

CHEMISTRY OF s AND p-BLOCK ELEMENTS-I

s-BLOCK OR GROUP I ELEMENTS

Alkali metals. These belong to group I of s-block of the modern periodic table. Group I elements include, lithium (${}_{3}\text{Li}$), sodium, (${}_{11}\text{Na}$), potassium (${}_{19}\text{K}$), rubidium (${}_{37}\text{Rb}$), cesium (${}_{55}\text{Cs}$) and francium (${}_{87}\text{Fr}$). Francium is radioactive. These elements are called alkali metals because their hydroxides are very strong alkalies.

ELECTRONIC CONFIGURATION

All these elements have one electron in s-orbital of their outermost major shell, *i.e.*, all alkali metals have ns^1 configuration.

The electronic configuration of these elements is given in the following table 3.1.

Table 3.1 Physical Properties Of Alkali Metals

Property	Lithium ${}_{3}\text{Li}$	Sodium ${}_{11}\text{Na}$	Potassium ${}_{19}\text{K}$	Rubidium ${}_{37}\text{Rb}$	Cesium ${}_{55}\text{Cs}$
Atomic number	3	11	19	37	55
Electronic configuration	$[\text{He}]2s^1$	$[\text{Ne}]3s^1$	$[\text{Ar}]4s^1$	$[\text{Kr}]5s^1$	$[\text{Xe}]6s^1$
Atomic radius, Å	1.23	1.57	2.03	2.16	2.35
Ionic radius, Å M^+	0.68	0.97	1.33	1.48	1.69
Ionisation energies					
KJ/g-atom	527	502	426.5	410	380.7
	7305	4569	3075	2661	2426.7
$E^\circ, \text{M}^+/\text{M}(\text{V})$	-3.04	-2.71	-2.92	-2.99	-3.02
Electronegativity	1.0	0.9	0.8	0.8	0.7
Heat of atomisation	159	108.8	87.9	81.6	78
(at 298 K, 1 atm), KJ mol^{-1}					
Atomic volume	12.97	23.68	45.39	55.80	69.95
Atomic weight	6.94	22.99	39.10	85.47	132.91
Density, g/cc	0.53	0.97	0.86	1.53	1.90
Melting point, K	455	371	336.5	312	301.5
Boiling point, K	1609	1156	1032	973	943
Colour of the flame	Carmine red	Yellow	Violet	Reddish violet	Blue
Ionic conductance of M^+ ions, Ω^{-1}	33.5	43.5	64.6	67.5	68.0

GENERAL TENDENCIES OR TRENDS IN PHYSICAL PROPERTIES

All alkali metals resemble closely in their physical and chemical properties because of their identical ns^1 configuration. The important physical properties of these elements are given in the table 3.1. The properties of francium are not included in the table because very little is known about this recently discovered radioactive element. The general trend in the physical properties of these elements can be explained in terms of :

(i) loose binding of valence s -electron and (ii) size of their atoms and ions.

Following physical properties of alkali metals can be explained on these concepts :

1. Atomic and ionic radii. Atoms of the alkali metals have the largest size in their respective periods. Even the $+1$ ions formed by the alkali metals by the loss of s -electron have a large size.

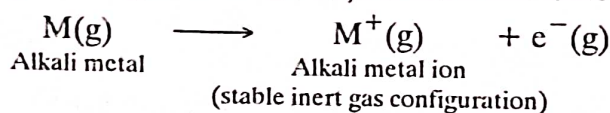
Within the group, the atomic as well as ionic radii of alkali metals increase with increase in atomic number. It is because of the increase in the number of energy shells. For example, the size of Na atom (having 3 shells) is larger than the size of lithium atom (having 2 shells).

2. Ionisation potential. On account of large atomic size, the outermost electron in an alkali metal is loosely held. Consequently alkali metals have low ionisation potentials.

On moving down the group, the ionisation potential decreases. It is because the s -electrons of outermost shell are getting away from the nucleus due to the addition of new shells. Therefore, the attractive pull exerted by the nucleus on the outermost electron decreases. Hence, electron can be removed by expending less energy.

3. Oxidation state or valency. All alkali metals form unipositive ions.

Reasons. Due to their low ionisation energies, alkali metals readily lose an electron from the outermost s -orbital and attain stable noble gas configuration. Hence, these metals form univalent positive ions.



Alkali metals do not form dipositive ions because the second electron has to be pulled from noble gas core (fully filled orbitals are most stable due to symmetry and high exchange energy).

4. Electropositive or metallic character. The alkali metals have a greater tendency to lose electrons due to their low I.P. values. Consequently, these are strongly electropositive or metallic in character.

Down the group, the I.P. decreases and the tendency to lose electrons increases in the same order. Hence, the electropositive or metallic character increases in the downward direction.

5. These metals have silvery white lustre. All alkali metals have low ionisation energy because of their large size. When a beam of light strikes the metal surface, the electrical component of light wave interacts with the valence s -electrons of the metal. As a result, the valence s -electrons set into oscillatory motion. These moving electrons radiate electromagnetic energy in the form of light like other charged objects. The light reflected from metal surface makes them show lustre.

6. Photoelectric effect. When light of threshold energy falls upon a metallic face, it causes the emission of electrons from the metal. The phenomenon is called photoelectric effect.

7. These metals are malleable and ductile. Due to low ionisation energy, alkali metal ions (M^+) are held together by valence electron clouds in their metal lattices by electrostatic force of attraction. These forces are uniform in all directions and there are no preferred orientations of metal ions. Hence, the metal ions can easily move from one lattice position (or layer) to another. Thus, these can be drawn into wires (ductile) and beaten into sheets (malleable).

8. Soft character and low melting and boiling point. The experimental data of atomic volume and atomic radii of these elements indicate that these have the largest size in their atomic and ionic state. As a result, one valence s -electron per metal atom results in the loosely packed metal lattices of alkali metals.

