electrical and thermal conductivity (electrical conductivity of aluminium is twice that of copper).
- **Action of acids :** Aluminium dissolves in dilute mineral acids producing hydrogen.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(g)}$$
$$2Al_{(s)} + 3H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$$

With hot concentration H_2SO_4, SO_2 gas is liberated.

$$2Al + 6H_2SO_{4\,(conc.)} \xrightarrow{\Delta} Al_2(SO_4)_3 + 2SO_2\uparrow + 6H_2O$$

Nitric acid renders aluminium passive due to the formation of a protective layer of Al_2O_3 on its surface.

- **Action of alkalies :** Aluminium dissolves in strong alkali solutions to give colourless aluminium liberating hydrogen gas.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O \longrightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_{2\,(g)}$$
$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\substack{\text{Sodium metaaluminate}\\ \text{(soluble)}}}{2NaAlO_2} + 3H_2$$

Addition of a small amount of alkali to an aluminium salt solution precipitates aluminium hydroxide. On addition of more alkali, the hydroxide dissolves to form the aluminate ion.

$$2Al + 6NaOH \longrightarrow \underset{\text{Sodium aluminate}}{2Na_3AlO_3} + 3H_2\uparrow$$

- **Uses**
  - Aluminium is used extensively in industry and everyday life.
  - It forms many useful alloys with Cu, Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries.
  - It is used as a conductor for transmission of electricity.
  - Aluminium is also used in the alumino-thermite process for production of chromium and manganese from their ores.
  - It is used for making silvery paints for covering iron and other materials.

GROUP 14 ELEMENTS

- **General introduction :** Group 14 contains five elements, carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Carbon is an essential constituent of all organic matter. Silicon is an important constituent of all inorganic matter. Carbon in combined state occurs in all living tissues belonging to plant or animal kingdom.
- **Electronic configuration :**

Element	Symbol	Electronic configuration [noble gas] ns^2np^2
Carbon	$_6C$	[He] $2s^22p^2$
Silicon	$_{14}Si$	[Ne] $3s^23p^2$
Germanium	$_{32}Ge$	[Ar] $3d^{10}4s^24p^2$
Tin	$_{50}Sn$	[Kr] $4d^{10}5s^25p^2$
Lead	$_{82}Pb$	[Xe] $4f^{14}5d^{10}6s^26p^2$

- **Occurrence and abundance :**

Element	Abundance (ppm)	Ore
C	180	Free state (graphite, diamond and coal) Combined : Limestone ($CaCO_3$), calamine ($ZnCO_3$), siderite ($FeCO_3$),
Si	2,72,000 (second most abundant)	Silica (SiO_2), silicates
Ge	1.5	In ores of Ag and Zn
Sn	2.1	Tin stone : SnO_2
Pb	13	Galena : PbS, cerussite ($PbCO_3$)

Trends in Physical Properties

- **Atomic radii**
  - The atomic radii of group 14 elements are smaller than that of corresponding elements of group 13. Because if we move from left to right in a period, effective nuclear charge increases consequently the size of the atom decreases.

- The atomic radii of group 14 elements increase regularly on moving down the group mainly due to increase in the number of shells.

- **Melting and boiling points**
  - The melting and boiling points of group 14 elements are much higher than those of the elements of group 13. It is because these form four covalent bonds with each other and hence there exists strong binding forces between their atoms both in the solid as well as in the liquid state.
  - The melting and boiling points decrease on descending the group form carbon to lead because the $M-M$ bond becomes weaker since the atom size increases.

- **Ionisation energy**
  - The first ionization energies of the group 14 elements are higher than those of group 13 elements. This is because of their greater nuclear charge and smaller size.
  - The value of ionisation energy decreases on moving down the group, though not in a regular order. The ionisation energy of group 14 elements follows the order : C > Si > Ge > Sn < Pb

- **Oxidation state**

Element	Oxidation state
C	+4
Si	+4
Ge	+2, +4
Sn	+2, +4
Pb	+2, +4

As we move down, inert pair effect increases and stability of lower oxidation state increases.

