It is possible to prevent oligomerisation of heavier members and obtain Si = Si or S = S species if we prevent the approach of neighbouring molecules. Recently in 1981, Robert West prepared the first compound which contains Si = Si double bond. The groups attached to the Si-atom are so bulky that these prevent the approach of other molecules like water to very reactive silicon atoms as shown in fig. 3.34.

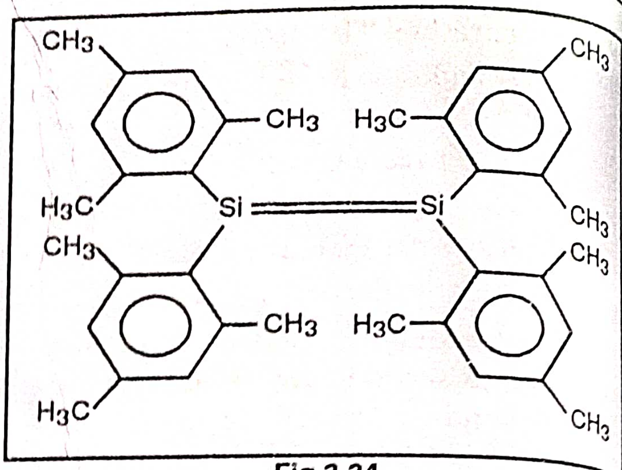

Fig 3.34.

Oxygen exists as O_2 while sulphur exists as S_8 and not S_2. Whether oligomerisation takes place or not in a species, depends upon the strength of σ and π-bond. If σ-bond is stronger than π-bond, then oligomerisation is preferred in a species. It can be explained on the basis of energy concept in the following equilibria.

(*i*)	$4O_2(g)$	$O_8(g)$
Bonds	$4\sigma + 4\pi$	8σ
Bond energy	4×493.8	8×142.3
	$= 1975.2$	$= 1138.4$

$$\Delta H = 1975.2 - 1138.4 = +836.8 \text{ kJ mol}^{-1}$$

(*ii*)	$4S_2(g)$	$S_8(g)$
Bonds	$4\sigma + 4\pi$	8σ
Bond energy	4×431	8×267.8
	$= 1724$	$= 2142.4$

$$\Delta H = 1724 - 2142.4 = -418.4 \text{ kJ mol}^{-1}$$

Since ΔH is negative in the case of sulphur, sulphur would prefer to oligomerise into S_8 units.

HYDRIDES (ELECTRON CONFIGURATION OF H^-–ION = $1s^2$)

"Hydrides are the binary compounds which are formed by the direct or indirect combination of hydrogen with metals, non-metals or metalloids." Strictly speaking, compounds of hydrogen with elements of low electronegativity should be called as hydride.

Classification of hydrides. Gibb (1941) classified hydrides in the following four types :

(*i*) Salt-like, ionic or saline hydride.
(*ii*) Molecular, volatile or covalent hydride.
(*iii*) Metallic hydride or Interstitial hydride.
(*iv*) Polymeric hydride.

The above hydrides are discussed below :

1. Saline or salt like hydrides. When hydrogen element combines with elements having very low electronegativity (0.9 to 1.2), we get salt-like hydrides. These elements belong to 1 or IA group except hydrogen). IIA group or 2 (except Be and Mg) and lanthanides. Aluminium hydride lies on the border line between salt-like and covalent hydrides.

General formula = MH_x where x = Group valency of the element, M.

Electronic configuration of H^--ion = $1s^2$.

It may be noted that due to endothermic character of H^- ion,

$$\frac{1}{2}H_2(g) + e^- \longrightarrow H^-(g)$$

$$\Delta H = +36 \text{ kcal mole}^- \ (= 150.6 \text{ kJ})$$

only the most electropositive metals (alkali and alkaline earth metals) form salt like hydrides.

Preparation. The preparation of some saline hydrides is given below.

1. Hydrides of IA or group I elements (Alkali metals). (*a*) **Lithium hydride.** (*i*) When molten lithium metal (975-1075 K) is treated with hydrogen, we get lithium hydride.

$$2Li + H_2 \xrightarrow{975 - 1075\ K} 2LiH \quad \text{(Lithium hydride)}$$

(*ii*) When lithium nitride is heated in a current of hydrogen, we get lithium hydride.

$$\underset{\text{Lithium nitride}}{2Li_3N} + 3H_2 \longrightarrow 6LiH + N_2$$

(*b*) **Sodium hydride.** When molten sodium metal (525 K) is treated with hydrogen, we get sodium hydride.

