Carbon Dioxide (CO_2) (Advanced)

Preparation

① By complete combustion of carbon and hydrocarbon in excess of air

- $C + O_2 \xrightarrow{\Delta} CO_2$
- $CH_4 + O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$

②
- $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 \uparrow + H_2O$
- $NaHCO_3 + HCl \rightarrow NaCl + CO_2 \uparrow + H_2O$

③ As a biproduct for manufacturing hydrogen

- $CO + H_2O \xrightarrow{\Delta} CO_2 + H_2$
- $CH_4(g) + 2H_2O \rightarrow CO_2(g) + 4H_2(g)$

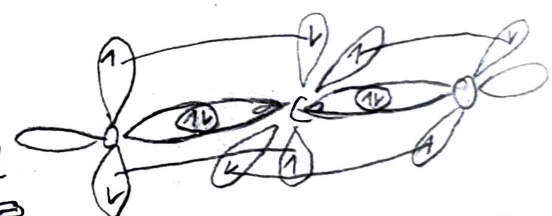
④ Fermentation

$C_6H_{12}O_6 \xrightarrow{Yeast} 2C_2H_5OH + 2CO_2$

⑤ By heating carbonates and bicarbonates

- $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
- $ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$

Structure



$:\ddot{O}=C=\ddot{O}:$ (sp hyb.)

Linear monomeric covalent compound

Due to Resonance, $O=C=O \longleftrightarrow :\overset{+}{O}\equiv C-\overset{\ominus}{O}:$

C=O bond acquire triple bond character and therefore bond length reduce to 115pm

Properties

① CO_2 is a colourless, odourless and tasteless gas, heavier than air.

② Non-poisonous gas, does not support life.

③ It is incombustible and non-supporter of combustion

However, some active metals reduce it to C.

$Mg/Na + CO_2 \rightarrow MgO/Na_2O + C$

④ Acidic Nature : $CO_2 + H_2O \rightleftharpoons H_2CO_3$ (carbonic acid)

Thus a solution of CO_2 in water is an equi mixture of CO_2, H_2CO_3, HCO_3^- & CO_3^{2-} which helps in maintaining pH of human blood b/w 7.26 and 7.42

(5) Reduction : When passed through red-hot coke

$CO_2 + C \rightarrow 2CO \uparrow$

(6) Photosynthesis : CO_2 in presence of sunlight and chlorophyll react with moisture to form glucose and starch.

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \uparrow$

(7) Action of lime water

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$

↓ excess

$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$

(8) Action of Ammonia

$CO_2 + 2NH_3 \longrightarrow [NH_2COONH_4] \longrightarrow NH_2\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$ (urea)

(9) Solubility – It is slightly soluble in water, solubility decreases with increase in temperature but inc with inc in pressure.

Dry Ice – Solid CO_2 is known as dry ice

* It is a soft, white solid resembling snow flakes. Under 1 atm pressure, it sublimes without liquefying, therefore does not wet the surface, and known as dry ice. It melts at above 5.2 atm pressure.

* Dry CO_2 gas is pressurised with/at 50-60 atm, refrigerated b/w -57°C & 30°C until it liquefies. Lowering of temp solidifies CO_2.

Uses

(1) As a fire extinguisher

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$

(2) Baking soda – sulphuric acid fire extinguisher

$2NaHCO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2CO_2 \uparrow + 2H_2O$

(3) Preparation of aerated waters

(4) In the manufacture of washing soda by Solvay ammonia process

(5) As a solvent to extract organic compounds

(6) Carbogen – 95% O_2 & 5% CO_2 for victims of CO poisoning & pneumonia patients.

Dry ice (Solid CO_2)

(1) As a refrigerant under name 'drikold'.

(2) As a freezing mixture

(3) Making cold baths in laboratories

(4) Making ice-creams

(5) Curing local burns

(6) Artificial rain by spraying dry ice over clouds.

(7) In film industry for artificial fog and cloud.

