Inorganic chemistry II
Second stage / First semester
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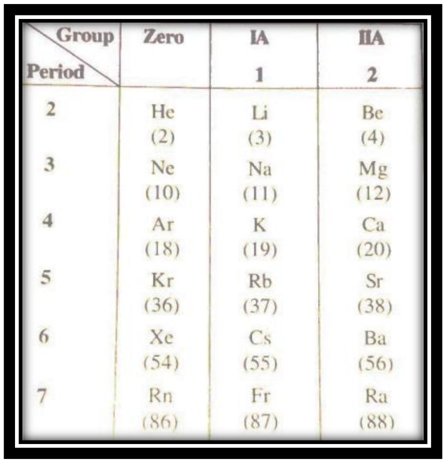
Alkali Metals and their Compounds (Group IA or 1, ns1^{1})

POSITION OF ALKALI METALS IN PERIODIC TABLE:-

The members of Group IA or 1, except hydrogen are called the alkali metals, because they react with water to form alkaline solutions. All the group IA elements are soft silvery-grey metals. Their valence electron configurations are ns^{1}, where n is the period number, and their physical and chemical properties are dominated by the ease with which the single valence electron can be removed. The group IA of the periodic table consists of six elements-lithium, sodium, potassium, rubidium, cesium and francium besides hydrogen. These elements are collectively called as alkali metals and group IA is known as alkali group as the hydroxides of these metals are soluble in water and these solutions are highly alkaline in The word alkali has been derived from Arabic word 'Alquili' meaning the ashes of plants from which compounds of sodium and potassium were first isolated. They are soft enough to cut with a knife . The alkali metals are the most reactive of all metals, reacting readily with water and air. The alkali metals, being reactive in nature, are never found free in nature but always found in combined state. The alkali metals are so reactive that, they must be stored under oil. This prevents the reaction of alkali metals with oxygen and water vapour in the air.

Of all the alkali metals, only sodium and potassium are found in abundance in nature, i.e., they are seventh and eighth most abundant elements by weight in earth's crust. Their compounds are very common and have been known and used from very early times. The last member, francium, occurs only in traces as a radioactive decay product because its half life period is very small, i.e., 21 minutes. Thus, not much is known about this element. The following table shows the percentage and relative abundance of alkali metals in earth's crust by weight.

Element	Percentage	Relative abundance
Li	0.0018	35
Na	2.27	7
K	1.84	8
Rb	0.0078	23
Cs	0.00026	46

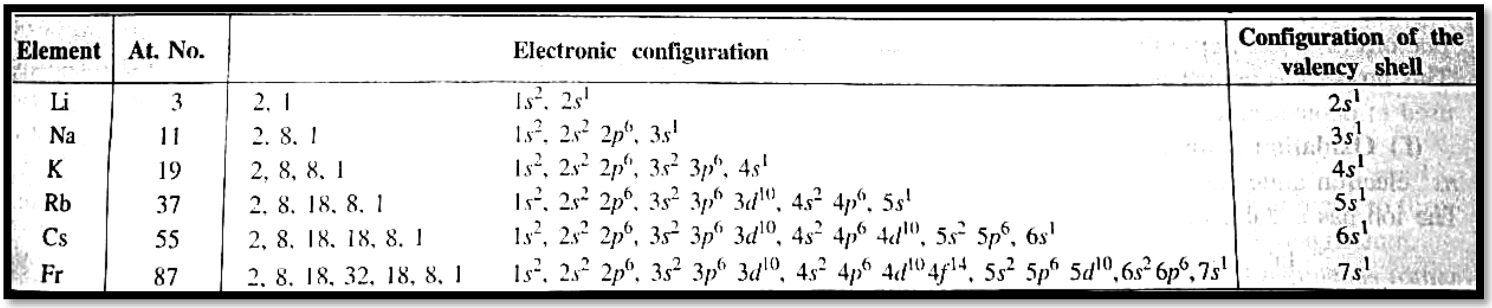


Group / Period	Zero	IA 1	IIA 2
2	He (2)	Li (3)	Be (4)
3	Ne (10)	Na (11)	Mg (12)
4	Ar (18)	K (19)	Ca (20)
5	Kr (36)	Rb (37)	Sr (38)
6	Xe (54)	Cs (55)	Ba (56)
7	Rn (86)	Fr (87)	Ra (88)

Each alkali metal occupies a place just after a member of Zero group. Except first period, rest of the six periods of the periodic table start with a member of alkali group. Next to the elements of Zero group, alkali metals form the most homogeneous of all the groups of the periodic table. The members of this group show a marked resemblance in their properties and possess the same electronic configuration. There is gradual gradation in the properties with the increase of atomic number. This justifies their inclusion in the same group of the periodic table.

