→ s-Block elements:-

- In the atom of these elements the last electron enters the s-orbital of the ultimate or outermost shell. i.e. last e- goes to ns orbital where n represents the number of the outermost shell or the number of the period.
- The elements of group 1 (IA) and group 2 (IIA) belong to this block.
- The valence shell electronic configuration of these elements varies from ns^1 to ns^2.

→ Group 1 or IA:-

- This group contains six elements which are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr).
- The elements of this group are called alkali metals because they form strongly alkaline oxides and hydroxides. Fr is a radioactive element.
- The elements are all metals, excellent conductors of electricity and typically soft and highly reactive.
- The have one loosely held valence electron in their outer shell, and form univalent, ionic and colourless compounds.
- The hydroxides and oxides are very strong base, and the oxosalts are very stable.
- Lithium, the first element in the group, shows considerable differences from the rest of the group.
- Sodium and potassium make up over 4% by weight of the earth crust and are essential elements for animal life.

- The metals were first isolated by Humphrey Davy in 1807 by the electrolysis of KOH and NaOH.

→ Electronic structure :→

- Group 1 elements all have one valency electron in their outer orbital.
- The single valence electron is a long distance from the nucleus, is only weakly held and is readily removed. In contrast, the remaining electrons are closer to the nucleus, more tightly held, and removed only with great difficulties.
- All group 1 elements show similarities in chemical behaviour because of similar electronic structure.

Element	Symbol	Atomic No.	Electronic structure or configuration
Lithium	Li	3	$1s^2 2s^1$ or $[He]\, 2s^1$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$ or $[Ne]\, 3s^1$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[Ar]\, 4s^1$
Rubidium	Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ or $[Kr]\, 5s^1$
Cesium/ Caesium	Cs	55	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[Xe]\, 6s^1$
Francium	Fr	87	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$ or $[Rn]\, 7s^1$

→ Group 2 or IIA :→

- This group contains six elements which are Beryllium (Be), Magnesium (Mg), Calcium (Ca), strontium (Sr), Barium and Radium (Ra).
- The elements of this group are called alkaline earth metals because their oxides are alkaline in character and occured in nature as earths. e.g. CaO (lime), SrO (strontia) & BaO (Baryta)

- Ra is a radioactive element and studied separately along with other radioactive elements.
- The group 2 elements show the same trends in properties as were observed with group 1. However, Be shows different properties from rest of group 2 elements and differs much more from them than Li does from the rest of group 1. because Be and Be^{+2} are very small in size.
- Be and Ba compounds are all very toxic.
- The group 2 elements are highly reactive but less reactive than group 1.
- They are divalent and generally form colourless ionic compounds.
- The oxides and hydroxides are less basic than group 1 and hence their oxosalts (carbonates, sulphates, nitrates) are less stable to heat.
- Mg^{+2} and Ca^{+2} are essential elements in the human body and Mg^{+2} is an important constituent of chlorophyll.

→ Electronic structure:-

- All group 2 elements have two s electrons in their outer shell
- Group 2 elements show similarities in chemical behaviour because of similar electronic structure.

Element	Symbol	Atomic No.	Electronic structure or configuration
Beryllium	Be	4	$1s^2 2s^2$ or $[He] 2s^2$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$ or $[Ne] 3s^2$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[Ar] 4s^2$
Strontium	Sr	38	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ or $[Kr] 5s^2$
Barium	Ba	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$ or $[Xe] 6s^2$
Radium	Ra	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$ or $[Rn] 7s^2$

→ Comparative study of s-Block elements:→

1. Physical state:-

- Group 1 elements are extremly soft and readily fused (except Li). They are highly malleable and ductile. When freshly cut, they have a bright lusture which is quickly tarnished as soon as metal comes in contact with atmosphere.
- Group 2 elements have a greyish white lusture when freshly cut and are malleable and ductile. Alkaline earth metals are harder than alkali metals.

2. Atomic and Ionic radii :→

- As we move from Li to Fr in group 1, an extra shell of electrons is added to each element. The addition of extra shell increases the atomic and ionic radius.

	Li	Na	K	Rb	Cs
Atomic/metallic radii (A°)	1.52	1.86	2.27	2.48	2.65
Ionic radii (A°) in six coordinate	0.76	1.02	1.38	1.52	1.67

- In group 2, the atomic and ionic radii also increases on moving from Be to Ra due to addition of extra shell of electrons.

	Be	Mg	Ca	Sr	Ba	Ra
Atomic/metallic radii (A°)	1.12	1.60	1.97	2.15	2.22	–
Ionic radii (A°) in six coordinate	0.31	0.72	1.00	1.18	1.35	1.48

- The atomic radii of alkaline earth metals are smaller than alkali metals. It is due to fact that alkaline earth metals have high nuclear charge.

3. Density:-

- The densities of alkali metals are quite low due to the large atomic volume. Li, Na and K are lighter than water. The densities increase with the increase in atomic number from Li to Cs. Increase in density is due to fact that atomic weight increases more than atomic volume. K is however, lighter than Na which is due to an unusual increase in atomic size of K.

	Li	Na	K	Rb	Cs
Density (g/cm)	0.54	0.97	0.86	1.53	0.90

- The densities of alkaline earth metals decreases slightly upto Ca after which it increases. Irregular variation of the density is due to the difference in crystal structures of these elements.

	Be	Mg	Ca	Sr	Ba	Ra
Density (g/cm)	1.85	1.74	1.55	2.63	3.62	5.5

- The alkaline earth metals are denser than alkali metals in same period. This is due to fact that the elements of group 2 can be packed more tightly due to their greater nuclear charge and smaller size.

4 Ionisation energy:-

- Alkali metals have only one valence e- (ns^1) and it is weakly bonded. so it can be remolved easily and hence alkali metals have low ionisation energies.
- As we move down in a group from Li to Cs, value of ionisation energy decreases due to increase in atomic size.
- The second ionisation energies are fairly high, since the second electron is removed from M^+ ion which has stable noble gas configuration

	Li	Na	K	Rb	Cs
First I.E. (KJ/mol)	520.1	495.7	418.6	402.9	375.6
Second I.E. (KJ/mol)	7296	4563	3069	2650	2420

- The ionisation energies of alkaline earth metals decreases as we move from top to bottom in group. Ra has higher ionisation energy than Ba.

	Be	Mg	Ca	Sr	Ba	Ra
First I.E. (KJ/mol)	899	737	590	549	503	509
second I.E. (KJ/mol)	1757	1450	1145	1064	965	979
Third I.E. (KJ/mol)	14847	7731	4910	—	—	3281

- Third ionisation energies are high. because third electron is removed from M^{+2} ion which has stable noble gas configuration.

- First ionisation energies of alkaline earth metals are higher than those of alkali metals whereas second ionisation energies of alkali metals are higher than those of alkaline earth metals.

5. m.p. and b.p. :→

- The m.p. and b.p. are very low for alkali metals due to presence of weak interatomic bonds. Weak bonds are due to large atomic size and single valence electron.
- On moving from top to bottom, m.p. and b.p. are decrease from Li to Cs because with increasing atomic size, replusion between non-bonding e⁻ increases.

	Li	Na	K	Rb	Cs
m.p. (°c)	181	98	63	39	28.5
b.p. (°c)	1347	881	766	688	705

- m.p. and b.p of alkaline earth metals do not show any trend. However m.p. & b.p of these elements are higher than those of alkali metal. Because these elements form strong bond due to two valence electrons.

	Be	Mg	Ca	Sr	Ba	Ra
m.p. (°c)	1287	649	839	768	727	700
b.p. (°c)	2500	1105	1494	1381	1850	1700

6. Electropositive character or metallic character:-

- Alkali metals easily lost valence shell electron due to low ionisation energy and show electropositive character which increases from Li to Cs.
- Alkaline earth metals also show electropositive character by loosing two valence electrons but their electropositive character is less than alkali metals due to high ionisation energies.

7. Oxidation state:-

- Alkali metals show +1 oxidation state due to presence of 1 valence electron.
- M^+ ion of alkali metals have no unpaired electron and hence diamagnetic and colourless.
- All the compound of alkali metals are colourless (except permaganates and dichromates)
- Alkaline earth metals show +2 oxidation state because they have two valence shell electrons. The second ionisation energies for alkaline earth metals are higher than first ionisation energies. It appears that these metals should form univalent ion rather than bivalent ions. But actually these elements give bivalent ions. This is due to fact that M^{+2} ions are extensively hydrated to form hydrated ions, $[M(H_2O)_x]^{+2}$. and in this process large amount of energy is released which is known as hydration energy.

This hydration energy counterbalance the higher value of second ionisation energy.

8. Electronegativity:-

- Alkali metals have high electropositive character and tendency to lost their ns^1 electron. Because of this electropositive character, these metals have very little electronegative character. Electronegative character decreases from Li to Cs.

	Li	Na	K	Rb	Cs
Pauling's electronegativity	1.0	0.9	0.8	0.8	0.7

- Alkaline earth metals are smaller in size than alkali metals and hence they have high value of electronegativities. Electronegative character decreases from Be to Ra.

	Be	Mg	Ca	Sr	Ba
Pauling's electronegativity	1.5	1.2	1.0	1.0	0.9

9. Conductivity:-

- Alkali metals are good conductor of heat and electricity due to weakly bonded ns^1 e^-.
- In Alkaline earth metals, two valence electrons are free to move throughout the metal struture. So, these metals are good conductor of heat and electricity.