Carbon Monoxide (CO)

Advanced

Preparation

① Incomplete combustion of carbon

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

② Heating heavy metals eg with carbon.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$ZnO + C \longrightarrow Zn + CO$$

③ Laboratory preparation

(i) From Formic Acid

$$HCOOH \xrightarrow[373K]{H_2SO_4} CO + H_2O$$

(ii) From Potassium ferrocyanide

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

④ Commercial Preparation.

a) By passing steam over red hot coke

$$C(s) + H_2O(g) \xrightarrow{473\text{-}1273K} \underbrace{CO(g) + H_2(g)}_{\text{Water Gas}}$$ (Synthesis Gas)

The ~~reaction~~ mixture is known as Water Gas and used to prepare H_2 also.

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

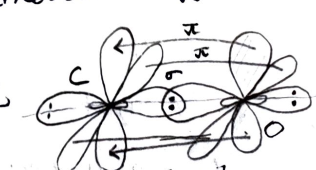
Structure

⇒ Electron Dot structure → $\ddot{C}::\ddot{O}:$

⇒ C has six electrons while O has 8. Therefore O donates a pair of electron to form a triple bond. Experiments suggest an existence of C≡O triple bond [:C≡O:]

⇒ Due to this backdonation of electron from O to C, CO has very less dipole moment

⇒ CO is sp hyb. and a linear molecule



[CO]

Properties

(1) CO is colourless and odourless gas and a neutral oxide, toxic in nature.
It reacts with haemoglobin to form a complex called carboxyhaemoglobin (300 times more stable than oxyhaemoglobin) which prevents transportation of oxygen from lungs to other body parts leading to oxygen deficiency causing unconsciousness and death.

(2) Powerful reducing agent
$ZnO/CuO + CO(g) \xrightarrow{\Delta} Zn/Cu + CO_2$

(3) Due to presence of lone pair of C, acts as ligand and form metals carbonyls.
$Ni^0 + 4CO \rightarrow Ni(CO)_4$ $\quad$ $Fe + 5CO \rightarrow Fe(CO)_5$

(4) An important fuel — burns with a blue flame.
$2CO + O_2 \rightarrow 2CO_2$ $\quad$ $\Delta H_f = -56.5\ KJ/mol^{-1}$

(5) Sparingly soluble in water and combines readily with O, Se, F
$CO + S \rightarrow COS$; $CO + Cl_2 \rightarrow COCl_2$ (phosgene)

Carbon suboxide (C_3O_2)

Preparation
By dehydrating malonic Acid with P_4O_{10}

$$HO-C(=O)-CH_2-C(=O)-OH \xrightarrow[150°C]{P_4O_{10}} O=C=C=C=O + 2H_2O$$

// The reaction shows that C_3O_2 is the anhydride of malonic acid

Properties

(1) It is a foul smelling gas, stable at $-78°C$, (bpt $6°C$)

(2) At room temperature, polymerises to a yellow solid and at higher temperature red and purple solid.

(3) $C_3O_2 + 2H_2O \longrightarrow CH_2(COOH)_2$ $\quad$ $C_3O_2 + 2HCl \longrightarrow CH_2(COCl)_2$

$C_3O_2 + 2NH_3 \longrightarrow CH_2(CONH_2)_2$

(4) It is a linear molecule

The other stable suboxide is $C_{12}O_9$ (white solid), anhydride of mellitic acid $C_6(COOH)_6$

Carbonic Acid (H_2CO_3)

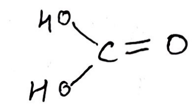
Advanced.

aq. soln' of CO_2 is known as carbonic acid

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

∴ CO_2 is also known as carbonic anhydride

* It is known to exist only in solution and not isolated in free state



Properties

① It is a weak dibasic acid

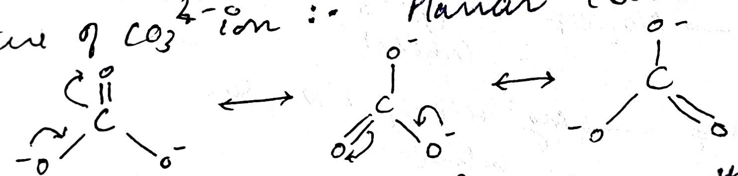
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

② Due to its dibasic nature, it gives rise to two series of acidic salts :-

(i) carbonates i.e normal salt (CO_3^{2-} ions)
(ii) Bicarbonates i.e acidic salts (HCO_3^- ion)

Carbonates and Bicarbonates

Structure of CO_3^{2-} ion :- Planar (Bond angle 120°)



(sp^2 hyb)

There are three canonical forms, therefore each C–O bond has $\frac{1}{3}$ rd double bond character.