Thus : (i) These metals are soft and can be cut with a knife.

(ii) Since small amount of energy is needed to break the weak metallic bonds, these metals have low melting and boiling points. This trend decreases down the group because the size of atoms increases with increase in atomic number in a group.

9. **Electronegativity and electron affinity.** Due to their strong electropositive character, alkali metals have little tendency to attract or accept electrons. Therefore, they have very low electronegativity and electron affinity values.

10. **Atomic volume.** As we go down the group, the atomic radius goes on increasing because of the increase in number of shells. Thus, the atomic volume of elements increases down the group.

11. **Density.** Mass per unit volume is called density of an element. As we go down the group, the atomic volume goes on increasing and hence atomic radii also increase. Atomic mass of elements also increase. The overall effect is that density increases. However, potassium has less density than sodium. It might be due to some structural changes in potassium.

12. **Electrical conductivity.** (a) Due to their low ionisation energy, these metal ions are embedded in a sea of electrons. This sea is very diffuse. So, the bonding in the metal is relatively weak. Hence the valence electrons move freely from one metal ion to other. These movements of electrons are responsible for the high electrical conductivity of the metals.

(b) **Covalent bonding.** Alkali metals also form covalent compounds.

For example :

(i) The diatomic molecules like Na_2 , K_2 , Cs_2 etc. are formed to some extent in their vapour states. The metal atoms are bonded through covalent bonds in these molecules. The strength of the covalent bond decreases down the group because of the increase in size of atoms down the group.

(ii) Organometallic compounds like CH_3Li , $\text{C}_2\text{H}_5\text{Li}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Na}$ etc. possess covalent bond between metal and the carbon atom.

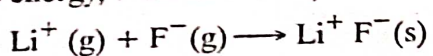
(iii) Due to small size of Li^+ ion, these get heavily hydrated in aqueous solutions as compared to large sized Cs^+ ion (aq). Hence conductivity of Li^+ ion in aqueous solution is less than that of Cs^+ ions.

13. **Ionic compound formation.** Due to low ionisation energy, these metals are highly electropositive. So, these react with highly electronegative elements (halogens, chalcogens etc.) through transfer of electrons. The compounds so formed have high difference of electronegativity. Hence, these form ionic compounds.

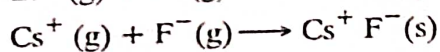
14. **Lattice energies.** Alkali metals form ionic solids which consist of cations and anions. The lattice energy of ionic solid is defined as :

'The energy released when one mole of a crystal is formed from the constituent ions present in the gaseous state.'

Since the cations and anions are held together by strong electrostatic forces of attraction, a large amount of energy called lattice energy is released. Thus, ionic solids have minimum energy (because of the release of high lattice energy) and maximum stability. For example, LiF (lattice energy, 1034 kJ mol^{-1}) is more stable than CsF (lattice energy, $743.9 \text{ kJ mole}^{-1}$).



$$\Delta H = \text{Lattice energy of LiF} = -1034 \text{ kJ}$$



$$\Delta H = \text{Lattice energy of CsF} = -743.9 \text{ kJ}$$

According to 'Coulomb's law, the coulombic forces of attraction vary directly as the product of charge (valency) on the ions. Thus, greater the charge on the ions, greater should be the lattice energy. Thus, lattice energy of the ionic solids decreases in the order.

bi-bivalent ionic solids like

magnesium sulphide (Mg^{2+} , S^{2-})

bi-univalent ionic solids like

calcium fluoride (Ca^{2+} , 2F^-) > uni-univalent ionic solids like
lithium fluoride (Li^+F^-)

For ionic solids

(i) having cations of same charge (valency) and (ii) having same anion the lattice energy decreases with increase in size of the cation.

For example, for the same anion (I^-), the lattice energy of lithium iodide (Li^+I^-) is greater than lattice energy of cesium iodide (Cs^+I^-) because the size of Li^+ is smaller than that of Cs^+ ion. Thus, we conclude that

'the lattice energies of ionic compounds of alkali metals having a same given anion decreases with increase in atomic number of the alkali metal.'

15. Colouration of the flame. All these elements impart colour to the bunsen flame. When energy is supplied to these elements or their salts (especially chlorides because of their more volatile nature), their electrons get excited to higher energy states. When such electrons fall back to their original energy levels, the extra energy is emitted in the form of visible light.

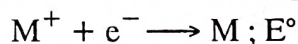
For the same excitation energy (of bunsen flame), the energy level to which the electron in lithium (higher ionisation energy, I.E.) rises is lower than the level to which the electron in sodium (lower I.E.) rises and this in turn is lower than level to which the electron on potassium rises and so on. As a result

(i) When the electron returns to the ground state, the energy released is lowest in Li and increases in the order $\text{Li} \rightarrow \text{Cs}$.

(ii) The frequency of light emitted in the bunsen flame will be minimum in case of Li and thus it will impart red colour to the flame. It increases in the order, $\text{Li} \rightarrow \text{Cs}$. Thus, the colour of flame is golden yellow in Na, pale violet in K and violet in rubidium and cesium.

16. Heat of atomisation. As we go down the group, the size of alkali metal atom goes on increasing. Thus, the distance between the adjacent atoms goes on increasing and the forces holding the metal atoms in their crystal lattice goes on decreasing. Hence the energy needed to convert them into atoms, i.e., heat of atomisation goes on decreasing down the group.