→ Comparative study of s-Block elements :- (Part-2)

10. Photoelectric effect. (Effect of light):-

- The ns^1 electron of alkali metal is so weakly held with nucleus that even the low energy photon (i.e. light) can eject this electron from metal surface. This ejection of proton is called photoelectric effect. Due to this property, K and Cs are used in photoelectric cell.
- Alkaline earth metals do not show this property due to high ionisation energy.

11. Colouration to the flame:-

- When we heat alkali metals and their salts in busen burner, colour is imparted by the atom due to excitation of electron.
- This property of alkali metals is used to detect their presence in salt by a test, known as flame test.

Li – Crimson red
Na – Golden yellow
K, Rb, Cs – violet colour

- Alkaline earth metals also give colour to the flame but Be and Mg do not show colour due to smaller size and hence electrons are not excited to the higher energy level by the energy of the flame.

Ca – Brick red
Sr – Crimson red
Ba – Apple green
Ra – red

12. Polarising power:-

- Alkali metal cations (M^+) are larger in size and hence less tendency to polarise anions.

- Li salts are slightly covalent while other alkali metal salts are ionic.
- In Alkaline earth metals, polarising power of M^{+2} cations decreases from Be^{+2} to Ra^{+2}. Therefor Be^{+2} has a tendency to form covalent compounds.

13. Reducing properties:-

- Alkali metals have strong tendency to lose their ns electron and hence act as strong reducing agent.
- Li has smallest size among alkali metals, still lithium acts as strong reducing agent. because Li atom has high hydration energy. this hydration energy compensates ionisation energy of Li atom. Due to this Li has high value of Oxidation potential. ($E^\circ = +3.04\,V$)
- Alkaline earth metals also have strong tendency to lose their ns electron and hence act as strong reducing agent. The strength as a reducing agent increases downwards from Be to Ba.
- The oxidation potentials of alkaline earth metals are lower than those of alkali metals because of their higher sublimation and ionisation energies. Hence alkaline earth metals are weaker reducing agents than the alkali metals.

14. Hydration energy:→

$$\text{Degree of hydration} \propto \frac{1}{\text{size of cation}} \quad \text{and} \quad \text{Hydration energy} \propto \frac{1}{\text{size of cation}}$$

- Hydration is a exothermic process. The energy released when on gm mole of an ion in the gaseous state is dissolved in water to get it hydrated is called hydration energy.

- In alkali metal ions, the degree of hydration and hydration energy decrease from Li^+ to Cs^+.
- In alkaline earth metals, degree of hydration and hydration energy decrease from Be^{+2} to Ba^{+2}.
- Alkaline earth metals have high value of hydration energy than alkali metals due to smaller size.

15. Occurance :-

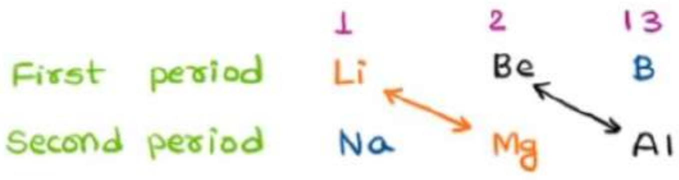
- Due to high reactivity, alkali metals and alkaline earth metal occur in nature in combined state.
- Alkali metals occur in the form of chloride, sulphate and nitrate while alkaline earth metals occur in the form of silicates, carbides and sulphates.

16. Complexation tendency:-

- Alkali metals have low complexation tendency due low charge and larger size.
- Alkaline earth metals have high complexation tendency than alkali metals due to high charge and smaller size.

17. Diagonal relationship:-

- Both Li (alkali metal) and Be (alkaline earth metal) show diagonal relationship.



→ Anomalous behaviour of Lithium :-

- Lithium shows different properties from other alkali metals due to following reasons -

(i) The size of Li and Li^+ ion is the smallest of all the alkali metal ions.

(ii) The polarising power of Li^+ ion is the greatest of all the alkali metal ion.

(iii) Li has highest ionisation energy and electronegativity as compared to other alkali metals.

- Lithium shows following different properties from other alkali metals -

1. Li^+ has high polarising power and hence forms covalent bond. Thus Li salts are soluble in non-polar solvents (e.g. organic solvents). However the salts of other alkali metals are insoluble in organic solvents.
2. Li is only alkali metal which reacts with N and Si to form lithium nitride (Li_3N) and lithium silicide (Li_6Si_2, dark violet and hygroscopic).
3. Li is much harder and lighter than the other alkali metals.
4. Its melting point and boiling point are high and it can be melted in dry air without losing its lusture.
5. Due to high ionisation energy, Li does not react with O_2 below 0°c, reacts slowly with H_2O liberate H_2.
6. Li is least reactive metal of all alkali metal.
7. Li^+ ion show a tendency to form complexes with NH_3, H_2O and form large number of organo lithium compounds.

8. When burnt in air, Li gives only monoxide, Li_2O (O^{-2}) while other alkali metals form peroxide (O_2^{-2}) and super oxide (O_2^-).
9. When acetylene gas is passed over heated Li metal, it does not form lithium acetylide, while other alkali metals form metal acetylide.
10. Li when heated in NH_3, it forms imide (Li_2NH), while other alkali metals form amides. (MNH_2)
11. Li is only alkali metal whose salts (e.g. LiCl) may undergo hydrolysis.
12. Due to low electropositive character of Li, its various salts are less stable and, therefore, decompose to give oxide

$$2\,LiOH \longrightarrow Li_2O + H_2O$$
$$4\,LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$
$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

13. Some of Salts of Li like Li_2CO_3, Li_3PO_4 and LiF are insoluble in water while corresponding salts of other alkali metals are soluble. The solubility of salts of other alkali metals is due to the weak electrostatic force of attraction.
14. Li_2O dissolves in H_2O slowly while other oxides dissolve easily.
15. LiOH is less soluble in water and weaker base than NaOH and KOH. LiOH decomposes into Li_2O on heating, whereas other alkali metal hydroxides sublimate.

16. LiCl is deliquescent and is soluble in alcohol as well as in pyridine. It forms the hydrates $LiCl \cdot 2H_2O$. Chlorides of other alkali metals do not show this behaviour.

17. $LiCO_3$ decomposes on heating to form Li_2O and CO_2 while other carbonates do not decomposes. The small size of Li^+ ion makes Li_2O lattice more stable than Li_2CO_3 lattice. However large size of other alkali metal ion make M_2O lattice less stable than M_2CO_3 lattice and hence they do not decompose.

18. $LiNO_3$, on heating, forms Li_2O, NO_2 and O_2, while other alkali metal nitrates form nitrites and O_2.

$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$

$$NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

19. Lithium hydro sulphide (LiSH) is thermally unstable while the hydro sulphides of other alkali metals are thermally stable.

20. Lithium per chlorate ($LiClO_4$) is soluble in alcohol, acetone and ethyl acetone, while perchlorates of other alkali metals are almost insoluble in these solvents. The solubility of $LiClO_4$ is due to strong solvation of Li^+ ion.

21. Li_2SO_4 is the only alkali metal sulphate which does not form double salts such as alum.

→ Anomalous behaviour of Beryllium: Dissimilarities with other alkaline earth metals:-

- Beryllium shows different properties from other alkaline earth metals due to following reasons-

(i) The size of Beryllium (0.90A°) is the smallest of all the alkaline earth metals.

(ii) Beryllium has highest electronegativity as compared other alkaline earth metals.

- Beryllium shows following different properties from other alkaline earth metals-

1. Hardness:- Beryllium is the hardest of all the elements of its group.

2. Melting and boiling points:- The melting points and boiling points of beryllium are the highest.

3. Formation of covalent compounds:- when beryllium reacts with another element, the electronegativity difference is not so large and the bond is, therefor, covalent.

4. Reaction with water:- Beryllium does not react with water even at high temperature. Other alkaline earth metals decompose water liberating H_2 gas.

$$Mg + H_2O \longrightarrow MgO + H_2 \uparrow$$

5. Reaction with hydrogen:- Beryllium does not react with hydrogen directly to form its hydride. However, its hydrides can be prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.

6. Reaction with alkali:- Beryllium reacts with alkalies to form hydrogen. Other alkaline earth metals do not react with alkalies.

$$Be + NaOH \longrightarrow Na_2BeO_2 \text{ (sodium beryllate)} + H_2 \uparrow$$

7. **Behaviour of oxides and hydroxides:-** The oxides and hydroxides of beryllium are amphoteric i.e. dissolve in both acids and alkalies to form salts.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

The oxides and hydroxides of other alkaline earth metals are basic.

8. **Behaviour of carbides:-** Beryllium carbide is decomposed by water to form methane (CH_4).

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

The carbides of other alkaline earth metals are decomposed by water to form acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

9. **Behaviour of nitrides:-** Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. **Number of molecule of water of crystallisation:-** The salts of Be^{+2} ion cannot have more than four molecules of water of crystallisation while other alkaline earth metals have more than four molecules of water of crystallisation.