Preparation

① By passing CO_2 through an alkali

$$2NaOH + CO_2 \longrightarrow Na_2CO_3\downarrow + H_2O$$
$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$
(excess)

carbonate form changes to bicarbonate on excess passage of CO_2

② By precipitation :- $Na_2CO_3 + BaCl_2 \longrightarrow BaCO_3\downarrow + NaCl$

③ From oxides :-

$$\begin{matrix} K_2O \\ Na_2O \end{matrix} + CO_2 \longrightarrow \begin{matrix} K_2CO_3 \\ Na_2CO_3 \end{matrix}$$

Properties

① Except alkali metal carbonates, all the carbonates are insoluble in water.
Bicarbonates of alkali metals (except Li) are known in solution state. Bicarbonates of alkali metals (except Li) are known only in solid state, rest are known only in solution state.

② Action of heat
All bicarbonates decompose on heating
$MHCO_3 \xrightarrow{\Delta} M_2CO_3 + CO_2\uparrow + H_2O$ —(1)

The carbonates formed further decomposes except alkali metal carbonates but Li_2CO_3

$ZnCO_3/CuCO_3 \xrightarrow{\Delta} ZnO/CuO + CO_2\uparrow$

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

③ Both carbonates and bicarbonates are decomposed by acids due to evolution of CO_2
e.g $CaCO_3 + HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O$

④ Action of $MgSO_4$ – Soluble carbonates gives a white ppt. whereas bicarbonates do not

• $Na_2CO_3 + MgSO_4 \rightarrow Na_2SO_4 + MgCO_3\downarrow$ (white)

• $2NaHCO_3 + MgSO_4 \rightarrow Mg(HCO_3)_2 + Na_2SO_4$ (Soluble)

However on heating, the soluble bicarbonate gives a white ppt of carbonate according to Reaction (1)

⑤ Hydrolysis – on hydrolysis both forms alkaline soln but carbonates gives pink colour to phenolphthalein whereas bicarbonates do not suggesting carbonates to be stronger bases than bicarbonates

Cyanogen $(CN)_2$
Due to resemblance with halogens, it is known as pseudohalogen // just to know

Structure : $:N\equiv C-C\equiv N:$ (Both C & N are sp)

Preparation : ① $4HCN + O_2 \xrightarrow{Ag} 2(CN)_2 + 2H_2O$
② $CuSO_4 + 2KCN \rightarrow K_2SO_4 + Cu(CN)_2 \longrightarrow CuCN + \frac{1}{2}(CN)_2$

Properties :- Colourless, extremely poisonous & flammable gas
• Burns in air with violet flame
$(CN)_2 + O_2 \longrightarrow 2CO_2 + N_2$ //explosive
• In basic medium
$(CN)_2 + 2KOH \rightarrow KCN + KCNO + H_2O$

(Advanced)

Silicon (Si)

Silicon is obtained by reduction of silica.
It exists in two allotropic forms—

① Amorphous silicon

Preparation: * $SiO_2 + 2Mg \rightarrow Si + 2MgO$

Properties: • Brownish powder

• Burns brilliantly in oxygen

$Si + O_2 \rightarrow SiO_2$

• Decomposes steam at red heat

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

• It dissolves in the mixture of HNO_3 & HCl

• $Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2$

$Si + Na_2CO_3 \rightarrow Na_2SiO_3 + C$

• $2Mg + Si \rightarrow Mg_2Si$

• $Si + 2F_2 \rightarrow SiF_4$

Amorphous form is chemically more reactive than crystalline form.

② Crystalline form

Preparation: * $SiO_2 + 2C \rightarrow Si + 2CO$

On strongly heating amorphous silicon, it fuses; on cooling, it solidifies to give crystalline form.

Properties: very hard

4 * It does not burn in oxygen but combines with fluorine

• dissolves in a mixture of HNO_3 & HF.

• $Si + Na_2CO_3 \rightarrow Na_2SiO_3 + C$ // same as amorphous silicon

High Purity Si

$SiCl_4 + Mg \rightarrow Si + 2MgCl_2$ // $MgCl_2$ being water soluble washed away and purification takes place by (zone refining).

