# INORGANIC POLYMERS

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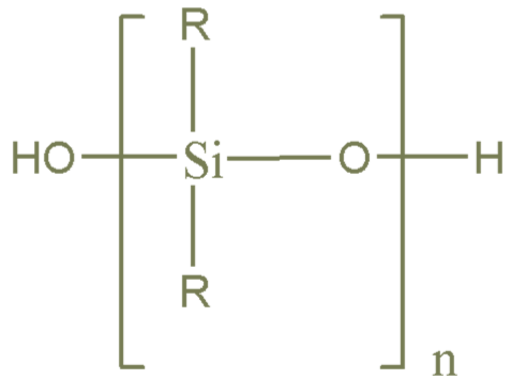
# Introduction

- Macromolecules that contain elements other than carbon as part of their principal backbone structure
- In nature-mica, clays, talc etc.
- Typical examples-silicones, silicates, zeolites, phosphazenes etc.

# SILICONES

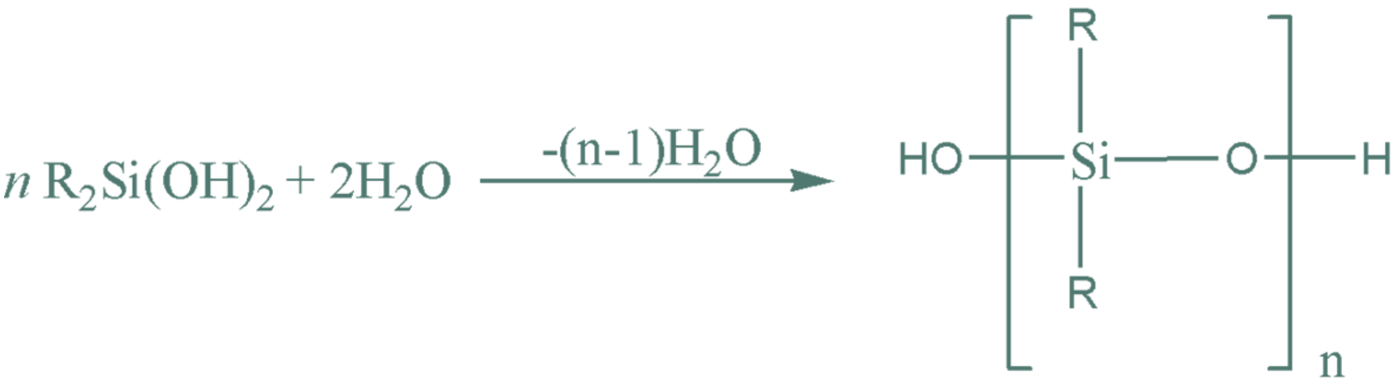
# Silicones

- Synthetic organosilicon polymers containing repeated $R_2SiO$ units held together by Si-O-Si linkages
- <<<<<<<<<<<<<structure



# Preparation of silicones

$$2RCl + Si \xrightarrow[573\ K]{Cu\ powder} R_2SiCl_2 + 2H_2O \longrightarrow \underset{\text{Silanol}}{R_2Si(OH)_2} + 2H_2O$$




Silicone

- Straight chain and cyclic forms are possible
- Chain growth may regulated using by adding $(CH_3)_3SiCl$ during hydrolysis
- Hydrolysis of alkyl trichlorosilane gives complex cross-linked polymers

# Types of silicones

- Silicone fluids
  - Straight chain polymers + cyclic polymers
  - 20-500 units
  - Variying BP and viscosities
- Silicone elastomers or silicone rubbers
  - Linear polymers
  - 6000-6 lakh Si units
- Silicone resins
  - Cross linked polymers
  - Harder and stiffer than rubber

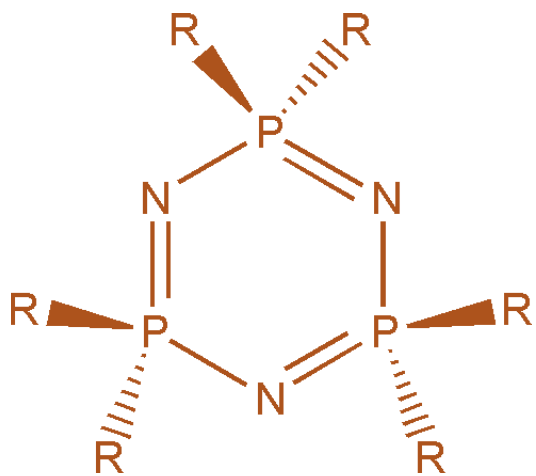
# Properties and applications of silicones