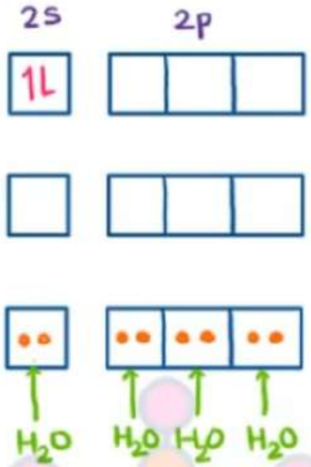
Explaination:- In case of Be^{+2} ion there are only four orbitals available in its outermost shell. These four orbitals accept e^- pairs from O-atom atom of each H_2O molecule.

On the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell.

Valence shell of Be →

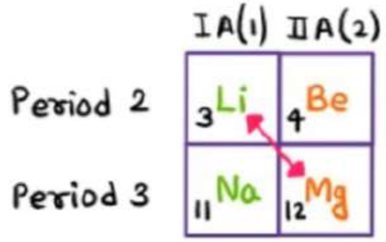
Valence shell of Be^{+2} ion →

Attachment of four H_2O molecules with Be^{+2} ion →



11 **Formation of complex compounds:-** Be^{+2} forms many stable complex compounds due to small size. e.g. $[BeF_3]^-$, $[BeF_4]^{-2}$ etc. while M^{+2} ions of other alkaline earth metals form very few complex compounds.

→ Diagonal relationship of Li with Mg : Similarities between Li and Mg:-



Diagonal relationship of Li and Mg

- Li shows similar properties with the Mg, lying its right in 3rd period (i.e. diagonally opposite element) than with other members of its own group IA(1). This type of similartiy between Li and Mg is called diagonal relationship.
- Li shows following similar properties with Mg-

1. Atomic and ionic radius:-

Atomic radius	Ionic radius
Li = 1.225 A°	Li^+ = 0.60 A°
Mg = 1.365 A°	Mg^{+2} = 0.65 A°

2. Atomic volume:- The atomic volume of solid Li and Mg are similar.

$$\text{Atomic vol.} = \frac{\text{Atomic weight}}{\text{density}}$$

Li = 12.97 C.C. Mg = 13.97 C.C.

3. Electronegativity:-

L = 1.00 Mg = 1.20

4. High polarising power (i.e. ionic potential) and its effect:-

- Li^+ and Mg^{+2} both the ions have high polarising power i.e. ionic potential (charge/radius ratio) of both the ions is high.
- Due to high polarising power, both the ions have great tendency to form hydrates with definite number of water molecules.

e.g. $LiCl \cdot 2H_2O$, $LiClO_4 \cdot 3H_2O$, $LiNO_3 \cdot 3H_2O$

$MgCl_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$

- Due to high polarising power, halides of both ions are covalent in nature.
- Due to high polarising power, their nitrates and carbonates have low thermal stability and decomposes easily on heating.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

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

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

5. Enthalpies of vaporisation:- Both the elements have comparable enthapy of vaporisation.

6. Melting points:- Li = 1336°C , Mg = 1100°C

7. Hardness:- Li and Mg are harder than the other members of their respective groups. However, hardness of Li is comparable with that of Mg.

8. Action of H_2O :- Like Mg, Li decomposes water slowly to liberate H_2.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

9. Action of N_2 :- Both the elements combine with N_2 on heating to form their ionic nitrides, Li_3N and Mg_3N_2.

Both the nitrides readily decompose H_2O to liberate NH_3

$$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$
$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

10. Action of Cl_2 :- Both the elements react with Cl_2 to form chlorides.

$$2Li + Cl_2 \longrightarrow 2LiCl$$
$$Mg + Cl_2 \longrightarrow MgCl_2$$

Chlorides of both show following similar properties:-

(i) Both are deliquescent (ii) Both are soluble in alcohol and water.

(iii) Both form hydrates (iv) Both undergo hydrolysis in hot water.

11. Combination with carbon:- On heating, both the elements combines with carbon to form the carbides, Li_2C_2 and MgC_2.

12. Action of O_2 (air) :- Both elements form oxides (Li_2O, MgO) when heating in air or O_2. Li_2O and MgO further not react with O_2 to form peroxide and superoxide.

13. **Nature of hydroxide :-** LiOH and $Mg(OH)_2$ are less soluble in water, less basic and decomposes on heating to form oxides.

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

14. **Solubilities of salts:-** Fluorides, carbonates and phosphates of both the metals are insoluble in water while chlorides, bromides, iodides and perchlorates of both the metals are soluble in oxygenated organic solvents.

15. **Unstability of hydrosulphides:-** Lithium hydrosulphide, LiSH and Magnesium hydrosulphide, $Mg(SH)_2$ are unstable under ordinary conditions. $Mg(SH)_2$ decomposes in aqueous solution to give $Mg(OH)_2$ and H_2S.

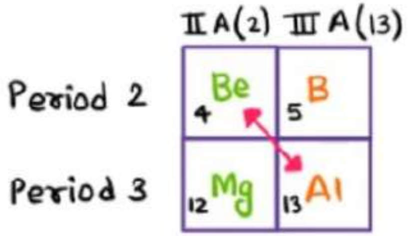
$$Mg(SH)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2H_2S$$

16. Li_2SO_4 and $MgSO_4$ do not form alum.

17. Alkyls of Li and Mg are soluble in organic solvents due to their covalent nature.

18. Li^+ and Mg^{+2} ions are strongly hydrated.

→ Diagonal relationship of Be with Al : Similarities between Be and Al :-



Diagonal relationship of Be and Al

- Be is placed diagonally opposite to Al in the periodic table, it shows diagonal relationship with Al, i.e. both these elements show many similar properties.
- Be–Al diagonal pair is considered to be an ideal diagonal pair in the periodic table and hence similarity between Be and Al is the best example of diagonal relationship.
- Be and Al shows diagonal relationship due to following reasons–

(i) Polarising powers (i.e. ionic potentials) of Be^{+2} (6·45) and Al^{+3} (6·00) are same.

(ii) Both the elements have same standard oxidation potential.

$$Be \longrightarrow Be^{+2} + 2e^- \quad , E^\circ_{ox} = +1{\cdot}70 \text{ volts}$$
$$Al \longrightarrow Al^{+3} + 3e^- \quad , E^\circ_{ox} = +1{\cdot}67 \text{ volts}$$

(iii) Electronegativity values of both the elements are the same.

$Be = 1{\cdot}5$, $Al = 1{\cdot}5$

(iv) Both the elements are weakly electropositive.

- Be and Al show following similar properties due to diagonal relationship –

1. Ionic radius :- $Be^{+2} = 0.31\ A^{\circ}$ and $Al^{+3} = 0.50\ A^{\circ}$

2. Extraction :- Both the metals are obtained by the electrolysis of their fused salts in the presence of the fluoride.

3. Heat of Vaporisation :- Both the elements have almost same values of heat of vaporisation.

   Be = 73.9 Kcal/atom Al = 67.9 Kcal/atom

4. Occurence :- In the nature, both the elements occur together in beryl, $3BeO, Al_2O_3 \cdot 6SiO_2$.

5. Formation of polymerised covalent hydrides :- Both the elements form polymerised hydrides which are covalent in nature.

6. Formation of covalent compounds :- Due to high polarising power, both the elements form covalent compounds.

7. Action of HNO_3 :- Both the elements do not react with HNO_3 due to formation of an inert and impervious film of their oxides on the metal surface.

8. Action of alkalies :- Both the elements liberates H_2 when dissolve in boiling alkalies.

$$Be + NaOH \longrightarrow \underset{\text{Sod. beryllate}}{Na_2BeO_2} + H_2\uparrow$$

$$Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sod. Aluminate}}{2NaAlO_2} + 3H_2\uparrow$$

9. Properties of oxides and hydroxides:- Both the metals burn in O_2 and form oxides. The oxides and hydroxides of both the metals are amphoteric in nature, i.e they are soluble in acids and alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Al_2O_3 + 6HCl \longrightarrow AlCl_3 + 3H_2O$$
$$Al(OH)_3 + 2HCl \longrightarrow AlCl_3 + 3H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

oxides of both the metals are extremely hard, non-volatile and very high melting point.

10. Halides:- Both the metals react with halogens to form halides

$$Be + Cl_2 \longrightarrow BeCl_2$$
$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

These halides have following properties –

(i) low m.p.
(ii) hydrolysed by water
(iii) Anhydrous (except fluorides) are covalent
(iv) dissolve in organic solvents
(v) fume in moist air
(vi) behave as Lewis acids.

11. Formation of carbides:- Both metals react with carbon to form carbides (Be_2C & Al_4C_3). These carbides evolve methane on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

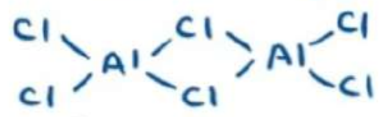
12. Formation of complexes:- Be^{+2} and Al^{+3} have strong tendency to form complexes. e.g. BeF_4^{-2}, $[Be(C_2O_4)_2]^{-2}$, AlF_6^{-3} and $[Al(C_2O_4)_3]^{-2}$

13. Properties of salts:- Salts of both the metals like nitrates, sulphates and chloride crystallise from aqueous solution as hydrates. They get easily hydrolysed in solution. The extent of hydrolysis of the salts of both the metals is almost comparable.

The carbonates of both the metals are unstable, except in atmosphere of CO_2.