1. Electronic Configuration

The arrangement or the distribution of electrons un various subshells in the atoms of alkali metals is given below



Element	At. No.	Electronic configuration		Configuration of the valency shell
Li	3	2, 1	$1s^2, 2s^1$	$2s^1$
Na	11	2. 8. 1	$1s^2, 2s^2\ 2p^6, 3s^1$	$3s^1$
K	19	2, 8, 8, 1	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6, 4s^1$	$4s^1$
Rb	37	2, 8, 18, 8, 1	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6, 5s^1$	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^6, 6s^1$	$6s^1$
Fr	87	2, 8, 18, 32, 18, 8, 1	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10} 4f^{14}, 5s^2\ 5p^6\ 5d^{10}, 6s^2\ 6p^6, 7s^1$	$7s^1$

The outermost shells of these elements have one electron and the penultimate (next to outermost) shells contain 8 electrons except in the first member, lithium, which contains 2 electrons. which is the atomic number of helium. Since, the last electron enters at s-orbital, these are called s-block elements.

Lithium shows somewhat abnormal properties as its electronic configuration is slightly different than the rest of the members. Because of their similarity in electronic configuration, (noble gas) ns^2 , they are placed in the same sub group, i.e., IA of the periodic table and closely resemble in their physical and chemical properties

2. Physical Properties

(a) All the alkali elements are silvery white solids. These are soft in nature and can be cut with the help of knife except the lithium. When freshly cut, they have a bright luster which quickly fades due to surface oxidation.

The silvery luster of alkali metals is due to the presence of highly mobile electrons of the metallic lattice. There being only a single electron per atom, the metallic bonding is not so strong. As a result of this, these metals are soft in nature. However, the softness increases with increase of atomic number because there is continuous decrease of metallic bond strength on account of increase in atomic size. Bigger is the size of metal kernel weaker is the metallic bonding

(b) Atomic and ionic radii: Group IA atoms are the largest in their horizontal periods in the periodic table. When the outermost electron is removed to give a positive ion, the size decreases considerably. There are two reasons for this

(i) The outermost shell of electron has been completely removed.

(ii) The positive charge on the nucleus is now acting on lesser number of electrons, Le.. attraction increases which brings contraction in size.

Atomic as well as ionic size increases from Li to Fr due to the presence of one extra shell of electrons

	Li	Na	K	Rb	Cs
Metallic radii(pm)	152	186	227	248	265
Ionic radii (pm)	76	102	138	152	167

Atomic volume also increases as the atomic number increases.

	Li	Na	K	Rb	Cs
At. Volume (ml)	13.0	23.7	44.4	55.8	69.3

(c) Density: All are light metals. The densities are low. Lithium, sodium and potassium are lighter than water, for this very reason they float on water. Density gradually increases in moving down from Li to Cs. Potassium is, however, lighter than sodium.

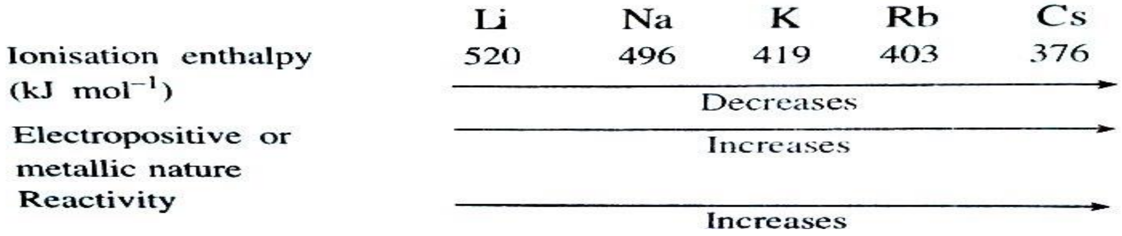
	Li	Na	K	Rb	Cs
Density (g/ml)	0.54	0.97	0.86	1.53	1.87

The reason for the low values is that these metals have high atomic volumes. The abnormal value of potassium is due to unusual increase in atomic size, i.e., atomic volume.