* Uses

* ① In high purity state, Si acts as semiconductor and is used in transistors and semiconductor devices and computer chips.

② Crystalline form is used to prepare alloys — Silicon bronze

Silicon Dioxide (SiO_2)

- Commonly known as 'silica'
- 95% of earth's crust is made up of silica and silicates

Crystallographic forms — Quartz, crystobalite and tridymite

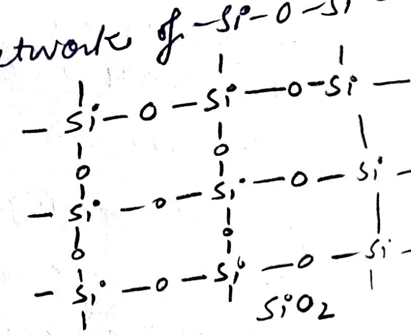
Amorphous form — Kieselghur and silica gel

Sand is crushed form of quartz.
Sandstone consists of sand particles bound together by iron oxide.
Flint consists of amorphous silica associated with quartz.

Kieselguhr is a white powder used in filtration plants and as an abrasive.

Structure

It consists of a three-dimension network of –Si–O–Si– linkages. It is therefore a covalent network solid. The entire structure is a giant molecule with 8-membered rings



Properties

① Relatively inert and has a very high melting point

*② It does not react with halogens (except F_2), dihydrogen and most acids (except HF)

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$
$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

* Due to formation of H_2SiF_6, SiO_2 present in glass dissolves and therefore HF cannot be stored in glass bottles.

③ It is insoluble in water but dissolves slightly when heated under pressure.

④ It behaves as an acidic oxide: $SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

⑤ $SiO_2 + Na_2O \rightarrow Na_2SiO_3$

* Silica Gel is used as a catalyst in petroleum industry and an absorbent in column chromatography.

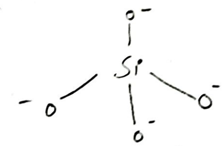
★ $SiCl_4 + 4H_2O \rightarrow SiO_2\cdot 2H_2O + 4HCl$ (silica gel)

★ $Si(OH)_4 \xrightarrow{\Delta} SiO_2\cdot 2H_2O$ (silicic acid)

Silicates

Advanced

- In silicates, the basic unit of structure is SiO_4^{2-} tetrahedron which may occur singly or by sharing oxygen atoms.



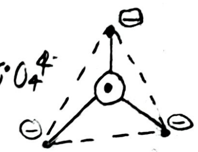
• → O atom
O → Si atom

Classification

① Orthosilicate :- They contain discrete SiO_4^{4-} units.

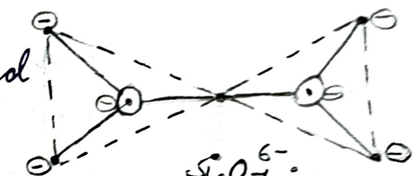
e.g. Phenacite (Be_2SiO_4) and Zircon ($ZrSiO_4$)
Forsterite (Mg_2SiO_4)

SiO_4^{4-}



② Pyrosilicate :- SiO_4^{4-} share one oxygen atom.

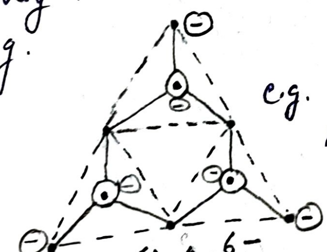
The simplest ion of this type is $Si_2O_7^{6-}$ ion. They are also know as island silicats e.g. Thortveitite $Sc_2[Si_2O_7]$
$Ln_2[Si_2O_7]$



$Si_2O_7^{6-}$ ion

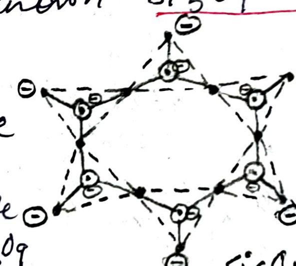
③ cyclic silicate : These involve silicate tetrahedra in which SiO_4 tetrahedra share two oxygen atoms. Only two such ions are known $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$.

e.g.