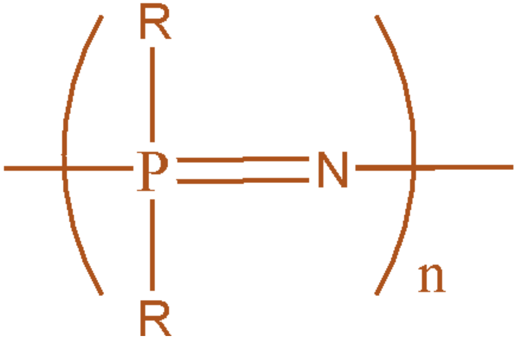
- Chemically inert and water repellent
- Resistant to heat, chemicals and oxidation (high Si-O, Si-C bond energy)
- Silicone fluids are used as lubricants, anti-foam agents, greases, high temp oil bath, vacuum pump etc.
- Silicone rubbers resistant to weathering (high thermal stability and low temp flexibility)-used in gaskets, seals, insulation, containers, surgical devices etc.
- Silicone resins –insulating coatings, varnishes, paints etc.

# Phosphazenes

# Phosphazenes (phosphonitrilic compounds)

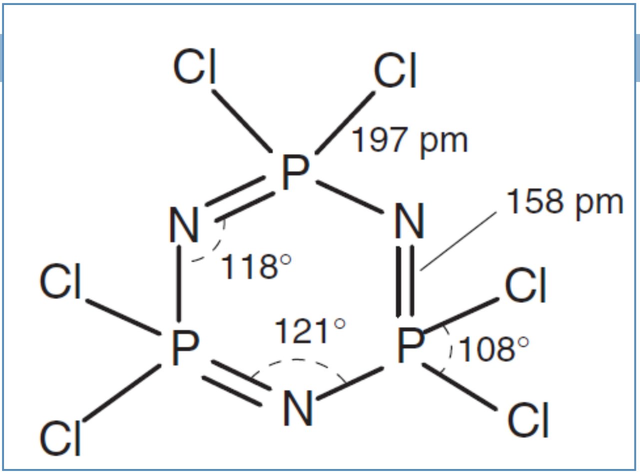
- N in +3, P in +5
- Cyclic phosphazenes and polyphosphazenes