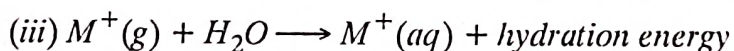
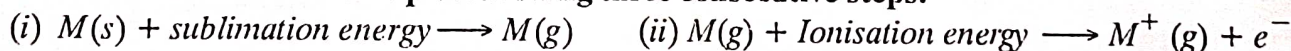
17. Reducing agent. Because of their large size, these elements have low ionisation energy. Thus, these have a great tendency to lose valence *s*-electron. Hence, these act as strong reducing agents. Their reducing power is measured in terms of their standard reduction potentials.



Greater the negative value of standard electrode reduction potential, stronger will be the reducing agent. For example, potassium ($\text{E}^\circ = -2.92 \text{ V}$) is stronger reducing agent than sodium ($\text{E}^\circ = -2.71 \text{ V}$).

Anomalous behaviour of lithium. Smaller size and higher ionisation energy of lithium as compared to other alkali metals indicates that it should be the lowest reducing agent. But the E° value of lithium (-3.04 V) indicates that it is as strong reducing agent as cesium ($\text{E}^\circ = -3.021 \text{ V}$). The discrepancy can be explained as follows :

The concept of ionisation energy is unable to explain fully the reducing power of an element because it is only a measure of the tendency of the neutral gaseous atom to form a gaseous ion. **The reducing power of an element is decided with the help of following three consecutive steps.**



In alkali metals

(a) The sublimation energy of all the elements is almost the same.

(b) Lithium has the highest ionisation energy while it decreases down the group.

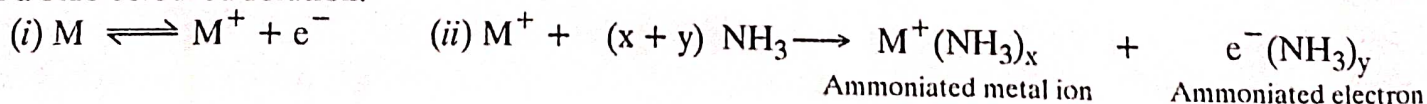
(c) Li^+ ion gets heavily hydrated and liberates highest hydration energy because of following reasons:

(i) The *smallest size of Li^+ ion causes maximum charge density around it.* As a result, maximum water molecules get attached to this ion.

(ii) In $\text{Li}^+(1s^2)$ 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 gaseous $\text{Li}(g)$ atom. Hence, it acts as the most powerful reducing agent in aqueous solution.

Trend down the group. Except lithium, the negative value of the reduction potential increases down the group. Thus, the power to act as reducing agent increases down the group.

18. Solution of alkali metals in liquid ammonia. All alkali metals (M), dissolve in liquid ammonia to form a blue coloured solution.



1. The above solution is blue due to ammoniated electrons. The electrons absorb photon and get excited to a higher energy level. As a result, an absorption band which has a maxima of 5000\AA is obtained which corresponds to blue colour. The colour is independent to nature of metal.

2. The solution is good conductor of electricity due to the presence of ammoniated electrons and ammoniated metal ions.

3. The dilute solution consists of free unpaired ammoniated electrons which are responsible for the reducing nature and paramagnetism of blue solution.

4. When more alkali metal is added to blue solution, a bronze coloured phase separates out and floats on the blue solution.

Further addition of alkali metal results in disappearance of blue colour and complete conversion to bronze solution takes place. This solution exhibits :

(i) very low densities,

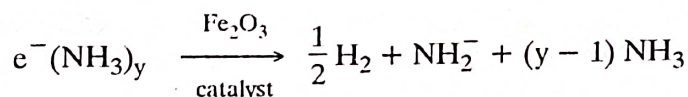
(ii) metallic lustre,

(iii) magnetic susceptibilities similar to pure metals and

(iv) metallic conductance. It is because the ammoniated metal ion and electrons form bonds like metallic bonds to give aggregates, M_2, M_3 etc.

5. Bronze solution on evaporation gives back the original metal. This suggests the reversible nature of the reaction.

6. The dilute solutions are metastable which give hydrogen and amide ions in the presence of ferric oxide as catalyst.



7. The density of blue solution is quite similar to that of pure ammonia.

8. These metal solutions in NH_3 are stronger reducing agents than that in water because the oxidising power of water is greater than that of ammonia.

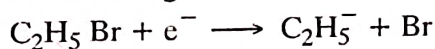
For example : (i) It reduces sodium nitrate to sodium hyponitrite.

(ii) It reduces metal halides to metals.

(iii) It removes hydrogen atom from monosubstituted acetylenes.



(iv) It removes halogen atom from organic halides.



CHEMICAL PROPERTIES AND TRENDS

All the alkali metals are highly reactive because of their :

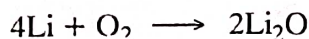
(i) low electronegativity (ii) low first ionisation energy (iii) low heat of atomisation.

These elements especially react with highly electronegative elements like chlorine and oxygen. Their important chemical properties are explained below :

1. Oxides. (i) All alkali metals react rapidly with molecular oxygen (or air) and get *tarnished*. That is why these elements are kept under hydrocarbon solvents like kerosene oil.

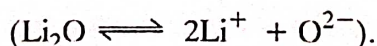
(ii) The nature of the oxide formed depends upon the nature of alkali metal. For example :

(a) Lithium burns in oxygen to form lithium monoxide only. No higher oxide is formed.

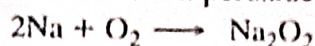


Lithium monoxide

Reason. Li^+ ion is a small sized ion. It has a strong positive field around it. It combines with oxide anion and restricts the spread of negative charge towards another oxygen atom. As a result, it prevents the formation of higher oxide. Li_2O is ionic

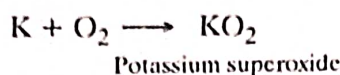


(b) Sodium burns in oxygen to form sodium peroxide and no superoxide is formed.