14. Formation of hydrated ions:- Both metals form hydrated ions. $[Be(H_2O)_4]^{+2}$ & $[Al(H_2O)_6]^{+3}$

15. Formation of bridged chlorides:- Both metals form bridged chlorides.



16. Formation of nitrides:- Both metals form nitrides when react with N_2. These nitrides give NH_3 on hydrolysis.

$$3Be + N_2 \longrightarrow Be_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

→ **S-block elements:-**

→ **Salient features of hydrides:→**

- Binary compounds of hydrogen with other elements whose electronegativity is lower than that of hydrogen are called hydrides.
- According to definition some compounds like H_2O, H_2S, NH_3, PH_3, H_2S, HF, HCl, HBr etc. are not considered as hydrides. Thus the term is not usually used for binary compounds of hydrogen with non-metals.
- Elements of group 1 or IA (Fr is an exception) and group 2 or IIA (Be and Mg are exceptions) form ionic or salt like hydrides

→ **Preparation:-**

1. By heating metal with H_2:→

$$2M + H_2 \xrightarrow{400^\circ C} 2MH \quad (M = Na \text{ or } K)$$

$$M + H_2 \xrightarrow{150-300^\circ C} MH_2 \quad (M = Ca, Sr, Ba)$$

LiH is prepared by reacting with H_2 at 600°C in an iron boat kept in a hard glass tube.

2. By heating carbonates with H_2:→

$$Rb_2CO_3 + H_2 \xrightarrow[Mg]{620-650^\circ C} 2RbH + CO_2 + H_2O$$

$$Cs_2CO_3 + H_2 \xrightarrow[\text{''}]{\text{''}} 2CsH + CO_2 + H_2O$$

3. By heating metal nitride with H_2:→

$$2\,LiN_3 + H_2 \longrightarrow 2\,LiH + 3N_2$$

4. Alexander's method:→

$$CaO + Mg + H_2 \xrightarrow{250^\circ C} CaH_2 + MgO$$

- A yield of 99.2% of CaH_2 is obtained in 2 hours.

→ Physical properties:-

- These hydrides are crystalline compounds with ionic lattices.
- These hydrides have high m.p and b.p.
- Conduct electricity in fuesd state.
- Except LiH they decompose on fusion.
- They are stoichiometric compounds.

→ Chemical properties:-

1. Thermal stability and reactivity order :-

- Hydrides of Li, Ca and Sr are most stable while others decompose above 400°C. Their thermal stability decrease with increasing size of cation in a group. Thus the order of thermal stability is as follows-

Group 1 $LiH > NaH > KH > RbH > CsH$

Group 2 $CaH_2 > SrH_2 > BaH_2$

- The order of reactivity of hydrides is as follows-

Group 1 $LiH < NaH < KH < RbH < CsH$

Group 2 $CaH_2 < SrH_2 < BaH_2$

3. Presence of H^- ion :- Electrolysis of these hydrides in the fused state liberates hydrogen at anode, showing the presence of H^- ion in them.

4. Action of protonic solvents:- They all vigorously react with protic solvents (i.e. gives H^+ ion) Such as H_2O, C_2H_5OH and NH_3 forming H_2 and base

$$MH \rightleftharpoons M^+ + H^-$$

$$H^- + H_2O \longrightarrow OH^- + H_2$$

$$H^- + NH_3 \longrightarrow NH_2^- + H_2$$

$$H^- + C_2H_5OH \longrightarrow OC_2H_5^- + H_2$$

5. Reducing properties:- All these hydrides show reducing properties at high temp due to formation of atomic hydrogen. These hydrides are used to reduce metal oxides.

$$4NaH + Fe_3O_4 \longrightarrow 3Fe + 4NaOH$$

$$4NaH + SiCl_4 \longrightarrow SiH_4 + 4NaCl$$

$$MH + CO_2 \longrightarrow HCOOM$$

(M = Li, Na, K)

6. These hydrides have no geometry due to ionic nature.

7. Decomposition by SO_2 :-

$$2KH + 2SO_2 \longrightarrow \underset{\text{Pot. dithionite}}{K_2S_2O_4} + H_2\uparrow$$

$$CaH_2 + 2SO_2 \longrightarrow \underset{\text{Cal. dithionite}}{CaS_2O_4} + H_2\uparrow$$

8. Reaction with N_2 :-

$$3CaH_2 + N_2 \longrightarrow Ca_3N_2 + H_2\uparrow$$

$$LiH \xrightarrow{+N_2} \underset{\text{Li-amide}}{LiNH_2} \xrightarrow{+N_2} \underset{\text{Li-imide}}{LiNH} \xrightarrow{+N_2} \underset{\text{Li-Nitride}}{Li_3N}$$

$$CsH + N_2 \xrightarrow{\Delta} CsNH_2$$

9. Reaction with $AlCl_3$:-

$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

→ Uses:-

- Ionic hydrides are used as condensing agents in Claisen and Aldol condensation.
- These hydrides are used as reducing agents.

→ **Ionic hydrides of s-block elements:-**

(i) **Lithium hydride, LiH:→**

→ **Preparation:→**

1. From Lithium and H_2 gas:-

$$2Li + H_2 \xrightarrow{700-800°C} 2LiH$$

2. From Lithium nitride and H_2 gas:-

$$2Li_3N + 3H_2 \longrightarrow 6LiH + N_2$$

→ **Physical properties:-**

1. white solid compound.
2. m.p. = 680°C

→ **chemical properties:-**

1. Reaction with H_2O:-

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

2. Reaction with anhydrous $AlCl_3$:-

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

3. Fused LiH, on electrolysis, gives Li at cathode and H_2 at anode like other ionic compounds.

4. Reaction with diborane :-

$$2LiH + B_2H_6 \xrightarrow{ether} 2LiBH_4$$

5. It turns blue on exposure to light whithout any change in composition.

6. LiH is the most stable of all the alkali metal hydrides and also chemically active. It is stable at ordinary temp. and is not affected by dry gases like Cl_2, HCl or O_2.

7. It is a powerful reducing agent and hence reduces oxides, chlorides, sulphides and CO_2.

→ Uses :-

- used as strong reducing agent in organic synthesis.
- In the preparation of $LiAlH_4$.
- As a convenient source of H_2 for air-sea rescue balloons.
- In the preparation of $LiBH_4$ which is used in jet propulsion.

→ Structure :- It crystal has face-centered cubic structure (like NaCl)

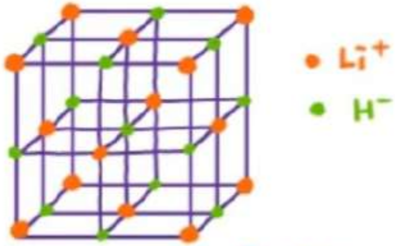


fig :- Structure of LiH.

(ii) Sodium hydride, NaH :→

→ Preparation :-

1. From sodium metal and H_2 gas :-

$$2Na + H_2 \xrightarrow{365^\circ c} 2NaH \text{ (colourless)}$$

- Reaction mixture is kept in nickel boat and heated in glass tube

→ Physical properties:-

1. Colourless crystalline substance.

→ chemical properties:-

1. On heating above 330°c it is decomposed into its elements.
2. Reaction with H_2O:-

$$NaH + H_2O \longrightarrow NaOH + H_2$$

3. Reaction with CO_2:-

$$NaH + CO_2 \longrightarrow \underset{\text{sod. formate}}{HCOONa}$$

4. Reaction with diborane:-

$$NaH + B_2H_6 \xrightarrow{\text{ether}} \underset{\text{Sod. borohydride}}{NaBH_4}$$

5. on electrolysis, fused NaH gives H_2 at anode and Na at cathode.
6. Reaction with trimethylborate:-

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + \underset{\text{Sod. methoxide}}{3NaOCH_3}$$

→ Uses:-

- NaH is used as reducing agent.
- NaH is used to prepare $NaBH_4$ which is a reducing agent.

→ Structure:-

- NaH has a face-centered cubic lattice.

(iii) Potassium hydride, KH :→

→ Preparation:→

1. From potassium and H_2 gas :→

$$2K + H_2 \xrightarrow{360^\circ C} 2KH$$

→ Physical properties:→

1. White needle-like crystalline solid.

→ Chemical properties:→

1. It ignites spontaneously in Cl_2 or O_2.
2. Decomposes on heating.
3. Reaction with H_2O :→

$$KH + H_2O \longrightarrow KOH + H_2$$

4. Reaction with CO_2:-

$$KH + CO_2 \longrightarrow \underset{\text{Pot. formate}}{HCOOK}$$

→ Structure:-

- It has NaCl like structure.

(iv) Calcium hydride, CaH_2: Hydrolith :→

→ Preparation:→

1. From fused calcium metal and H_2 gas:-

$$Ca + H_2 \xrightarrow{400-500^\circ C} CaH_2$$

→ Physical properties:→

1. Colourless crystalline compound.
2. m.p. = 816°C

→ Chemical properties:→

1. On electrolysis, fused salt gives H_2 at anode and Ca at cathode.
2. Reaction with water:-

$$CaH_2 + 2H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2} + 2H_2$$

3. Reaction with CO_2:-

$$CaH_2 + CO_2 \longrightarrow (HCOO)_2Ca \text{ (Calcium formate)}$$

– Use :-

- It is used for millitary purpose as a source of H_2 for balloons and hence the name of hydrolith.
- It is used as a reducing agent in metallurgical processes.
- To determine the traces of water in organic solvents.

→ Structure:-

- Ca^{+2} ions in CaH_2 are in a slightly disorted hexagonally close-paked arrangement. The unit cell of this hydride is orthorhombic.