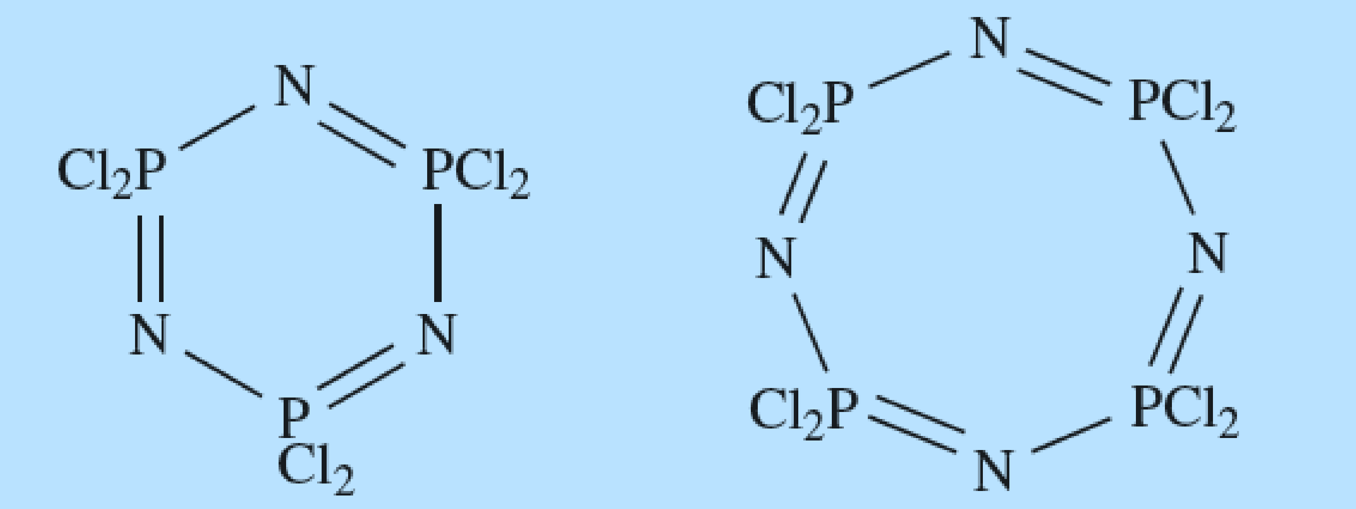


# Preparation

$$n\,NH_4Cl + n\,PCl_5 \rightarrow (NPCl_2)_n + 4n\,HCl$$



# Reactions of cyclic and polyphosphazenes

- Reaction with phenyl lithium, grignard reagent (alkylation)
- Reaction with sodium methoxide (acylation)

# Properties and applications

- High thermal stability, properties can control by changing substituents
- Ultra hydrophobic, retard flame
- Sealing agent for semiconductors
- Good elastomer, flexible even at low temperature- resistant to chemicals-used in fuel lines, gaskets, shock absorbers etc.

# S-N compounds

$S_4N_4$

$S_2N_2$

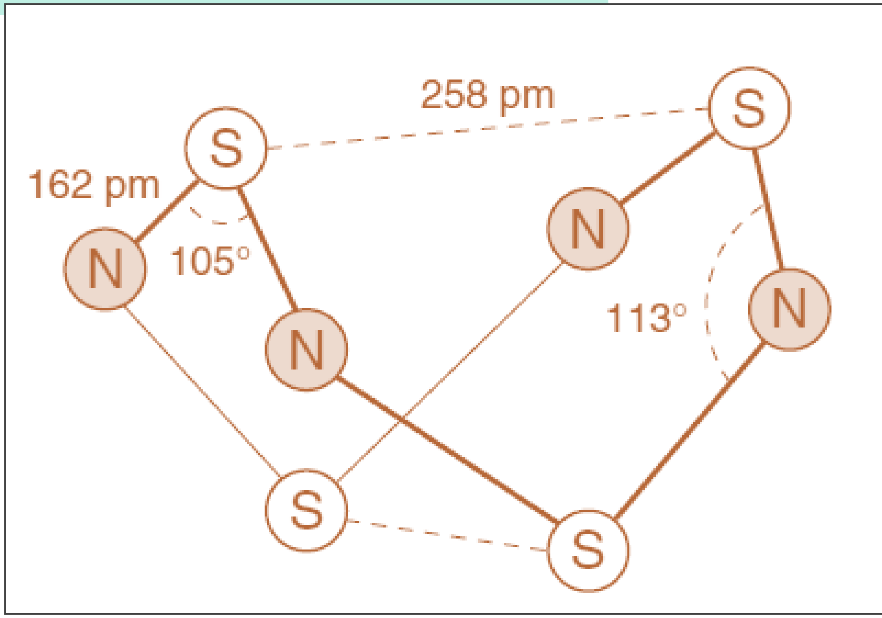
$(SN)_x$

# $S_4N_4$ TETRASULPHUR TETRANITRIDE

- Preparation

$$6\ S_2Cl_2 + 4\ NH_4Cl \rightarrow S_4N_4 + S_8 + 16\ HCl$$

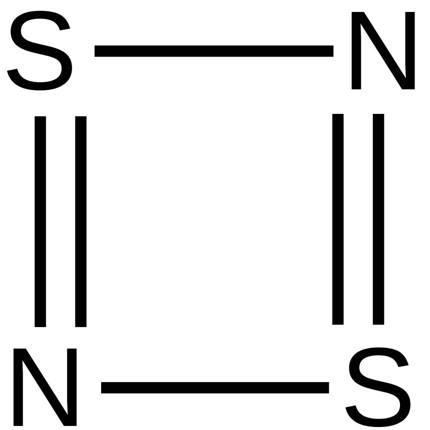
$$6\ S_2Cl_2 + 16\ NH_3 \rightarrow S_4N_4 + S_8 + 12\ NH_4Cl$$