Reason. Na^+ ion is larger in size than Li^+ ion. The positive field around Na^+ ion is weaker than Li^+ ion. This positive field is so weak that it cannot prevent the conversion of oxide anion (O^{2-}) into a peroxide ion (O_2^{2-}). However, it is strong enough to prevent the conversion of peroxide to superoxide. The peroxide contains $(-\text{O}-\text{O}-)^{2-}$ ion.

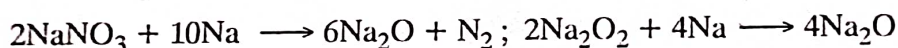
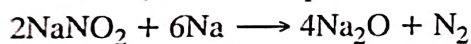
(c) Potassium, rubidium and cesium react with oxygen to form superoxides, viz. KO_2 , RbO_2 and CsO_2 .



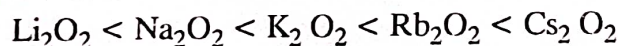
Reason to form superoxide. K, Rb and Cs ions are large sized ions. These have, thus, very weak positive field around them. This positive field is so weak that it cannot prevent the conversion of peroxide (O_2^{2-}) anion to superoxide anion (O_2^-).

Nature of superoxides. The superoxides have tetragonal lattice of calcium carbide type. The superoxide anion $(\ddot{\text{O}}-\ddot{\text{O}})^-$ contains three electron bond. Thus, it is *paramagnetic* and *coloured*.

Nature of normal oxides. These have antifluorite oxide structure. Only lithium metal forms normal oxide (Li_2O) by the direct reactions with oxygen. Normal oxides of other alkali metals are formed indirectly i.e., by the reduction of their nitrites, nitrates or peroxide with metal itself.



Stability. We know that binary compounds of alkali metals with oxygen are monoxides (M_2O), peroxides (M_2O_2) and super oxide (MO_2). Their stability increases with decreasing charge density on cations and increasing charge density on the anions :



and monoxide > peroxides > superoxides.

Reasons for above trend of stability

(i) The negative charge on O_2 (or O_2^{2-}) ions gets polarised on one oxygen atom because of high polarizing power of small sized Li^+ ions. As a result, the other oxygen atom sets free from the diatomic anions.

(ii) The larger sized cations like Cs^+ form a close packed lattice with larger sized anions. As a result, their lattice energy increases.

Basic nature. All monoxides are soluble in water and form strongly alkaline solutions. Their alkalinity increases down the group.

Oxidants. Alkali metal peroxides act as powerful oxidising agents. The superoxides are even more powerful oxidants than fluorine.

Colour. The oxides of alkali metals are obtained by the direct combination of elements in ammonia (under high pressure and low temperature for Li^+ and Na^+ superoxides). The colour of these oxides deepens with the increase in the molecular mass of their compounds. (See table 3.2).

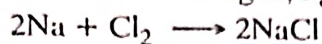
II. Hydroxides. The alkali metals react violently with water (except lithium which reacts with hissing sound) to form hydroxides. The reactions are exothermic which help in the liberation of electrons (reducing agents) from alkali metals which reduce H^+ ions (in H_2O) to hydrogen gas. In higher alkali metals like Na , K etc., hydrogen evolved also catches fire. This fire should not be extinguished with water but with carbon tetrachloride (pyrene) which forms a protective layer over the fire.

The hydroxides of alkali metals are the strongest bases. The strength of the base depends upon the ease with which the hydroxide ions get separated from the alkali metal cation. Following factors are responsible for the separation of OH^- ions from cations.

(i) *Internuclear distance between metal atom and the oxygen atom of hydroxide ion ($-\text{OH}^-$)*. As we move down the group from Li to Cs, the cation size increases. Thus, the internuclear distance between metal atom and the oxygen atom of OH^- ion increases. This results in easier separation of OH^- ion from the metal. Hence the strength of bases increases from LiOH to CsOH .

(ii) *Polarity of bond*. Greater the polarity of alkali metal $-\text{OH}$ bond, greater is the ease with which OH^- ions are formed. Since the electronegativity of alkali metals decreases down the group, the electronegativity difference between alkali metal and oxygen atom of OH group increases. This results in easier separation of hydroxide ions from the metal ion. Hence strength of the bases increases from LiOH to CsOH .

III. Halides. Alkali metals readily combine with halogens to form metal halides having the formula M^+X^- where M is an alkali metal and X is the halogen, e.g.,



The ease with which alkali metals form their halides increases in moving down the group from Li to Cs.

Highly electropositive alkali metals (M) react with highly electronegative halogens (X where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) to form metal halides, M^+X^- . M^+X^- are ideal ionic compounds in which ions are present even in solid state. The structure and stability of these compounds can thus be explained on the basis of their lattice energies and radius ratio effects.

Table 3.2.

Different metal oxides	Colour		Different oxides of the same metal	Colour
	in cold	in hot		
Li_2O	White	White	Na_2O	White
K_2O	White	Pale yellow	Na_2O_2	Pale yellow
Rb_2O	Pale yellow	Golden yellow	NaO_2	Yellow
Cs_2O	Orange red	Purple and then black		

(i) **Lattice energy*** effect. Lithium fluoride (LiF) is insoluble in water while other alkali metal fluorides are soluble in water. It is because of the combination of very small Li^+ ion with very small F^- ion. The lattice energy of LiF is very high and hence it does not dissolve in water.

(ii) **Radius ratio**** effect. For the same halide ion (Cl^-), the co-ordination number of alkali metal ion increases with an increase in the size of the cation.

For example :

(a) The radius ratio of CsCl ($\text{Cs}^+/\text{Cl}^- = 0.93$) allows a co-ordination number of 8.

(b) The radius ratio of NaCl ($\text{Na}^+/\text{Cl}^- = 0.52$) allows a co-ordination number of 6.