(d) Melting and boiling points: The energy binding the atoms in the crystal lattices of these metals is relatively low on account of a single electron in the valency shell. Consequently, the metals have low melting and boiling points. These decrease in moving down from Li to Cs as the metallic bond strength decreases or cohesive force decreases.

	Li	Na	K	Rb	Cs
Melting point (K)	454	371	336	312	302
Boiling point (K)	1615	1156	1032	961	944

(e) Ionisation energies and electropositive character: Due to their large size, the outermost electron is far from the nucleus and can easily be removed. Their ionisation energies or ionisation enthalpies are relatively low. Thus, the metals have a great tendency to lose the ns electron to change into M^+ ions. These metals are highly electropositive in nature. As the ionisation enthalpy decreases from Li to Cs, the electropositive character increases, i.e., metallic character increases. The reactivity of these metals increases from Li to Cs.



The ns^1 electron is so loosely held that even the low energy photons (light) can eject this electron from the metal surface. This property is termed as photoelectric effect. K and Cs are used in photoelectric cells which are sensitive to blue light.

(f) Oxidation states: The alkali metals can lose their ns^1 electron quite easily to form univalent positive ion, M^+. The ion has a stable configuration of an inert gas.

Li^+ He-configuration

Na^+ Ne-configuration

K^+ Ar-configuration

Rb^+ Kr-configuration

Cs^+ Xe-configuration

The energy required to pull out another electron from M^+ ion is very high, i.e., the second ionisation enthalpy values are high.

	Li	Na	K	Rb	Cs
I_2 (KJ/mol)	7298	4562	3051	2633	2230

Consequently, it is not possible for alkali metals to form M^{2+} ions under ordinary conditions. These metals, thus show only one oxidation state, i.e., +1 oxidation state. These metals are univalent in nature and show electrovalency, i.e., form electrovalent compounds.

Since the electronic configuration of M^+ ions are similar to those of inert gases, these ions have no unpaired electrons and consequently are colourless and diamagnetic in nature.

(g) Hydration of ions, hydrated radii and hydration energy: The salts of alkali metals are ionic and soluble in water. The solubility is due to the fact that cations get hydrated by water molecules.

$$M^+ + \ aq. \longrightarrow \underset{\text{Hydrated cation}}{[M(aq.)]^+}$$

The smaller the cation, the greater is the degree of its hydration. Thus, the degree of hydration of M+ ions decreases from Li^+ to Cs^+. Consequently the radii of the hydrated ion decreases from Li^+ to Cs^+.

	$[Li(aq.)]^+$	$[Na(aq.)]^+$	$[K(aq.)]^+$	$[Rb(aq.)]^+$	$[Cs(aq.)]^+$
Hydrated radii(^{0}A)	3.40	2.76	2.32	2.28	2.27

The ionic conductance of these hydrated ions increases from $[Li(aq.)]^+$to $[Cs(aq.)]^+$.

	$[Li(aq.)]^+ <$	$[Na(aq.)]^+ <$	$[K(aq.)]^+ <$	$[Rb(aq.)]^+ <$	$[Cs(aq.)]^+$
Ionic mobility at infinite dilution	33.5	43.5	64.5	67.5	68

Hydration of ions is an exothermic process. The energy released when one gram mole of an ion is dissolved in water to get it hydrated is called hydration energy. Since the degree of hydration decreases from Li^+ to Cs^+ , the hydration energy of alkali metal ion also decreases from Li^+ to Cs^+.

Alkali metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+
Hydration energy (KJ/mol)	-506	-406	-330	-310	-276

(h) Electronegativity: The tendency to attract electrons is low as the alkali metals are electropositive. The electro negativity, thus, decreases from Li to Cs as the electropositive character increases.

(i) Conductivity : The alkali metals are good conductors of heat and electricity. This is due to the presence of loosely held valency electrons which are free to move throughout the metal structure.