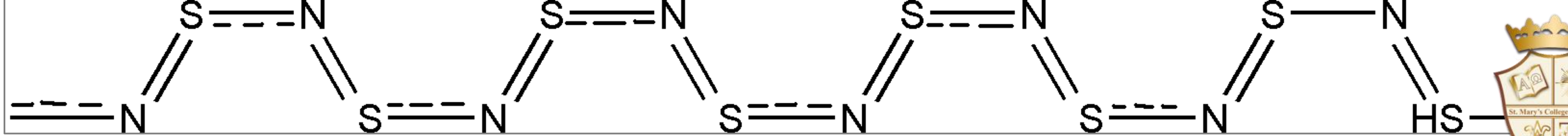



- Cage like cradle structure
- Stable to air-tends to detonate on hammering (decompose to N and S)

# $S_2N_2$ DISULPHUR DINITRIDE

- Preparation
  - $S_4N_4 + 8Ag \rightarrow 4\ Ag_2S + 2N_2$
  - $S_4N_4 + Ag_2S \rightarrow 2\ S_2N_2$
- Structure
- Properties and application
  - Tend to detonate
  - Easily polymerise





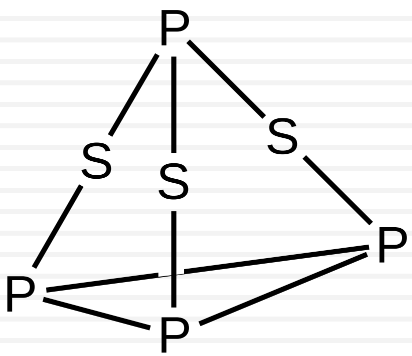
# Polythiazil, (SN)x

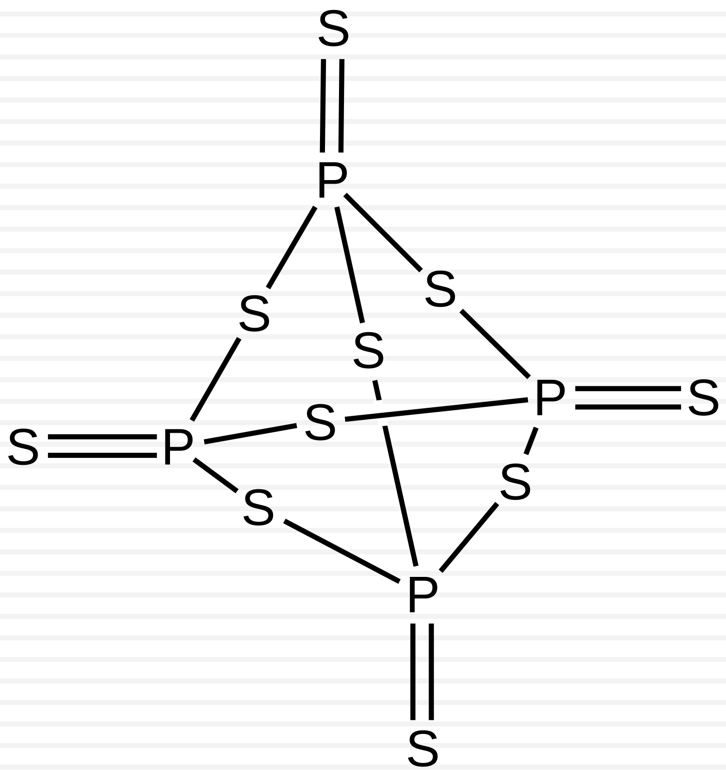
- Preparation
  - Polymerisation of $S_2N_2$ at RT
  - $x/2\ S_2N_2(s) \rightarrow (SN)_x\ (s)$
- Structure
  - Planar parallel chains-alternate single and double bond
- Properties and application-
  - covalent polymer with metallic properties-forms lustrous crystals-chemically inert-explosive when compressed-electrode-efficiency of solar cell can increase

# S-P compounds

$P_4S_3$

$P_4S_{10}$



# Sulphur-phosphorous compounds

- **$P_4S_3$**
  - Tetrahedral array of P atoms
  - $P_4 + 3S \rightarrow P_4S_3$ (>100°C)
  - Most stable sulphide of P
  - Used in match industry ($P_4S_3$ + $KClO_3$ match head)

- **$P_4S_{10}$**
  - Tetrahedral array of P atoms
  - $P_4 + 10S \rightarrow P_4S_{10}$ (>300°C)
  - Sensitive to moisture (form $H_3PO_4$)
  - Lawesson's reagent (Anisole + $P_4S_{10}$) is a thionating agent in org synthesis
  - Production of pesticides