→ s Block elements:→

→ Solvation tendencies:→

1. Group 1 (Alkali metals):→

- All the simple salts dissolve in water, producing ions and consequently the solution conduct electricity.
- Since Li^+ ions are small, it might be expected that solutions of lithium salts would conduct electricity better than solutions of the same concentration of sodium, potassium, rubidium or cesium salts. The small ions should migrate more easily towards the cathode, and thus conduct more than the larger ions. However, the order of ionic mobility in the opposite order -

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

The reason for this opposite order is hydration. since Li^+ is very small, it is heavily hydrated. This makes the radius of the hydrated ion large, and hence it moves slowly. In contrast, Cs^+ is the least hydrated, and the radius of the hydrated Cs^+ ion is smaller than the radius of hydrated Li^+, and hence hydrated Cs^+ moves faster and conducts electricity more readily.

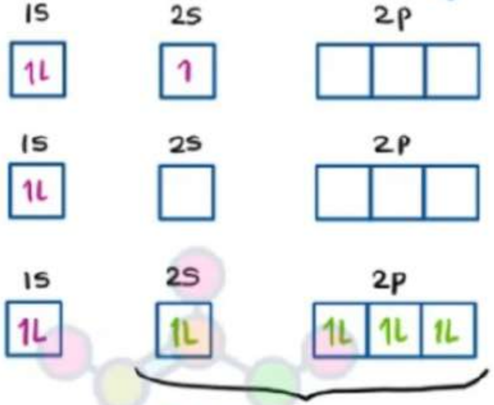
- The hydration number is the average number of water molecules associated with metal ion and is measured using conductivity cell.
- Some water molecules touch the metal ion and bond to it forming a complex. These water molecules consititute the primary shell of water. Thus Li^+ ion is tetrahedrally surrounded by four water molecules. The oxygen atoms of water molecules form coordinate bond with Li^+ ion using lone pairs.

- The tetrahedral structure is predict on the basis of VSEPR theory and alternatively sp^3 hybrid orbitals are predict on the basis of valence bond theory.

Electronic structure of Li

Electronic structure of Li^+

Electronic structure of Li^+ ion with four water molecules bonded, using a lone pair on oxygen to form coordinate bond



Four electron pairs
(Tetrahedral, sp^3 hybridisation)

- With the heavier ions, particularly Rb^+ and Cs^+, the number of water molecules increases to six. VSEPR theory predicts an octahedral structure. VBT also indicates d^2sp^3 hybridisation for octahedral geometry.

- A secondary layer of water molecules further hydrates the ions, though these are only held by weak ion-dipole attractive force. The strength of such forces is inversely proportional to the distance, that is to the size of the metal ions. Thus the secondary hydration decreases from lithium to cesium and accounts for Li^+ being the most heavily hydrated.
- The simple salts are all soluble in water, and so in qualitative analysis these metals need to be precipited as less common salts.

- Na^+ is precipitated by adding zinc or copper uranyl acetate and precipitated as sodium zinc uranyl acetate whereas K^+ is precipitated by adding sodium cobaltnitrate and precipitated as potassium cobaltnitrate.
- If a salt is insoluble, its lattice energy is greater than the hydration energy.

lattice energy > hydration energy → Salt is insoluble

lattice energy < hydration energy → Salt is soluble

- The solubility of most of the salts of group 1 elements in water decreases on descending the group. because on descending the group, the lattice energy only changes slightly, but free energy of hydration changes rather more. for example, difference in lattice energy between NaCl and KCl is 67 KJ/mol, and the difference in $\Delta h_{(hydration)}$ for Na^+ and K^+ is 76 KJ/mol. Thus KCl is less soluble than NaCl.
- The solubilities of fluorides and carbonates of group 1 elements increases on descending the group. The reason for this is that ~~their~~ lattic energies change more than the hydration energies on descending the group.
- The lattice energy depends on electrostatic attraction between ions, and is proportional to the distance between the ions, that is proportional to $1/(r^+ + r^-)$

$$\text{Lattice energy} \propto \frac{1}{(r^+ + r^-)}$$

lattic energy will very most when r^- is small, that is with F^-, and very least when r^- is large. (with I^-)

- The weight of solute dissolving does not provide a very useful comparision of the solubilities, because the molecular weight differs.
- The easiest way to compare the number of ions is to compare the solubilities as molar quantities.

2. Group 2 (Alkaline earth metals):-

- The solubility of most salts decreases with increased atomic weight though the usual trend is reversed with the fluorides and hydroxides in this group.
- solubilities depends on the lattice energy of solid and hydration energy of the ions.
- The lattice energies of group 2 compounds are much higher than the value for group 1 compounds because of the effect of the increased charged on group 2 ions.
- Taking any one particular negative ion, the lattice energy decrease as the size of the metal increases. The hydration energy also decreases as the metal ion becomes larger. For a substance to dissolve the hydration energy must exceed the lattice energy.

- In case of chlorides of group 2 metals, on descending the group metal ions becomes larger and so both the lattice energy and the hydration energy decrease. A decrease in lattice energy favors increased solubility, but decrease in hydration energy favors decreased Solubility. These two factors thus change in opposite directions, and the overall effect depends on which of two has changed most.
- with most compounds, on descending group, the hydration energy decreases more rapidly than the lattice energy, hence the compound become less soluble as the metal gets larger.

- In case of fluorides and hydroxides the lattice energy decreases more rapidly than the hydration energy, and so their solubility increases on desending the group.

→ s-Block elements:→

→ complexation tendencies:→

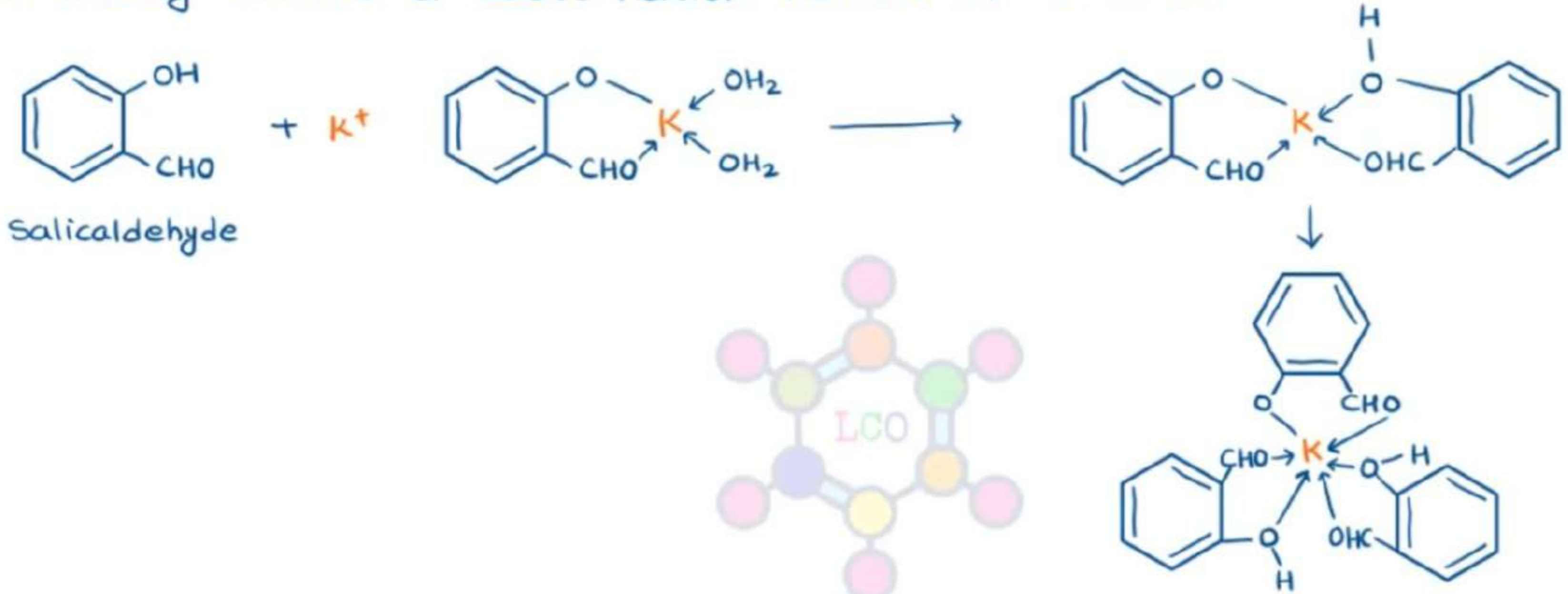
→ Group 1 elements (Alkali metals):→

- The factors favoring complex formation are small size, high charge and empty orbitals of low energy. But group 1 metal ions are very large and have a low charge (+1). Therefore these metal ions have weak tendency to form complexes.
- A number of aqua complexes are known such as $[Li(H_2O)_4]^+$ and a primary hydration shell of four H_2O molecules arranged tetrahedrally is found in various crystalline salts. Na^+ and K^+ also have same primary hydration shell, but Rb^+ and Cs^+ coordinates six H_2O molecules.
- Stable complexes are formed with phosphine oxides.