(j) Specific heats: The specific heat values decrease from Li to Cs.

	Li	Na	K	Rb	Cs
Specific heat at 0^0C	0.94	0.29	0.17	0.08	0.05

This is due to the decrease in the metallic bond strength from Li to Cs.

(I) Flame colouration: The alkali metals and their salts impart a characteristic colour to flame .

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Pale violet	Red violet	Violet

The reason for flame colouration is that the energy of the flame causes an excitation of the outermost electrons which on return to their original position give out the energy so absorbed in the visible region. The energy released is minimum in the case of Li^+ and increases in order Li^+, Na^+, K^+, Rb^+, Cs^+. Thus, the frequency of the light emitted increases in accordance with the formula $E = hv$. The frequency of light in lithium is minimum which corresponds to red region of the spectra.

(m) Reducing nature: An element, which acts as a reducing agent, must have low ionisation energy. Alkali metals act as strong reducing agents as their ionisation energy values are low. Since ionisation energy decreases on moving down from Li to Cs, the reducing property increases in the same order. Thus, Li is weakest reducing agent while Cs is the strongest reducing agent amongst alkali metals in free state. The tendency of an element to lose an electron in solution is measured by its standard oxidation potential value (E). Since alkali metals have high E_{ox} values, these are strong reducing agents. Because their standard oxidation potentials are so strongly positive, the alkali metals can even reduce water.

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq.)} + H_{2(g)}$$

However, it is observed that Li is the strongest reducing agent amongst alkali metals in solution as E^0_{OX} value of Li is maximum.

	Li	Na	K	Rb	Cs
Oxidation potential (V)	+3.05	+2.71	+2.925	+2.93	+2.927

It looks surprising at first sight that lithium having high value of ionisation energy amongst alkali metals acts as strongest reducing agent in solution. This can be explained if we understand the fact that ionisation energy is the property of an isolated atom in gaseous state while oxidation potential is concerned when the metal atom goes into the solution.

The ionisation energy involves the change of gaseous atom to gaseous ion,

$$M_{(g)} \rightarrow M^+_{(g)} + e^-$$

while oxidation potential involves the following change:

$$M_{(s)} \rightarrow M^+_{(aq.)} + e^-$$

The above change occurs in three steps:

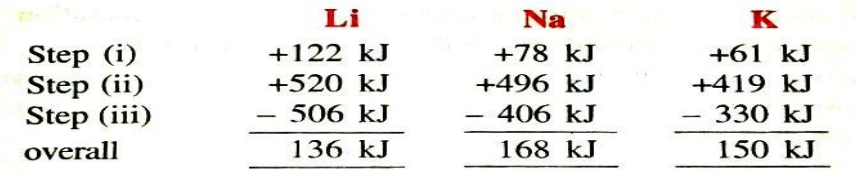
(i) $M(s) \rightarrow M(g)$ - sublimation energy

(ii) $M(g) \rightarrow M^+(g) + e^-$ ionisation energy

(iii) $M^+(g) + H_2O \rightarrow M^+(aq)$ + hydration energy

Sublimation energy is nearly same for all the alkali metals.

The energy required in (ii) step is the ionisation energy which is highest for lithium. Li^+ ion is smallest in size, hence it has maximum degree of hydration. Thus, in (iii) step, maximum hydration energy is released in lithium.



	Li	Na	K
Step (i)	+122 kJ	+78 kJ	+61 kJ
Step (ii)	+520 kJ	+496 kJ	+419 kJ
Step (iii)	– 506 kJ	– 406 kJ	– 330 kJ
overall	136 kJ	168 kJ	150 kJ

Thus, with greater ease the following overall change occurs in lithium and it acts as a strongest reducing agent :

$$M_{(S)} \longrightarrow M^+_{(aq.)} + e$$

It is, therefore, concluded that highest reducing power of lithium in solution is due to its large heat of hydration.

3. Chemical Properties

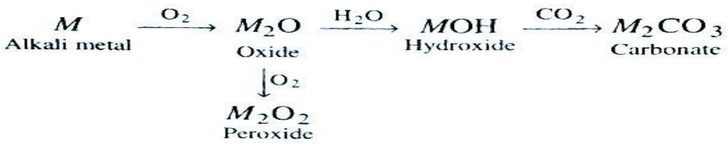
Alkali metals are highly reactive metals and the reasons for high reactivity are :

(i) They have low values of ionisation energies and readily lose their valence electron to form M^+ ion.