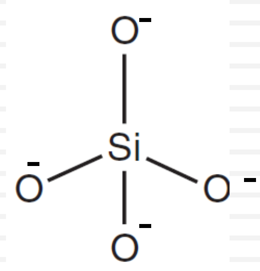
# Silicates

Si-O 3.5-1.8=1.7

50% ionic and covalent

Tetrahedral

$SiO_4^{4-}$



# Classification of silicate

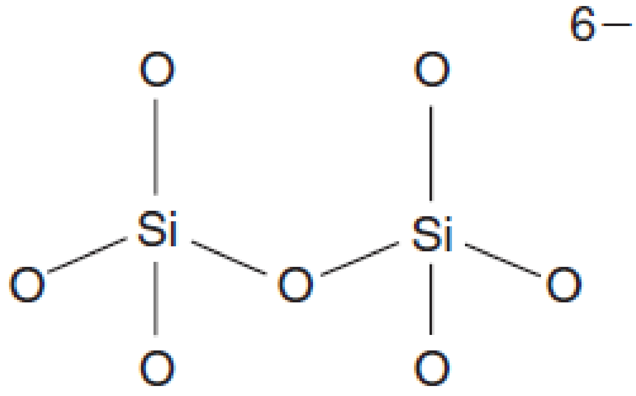
- Orthosilicate
- Pyrosilicate
- Cyclic silicate
- Chain silicate
- Sheet silicate
- 3D silicate

# Orthosilicate

- Simple silicate containing discrete $SiO_4^{4-}$ tetrahedra
- Eg: Zircon ($ZrSiO_4$); Forestrite ($Mg_2SiO_4$), Willemite ($Zn_2SiO_4$)

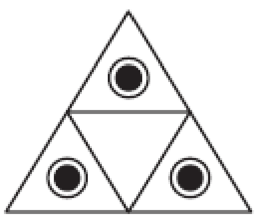
# Pyrosilicate

- Contain $Si_2O_7{}^{6-}$ units
- Possess island structure
- Eg: *thortveitite* , $Se_2Si_2O_7$ , *and hemimorphite* , $Zn_4(OH)_2Si_2O_7$

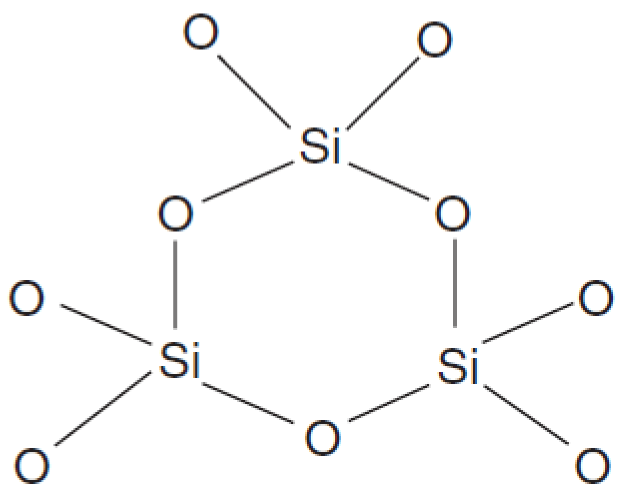


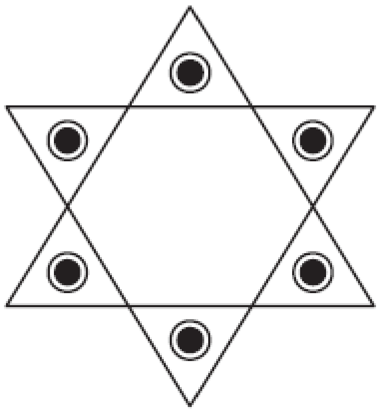
# Cyclic silicate (ring silicate)

- Contain ring structures $(SiO_3{}^{2-})_n$
- 2 oxygen atoms are shared
- Eg: wollastonite, beryl