$Pb^{2+} > Pb^{4+}$, $Ge^{4+} > Ge^{2+}$

$Pb^{2+} > Sn^{2+} > Ge^{2+}$

- **Electropositive character–metallic character**

Group 14 elements are less electropositive than group 13 elements.

Element	Metallic character
C	Non-metal
Si	Non-metal
Ge	Metalloid
Sn	Metal
Pb	Metal

- **Catenation (Tendency to form chains)**
  - Catenation is the property of elements to form long chains or rings by self-linking of their own atoms through covalent bonds.
  - Carbon shows a remarkable ***catenation*** due to smaller size and high electronegativity. So that C – C bond is extremely stable.

- **Allotropy :** Allotropy (Greek: allos = other, tropos = manner) is the phenomenon of existence of the same substance (element or compound) in two or more forms, in the same physical state, having different properties. Different forms are called allotropes or allotropic modifications.

Except lead, all other elements of group 14 show allotropy.

Element	Allotropic form
C	Crystalline : graphite and diamond Amorphous : coal, coke and charcoal
Si	Crystalline and amorphous
Ge	Two crystalline forms
Sn	Three forms : grey tin, white tin, rhombic tin

Chemical Properties

- **Reactivity :** The elements of this group are relatively less reactive but reactivity increases down the group. Lead often appears more unreactive than expected. This is partly due to surface coating of the oxide and partly due to the high overpotential for the reduction of H^+ to H_2 at a lead surface.
  - **Reactivity towards air :** These elements react with the oxygen of the air on strong heating when their oxides are formed.

    $C + O_2 \rightarrow CO_2$; $Si + O_2 \rightarrow SiO_2$

    $Ge + O_2 \rightarrow GeO_2$; $2Pb + O_2 \rightarrow 2PbO$

    Monoxides CO, SiO, GeO are also known. SiO is unstable.
  - **Reactivity towards water :** C, Si, Ge are unaffected by water. However, on red heating, these elements except lead decompose steam.

    $C + H_2O \rightarrow CO + H_2$

    $Si + 2H_2O \rightarrow SiO_2 + 2H_2$

    $Sn + 2H_2O \rightarrow SnO_2 + 2H_2$

    Lead is unaffected by water, probably, because of a protective oxide film.
  - **Reactivity towards acids :** Non-oxidising acids do not attack carbon and silicon. Germanium is not attacked by dilute HCl. However, when metal is heated in a stream of HCl gas, germanium chloroform is formed.

    $Ge + 3HCl \rightarrow GeHCl_3 + H_2$

    Tin dissolves slowly in dilute HCl but readily in concentrated HCl.

    $Sn + 2HCl \rightarrow SnCl_2 + H_2$

    Lead dissolves in dilute HCl.
  - **Reactivity towards alkalies :** Carbon is unaffected by alkalies. Silicon react slowly with cold aqueous NaOH and readily with hot solution giving solution of silicate.

    $Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$

    Sn and Pb are slowly attacked by cold alkali but readily by hot alkali giving stannates and plumbates. Thus, Sn and Pb are somewhat amphoteric.

    $Sn + 2NaOH + H_2O \rightarrow Na_2SnO_3 + 2H_2$

    $Pb + 2NaOH + H_2O \rightarrow Na_2PbO_3 + 2H_2$

- **Oxides**

MO	Nature
CO	Neutral
GeO	Acidic
SnO	Amphoteric
PbO	Amphoteric

- Carbon dioxide is gas at ordinary temperature. CO_2 has discrete molecules because carbon for ms $p\pi$-$p\pi$ bonds with oxygen or held together by weak van der Waals forces and hence exists as a gas at ordinary temperature. Whereas SiO_2 has three dimensional network structure, hence exists as a solid at room temperature. GeO_2, SnO_2, etc., are also network solids.