  Exampls:- $[LiX \cdot 4Ph_3PO]$, $[LiX.5Ph_3PO]$ and $[NaX.5Ph_3PO]$

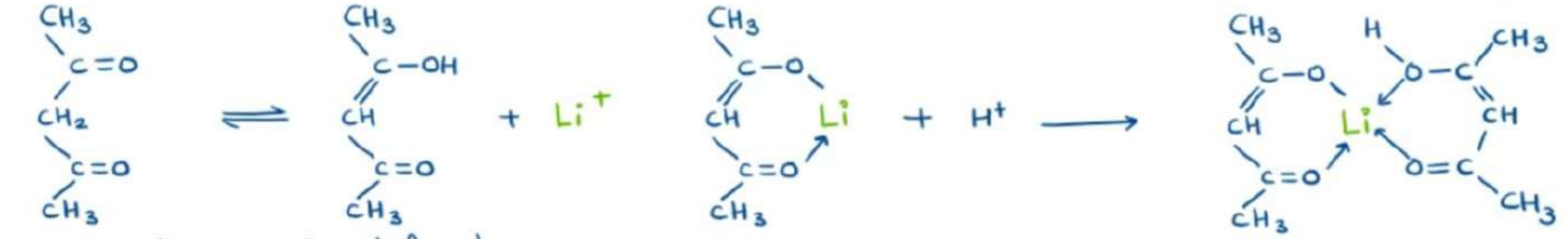
  where X is large anion such as ClO_4^-, I^-, NO_3^- and SbF_6^-.
- There is slight tendency to form ammine complexes such as $[Li(NH_3)_4]I$.
- Weak complexes of sulphates, peroxosulphates, thiosulphates and hexacyanoferrates are known in solution.
- However, some organic chelating agents (particularly salicaldehyde and β-diketones) are extremely strong complexing agents, and Group 1 ions form complexes with these. These ligands are very strong complexing agents because they are multidentate, that is they have more than one donor so they form more than one bond to metal, and also because they form a ring or chelate compound by bonding to the metal.

Examples:- salicaldehyde, acetylacetone, benzoylacetone, methyl salicylate, o-nitrophenol and o-nitrocresol.
The metal usually attains a coordination number of 4 or 6.



Salicaldehyde

Potassium salicaldehyde complex



Acetyl acetone (keto form)

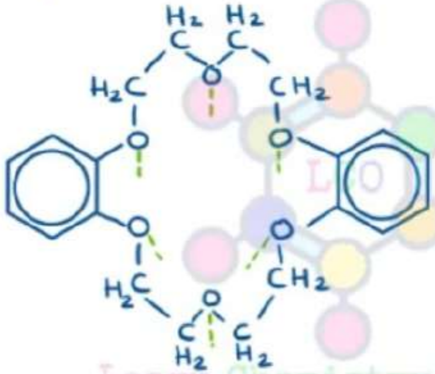
(enol form)

Lithium acetylacetone complex

- Alkali metal ions also form complexes with crown ethers and cryptates.
- Crown ethers are complexing agents first synthesized by Pedersan in 1967. Some crown ethers are given below-

(i) dibenzo 18 crown 6 :→

- The name indicates that there are two benzene rings in the compound, 18 atoms makes up a crown shape ring, and six of the ring atoms are oxygen. These six oxygen atoms may complex with a metal ion, even with large ions like Group 1 ions that are not very good at forming complexes.

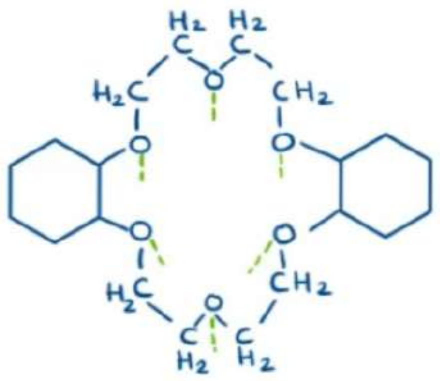


dibenzo 18 crown 6

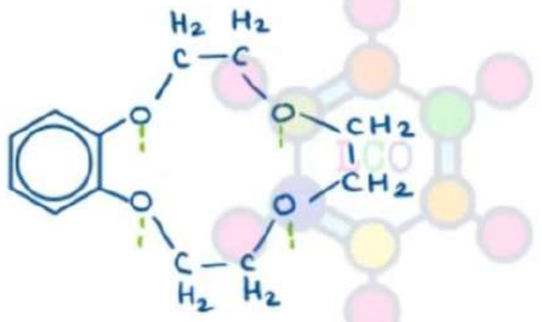
- The organic part of the molecule is puckered to give the crown arrangement, and the oxygen atoms with their lone pairs are nearly planar about the metal ion at the centre of the ring.
- The bonding of metal ion to the polyether is largely electrostatic and metal ion fits in to center hole of the polyether.
- The polyethers form complexes selectively with the alkali metal ion. The size of the ring opening in the crown determines the size of the metal ion which may be accommodated. For example crown-4 is selective for Li^+, crown-5 is for Na^+ and crown-6 is for K^+.

- Crown ethers form a number of crystalline complexes, but more importantly they are sometimes added to organic solvents to make them dissolve inorganic salts which, being ionic, would not normally dissolve.
- Polyethers of this type act as ion carriers inside living cells to transport ions across the cell membranes, and thus maintain the balance between Na^+ and K^+ inside and outside cells.

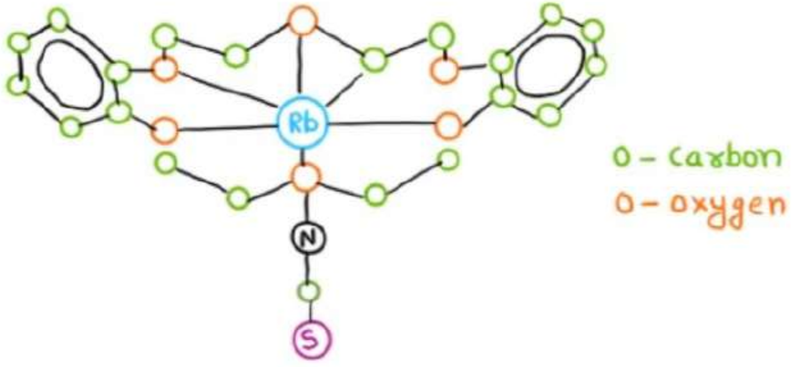
(ii) dicyclohexyl 18 crown 6



(iii) benzo 12 crown 4



(iv) RbCNS (dibenzo 18 crown 6) complex



- The cryptates are three dimensional equivalents of the crown ethers, but contain nitrogen atoms which provide branching and act as extra donor sites in addition to the oxygen atoms to bond to the metal ion.
- They are called cryptates because they wrap round and hide the cation.
- A typical crypt is the molecule $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$. This is called cryptand-222.

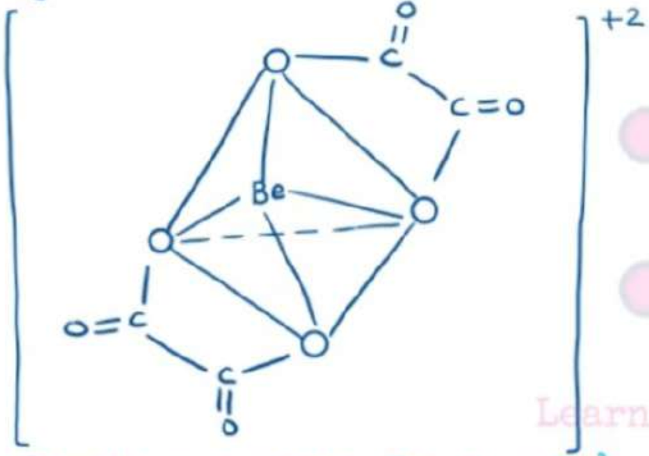
- Cryptand-222 forms a complex [Rb(crypt)]CNS·H_2O in which six oxygen atoms and two nitrogen atoms bonded to the metal ion, giving the metal ion a coordination number of 8. The ligand completely wraps round the metal ion and hiding it. The complex presents hydrocarbon exterior and so is soluble in organic solvents. such complexes are used for solvent extraction, stabilising uncommon oxidation states and promoting otherwise improbable reactions.
- A unusual compound $[Na(cryptand\text{-}222)]^+Na^-$ can be formed by cooling a solution of Na in ethylamine with cryptand-222. This is a golden yellow, diamagnetic solid which is only stable below -10°c.

Fig:- cryptand-222 ligand

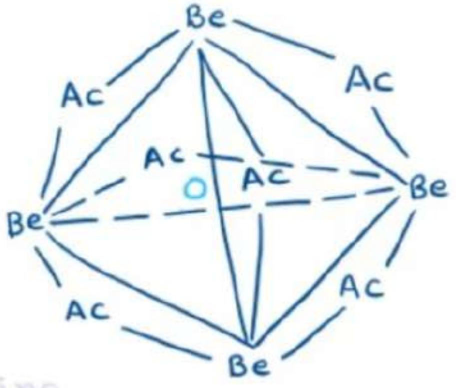
→ Group-2 elements (Alkaline earth metals):→

- Group-2 elements have also lesser tendency to form complexes.
- All the elements in the group form divalent ions, and these are smaller than the corresponding Group 1 ions. Hence Group-2 elements are better at forming complexes than Group 1 elements.
- Be is appreciably smaller than the others, and so Be forms many complexes.
- Mg and Ca also show much tendency to form complex in solution, and these are usually with oxygen-donor ligands.