(c) **Covalent character.** According to Fajan's rule, the covalent character of the halides increases with decreasing cationic size ($\text{Li}^+ > \text{Na}^+ > \text{Rb}^+$ etc.) and increasing anionic size ($\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$). Thus, LiF , LiCl , LiBr , LiI are soluble in alcohol and pyridine but not in water. KI is soluble in alcohol but KCl and NaI are not. Their solubility in water is in the following order :

(i) $\text{LiF} < \text{NaF} < \text{KF} < \text{KbF} < \text{CsF}$

It is because the lattice energy of LiF is the highest and that of the CsF is the least among above alkali metal fluorides. Similarly :

(ii) $\text{LiF} < \text{LiCl} < \text{LiBr} < \text{LiI}$

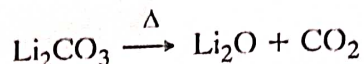
(iii) $\text{KF} < \text{KCl} < \text{KBr} < \text{KI}$

* Lattice energy is the amount of energy required to convert one mole of ionic lattice into gaseous ions. The lattices with smaller ions have higher lattice energies.

** Radius ratio is the ratio of size of cation and anion in an ionic solid.

Polyhalides formation. Except Li^+ and Na^+ , other alkali metal ions form polyhalides with I_3^- (e.g., KI_3), ICl_2^{2-} , ICl_4^- , IBrF^- etc. Li^+ and Na^+ ions do not form polyhalides because the charge density on small sized Li^+ and Na^+ ions polarizes the polyatomic anions.

IV. Carbonates. Alkali metals form carbonates of general formula, M_2CO_3 . These carbonates are very stable because of their highly electropositive and basic nature. These melt without decomposition. However, among all these carbonates, only lithium carbonate (Li_2CO_3) decomposes on heating to form lithium oxide Li_2O and carbon dioxide.

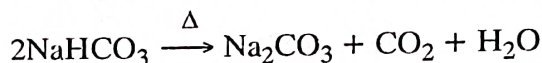


Reason. Li^+ ion is small in size and forms Li_2O lattice which is more stable than Li_2CO_3 lattice. Other alkali metals (Na, K, Rb, Cs) are larger in size than lithium. So, their M_2O lattices are less stable than M_2CO_3 lattices. Hence M_2CO_3 ($\text{M} = \text{Na, K, Rb, Cs}$) does not decompose.

However, at temperatures over 1273 K, these decompose into oxides.

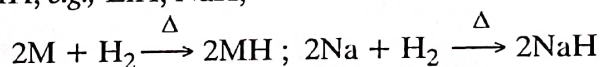
Solubility. Due to small size of Li^+ , Li_2CO_3 has more covalent character. So, it is insoluble in water while other carbonates are freely soluble in water. The solubility of carbonates increases down the group.

Since alkali metals are highly basic, these also form solid bicarbonates which decompose to carbonates on gentle heating.



Lithium does not form solid bicarbonate but exists in solution form. All bicarbonates are soluble in water and form alkaline solution.

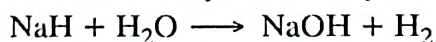
V. Hydrides. All alkali metals combine with dry hydrogen on heating to form white crystalline ionic hydrides of the general formula MH , e.g., LiH , NaH ,



Ionic character. The ionic character of these hydrides increases down the group from LiH to CsH . It is because as we go down the group, the ionisation potential of the elements decreases and electrons are easily available to hydrogen to form stable hydride ion $\text{H}^- (1s^2)$.

Stability. The stability of these hydrides decreases from LiH to CsH . It is because as we go down the group, the size of central alkali metal increases and the bond between central atom and hydrogen increases. Longer the bond, weaker it is.

Action with water. These hydrides are readily attacked by water to form hydrogen, e.g.,



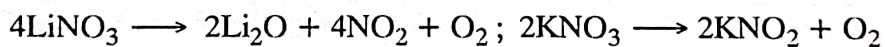
The reactivity of hydrides increases down the group. It is because, the size of $\text{M}-\text{H}$ bond, increases down the group. Longer the bond, weaker it is and breaks easily. Thus, LiH is least reactive while CsH is highly reactive.

ANOMALOUS BEHAVIOUR OF LITHIUM

It has been observed that the properties of lithium metal differ from other alkali metals (congeners) in many respects. The *main reasons for its different behaviour* as compared to other alkali metals are :

- (i) The size of Li-atom and Li^+ ion is **extremely small** as compared to other alkali metals.
- (ii) The *electronegativity and ionisation potential* of Li-atom is the highest among the alkali metals.
- (iii) **Polarizing power** of Li^+ - ion is highest among alkali metals. Thus, its tendency for covalent bond formation and solvation increases. The increased covalent character of Li-compounds makes them more soluble in organic (non-polar) solvents. Other alkali metal compounds are, however, not soluble in the organic solvents. Based on above reasons, lithium differs from its congeners (other alkali metals) in following respects.