$Si_3O_9^{6-}$

e.g. Benitoite $BaTiSi_3O_9$
Wallastonite $Ca_3Si_3O_9$

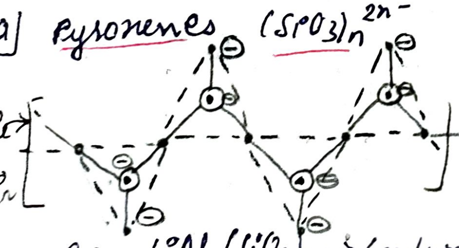


$Si_6O_{18}^{12-}$

e.g. Beryl $Be_3Al_2Si_6O_{18}$

④ Infinite chain silicate :- Indefinite linkage gives two types of chain silicates. They also share two (or three) oxygen atoms.

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

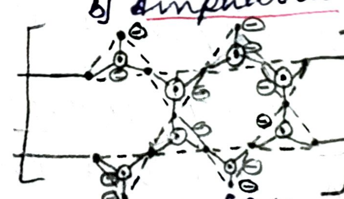


Single Chain

$MgSiO_3$
$CaMg(SiO_3)_2$
$NaAl(SiO_3)_2$

e.g. $LiAl(SiO_3)_3$ → Spodumene

b) Amphiboles. $(Si_4O_{11})_n^{6n-}$



← Double Chain

e.g. asbestos $[CaMg_3O(Si_4O_{11})]$

★ Amphiboles have two type of units terminal/upper units share 2 & middle unit 3 O atoms

(5) Two Dimensional sheet silicates

The sharing of three oxygen atom per SiO_4 tetrahedra results in a two dimensional sheet of emperical formula $(Si_2O_5)_n^{2n-}$ e.g. Mica $KAl_2(OH)_2(Si_3AlO_{10})$, clay

(6) Three Dimensional sheet silicates

Complete sharing of all four oxygen atoms in tetrahedra gives a three dimensional network of emperical formula $(SiO_2)_n$ i.e silica.

This type of structure is characteristics of three three forms of silica i.e. quartz, tridymite and ~~crystablobalite~~ crystallobalite

Isomorphous replacement of Si^{4+} by a combination of Al^{3+} and other metal ions (to attain electrical neutrality) gives minerals as (i) zeolite, (ii) feldspar (iii) ultramarines.

(i) Zeolite = They have porous structures and, H_2O, NH_3 & CO_2 molecules can pass through cavities. Thus they are used as ion exchanges and water softners.

General formula. $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$

★ They are used as catalyst in petrochemical industries e.g. (ZSM-5) used to convert alcohol directly into gasoline

(ii) Feldspar = Most abundant of all mineral and almost 67% of all igneous rocks consist of feldspar.

e.g. orthoclase feldspar $KAlSi_3O_8$, Anorthite - $CaAl_2Si_2O_8$

(iii) ultramarines - They do not contain water and some extra anions such as Cl^-, S_2^- are also present. They are used as pigments, also known as artificial Lapis Lazuli

e.g. $Na_8(AlO_2)_6(SiO_2)_6S_2$

Sodium silicate (Na_2SiO_3) - Also known as water glass

Preparation: $Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$

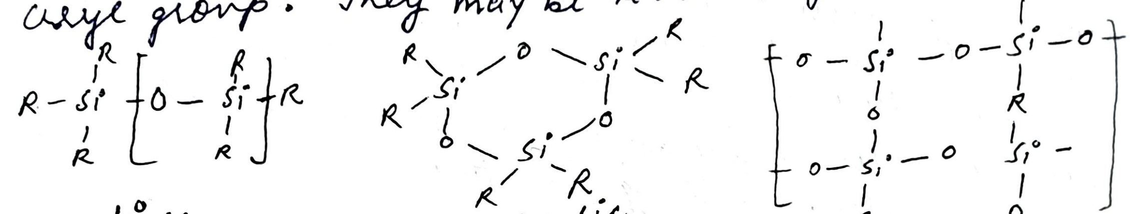
Properties: Soluble in water and alkaline due to hydrolysis

uses: In fireproofing ~~and~~ of wood and textiles.