(d) $Si_3O_9{}^{6-}$

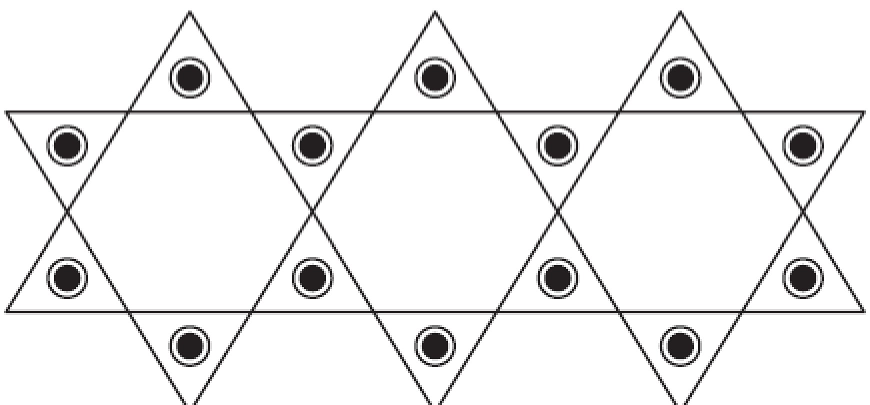


(e) $[Si_6\ O_{18}]^{12-}$

# Chain silicate

- 2 oxygen atoms are shared
- Single chain silicates and double chain silicates
- Single chain silicates contain ($SiO_3$ $^{2-}$)n chains (Examples spodumene and diopside)
- Double chain silicates contain ($Si_4O_{11}$$^{6-}$)n double chains (Eg: asbestos, tremoline)

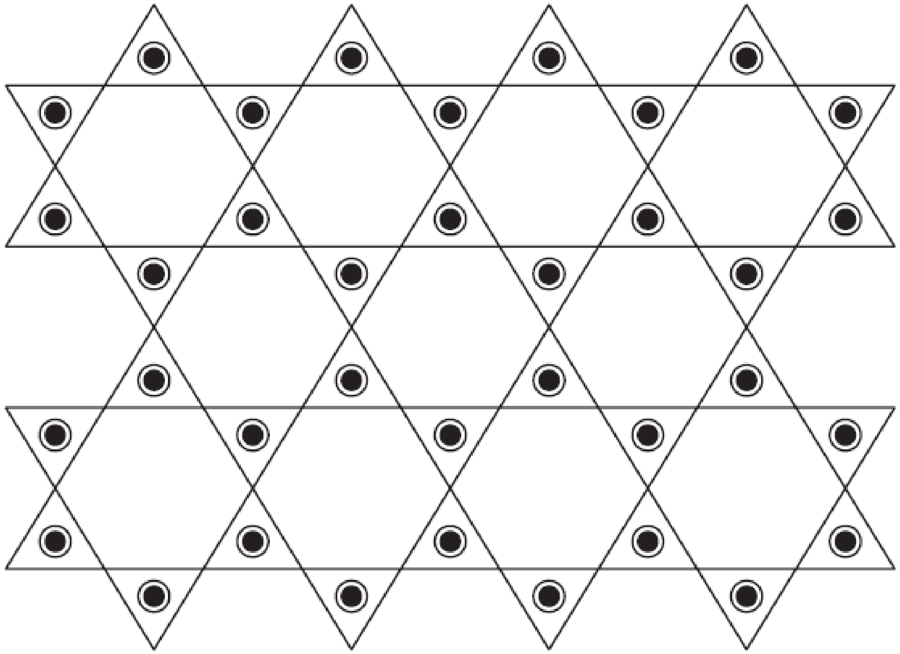




(f) $[Si_4O_{11}]_n^{6-}$

# Sheet silicate

- When $SiO_4^{4-}$ tetrahedra shares 3 corners
- Infinite 2D sheet, empirical formula $(Si_2O_5^{2-})n$
- Eg: Kaolinite, talc



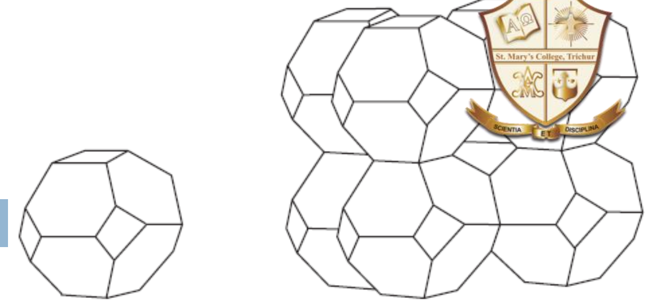
(g) $[Si_4O_{10}^{4-}]_n$

# 3D silicate

- When $SiO_4^{4-}$ tetrahedra shares all 4 corners
- empirical formula $(SiO_2)_n$
- Eg: quartz, tridymite, cristobalite etc.
- Si may be replaced by other cations to form feldspars, zeolites and ultramarines

- Feldspars are aluminosilicate salts of $K^+$, $Na^+$, $Ca^{2+}$ or $Ba^{2+}$ and constitute an important class of rock-forming minerals
- Zeolites are crystalline, hydrated aluminosilicates that possess framework structures containing regular channels and/or cavities; the cavities contain $H_2O$ molecules and cations (usually group 1 or 2 metal ions).
- Ultramarines are splendidly coloured aluminosilicates containing anions like chloride, sulphate etc.