1. **Hardness.** It is harder and lighter than other alkali metals.
2. **M.pt. and b.pt.** Its melting and boiling points are higher as compared to other alkali metals. When heated in dry air, it melts without losing brilliance.
3. **Action with oxygen.** It reacts with oxygen above 373 K to form lithium oxide (Li_2O). Other alkali metals, however, form peroxides and superoxides also. It is because of the smallest size of lithium among alkali metals.
4. **Solubility of salts.** (a) *Lithium oxide* dissolves in water slowly while other alkali metal oxides react vigorously.
(b) *Lithium hydroxide* is a weak base and is sparingly soluble in water. Other alkali metal hydroxides are strong alkalies and are highly soluble in water.
(c) LiF , Li_2CO_3 and Li_3PO_4 are insoluble in water but the corresponding compounds of other alkali metals are soluble.
(d) **Lithium chloride (LiCl).** It is deliquescent and is soluble in organic solvents like pyridine and alcohol. The solubility in these solvents is due to the covalent nature of LiCl .
(e) **Lithium perchlorate (LiClO_4).** Due to strong solvation of small sized Li^+ - ion, it is soluble in ethyl acetate, alcohol and acetone. The perchlorates of other alkali metals are not soluble in above solvents because of the large size of their ions.
5. **Action with small anions.** Small anions like *hydrides* (H^-), *carbides* (C^{4-}) and *nitrides* (N^{3-}) react with small Li^+ -ions to give stable compounds because of the liberation of high lattice energy. Thus lithium hydride is far more stable to heat than hydrides of other alkali metals.
6. **Action with acetylene (ethyne).** When acetylene gas is passed over heated lithium, *lithium acetylide* is not formed. Other alkali metals, however, form acetylides.
7. **Action with ammonia.** When heated with ammonia, lithium forms *lithium imide* (Li_2NH). The other alkali metals (M) form *amides*, MNH_2 .
8. **Formation of double salts.** Li_2SO_4 does not form double salts while other alkali metal sulphates form double salts like alum [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$].
9. **Formation of complexes.** Li^+ -ion forms complexes with water (called hydrates), ammonia (called ammines) etc. It also forms a large number of organolithium compounds.
10. **Stability of salts.** (a) *Lithium hydrogen sulphide* (LiHS) is thermally unstable while hydrosulphides of other alkali metals are stable and fuse without decomposition.
(b) *Lithium nitrate* decomposes on heating to give Li_2O , NO_2 and O_2 while other alkali metal nitrates give nitrites and oxygen.



Reason. The small size of Li^+ makes Li_2O lattice more stable than LiNO_3 lattice. On the other hand, the larger size of other alkali metal ions makes the M_2O lattice less stable than MNO_3 . However, the MNO_2 lattice being more stable than M_2O lattice, their nitrates form MNO_2 and O_2 .

(c) *Lithium carbonate* (Li_2CO_3) is thermally unstable and decomposes on heating to give Li_2O and CO_2 . It is because the small size of Li^+ -ion makes Li_2O lattice more stable than Li_2CO_3 lattice. The larger size of other alkali metal ions makes the M_2O lattice less stable than M_2CO_3 lattice. Thus M_2CO_3 does not decompose.

(d) *Lithium hydroxide* (LiOH) is thermally unstable and decomposes to Li_2O and water at red heat. Hydroxides of other alkali metals sublime unchanged as $(\text{MOH})_2$.

COMPLEXATION OF ALKALI METAL IONS

Although alkali metal cations are not conducive to co-ordinate with ligands because of their large size and electron configuration, yet chelating groups like salicylaldehyde, crown ethers, cryptands etc., do impose

some acceptor properties on them. As a result, covalent compounds are formed. The stability of these covalent compounds is influenced by the increasing atomic number of alkali metals. It is because as we go down the alkali metal group :

(i) There is an increased ease of ionisation which weakens the tendency to accept electrons.

(ii) There is an increase in the size of atom which raises the maximum co-ordination number.

This explains well the stability of 4-covalent compounds of sodium and 6-covalent compounds of potassium, rubidium and caesium.

Crown ethers. These are the macrocyclic polyethers which contain the repeating units $(-CH_2CH_2-O)_n$.

Cryptands. These are the polycyclic compounds having chiefly donor atoms like O, S, N (present in the bridges) which bind the metals and most ions very strongly.

Following procedure is used to name crown ethers.

1. The first number in the crown ether {e.g., dibenzo [18] - crown-6} name designates the number of atoms in the ring (usually given in the square brackets i.e., []). In the above example, [18] represents 18-membered macrocyclic ring.

2. The second number in the crown ether name designates number of oxygen (or other donor) atoms. For example, in above (1) crown ether, 6 represents number of oxygen atoms.

3. The substituents in the crown ether are denoted by a prefix such as benzo, dicyclohexano etc. For example, in above (1) crown ether, dibenzo represents two benzo substituents.

Nomenclature of Cryptands. The cryptands, which present a more spherical, rather than crown like structure have some what different nomenclature.

Each host is denoted by a series of numbers indicating the number of donor atoms in each of the bridges between the bridge head atoms. Thus fig 3.1 is called [2, 2, 2] cryptand*.

Cryptands (Macrocyclic ligands). These are the macrocyclic ligands which contain the intermolecular cavities of three dimensional shape (crypts). Their complexes are called cryptates. In their complexes with alkali and alkaline earth cations, these show much enhanced stabilities with respect to crown ethers. The effect is called cryptate effect. For example :