Silicones

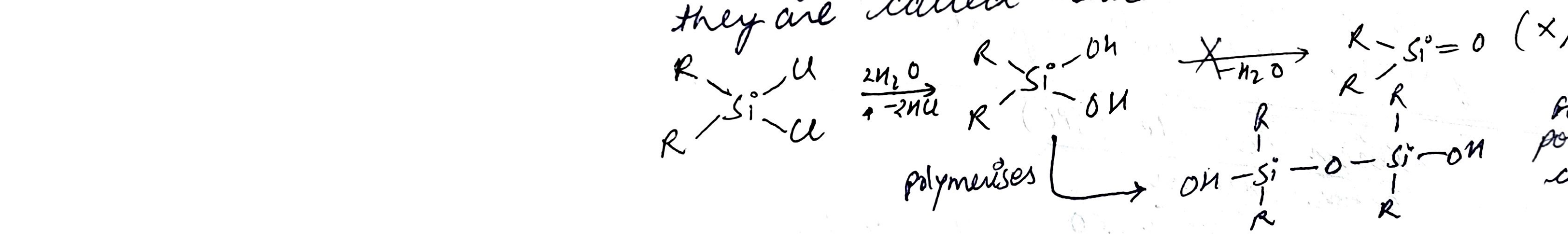
(Advanced)

* Silicones are polymeric organosilicon compounds having Si–O–Si linkages. These compounds have the general formula $(R_2SiO)_x$ where R is alkyl or aryl group. They may be linear, cyclic or cross linked



Linear — cyclic — Branched

* Although due to similar formula like ketones $R_2C=O$, they are called silicones, but their structure is different



further polymerisation can occur

Preparation

① $R_2SiCl_2 \xrightarrow[-2HCl]{2H_2O} R_2Si(OH)_2 \xrightarrow{-H_2O} R_2Si(OH)-O-Si(OH)R_2 \xrightarrow{\text{polymerises}} [-O-SiR_2-O-SiR_2-]$

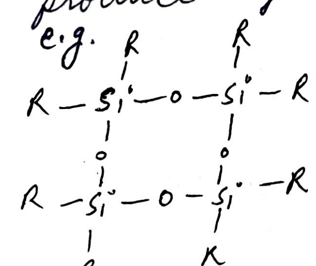
② $(CH_3)_3SiCl \xrightarrow{H_2O} (CH_3)_3Si-OH + HCl$

condensation $\downarrow -H_2O$

$(CH_3)_3-Si-O-Si-(CH_3)_3$ — Hexamethyldisiloxane has no –OH group, therefore cannot polymerise further

③ Hydrolysis under carefully controlled condition can produce cyclic structures with 3, 4, 5 or 6 Si atom

e.g.



Tetrakis cyclodimethyl siloxane

④ Hydrolysis of $RSiCl_3$ gives a cross linked or branched system.

★ If some R_3SiCl is mixed with R_2SiCl_2 then R_3SiCl will block end of straight chain. Therefore it is used to control the chain length.

$$n\,HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \xrightarrow[-H_2O]{poly...} -O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O\right)\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

(Blocking)

Properties and uses

① Depending upon chain length, silicons may be liquid, oil, greese or rubber. As chain length increases viscosity inc. and their nature changes from liquid to oil to greese to rubber or resins both at low & high temp

② They are better lubricants than graphite

③ They are water-repelling in nature

④ Have high thermal stability, high di-electric strength and resistant to oxidation and chemicals.

⑤ They are good ~~conductors~~ of electrical insulators

⑥ They are used for water proofing of fabrics

⑦ Being biocompatible, used in surgical and cosmetic plants.

Silicon Carbide (SiC)

Also known as "Carborundum"

Preparation: $SiO_2 + 3C \rightarrow SiC + 2CO$

It is obtained when a mixture of sand, carbon and common salt and saw dust is strongly heated in an electric furnace. NaCl acts as flux

Properties: Hard like diamond

② It is colourless in pure form, however commercial products show tint of yellow, blue or green

③ Chemically inert and not attacked by even HF

However, it decomposes when fused with alkalies

$$4NaOH + SiC + 2O_2 \rightarrow \underbrace{Na_2SiO_3 + Na_2CO_3}_{\text{soluble}} + 2H_2O$$

Uses
① Abrasive for cutting and grinding
② Preservative for egg
③ Filler in soap industry
④ Paint industry and calnico printing
⑤ Adhesive for joining pieces of china clay
⑥ For preparing silica gel.