$$2Na + H_2 \xrightarrow{525\ K} 2NaH \quad \text{(Sodium hydride)}$$

(*c*) **Potassium hydride.** When molten potassium metal (675 K) is treated with hydrogen, we get potassium hydride.

$$2K + H_2 \xrightarrow{675\ K} 2KH \quad \text{(Potassium hydride)}$$

(*d*) **Rubidium and Cesium hydrides.** When molten rubidium and cesium hydrides (955 K) are treated with hydrogen, we get rubidium hydride and cesium hydride respectively.

$$2Rb + H_2 \xrightarrow{955\ K} 2RbH \quad \text{(Rubidium hydride)}$$

$$2Cs + H_2 \xrightarrow{955\ K} 2CsH \quad \text{(Cesium hydride)}$$

2. Hydrides of IIA or group 2 elements (alkaline earth metals). Except beryllium and magnesium metals, all the alkaline earth metals (Ba, Sr, Ca) form hydrides with hydrogen at 1075-1125 K.

$$\underset{\text{Calcium}}{Ca} + H_2 \xrightarrow{1075\ K} CaH_2 \quad \text{(Calcium hydride or hydrolith)}$$

$$\underset{\text{Barium}}{Ba} + H_2 \xrightarrow{1075\ K} BaH_2 \text{ (Barium hydride)}$$

$$\underset{\text{Strontium}}{Sr} + H_2 \xrightarrow{1125\ K} SrH_2 \quad \text{(Strontium hydride)}$$

3. Hydrides of lanthanides. The true ionic nature of lanthanide hydrides is doubtful. However, hydrides of some lantanides are large in number and are ionic. For example, the heat of formation of cerium hydride, $Ce\,H_{2.8}$ is 42.3 kcal/mole and is ionic. Many hydrides of lanthanides are non-stoichiometric like metallic hydrides.

4. Hydrides of actinides. Uranium absorbs hydrogen rapidly at 525 K to form uranium hydride, UH_3 (black powder).

$$2U + 3H_2 \xrightarrow{525\ K} 2UH_3$$

Properties. Properties of some saline hydrides are given below.

(*i*) *Physical state*. These are colourless and crystalline stoichiometric compounds with ionic lattices.

(*ii*) *Density, melting and boiling point*. Due to strong polar bonds in the ionic lattice of metal hydrides :

(*a*) The volume of the hydride decreases. Thus, the density of hydrides becomes more than the metal of which it is made of.

(*b*) The melting and boiling points of hydrides become high.

(*c*) The metal hydrides show *electrical conductivity* in their fused state.

(*iii*) *Solubility*. These are soluble in molten alkali metal halides.

For example, CaH_2 dissolves in LiCl + KCl at 635 K. It is insoluble in common solvents.

(*iv*) *Stability*. LiH, CaH_2 and SrH_2 are very stable. LiH is the only hydride which can be melted without decomposition. All other hydrides undergo decomposition above 675°C. Heats of formation ($kJ mole^{-}$) and relative stability of hydrides of group IA and IIA elements are given below :

Group IA or 1					Group IIA or 2		
LiH	NaH	KH	RbH	CsH	CaH_2	SrH_2	BaH_2
90.4	58	59	56.4	54.4	188.7	177	171

(*v*) *presence of hydride ion* (H^- *ion*). When electric current is passed through fused lithium hydride (or solution of CaH_2 in LiCl + KCl at 635 K), we get hydrogen gas.

$$LiH \overset{\Delta}{\rightleftharpoons} Li^+ + H^-$$

At cathode $\quad Li^+ + e^- \longrightarrow$ Li metal

At anode $\quad H^- - e^- \longrightarrow$ H atom (unstable)

$$H + H \longrightarrow H_2 \uparrow$$

(*vi*) *Action of air*. These are easily oxidised by air. Some burn spontaneously at room temperature.

(*vii*) *Action of water*. These react with water to form hydrogen gas.

$$LiH + H_2O \longrightarrow LiOH + H_2$$

Since above reaction goes to completion, lithium hydride is a stronger base than lithium hydroxide in aqueous solution.

(*viii*) *As a reducing agent*. These are good reducing agents.