(ii) They have low heat of atomisation and easily come into vaporised form.

(iii) They have high heats of hydration.

(a) Reactivity towards air: On exposure to moist air, all alkali metals except lithium tarnish quickly. The effect of atmosphere increases from Li to Cs. These are, therefore, always kept under kerosene to protect them from air.



Lithium when heated in air combines with nitrogen to form nitride, it is due to diagonal relationship with magnesium. All alkali metals react directly with most nonmetals (other than the noble gases). However, only lithium react with nitrogen, which it reduces to the nitride ion.

$$6Li_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2Li_3N_{(s)}$$

(b) Reactivity towards water: Alkali metals decompose water with the evolution of hydrogen.

$$2M + 2H_2O \rightarrow 2MOH + H_2\uparrow$$

Lithium decomposes water slowly. Sodium reacts with water quickly, K, Rb and Cs react with water vigorously. The decomposition is highly exothermic and the evolved hydrogen sometimes inflames. Thus, the reactivity towards water increases from Li to Cs. This is due to increase of electropositive character in the same order.

[The oxidation potential of lithium is highest amongst alkali metals, i.e., free energy released in the case of lithium is maximum ($\Delta G = nFE^0_{OX}$). In view of this, it looks rather surprising that lithium reacts gently with water whereas potassium which liberates less energy, reacts violently and catches fire. The explanation lies in the kinetics (the rate at which reaction proceeds) rather than in the thermodynamics (that is total amount of energy released). Potassium has a low melting point and heat of reaction is sufficient to make it melt or even vaporise. The molten metal spreads out and exposes a larger surface to the water, so it reacts even faster, gets even hotter and catches fire.]

The alkali metals also react with alcohols forming alkoxides with the evolution of hydrogen. This reaction is used in preliminary test of alcoholic group.

$$\underset{\text{Ethyl alcohol}}{2Li + 2C_2H_5OH} \longrightarrow \underset{\text{Lithium ethoxide}}{2C_2H_5OLi} + H_2\uparrow$$

(**c) Affinity for non-metals:** Alkali metals have great affinity for non-metals.

(i) Reactivity towards hydrogen: The alkali metals combine directly with hydrogen to form crystalline hydrides of the formula MH. These hydrides are ionic and contain the hydride ion, H^{1-}.

$$2M + H_2 \longrightarrow 2MH$$

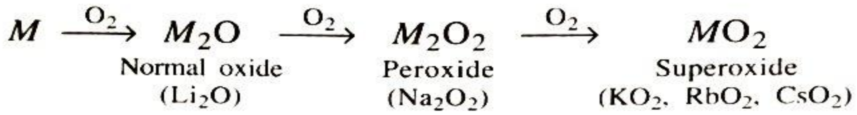
The electrolysis of the fused hydride (LiH) yields hydrogen at anode [other hydrides decompose before melting.] The hydrides react with water liberating hydrogen.

$$MH + H_2O \longrightarrow MOH + H_2\uparrow$$

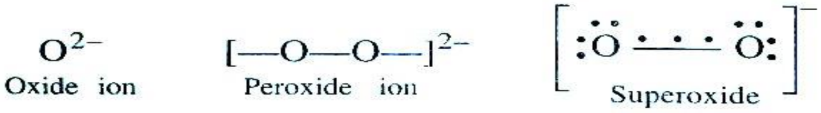
The ionic character of the bonds in these hydrides increases from LiH to CsH and their stability decreases in the same order. They are powerful reducing agents especially at high temperatures.

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

(ii) Reactivity towards oxygen (oxides and hydroxides): Affinity towards oxygen increases. When heated in atmosphere of oxygen, the alkali metals ignite and form oxides. On combustion Li forms Li_2O; sodium gives the peroxide, Na_2O_2: and potassium, rubidium and cesium give superoxides, MO_2.



