Table : 16.3

Property	Alkali metal	Alkaline earth metal
Physical state	**(a)** All are silvery white metals. **(b)** Light soft, malleable, and ductile metals with metallic luster. **(c)** Both are diamagnetic and colorless in the form of ions.	**(a)** All are greyish white. **(b)** Relatively harder.
Atomic and ionic radii	**(a)** Largest size in their respective period. **(b)** Down the group, atomic and ionic radii increases for gaseous species.	**(a)** Smaller than alkali metals. **(b)** Down the group, atomic and ionic radii increases for gaseous species.
Density	**(a)** All are light metals. **(b)** Density increases gradually from Li to Cs. **(c)** Li is lightest known metal among all. **Exception:** K is lighter than Na because of low density.	**(a)** Heavier than alkali metals. **(b)** Density decrease slightly up to Ca after which it increases. **(c)** Density of Mg is greater than Ca.
M.pt and B.pt	**(a)** The lattice energy of these atoms in metallic crystal lattice is relatively low and thus these possess low m.pt. and b.pt. **(b)** Lattice energy decreases from Li to Cs and thus m. pt. and b. pt. also decrease from Li to Cs.	**(a)** Melting points and boiling points are more than that of alkali metals due to smaller size and close packed structure. **(b)** Do not show any regular trend.
Ionization energy	**(a)** Due to unpaired electrons in *ns* sub shell as well as due to their larger size, the outermost electron is far from the nucleus, the removal of electron is easier and these have low values of ionization potential. **(b)** I. P. of these metals decreases from Li to Cs. **(c)** I.E. decrease ↓ ; Electropositive and matalic character increases ↓	**(a)** Due to smaller size, electrons are tightly held as compared to alkali metal, so more I.E. than alkali metals. **(b)** The IP values decrease with increase of atomic radii from Be to Ba. **(c)** I.E. decrease ↓ ; Electropositive and metalic character increases ↓
Flame colour	**(a)** Both produces characteristic colour in Bunsen flame due to easy excitation of electron to higher energy levels. **(b)** Characteristic flame colours are: Li — Crimson, Na — Golden Yellow, K — Pale violet, Rb and Cs — Violet. **(c)** Energy released $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ **(d)** The flame energy causes an excitation of the outermost electron which on reverting back to its initial position gives out the absorbed energy as visible light.	**Exception: (a)** Be and Mg do not show any colour as their electrons are more strongly bound. **(b)** Ca — Brick red, Sr — Blood red, Ba — apple green, Ra — Crimson. **(c)** Be and Mg atoms due to their small size, bind their electrons more strongly because of higher effective nuclear charge. Hence, these posses high excitation energy and are not excited by the flame energy and do not show any colour.
Conduction power	Both are good conductor of heat and electricity.	
Hydration of ions	**(a)** Hydration represents the dissolution of a substance in water to absorb water molecule by weak valency forces. Hydration of ions is the process which ions on dissolution in water get hydrated. **(b)** Smaller the cation, greater is the degree of hydration. Hydration energy. $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ **(c)** Li^+ being smallest in size has maximum degree of hydration. **Consequence:** Lithium salts are mostly hydrated and moves very slowly under the influence of electric field.	**(b)** Hydration energy: $Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$
Electro-negativity	**(a)** These metals are highly electropositive and thereby possess low values of electronegativities. **(b)** Electronegativity of alkali metals decreases down the group.	**(a)** Their electronegativites are also small but are higher than that of alkali metals. **(b)** Electronegativity decrease from Be to Ba.

Standard oxidation potential and reducing properties	**(a)** Since alkali metals easily lose ns^1 electron, they have high values of oxidation potential. That is $M(s) \rightarrow M^+(aq) + e^-$	**(a)** They lose two electrons to give M^{+2} ion.
Oxidation no and valency	These elements easily form univalent +ve ion by losing solitary ns^1 electron due to low IP value.	The IP_1 of these metals are much lower than IP_2 and thus it appears that these metals should form univalent ion rather than divalent ions but in actual practice, all these metals give bivalent ion.
Photoelectric effect	Except Li all group elements show.	

10. Hydration of Ions. The alkali metal ions are *extensively hydrated. The smaller the size of the ion, the greater is the degree of hydration*. Thus, Li^+ ion, which is smallest in size and has the highest charge/size ratio amongst the alkali metal ions, gets much more hydrated (*i.e.*, holds more water molecules in its hydration sphere) than Na^+ ion and the latter gets more hydrated than K^+ ion and so on. The degree of hydration decreases on moving down the group form Li^+ to Cs^+. As a result of the difference in degree of hydration, ionic radii of hydrated alkali metal ions *decrease* from Li^+ to Cs^+, *i.e.*, Li^+ ion, which should have been smallest, is actually largest in size in aqueous solutions. Thus, the ionic radii *in aqueous solutions* decrease in the order.

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

It is for this reason that Li^+ ion has the *lowest* and Cs^+ ion has the *highest mobility* in an electric field.

11. Oxidation States. All the alkali metals exhibit an oxidation state of +1. This is because these metals *can lose their solitary outermost electron easily*. The second ionisation energy is so high that the second electron is very rarely lost.