Element	Oxides
C	CO, CO_2, C_3O_2, C_5O_2, $C_{12}O_9$
Ge	GeO, GeO_2
Sn	SnO, SnO_2
Pb	PbO (litharge), PbO_2, Pb_3O_4 (sindur)

- **Halides**
  - Group 14 elements form tetrahalides of the type MX_4 and few dihalides MX_2.
  - All these tetrahalides are covalent (except $PbBr_4$ and PbI_4) formed by sp^3 hybridisation.
  - The thermal stability of tetrahalides of group 14 elements with a common halogen decreases with increasing atomic number *i.e.*, $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$.
  - While thermal stability of tetrahalides with a common central atom decreases with increase of atomic mass of halogen because of the decrease in $M-X$ bond energy from M–F to M–I *i.e.*,
  $$MF_4 > MCl_4 > MBr_4 > MI_4$$
- **Hydrides :** All elements form hydrides and C has maximum number of hydrogen compounds.

Elements	Name of hydrides	General formula
C	Alkanes	C_nH_{2n+2}
	Alkenes	C_nH_{2n}
	Alkynes	C_nH_{2n-2}
S	Silanes	Si_nH_{2n+2} (n = 1 to 7)
Ge	Germanes	—
Ti	Stannanes	—
Pb	Plumbane	PbH_4

- **Carbides :** Binary compounds of carbon with elements which are nearly same or more electropositive than carbon are called carbides.

Carbides

- **Ionic carbides** — With group 1, 2 and group 13 (except B) and Zn, Cd, etc.
  - **Methanides** — Give methane on hydrolysis (C^{4-}) *e.g.*, Be_2C, Al_4C
  - **Acetylides** — Give acetylene (C_2H_2) upon hydrolysis, contain C_2^{2-} unit. *e.g.*, : CaC_2, BeC_2, MgC_2, etc.
  - **Allylides** — Give methyl acetylene ($CH_3C\equiv CH$) on hydrolysis, contains C_3^{4-} ions *e.g.* Mg_2C_3
- **Covalent carbides** — Only Si and B SiC, B_4C
- **Metallic carbides** — Formed by transition elements

- **Anomalous properties of carbon :** Carbon differs from other elements of group 14 because of its smaller size, high electronegativity, absence of d-orbitals and high tendency of catenation.

Property	Carbon	Other elements
Hardness	Hardest	less hard
M.pt. and B.pt.	High	low
Maximum covalency	4	6
Multiple bonds	$p\pi$-$p\pi$ (high extent)	$p\pi$-$d\pi$ (low extent)
Catenation	very high tendency	very low
Tetrahalides	does not undergo hydrolysis	undergo hydrolysis

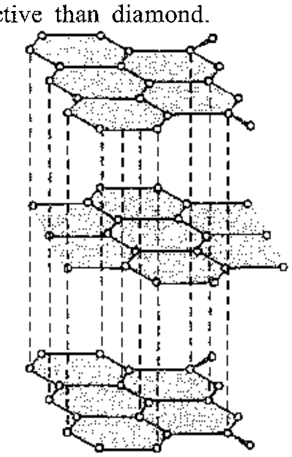
CARBON

- Carbon is found in many different forms and compounds. It is in the food we eat, the clothes we wear, the cosmetics we use and the gasoline that fuels our car. In addition, carbon is a very special element because it plays a dominant role in the chemistry of life. Carbon exists in two allotropic forms crystalline and amorphous.

Crystalline Forms

Graphite : Hybridisation - sp^2

- Highly conductive due to delocalised π-electron cloud.
- Leaves a black mark on paper and is called black lead or plumbago.
- Two dimensional sheet structure.
- More reactive than diamond.



Structure of graphite

$$\text{Graphite} \xrightarrow[\text{50000-60000 atm}]{1600°C} \text{Diamond}$$

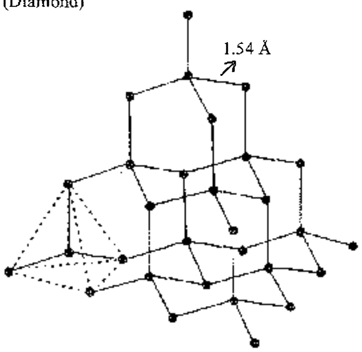
- **Uses**
  - as reducing agent in steel manufacturing.
  - as lubricant, electrodes for dry cell, moderator for fast moving neutron in nuclear reactors.
  - for making core of lead pencils.
  - industrial lubricant ***oildag*** is a suspension of graphite in oil and colloidal solution of graphite is called ***aquadag***.