(*a*) LiH reduces organic acids to alcohols.

$$\underset{\text{Organic acid}}{RCOOH} + 2LiH \longrightarrow \underset{\text{Alcohol}}{RCH_2OH} + Li_2O$$

(*b*) NaH reduces Fe_3O_4 to Fe and CO_2 to sodium formate, HCOONa on heating.

$$Fe_3O_4 + 4NaH \overset{\Delta}{\longrightarrow} 3Fe + 4NaOH; \; CO_2 + NaH \overset{\Delta}{\longrightarrow} HCOONa \text{ (sodium formate)}$$

(*c*) LiH (ether solution) reacts with aluminium chloride to form another reducing agent, $LiAlH_4$.

$$\underset{\text{(Ether solution)}}{4LiH + AlCl_3} \longrightarrow 3LiCl + \underset{\text{Lithium aluminium hydride}}{LiAlH_4}$$

$LiAlH_4$ further reacts with $AlCl_3$ to form aluminium hydride

$$3LiAlH_4 + AlCl_3 \longrightarrow 3LiCl + 4AlH_3$$

(*d*) NaH (ether solution) reacts with diborane to form another reducing agent, $NaBH_4$

$$2NaH + \underset{\text{Diborane}}{B_2H_6} \overset{\text{Ether}}{\longrightarrow} \underset{\text{Sodium borohydride}}{2NaBH_4}$$

II. Molecular or covalent hydrides. These are the largely covalent compounds formed by the highly electronegative elements of IIIA (or 13), IVA (or 14), VA (or 15), VIA (or 16), and VIIA (or 17) group through sharing of electrons with hydrogen atom.

Hydrides of highly electronegative atoms (N, O, F) are NH_3, H_2O and HF. These hydrides exhibit *hydrogen bonding*. In the solid state, the molecules (with atoms involving covalent bonds) are held together by *weak van der Waals forces*.

Preparation. Covalent hydrides are prepared as follows :

(*i*) By the direct action of hydrogen on elements

$$H_2 + F_2 \longrightarrow 2HF \text{ (Hydrofluoric acid)}$$

(ii) By the action of nascent hydrogen on metals or their compounds.

$$\underset{\text{Arsenous (III) chloride}}{AsCl_3} + 6H \longrightarrow \underset{\text{Arsine}}{AsH_3} + 3HCl$$

$$SbCl_3 + 6H \longrightarrow \underset{\text{Stibine}}{SbH_3} + 3HCl\ ;\ GeCl_4 + 8H \longrightarrow \underset{\text{Germane}}{GeH_4} + 4HCl$$

(iii) By the action of water or dilute acids on nitrides, phosphides, borides, carbides, silicides etc. of metals.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3 \text{ (Ammonia)}$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \text{ (Phosphine)}$$

$$Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6 \text{ (Diborane)}$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow \text{ (Methane)}$$

$$\underset{\text{Magnesium silicide}}{Mg_2Si} + 4HCl \longrightarrow 2MgCl_2 + \underset{\text{Silane}}{SiH_4}$$

(iv) By the action of reducing agent like lithium aluminium hydride, $LiAlH_4$ (ether solution) on certain metal halides.

$$SnCl_4 + LiAlH_4 \xrightarrow{\text{Ether}} LiCl + AlCl_3 + SnH_4 \text{ (Stannane)}$$

$$GeCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + GeH_4 \text{ (Germane)}$$

(v) Some hydrides are formed by indirect methods. For example, when sodium acetate is heated with sodalime (NaOH + CaO), we get methane (a hydride of carbon).

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow[\Delta]{CaO} Na_2CO_3 + \underset{\text{Methane}}{CH_4}$$

Properties. The properties of covalent hydrides depend upon the electronegativity difference between hydrogen and the atom bonded to it. Due to their covalent character, these exhibit following properties :

(i) They possess low melting and boiling points. (ii) They are volatile in nature.

(iii) They are non-conductor of electricity.

(iv) As we move from left to right along a period in the periodic table, the acidic character of hydrides increases with increase in atomic number. For example, the acidic nature of hydrides of second period elements is as follows :

LiH	NH_3	H_2O	HF
Strong base	Weak base	Neutral	Strong acid

III. Metallic or interstitial hydrides. The hydrides formed by some of the transition metals (electronegativity 1.2 to 1.4) are called metallic hydrides. These are also called interstitial hydrides. It is because the hydrogen atoms seem to occupy interstitial positions in their metallic lattices and form solid solutions.

Preparation. Following are the few methods to prepare non-stoichiometric and stoichiometric hydrides.

(a) **Non-stoichiometric hydrides.** (i) *Direct method.* Palladium metal adsorbs 900 times its volume of hydrogen at high temperature to form palladium hydride (non-stoichiometric), $PdH_{0.6}$.