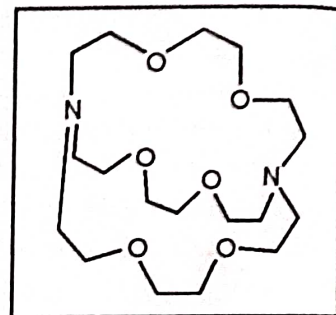


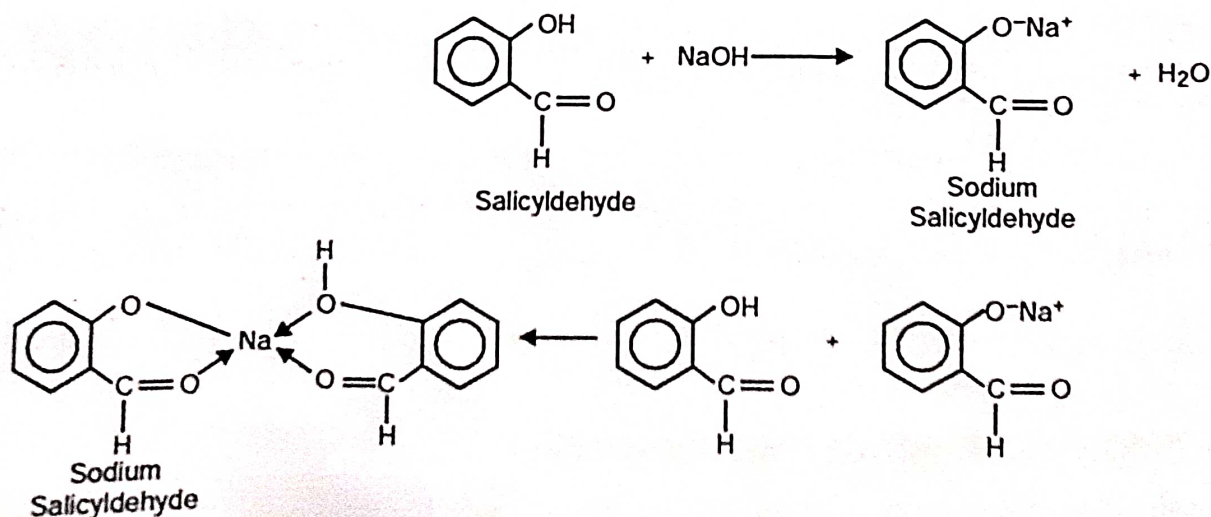
Fig. 3.1.

“the K^+ -complex of [2, 2, 2] cryptand is more stable than the corresponding diaza [18] crown-6 complex by a factor of 105. It is also more stable than valinomycin (see page 54) potassium complex by a factor of 104.”

The stability of 4-covalent compounds of sodium and 6-covalent compounds of potassium, rubidium and cesium

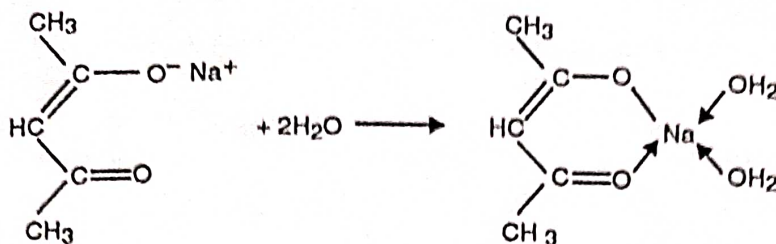
(a) 4-covalent compounds of sodium.

(1) When sodium hydroxide is added to salicyldehyde, a sodium salt of the salicyldehyde is formed which takes up a further molecule of salicyldehyde to form a covalent compound.



*Because there are two (2), two (2) and two O-atoms between bridged atoms, N and N.

(2) When anhydrous sodium derivative of acetyl acetone is hydrated, a dihydrate is formed. This hydrate is a covalent compound because it is soluble in non-polar solvents like toluene.



(b) 6-Covalent compounds. A 6-covalent compound of cesium, tris (salicyldehidato) cesium is shown in Fig. 3.2.

M^+ ions of alkali metals have large size and low charge. So, these are very weakly complexed by simple anions.

For example, F^- ions in 1 M fluoride solution, where the order falls from Li to Cs, chelation is essential to form a complex. But lithium is exception to it. Alkali metals form complexes with nitrophenol, β -diketones etc. Some of these complexes indicate ionic nature while others covalent. For example, although metal-ligand bonds in hexafluoroacetyl acetate complexes are doubtless quite polar yet these complexes are sublimable at 475 K. Anhydrous β -diketonates do not dissolve in organic solvents. So, these are ionic in nature. But in the presence of co-ordinating ligands including water, the complexes attain covalent nature and become soluble in the organic solvents including hydrocarbons.

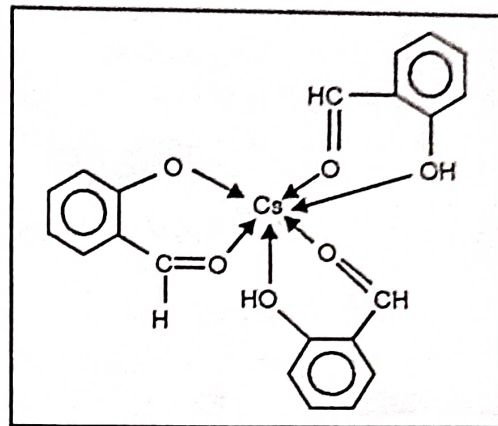


Fig. 3.2. Tris (salicyldehidato) cesium

For example, tetramethylethylene diamine lithium hexafluoroacetylacetate is soluble in benzene while sodium benzoylacetylacetate is soluble in toluene. This behaviour is helpful for solvent extraction procedures for alkali metal ions. For example :

(i) Cs^+ can be extracted from aqueous solutions with the help of 1, 1, 1-trifluoro-3 (2-thionyl) acetone (TTA) in $MeNO_2$ -hydrocarbons.

(ii) Trioctylphosphine oxide adduct $Li(C_6H_5COCHCOC_6H_5) [OP(octyl)_3]_2$ can be extracted from aqueous solutions into p-xylene. This process can also be used to separate lithium from other alkali metal ions.

Lithium forms many complexes with ethers, amines, carboxylates, dialkylamides, alkoxides and many other ligands having structures usually quite different from those of the other M^+ ions. In many compounds, Li has co-ordination number 3 to 7. Some examples are :

(i) $LiNO_3$ (diacetamide) is five co-ordinate with $Li-NO_3$.

(ii) $LiBF_4 [OP(NMe_2)_3]$ is soluble in benzene and has strong Li-F interactions.

(iii) $LiI-(en)_3$ (en = ethylenediamine, $CH_2NH_2NH_2CH_2$) has Li^+ in a distorted octahedron of N-atoms.