Diamond : Hybridisation - sp^3

- Purest form of carbon.
- Hardest natural substance known.

- Bad conductor of heat and electricity.
- It is chemically inert and not attacked by acids, alkalies and salts.

$$\underset{\text{(Diamond)}}{C} + O_2 \xrightarrow{900°C} CO_2$$



Structure of diamond

- **Uses :** Diamond is used as a gem stone on account of reflection and refraction of light. Impure diamonds (black) are used in knives for cutting glass, "diamond studded saws" in drill bits, as rock borers and is also used as polishers.

Fullerene

- In fullerenes C atoms are arranged in a spherical or eliptical structure.
- C_{60} is made from pentagonal and hexagonal rings of carbon atoms. C_{60} is known as Buckminster fullerene.
- Fullerenes are highly soluble in non-polar solvents.
- C_{70} has recently been discovered.
- All the carbons are equivalent and sp^2-hybridised.

Amorphous Forms

Name	Properties	Uses
Coal	Crude form of carbon. Formed by slow decomposition of vegetables. Present as peat (C = 60%), lignite (C = 67%), Bituminous (C = 88%), steam coal (C = 93%), anthracite (C = 95%)	As fuel. For manufacturing of coal gas, coal tar and coke. For manufacture of synthetic petrol.
Coke	Contains 80-95% carbon. Formed by destructive distillation of coal in absence of air.	As reducing agent in iron and steel industry. For making fuel gases and graphite.
Charcoal	Obtained by burning of wood, cellulose, etc. Wood charcoal is porous and has very large surface area. Most active form of carbon.	As adsorbent. For making filters in cigarettes. To remove offensive odour from air.

Oxides of carbon

Carbon monoxide, CO

- It is found in small amounts in volcanic gases, chimney gases, exhaust gases of internal combustion engines and coal gas.

Preparation of CO:

$$HCOOH \xrightarrow[-H_2O]{H_2SO_4} CO$$
$$\underset{\text{(sufficient)}}{2C + O_2} \longrightarrow CO$$
$$ZnO + C \xrightarrow{-Zn} CO$$
$$Zn + CO_2 \xrightarrow{-ZnO} CO$$
$$CO_2 + C \longrightarrow CO$$

Reactions of CO:

$$CO \xrightarrow[Fe]{180°C} Fe(CO)_5$$
$$CO \xrightarrow{O_2} CO_2$$
$$CO \xrightarrow{Fe_2O_3} Fe + CO_2$$
$$CO \xrightarrow[Cu(OH)_2]{\text{Fehling's solution}} Cu_2O + CO_2$$
$$CO \xrightarrow{I_2O_5} I_2 + CO_2$$
$$CO \xrightarrow{S} COS$$
$$CO \xrightarrow{NaOH} HCOONa$$
$$CO \xrightarrow[80°C]{Ni} Ni(CO)_4$$

- **Uses**
  - CO is an important constituent of fuel gas *viz* water gas ($CO + H_2$) and producer gas ($CO + N_2$).
  - Used in manufacturing of methyl alcohol, acetic acid, sodium formate, etc.
  - Used as reducing agent in metallurgical processes.
  - Used in purification of Ni in Mond's process.

Carbon dioxide, CO_2

- Present in atmosphere (0.03-0.05%). It is produced during breathing of animals, burning of carbanous matter, etc.