(ii) *Electrolytic method.* Palladium, iron etc. metals when used as cathode, adsorb hydrogen during electrolysis. For example :

1. The hydrogen liberated at the iron cathode adsorbs on iron in the ratio, *100 volume H_2 : 1 volume Fe.*

2. The hydrogen liberated at the palladium cathode adsorbs on Pd in the ratio, *1000 volume H_2 : 1 volume Pd.*

(b) **Stoichiometric hydrides.** These are prepared by reduction method. For example, copper (I) hydride, CuH (Reddish brown powder) is prepared by the reduction of copper (II) salt solution with sodium hypophosphite at 345 K. X-ray diffraction data indicates that like metallic copper, Cu-atoms in CuH have a face centred cubic arrangement.

Properties. (*i*) These are grey to black in colour.

(*ii*) These show metallic lustre, electrical conductivity and hardness.

(*iii*) These are good reducing agents at high temperature. It is because at high temperature, the adsorbed atomic hydrogen reacts with oxidants and reduce them to lower oxidation state. For example, UH_3 (Uranium hydride) reduces

(*a*) $AgNO_3$ to Ag and (*b*) $CuSO_4$ to Cu metal.

(*iv*) Metallic hydride formation either involves absorption or evolution of heat. For example :

(*a*) Metals like Ag, Mo, U, Cu, etc. form hydrides with absorption of heat energy.

$$2Ag + H_2 + q \text{ kcal} \longrightarrow 2AgH$$

(*b*) Metals like palladium, thorium, titanium etc. form hydrides with the evolution of heat.

Problem 6. Metallic hydride formation either involves absorption or evolution of heat. Comment.

Structure. Much work has been done to know the exact state of hydrogen gas in metal lattice. The results interpreted from X-ray diffraction and density of metal hydrides are given below :

(*i*) The hydrogen atoms are present in the interstices (Fig. 3.35) between the metal atoms in the crystal lattice. When such a hydride is heated, hydrogen gas is given out.

(*ii*) In certain cases, the lattices of a metal and its hydrides are same. However, in certain other cases, metal hydride lattices get expanded and slightly distorted.

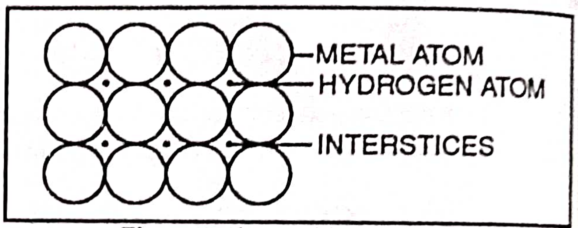

Fig. 3.35 Interstitial hydrides.

BASIC BERYLLIUM NITRATE

Preparation. The compound can be prepared in solution. It can be crystallised as hydrated salt by the action of nitric acid on the carbonates, hydroxides or oxides of beryllium. The hydrated solids do not give the anhydrous nitrate because the solid decomposes on heating to its oxide.

Anhydrous nitrate can be prepared with the use of ethyl acetate and liquid dinitrogen tetraoxide. Beryllium is unusual because it forms a basic nitrate in addition to the normal salt, $Be(NO_3)_2$

Reaction. $BeCl_2 \xrightarrow{N_2O_4} Be(NO_3)_2 \cdot 2N_2O_4 \xrightarrow[\text{325 K under vaccum}]{\text{Warm to}} Be(NO_3)_2 \xrightarrow{398\text{ K}} [Be_4O(NO_3)_6]$

Basic beryllium acetate

It is highly hygroscopic substance.

Structure. It has an unusual structure. The four Be-atoms are located at the four corners of a tetrahedron. The six NO_3^- groups are present along the six edges of the tetrahedron and the (basic) oxygen atom is present at the centre. It forms stable covalent molecules of the formula, $[Be_4O(R_6)]$ where R may be NO_3^-, $C_2H_5COO^-$, $C_6H_5COO^-$, $HCOO^-$, CH_3COO^- etc. Its basic beryllium acetate (fig. 3.36), NO_3^- groups act as bidentate ligands in forming a bridge between two Be-atoms.