Compounds of alkali metals with crown ethers and cryptates (or cryptands)

It has been found that ethers, polyethers and particularly macrocyclic poly ethers* (termed crown ethers) such as cyclohexyl-18-crown-6** [Fig. 3.3] form stable complexes with alkali metal cations (M^+). This

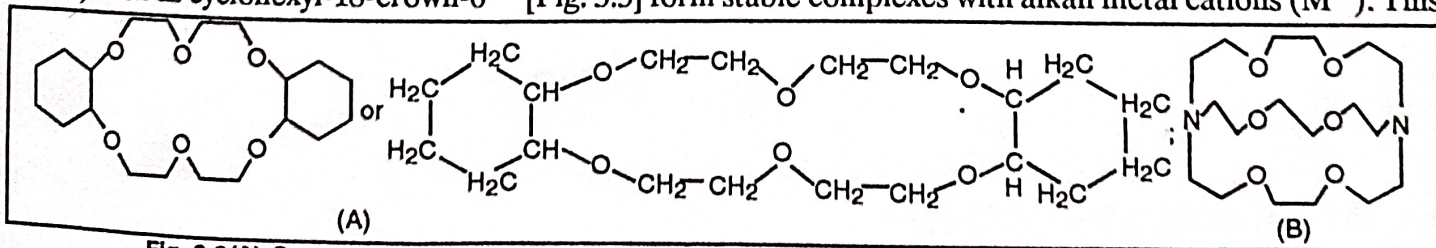


Fig. 3.3(A) Crown ether dicyclohexyl-18-Crown-6. (B) Structure of a Cryptate or 2, 2, 2-crypt ligand

*Macrocyclic polyethers were developed for the first time by C.J. Pederson (1960)

**In this crown ether, the prefix numeral 18 indicates the number of atoms in the heterocyclic ring while the suffix numeral 6 indicates the number of oxygen atoms. So, this crown ether is 18-membered, ring with six oxygen atoms.

stability depends upon the relative sizes of the polyhedra (hole size) and the concerned alkali metal ions. In these polyethers, the oxygen atoms point inward towards the metal ion with the rest of the molecule forming a crown shaped arrangement. These are hence named as crown ethers. The extra stability of crown ether complexes with alkali metal ions is attributed to their close fit. The size of the hole in which M^+ ion fits in, depends on the size of crown ether. For example, crown-4, crown-5 and crown-6 selectively complexes Li^+ , Na^+ and K^+ ions respectively. The solubility of alkali metal salts in organic solvents (say ethers) is greatly increased by these ligands. It is achieved by the large hydrophobic organic part in the crown ether.

$(C_2H_5)_2O$
Crown - 6 + $K \longrightarrow [K (Crown - 6)] + e^-$ (solvated). The effectiveness of tetrahydrofuran (THF) and dimethyl ethers of ethylene and diethylene glycols as media for reactions involving Na metal, may be due in part to slight solubility of Na but the driving force is infact the complexation of Na^+ by the chelate ethers.

Crown ethers have large complexity constants for alkali metals.

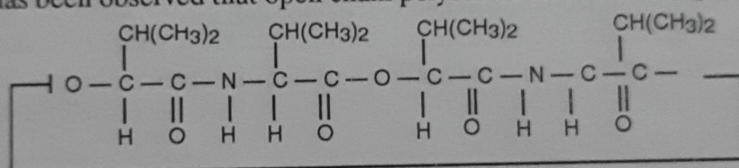
For cyclohexyl-crown-6 ether, the equilibrium constants are in the order $K^+ > Rb^+ >$

$Cs^+ > Na^+ > Li^+$. Crown ether (18-C-6) with side chain terminating in an NH_2 group is selective for Na^+ and K^+ in the transport of ions across a liquid membrane, thus mimicing (resembling closely) natural ion-selective transport agents like monensin.

Many of the natural agents are small polypeptides, of which valinomycin (see fig. below) is another.

Some ionophores having high preference to Li^+ are crown ethers with long aliphatic chains.

Some other macrocycles with functional groups may have utility for therapy in brain disorders for which Li^+ salts are used. It has been observed that open chain polyethers also form complexes with M^+ ions.



Valinomycin

Related macrocyclic polyethers are the cryptates or cryptands which are N, O compounds such as $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$.

Thus cryptates or cryptands may be defined as the polycyclic (macrocyclic) systems containing both nitrogen and oxygen atoms which have a great complexing ability.

The cryptate name comes from the term that the cations (metal ions) are burried in the structure.

An example of cryptate includes 2, 2, 2-crypt ligand (fig. 3.3B).

The cryptates bind M^+ strongly and often with high selectivity. The affinity of such a ligand for an ion depends on how well the ion fits into the cavity that the ligand can provide for it.

Selectivity as well as strength of complexation also depends on the solvent.

The ionic diameter, polyether ring and hole size of alkali metal ions are given below :

Cation	Ionic diameter (pm)	Polyether ring	Hole size (pm)
Li^+	152	14-Crown-4	120-150
Na^+	304	15-Crown-5	170-220
K^+	204	18-Crown-6	260-320
Rb^+	276	21-Crown-7	340-430

ALKALINE EARTH METALS

These belong to group 2 of *s*-block of the modern periodic table.

Group 2 elements include beryllium ($_4Be$), magnesium ($_{12}Mg$), calcium ($_{20}Ca$), strontium ($_{38}Sr$), barium ($_{56}Ba$) and radium ($_{86}Ra$).

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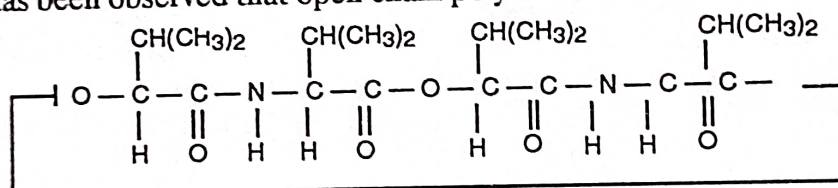
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