Preparation of CO_2:

$$\underset{\text{(excess)}}{C + O_2} \longrightarrow CO_2$$
$$CaCO_3 + HCl \xrightarrow{-CaCl_2} CO_2$$
$$Na_2CO_3 + HCl \xrightarrow{-NaCl} CO_2$$
$$ZnCO_3 \xrightarrow[-ZnO]{heat} CO_2$$
$$NaHCO_3 \xrightarrow[-Na_2CO_3]{\Delta} CO_2$$
$$CaCO_3 \xrightarrow{-CaO} CO_2$$
$$\text{sugar} \rightarrow \underset{C_6H_{12}O_6}{\text{glucose}} \xrightarrow[-C_2H_5OH]{\text{from fermentation}} CO_2$$

Reactions of CO_2:

$$CO_2 \xrightarrow{Mg} MgO + C$$
$$CO_2 \xrightarrow{C} CO$$
$$CO_2 \xrightarrow[H_2O]{} H_2CO_3$$
$$CO_2 \xrightarrow{Ca(OH)_2} CaCO_3$$
$$CO_2 \xrightarrow[H_2O]{\text{sunlight}} \underbrace{C_6H_{12}O_6 + 6CO_2}_{\text{photosynthesis}}$$
$$CO_2 \xrightarrow{M_2O} M_2CO_3$$

- **Uses**
  - In manufacturing of aerated drinks.
  - Used in manufacturing of washing soda by Solvay ammonia process.
  - Used as refrigerant under the commercial name drikold.
  - Used as fire extinguisher.
  - Carbogen, a mixture of O_2 (95%) and CO_2 (5%) is used for artificial respiration for pneumonia patients and victims of CO poisoning.

COMPOUNDS OF SILICON

Silicon Tetrachloride, $SiCl_4$

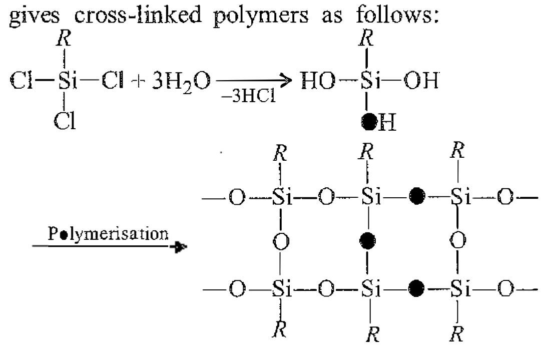
- **Preparation :** Silicon tetrachloride can be prepared by heating silicon or silicon carbide with chlorine or by passing dry Cl_2 gas over an intimate hot mixture of silica and carbon.

$$Si_{(s)} + 2Cl_{2(g)} \xrightarrow{\Delta} SiCl_{4(l)}$$
$$SiC_{(s)} + 4Cl_{2(g)} \xrightarrow{\Delta} SiCl_{4(l)} + CCl_{4(l)}$$
$$SiO + 2C + 2Cl_2 \xrightarrow{\Delta} SiCl_{4(l)} + 2CO_{(g)}$$

- **Properties**
  - $SiCl_4$ is a colourless, fuming liquid with boiling point 56.8°C.
  - $SiCl_4$ is hydrolysed to silicic acid.
    $$SiCl_4 + 2H_2O \xrightarrow{\Delta} \underset{\text{Silicic acid}}{Si(OH)_4} \xrightarrow{\Delta} \underset{\text{Silica gel}}{SiO_2 \cdot xH_2O_{(s)}}$$
  - High temperature hydrolysis of $SiCl_4$ yields finely powdered silica.
    $$SiCl_{4(g)} + 4H_2O_{(l)} \xrightarrow[O_2\text{-}H_2 \text{ fumes}]{\text{high temp.}} SiO_{2(s)} + 4HCl_{(g)}$$
  - Reduction of $SiCl_4$ with hydrogen gas gives highly pure silicon.
    $$SiCl_{4\,(g)} + 2H_{2\,(g)} \xrightarrow{\Delta} Si_{(s)} + 4HCl_{(g)}$$
  - Pyrolysis of $SiCl_4$ with silicon gives a number of perhalosilanes with general formula Si_nCl_{2n+2} (n = 2 to 6)
    $$2SiCl_4 + Si \xrightarrow{\Delta} Si_3Cl_8$$
- **Uses**
  - Silicon tetrachloride is used in the preparation of silica gel, silicones, esters of silicic acid and pure silica.
  - $SiCl_4$ is used as smoke screen in warfare.