- The tetrafluoroberyllates, $M_2[BeF_4]$ are well known complex ions and resembles the sulphates in properties. In most case, Be is four coordinate in complexes and tetrahedrally arranged.
- In similar way, $BeCl_2 \cdot D_2$ is also formed where D is an ether, aldehyde or ketone which has oxygen donor atom.
- Many stable chelate complexes of Be are known, inculding Beryllium oxalate, with β-diketones such as acetylacetone and with catechol. In all these complexes, Be^{+2} ion is tetrahedrally coordinated.



Beryllium oxalate $[Be(ox)_2]^{-2}$



Basic beryllium acetate $[Be_4O(CH_3COO)_6]$

- Basic beryllium acetate is formed if $Be(OH)_2$ is evaporated with acetic acid. In structure, a central oxygen atom is surrounded by four beryllium atoms located at the corners of a tetrahedron, with six acetate groups arranged along the six edges of a tetrahedron.
- Basic beryllium is soluble in organic solvent and covalent in nature. Its m.p. is 285°c and b.p. is 330°C.

- Be compounds are sweet in taste but toxic. This is due to their very high solubility and their ability to form complexes with enzymes in body. Be displaces Mg from some enzymes because it has a stronger complexing ability. Contact with the skin causes dermatitis and inhaling dust or smoke causes a disease called berylliosis which is rather like silicosis.
- Mg forms a few halide complexes such as $[NEt_4][MgCl_4]$, but Ca, Sr, and Ba do not.
- Mg forms most important complex of the planat which is chlorophyll.

The Mg is at center of a flat heterocyclic organic ring system called a porphyrin, in which four nitrogen atoms are bonded to Mg. chlorophyll is the green pigment in plants which absorbs light in the red region from sun light, and makes the energy available for photosynthesis. In this process CO_2 is converted into sugars

$$6CO_2 + 6H_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2$$

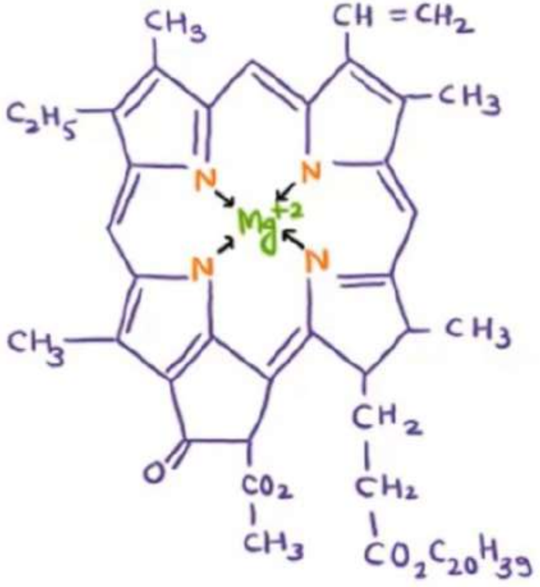


fig:- chlorophyll.

- Photosynthesis is commonly associated with higher plants, alage and certain green, brown, red and purpule bacteria.
- Calcium and the rest of the group only form complexes with Strong complexing agents such as acetylacetone (two donor atoms) or EDTA (six donor atoms).

$$Ca^{+2} + [H_2EDTA]^{-2} \rightarrow [Ca(EDTA)]^{-2} + 2H^+$$

- Titrations are performed using EDTA in buffer solutions to estimate the amounts of Ca^{+2} and Mg^{+2} present to determine the hardness of water.
- Titrations of Ca^{+2} and Mg^{+2} are performed at higher pH than those of many other metals (Zn^{+2}, Cd^{+2}, Pb^{+2}) as their complexes are less stable, and at lower pH values the EDTA is protonated instead of the Ca or Mg complex forming.
- EDTA is sometimes added to detergents to soften the water.
- Group-2 elements also form complexes with crown ethers and cryptates.

→ S-Block elements:→

→ Functions in biosystem:→

- Living organisms require at least 27 elements, of which 15 are metals.
- Metals required in major quantities are K, Mg, Na and Ca.
- Minor quantities of Mn, Fe, Co, Cu, Zn and Mo are required.
- Trace amounts of V, Cr, Sn, Ni and Al are required by at least some organism.
- Bulk quantities of Group 1 and Group 2 metals required to balance electric charge and osmotic pressure of cell.

1. Group 1 elements (Alkali metals):→

- Na and K have similar chemical properties but their biological functions are different. Na^+ are actively expelled from cells, whereas K^+ are not. This ion transport is sometimes called a Sodium pump. Sodium pump involves both the active expulsion of Na^+ and active take-up of K^+.
- In Animal cells, the concentration of K^+ is about 0.15M and the concentration of Na^+ is about 0.01M.
- In body fluids (lymph and blood) the concentrations of K^+ and Na^+ are about 0.003M and 0.15M respectively.
- The transport of ions requires energy, and this is obtained by hydrolysis of ATP. It is estimated that hydrolysis of one ATP molecule to ADP provides enough energy to move three Na^+ ions out of the cell, and two K^+ and one H^+ ions back in to the cell. The mechanism for ion transport involves polyethers natural to the organism.
- The different ratio of Na^+ and K^+ inside and outside cells produces an electrical potential across the cell membrane, which is essential for the functioning of nerve and muscle cells.

- The movement of glucose into cell is associated with Na^+ ions and they enter the cell together. This is favoured by a high concentration gradient. The Na^+ ions entering the cell in this way must be expelled. The movement of amino acids is similar.
- K^+ ions inside the cell are essential for the metabolism of glucose, synthesis of proteins and activations of some enzymes.

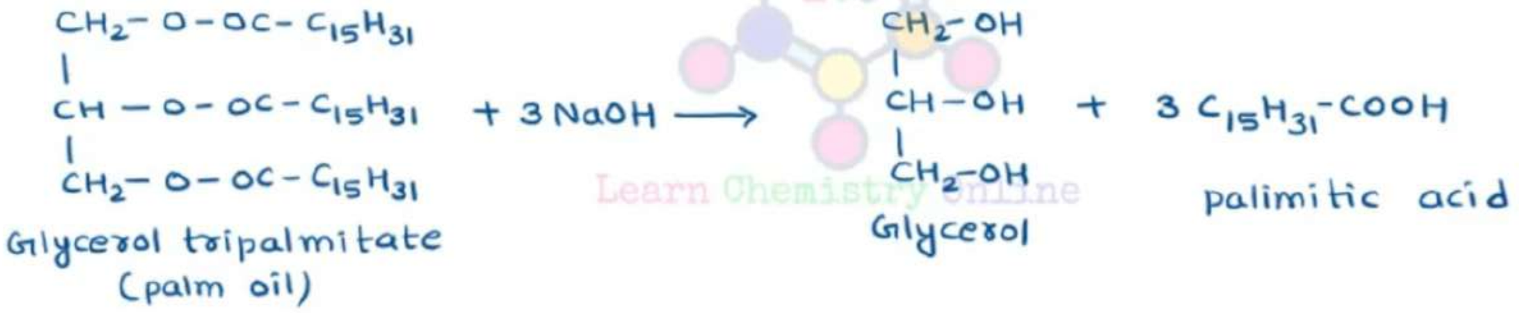
2. Group 2 elements (Alkaline earth metals):-

- Mg^{+2} ions are concentrated in animal cells, and Ca^{+2} are concentrated in the body fluids outside the cell, in much the same way that K^+ concentrates inside the cell and Na^+ outside.
- Mg^{+2} ions from a complex with ATP, and are consituents of phosphohydrolases and phosphotransferases, which are enzymes for reactions involving ATP and energy release. They are also essential for transmission of impulses along nerve fibres.
- Mg^{+2} is important in chlorophyll, in the green parts of plants.
- Ca^{+2} is important in bones and teeth as apatite $Ca_3(PO_4)_2$ and the enemal on teeth as fluoroapatite $[3(Ca_3(PO_4)_2) \cdot CaF_2]$
- Ca^{+2} ions are important in blood clotting, and are required to trigger the concentration of muscles and to maintain the regular heart beat.

→ Alkyls and aryls of s-block elements:→

→ Group 1 elements (Alkali metals):→

- The alkali metals replace hydrogen in organic acids, forming salts such as sodium acetate (sod. ethanoate (CH_3COONa) and potassium benzoate, C_6H_5COOK.
- Soap is a mixture of sodium salts of palmitic, oleic and stearic acids. Palmitic acid $C_{15}H_{31}COOH$ occurs in palm oil, oleic acid $C_{17}H_{33}COOH$ occurs in olive oil and stearic acid $C_{17}H_{35}COOH$ occurs in beef and mutton fat and tallow.
- Soap is made by the saponification (hydrolysis) of naturally occuring oils and fats. These fats and oils are esters of glycerol, and their hydrolysis with NaOH first breaks the ester to glycerol and fatty acids, neutralising the fatty acid to give sodium salts, i.e. the soap.



$$\begin{array}{l} CH_2-O-OC-C_{15}H_{31} \\ | \\ CH-O-OC-C_{15}H_{31} \\ | \\ CH_2-O-OC-C_{15}H_{31} \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3\,C_{15}H_{31}-COOH$$

Glycerol tripalmitate (palm oil) — Glycerol — palimitic acid

$$C_{15}H_{31}-COOH + NaOH \longrightarrow \underset{\text{Soap}}{C_{15}H_{31}-COONa} + H_2O$$

- Lithium stearate is also a 'soap' and is made from LiOH and some natural fat such as tallow.