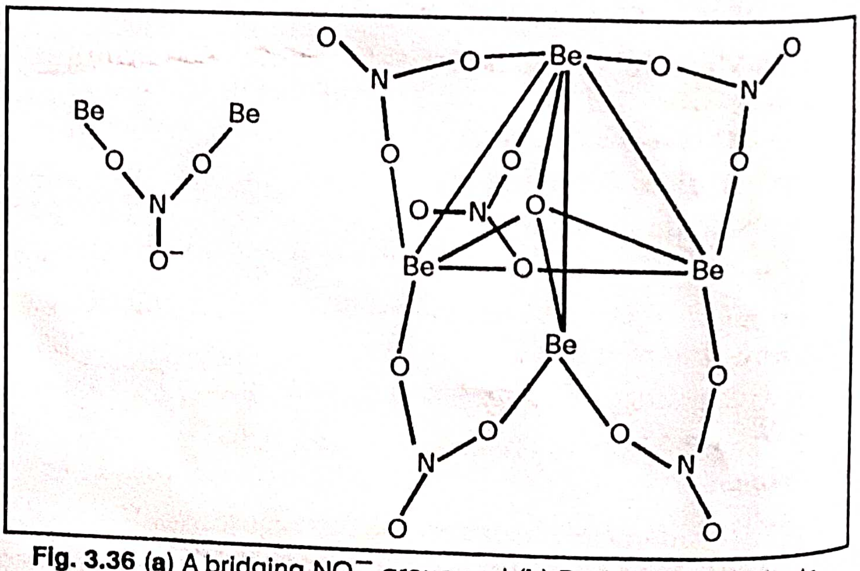

Fig. 3.36 (**a**) A bridging NO_3^- group and (**b**) Basic beryllium nitrate.

Basic beryllium acetate, $3Be(CH_3COO)_2BeO$ or $Be_4O(CH_3COO)_6]$

Preparation. Basic beryllium acetate can be prepared by following methods.

1. Parson's method. This compound is obtained by heating a mixture of beryllium carbonate and glacial acetic acid.

$$6BeCO_3 + 6CH_3COOH \longrightarrow 3Be(CH_3COO)_2 . BeO + 6CO_2 + 6H_2O$$

2. Urbain method. The compound can be prepared by evaporating a mixture of beryllium hydroxide and dilute acetic acid to dryness. The residue so obtained is dissolved in boiling glacial (anhydrous) acetic acid and cooled. The compound so formed is extracted with chloroform, in which it is soluble.

Properties. It is a volatile crystalline solid. It dissolves in non-polar organic solvents like chloroform and in lower alcohols.

When its solution in organic solvents is crystallised, it is obtained in the form of octahedral crystals. It is insoluble in water. It melts at 283°C and boils at 330°C without decomposition. It is a covalent compound. It is unaffected by water but gets hydrolysed when boiled with dilute sulphuric acid.

Structure. Its structure has been studied by X-ray methods. The molecule has a tetrahedral symmetry. The central oxygen atom is tetrahedrally surrounded by four beryllium atoms in such a way that the four acetate groups. According to Pauling and Sherman (1934), the crystal cell contains four molecules of basic acetate and the arrangement corresponds to the structure. See page 65, fig. 3.7.

SHORT QUESTIONS WITH ANSWERS

1. Why group 1 elements are metals ? Give their trend down the group.

   Ans. Group 1 elements have a greater tendency to lose electrons due to their low ionisation potential values. As a result, these are strongly electropositive or metallic in nature. Since their I.P. decreases down the group, their metallic character increases down the group.

2. Although Li has small size and high ionisation energy, it is stronger reducing agent than other alkali metals. Why ?

   Ans. The smallest size of Li^+ causes maximum charge density around it. As a result, maximum water molecules get attached to this ion. In Li^+ $(1s^2)$, the 1s electrons are not screened from the nucleus effectively. The hydration energy produced is so high that it pulls off the 2s electron from Li(g) atom. Hence, it acts as the most powerful reducing agent ($E^\circ_{Li^+/Li} = -3.04V$).

3. Describe the group trend for the solubility of fluorides of group 2 elements.

   Ans. Except BeF_2, all alkaline earth metal fluorides are insoluble in water because of their large value of lattice energies. Their solubility in water decreases down the group.

4. Why B^{3+} ions are not formed ?

   Ans. It is because the ionisation energy required to produce B^{3+} ions is very high. It is neither available from the hydration of ions in aqueous solution nor from the lattice energies of its ionic compounds.

5. $SnCl_2$ in a solid while $SnCl_4$ is a liquid. Why ?

   Ans. $SnCl_2$ is an ionic compound because less energy is required to remove two electrons from Sn to form Sn^{2+}. Since ionic compounds have high melting point, $SnCl_2$ is a solid. $SnCl_4$ is a covalent compound which is formed by the sharing of four valence electrons, because lot of energy is required for the removal of four electrons. $SnCl_4$ is a liquid because covalent compounds are held together by weak vander Waal forces and less energy is required to separate them, and hence have low melting point.

6. What is dry ice ? Why is it so called ?

   Ans. Carbon dioxide is a gas at room temperature, which on application of a slight pressure changes into **solid CO_2 called dry ice.** It is called dry ice because it sublimes without producing liquid carbondioxide. It does not wet a piece of cloth because it sublimes without melting.