The normal oxides contain O^{2-} ion, the peroxides contain O_2^{2-} ion and superoxides contain O_2^{1-} ion. The peroxides and superoxides become more stable with increase in atomic number of the alkali metal. The formation and stability of these oxides can be explained on the basis of lattice energy effects. Li ior being a small ion has a strong positive field around it and car stabilise only a small anion, O^{2-} whereas Nat being a large cation can stabilise a large ion and so on.



The normal oxides 'M_2O' react with water to form hydroxides.

$$M_2O + H_2O \rightarrow 2MOH$$

The basic nature of the oxides (M_2O) increases gradually on moving down in the group. The hydroxides (MOH) are colourless, strong alkaline and corrosive compounds. These are soluble in water and dissolve with the evolution of heat. The hydroxides are thermally stable except LiOH. The relative strength of the hydroxides increases from LiOH to CSOH.

$$CsOH > RbOH > KOH > NaOH > LiOH$$

The crystal structures of Li_2O, Na_2O, K_2O and Rb_2O are antifluorite structures. Cs_2O has an anti-$CdCl_2$ layer structure.

The higher oxides, viz., peroxides and superoxides are strong oxidising agents. They react with dilute acids forming hydrogen peroxide and oxygen respectively.

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$$

$$4KO_2 + 2H_2SO4 \rightarrow 2K_2SO_4 + 2H_2O + 3O_2$$

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

The peroxides are diamagnetic in nature (all the electrons are paired) and are regarded as the salts of the dibasic acid, H_2O_2. The superoxides are paramagnetic and coloured as odd electron bond is present between two oxygen atoms. Yellow colour of Na_2O_2 is probably due to the presence of small amount of superoxide. Superoxides are even stronger oxidising agents than peroxides.

(iii) Reactivity towards halogens: The alkali metals directly react with halogens forming the halides of the type MX.

$$2M + X_2 \rightarrow 2MX$$

The reactivity of alkali metals towards a particular halogen increases from Li to Cs. On the other hand, reactivity of halogens towards a particular alkali metal decreases from F_2 to I_2 i.e.,

$$F_2 > Cl_2 > Br_2 > 12$$

With the exception of certain lithium halides, the alkali metal halides are ionic compounds ($M^+ X^-$). The halides are crystalline and have high melting and boiling points. The fused halides are good conductors of electricity and are used for the preparation of alkali metals. All halides except LiF dissolve in water.

Alkali metal halides are colourless but on heating they turn yellow, blue, etc., owing to non-stoichiometry and crystal defects.

Halides of potassium, rubidium and caesium have a property of combining with extra halogen atoms forming polyhalides.

$$KI + 1_2 \rightarrow KI_3$$

[The insolubility of LiF in water can be explained in the following manner. The lithium ion has the highest energy of hydration as it is small in size in comparison to other alkali metal ions and thus it should have high solubility. However, the small Li^+ and F^- ions interact very strongly resulting in high lattice energy of LiF which is responsible for its insolubility (the ionic compounds, which possess low value of lattice energy, are freely soluble in water).]

(iv) Action with sulphur and phosphorus: Alkali metals directly combine with sulphur and phosphorus when heated with them. The monosulphides, M_2S, cannot be obtained by passing H_2S through their salt solutions as sulphides get hydrolysed.

$$M_2S + H_2O \rightarrow MOH + MHS$$

Phosphides on hydrolysis evolve phosphine.

$$3M + P \rightarrow M_3P$$

$$M_3P + 3H_2O \rightarrow 3MOH + PH_3$$

(d) Nature of oxysalts: Alkali metals readily react with oxyacids forming corresponding salts with evolution of hydrogen. Lithium salts behave abnormally due to polarising power of Li^+ ion (small size) and lattice energy effects. However, the salts of rest of the alkali metals behave similarly and there is a gradual gradation in their properties with the increase of atomic number.

(i) Nature of carbonates and bicarbonates: All the alkali metals form carbonates of the type M_2CO3. Since the alkali metals are highly electropositive, their carbonates are highly stable towards heat and readily soluble in water. As the electropositive character increases from Li to Cs, the stability of the carbonates increases in the same order.

$$Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$$

Li_2CO_3 decomposes on heating and is insoluble in water. The aqueous solutions of carbonates are alkaline. This is due to hydrolysis as carbonates are salts of strong bases and weak acid (H_2CO_3 carbonic acid).

$$M_2CO_3 + 2H_2O \longleftrightarrow \underset{\text{Strong alkali}}{2MOH} + \underset{\text{Weak acid}}{H_2CO_3}$$

The bicarbonates, $MHCO_3$, of the alkali metals, with the exception of lithium, are known in solid state. The bicarbonates. are soluble in water. On heating, bicarbonates decompose into carbonates with evolution of CO_2.

$$2MHCO_3 \longrightarrow M_2CO_3 + H_2O + CO_2$$

The abnormal behaviour of Li_2CO_3 towards heat can be explained in the following manner.