Silicones

- These are polymeric organo-silicon compounds containing Si–O–Si bonds. These have the general formula $(R_2SiO)_n$. Where R can be $-CH_3$ group (in majority of cases) or $-C_6H_5$ group. There may be linear silicones, cyclic silicones or cross-linked silicones.
- **Preparation :** Silicones are generally prepared by the hydrolysis of dialkyldichlorosilanes (R_2SiCl_2) or diaryldichlorosilanes (Ar_2SiCl_2), which are prepared by heating RCl with silicon at 300°C with copper as a catalyst.
  $$2RCl + Si \xrightarrow{Cu,\ 300°C} \underset{\text{Dialkyl dichlorosilane}}{R_2SiCl_2}$$
  - The hydrolysis of alkyl trichlorosilanes, RSiCl$_3$, gives cross-linked polymers as follows:



Cross-linked silicone

  - Silicones may be obtained in the form of oils, rubber or resins depending upon the extent of polymerization which depends upon reaction conditions and nature of alkyl groups.
- **Properties**
  - Silicones are water repellent and quite inert chemically.
  - These resist oxidation, thermal decomposition and attack by organic reagents.
  - These are also good electrical and thermal insulators and are antifoaming agents.
- **Uses**
  - Used for making water-proof papers, wools, textiles, wood, etc., after coating these articles with silicones.
  - Used as weather lubricants since viscosities of silicones do not change with changes in temperature.
  - Used as antifoaming agents, low temperature hydraulic fluids.
  - Their use in cosmetics is also known due to their biocompatibility.

Silicates

- Silicates can be considered as metal derivatives of silicic acid H_4SiO_4 or $Si(OH)_4$. Different silicates may have discrete SiO_4^{4-} tetrahedra or number of such units joined together by sharing of oxygens.
- Silicates are formed by heating metal oxide or metal carbonates with sand. *e.g.*,
  $$nNa_2CO_3 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_2(SiO_3)_n + nCO_2$$
- Silicates are classified in different types on the basis of number of oxygen atoms of SiO_4^{4-} shared with other tetrahedra.

Zeolites

- Zeolites are hydrated 3-dimensional aluminosilicates obtained by replacing some of the silicon atom in three-dimensional network silicate by Al^{3+}. They have general formula : $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$
- **Uses**
  - Zeolites are used as catalyst in petrochemical industries.
  - Used as molecular sieves.
  - Used for softening of water by ion-exchange method.

Type	No. of oxygen atoms shared	Basic unit	Example
Ortho silicates	No sharing	SiO_4^{4-}	Zircon–$ZrSiO_4$, Forestrite–Mg_2SiO_4
Pyrosilicates or islands	One oxygen atom shared	$Si_2O_7^{6-}$	Thortveitite–$Sc_2Si_2O_7$, Hemimorphite-$Zn_3(Si_2O_7) \cdot Zn(OH)_2 \cdot H_2O$
Cyclic or ring silicates	Two oxygen atoms per tetrahedron shared	$\left(SiO_3^{2-}\right)_n$ or $\left(SiO_3\right)_n^{2n-}$	Wollastonite–$Ca_3Si_3O_9$, Beryl–$Be_3Al_2Si_6O_{18}$
Chain silicates	Two oxygen atoms per tetrahedron shared	$\left(SiO_3\right)_n^{2n-}$ or $\left(Si_4O_{11}\right)_n^{6n-}$	Spodumene–$LiAl(SiO_3)_2$, Diopside–$CaMg(SiO_3)_2$
Sheet silicates (two dimensional)	Three oxygen atoms per tetrahedron shared	$\left(Si_2O_5\right)_n^{2n-}$ or $\left(Si_2O_5^{2-}\right)_n$	Kaolin–$Al_2(OH)_4(Si_2O_5)$, Talc–$Mg(Si_2O_5)_2Mg(OH)_2$
Three-dimensional silicates	All four oxygen atoms shared	$(SiO_3)_n$	Zeolites, Quartz, Feldspar, Ultramarines, etc.