- Lithium stearate is widely used to thicken hydrocarbon oils (lubricants) and therefore also known as detergent oil. It is also used to make greases for motor vehicles.
- Lithium shows strong tendency to form covalent bond than the other alkali metals.
- Lithium also shows diagonal relationship with magnesium. so, like magnesium, lithium also forms a number of covalent alkyls and aryls which are of great importance in the preparation of organometallic compounds.

Example:- $(LiCH_3)_4$ is typical covalent compound of Lithium. It is covalent, soluble in organic solvents, and can be sublimed or distilled.

- Alkyl lithiums are found in tetrameric or hexameric forms and can be prepared by reaction of alkyl halides (generallyl chlorides) with lithium metal in the presence of solvents such as light petroleum, cyclohexane, toluene or ether.

$$R-Cl + 2Li \longrightarrow Li-R + LiCl$$

- $LiCH_3$ is a electron defficient compound and hence exist as tetrameric (polymeric) molecule $(LiCH_3)_4$.
- Structure is considered as cube in which two tetrahedra, one of $(CH_3)_4$ and the other of Li_4 are interlinked with each other. These tetrahedra have common center
- Each Li-atom is linked with three CH_3 groups and each CH_3-group is linked with three Li-atoms.

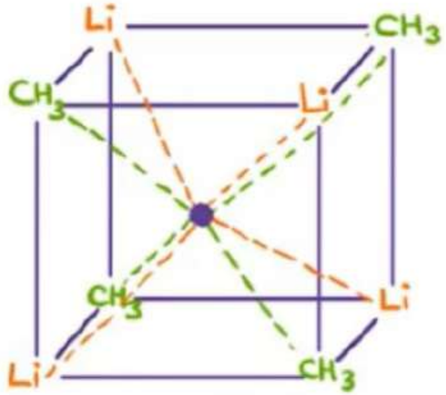


fig:- Structure of tetrameric $(CH_3Li)_4$ molecule.

- Lithium ethyl is also tetrameric in solid $(LiEt)_4$, but is hexameric $(LiEt)_6$ when dissolved in hydrocarbons. The structure of solid is similar to $(LiCH_3)_4$, and in case of hexamer, the Li atoms are arranged in octohedron geometry and six ethyl groups are at faces of octahedron, involving multicenter bonding.
- n-Butyl lithium is also tetrameric in solid $(LiBu)_4$. It is used as a polymerisation catalyst and for alkylation. It is also used as versatile reagent in the laboratory for the synthesis of aromatic derivatives and unsaturated derivatives such as vinyl and allyl lithium. Many of these reactions are similar to grignard reagent.

$$LiBu + ArI \longrightarrow LiAr + BuI \quad (Bu = \text{Butyl},\ Ar = \text{Aryl})$$

$$4\,LiAr + Sn(CH{=}CH)_4 \longrightarrow 4\,LiCH{=}CH_2 + Sn(Ar)_4$$

- Organometallic compounds of lithium can be used for the preparation of wide range of organometallic and organic compounds. (R = alkyl or aryl)

$$3\,LiR + BCl_3 \longrightarrow BR_3 + 3\,LiCl \quad (\text{organoboron compounds})$$

$$4\,LiR + SnCl_4 \longrightarrow SnR_4 + 4\,LiCl \quad (\text{organotin compounds})$$

$$3\,LiR + P(OEt)_3 \longrightarrow PR_3 + 3\,LiOEt \quad (\text{organophosphorus compounds})$$

$$2\,LiR + HgI_2 \longrightarrow HgR_2 + 2\,LiI \quad (\text{organomercury compounds})$$

$$LiR + R'I \longrightarrow R{-}R' + LiI \quad (\text{Hydrocarbon})$$

$$LiR + H^+ \longrightarrow R{-}H + Li^+ \quad (\text{Hydrocarbon})$$

$$LiR + Cl_2 \longrightarrow R{-}Cl + LiCl \quad (\text{Alkyl/Aryl halide})$$

$$LiR + HCONMe_2 \longrightarrow R{-}CHO + LiNMe_2 \quad (\text{Aldehydes})$$

$$LiR + 3CO \longrightarrow R_2CO + 2LiCO \quad \text{(Ketones)}$$

$$LiR + CO_2 \longrightarrow R\text{-}COOH + LiOH \quad \text{(carboxylic acid)}$$

- Alkyls of Na, K, Rb and Cs are usually prepared form the corresponding organomercury compounds.

$$2M + HgR_2 \longrightarrow Hg + 2MR$$

$$M = Na, K, Rb, Cs$$

These compounds are ionic M^+R^-, and are extremely reactive. They catch fire in air, react violently with most compounds except dinitrogen and saturated hydrocarbons are consequently difficult to handle.

→ Group 2 elements (Alkaline earth metals) :→

- Both Be and Mg form an appreciable number of compounds with M–C bonds. but only a few compounds have been isolated for Ca, Sr and Ba.
- Victor Grinard, a Frenchman, won the Nobel Prize for chemistry in 1912 for his work on organomagnesium compounds which are now called Grignard reagents.
- Grignard reagents are most versatile reagents in organic chemistry, and can be used to make alcohols, aldehydes, ketones, carboxylic acids, esters, amides and alkenes. These reagents are very important in inorganic chemistry too.
- Grignard reagents are prepared by the reaction of aryl or alkyl halide (Cl, Br or I) with Mg metal turning in dry organic solvent such as diethyl ether. Water and moisture must be excluded.

- The reaction often has a induction period before it starts, and may require the addition of a crystal of iodine to penetrate the oxide film on metal to make it start.
- very reactive magnesium can be prepared by reducing metal halides with potassium in the presence of KI.

$$\underset{\text{Grignard reagent}}{Mg + R\text{-}Br \xrightarrow[\text{ether}]{\text{dry}} RMgBr} \quad (R = \text{alkyl or aryl})$$

- All Grignard reagents are very reactive. Iodies are most reactive and chlorides are least reactive. Alkyl Grignard reagents are more reactive than aryl Grignard reagents.
- All Grignard reagents are rapidly hydrolysed by water to give the parant hydrocarbons.

$$2RMgBr + 2H_2O \longrightarrow 2RH + Mg(OH)_2 + MgBr_2$$

- Grignard reagents are not stored, but are made and used when required without isolating them. They are normally solvated and polymerised with halogen bridges.
- X-Ray structures of solid $PhMgBr \cdot 2Et_2O$ and $EtMgBr \cdot 2Et_2O$ show that the magnesium is tetrahedrally coordinated by bromine, the organic group and oxygen atom from ether molecules, but in solution there are several species.

Fig:- Structures of some Grignard reagent

- Some typical reactions of Grignard reagents are -

$$RMgBr + CO_2 \xrightarrow{Acid} R-COOH \text{ (carboxylic acid)}$$

$$RMgBr + R_2C=O \xrightarrow{H_2O} R_3-C-OH \text{ (tertiary alcohol)}$$

$$RMgBr + R-CHO \xrightarrow{H_2O} R_2-CH-OH \text{ (Secondary alcohol)}$$

$$RMgBr + HCHO \xrightarrow{H_2O} R-OH \text{ (Primary alcohol)}$$

$$RMgBr + O_2 \xrightarrow{Acid} R-OH \text{ (primary alcohol)}$$

$$RMgBr + S_8 \longrightarrow R-SH \text{ and } R_2S$$

$$RMgBr + I_2 \longrightarrow RI$$

$$RMgBr + H^+ \longrightarrow R-H$$

$$RMgBr + BeCl_2 \longrightarrow BeR_2$$

$$RMgBr + LiR \longrightarrow MgR_2$$

$$RMgBr + BCl_3 \longrightarrow BR_3$$

$$RMgBr + SiCl_4 \longrightarrow RSiCl_3 , R_2SiCl_2 , R_3SiCl , R_4Si$$

Alkyl and Aryl chlorosilanes

- Alkyl and aryl chlorosilanes are commercially important in the manufacture of silicones.

- When $BeCl_2$ reacts with Grignard reagents, then alkyls or aryls of beryllium formed.
- The compound $Be(CH_3)_2$ is dimerised in vapour state and polymerised in the solid.
- The structure of $Be(CH_3)_2$ is similar to $BeCl_2$ but bonding is, however, very different. The bond present is $3c-2e^-$ $(Be-CH_3-Be)$ which is similar to bond in $(BeH_2)_n$
- Organometallic compounds of Be can be prepared by following methods-

$$BeCl_2 + 2CH_3MgCl \xrightarrow{ether} Be(CH_3)_2 \cdot (Et_2O)_n + 2MgCl_2$$

$$BeCl_2 + 2LiEt \xrightarrow{ether} Be(Et)_2 \cdot (Et_2O)_n$$

$$Be + Hg(CH_3)_2 \xrightarrow{warm} Be(CH_3)_2 + Hg$$

- Similar reaction may be used to make dialkyls and diaryls of Mg, Ca, Sr and Ba. The Ca, Sr and Ba compounds are much more reactive than the corresponding magnesium compounds.
- The beryllium alkyls react with $BeCl_2$ to form 'Beryllium Grignard' compounds.

$$Be(CH_3)_2 + BeCl_2 \longrightarrow 2\,CH_3BeCl$$

These are less reactive than the corresponding magnesium (Grignard) reagents.