The Li^+ ion exerts a strong polarising action and distorts the electron cloud of the nearby oxygen atom of the large CO_3^{2-} ion. This results in the weakening of the C-O bond and strengthening of the Li-O bond. This ultimately facilitates the decomposition of Li_2CO_3 into Li_2O and CO_2. The lattice energy of Li_2O is higher than the lattice energy of carbonate. This also favours the decomposition of Li_2CO_3.

Lithium due to its less electropositive nature, does not form solid bicarbonate.

(**ii) Nature of nitrates:** Nitrates of the type, MNO_3, are known. These are colourless, soluble in water and electrovalen in nature. The nitrates do not undergo hydrolysis. With the exception of $LiNO_3$, the other nitrates decompose to nitrite and oxygen.

$$2MNO_3 \rightarrow 2MNO_2 + O_2$$

Lithium nitrate decompose to oxide on heating, it is due to diagonal relationship with magnesium.

$$2LiNO_3 \rightarrow Li_2O + 2NO_2 + O_2$$

(iii) Nature of sulphates: Sulphates of the type M_2SO_4 are known. With the exception of Li_2SO_4, other sulphates are soluble in water. The sulphates when fused with carbon form sulphides.

$$M_2SO_4 + 4C \rightarrow M_2S + 4CO$$

The sulphates of alkali metals form double salts with the sulphates of the trivalent metals like Fe, Al, Cr, etc. The double sulphates crystallise with large number of water molecules as potash alum, $K_2SO_4\ Al_2(SO_4)_3\ 24H_2O$ consists of 24 water molecules. Sulphate of lithium is not known to form alum.

(e) Solubility in liquid ammonia: The alkali metals dissolve in liquid ammonia without the evolution of hydrogen. The colour of the dilute solutions is blue. The metal atom loses electron and it combines with ammonia molecule.

$M \rightarrow M$ (in liquid ammonia) + e (ammoniated)

$M + (x + y)NH_3 \rightarrow [M(NH3)]^+ + e\ (NH_3)y$

Solvated electron

On heating its blue colour changes to bronze. It is ammoniated electron which is responsible for colour. The solutions are good conductors of electricity and have strong reducing properties. The solutions are paramagnetic in nature

When dry ammonia is passed over hot metal, amides are formed.

$$2M + 2NH_3 \rightarrow 2MNH_2 + H_2 \uparrow$$

Amide

The amides are decomposed by cold water with evolution of NH_3.

$$MNH_2 + H_2O \rightarrow MOH + NH_3$$

Recent studies proved the existence of $Li(NH_3)_4$,golden yellow solid.

(f) Formation of alloys: The alkali metals form alloys amongst themselves and with other metals. These combine with mercury readily forming amalgams

(g) Complex formation: Alkali metals have a very little tendency to form complexes. Lithium being small in size forms certain complexes but this tendency decreases as the size increases.

(h) Extraction of alkali metals: Alkali metals cannot be extracted by the application of common processes used for the extraction of metals due to following reasons:

(i) Alkali metals are strong reducing agents, hence cannot be extracted by reduction of their oxides and other compounds.

(ii) Being highly electropositive in nature, it is not possible to apply the method of displacing them from their salt solutions by any other element.

(iii) The aqueous solutions of their salts cannot be used for extraction by electrolytic method because hydrogen is discharged

at cathode instead of an alkali metal as the discharge potentials of alkali metals are high. However, by using Hg as cathode, alkali metal can be deposited. The alkali metal readily combines with Hg to form an amalgam from which its recovery is very difficult.

The only successful method, therefore, is the electrolysis of their fused salts, usually chlorides. Generally, another metal chloride is added to lower its fusion temperature.