# Zeolites

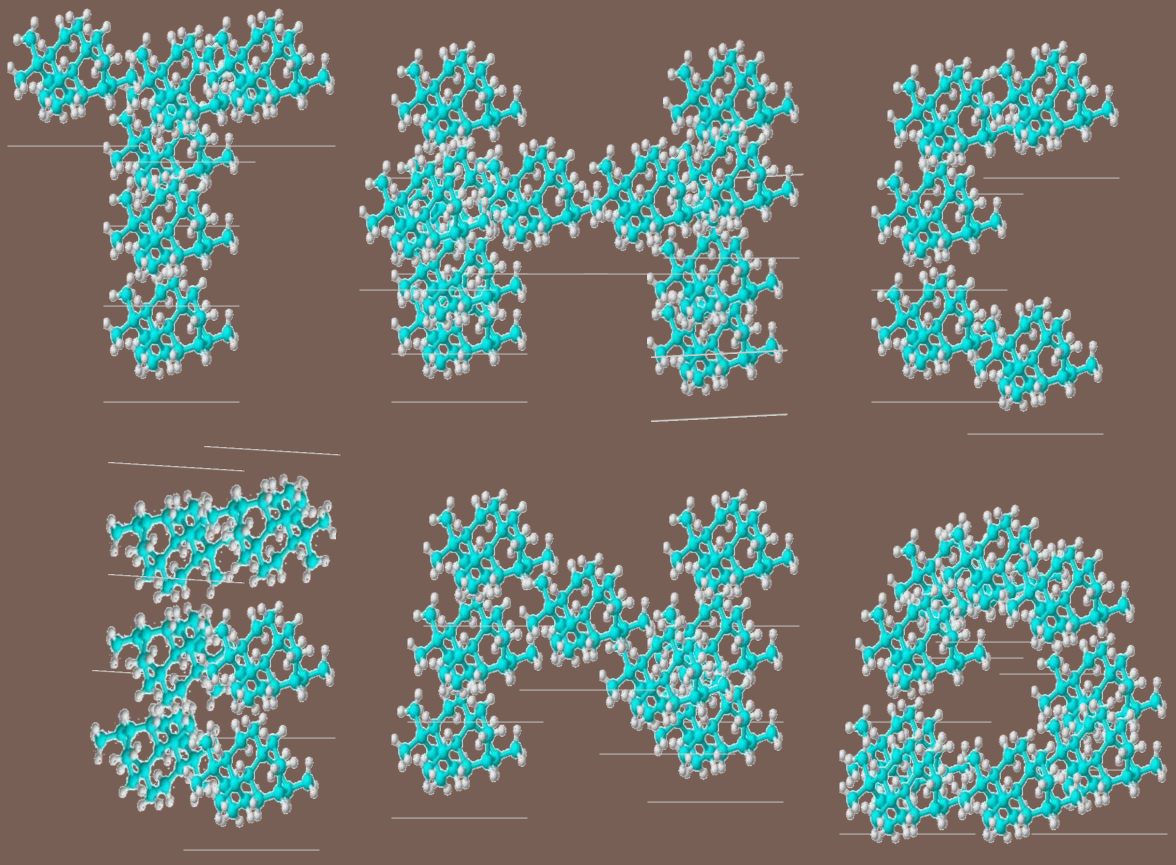


(a) (b)

- Crystalline aluminosilicates
- Gen formula $M^{n+}_{x/n}\left[Al_x Si_y O_{2x+2y}\right]^{x-}$
- Natural and synthetic
- Ion exchanger-soften hard water

$$2\,\text{Na-zeolite(s)} + \text{Ca}^{2+}\text{(aq)} \rightarrow \text{Ca-zeolite(s)} + 2\,\text{Na}^{+}\text{(aq)}$$

- Shape selective catalysis
  - Conversion of benzene to ethyl benzene, methanol to gasoline
- Molecular sieves
  - Depending upon the pore size small molecules passes

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