13. Reducing Properties, Oxidation Potentials. As is well known, **oxidation** *is a process in which electrons are lost* and **reduction** *is a process in which electrons are gained.* An *oxidising agent,* therefore, is a substance which can *accept* electrons while a *reducing agent* is a substance which can *lose* electrons. Consider the formation of sodium chloride by burning of sodium in chlorine. Sodium, on account of low ionisation energy, can *lose* an electron readily while chlorine, on account of its high electron affinity, can *accept* it readily.

$$\mathrm{Na}(s) \xrightarrow{\text{heat}} \mathrm{Na}(g)$$
$$\mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + e^-$$
$$1/2\ \mathrm{Cl}_2(g) + e^- \longrightarrow \mathrm{Cl}^-(g)$$
$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{Na}^+\mathrm{Cl}^-(s)$$
$$\mathrm{Na}(s) + 1/2\ \mathrm{Cl}_2(g) \longrightarrow \mathrm{Na}^+\mathrm{Cl}^-(s)$$

Thus, sodium is a reducing agent while chlorine is an oxidising agent. Evidently, an element which is a *reducing agent* must have *low ionisation energy* while an element which is an *oxidising agent* must have *high ionisation energy* (or *high electron affinity*). Since ionisation energy decreases on moving down from lithium to cesium, the reducing properties increase in the same order.

The tendency of an element to lose an electron *in solution* is measured by the standard oxidation potential of the element. The standard oxidation potentials of the alkali metals are given in Table 3.

TABLE 3.
Standard Oxidation Potentials of Alkali Metals

Element	Oxidation Reaction	Standard Oxidation Potential (volts)
Lithium	$\mathrm{Li} \longrightarrow \mathrm{Li}^+ + e^-$	3·04
Sodium	$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$	2·71
Potassium	$\mathrm{K} \longrightarrow \mathrm{K}^+ + e^-$	2·92
Rubidium	$\mathrm{Rb} \longrightarrow \mathrm{Rb}^+ + e^-$	2·99
Cesium	$\mathrm{Cs} \longrightarrow \mathrm{Cs}^+ + e^-$	3·02

These high values indicate that *alkali metals have a strong tendency to act as reducing agents and that lithium is the strongest of them all*. However, if we look at the ionisation energies of these elements (Table 2), it is seen that lithium has the highest value indicating that *it holds its electron most tightly*. This, at first sight, seems to be contrary to the maximum value of oxidation potential of lithium which indicates that *lithium gives off its electron most readily*. This anomaly can be explained if we recall that ionisation energy is the property of *isolated atom in the gaseous state* while oxidation potential concerns itself with *the metal as it goes into solution*.

Thus, ionisation energy involves only the following change :

$$\mathrm{M}(g) \longrightarrow \mathrm{M}^+(g) + e^-$$

Oxidation potential, on the other hand, involves the process

$$\mathrm{M}(s) \longrightarrow \mathrm{M}^+(aq) + e^-$$

which is considered to take place in three consecutive steps :

$$\mathrm{M}(s) \longrightarrow \mathrm{M}(g)$$
$$\mathrm{M}(g) \longrightarrow \mathrm{M}^+(g) + e^-$$
$$\mathrm{M}^+(g) + \mathrm{H_2O} \longrightarrow \mathrm{M}^+(aq)$$

In the first step, the metal (solid) is evaporated to the gaseous state in which the atoms get isolated from one another and become independent of one another. The energy required in this process is known as **sublimation energy** which is about the same for all the alkali metals. In the second step, the outer electron is pulled off from an isolated gaseous atom. The energy required for this change is the **ionisation energy** which, as mentioned above, is the highest for lithium. In the third stage, the gaseous ion gets hydrated. In this process, energy, known as **hydration energy**, gets *liberated*. The oxidation potential which gives the tendency for the overall change to occur, naturally depends on the *net effect of all the three steps*. *Lithium ion is hydrated to the maximum extent* and, therefore, the energy *liberated* in the third step is maximum in case of Li^+ ion. *The hydration energy of lithium ion (released in step 3) is so large that it compensates the energy required to knock off the electron* (*step* 2). This explains the higher oxidation potential of lithium, *i.e.*, the greater ease with which the overall change,

$$Li(s) \longrightarrow Li^+(aq) + e^-$$

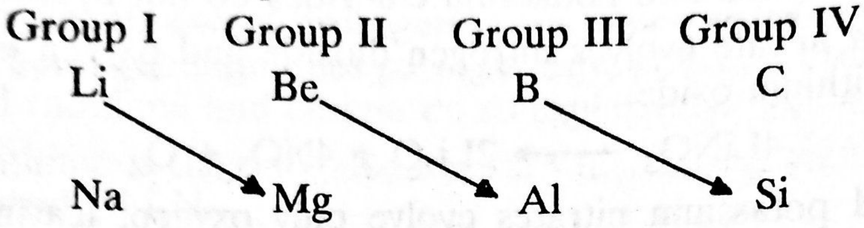
takes place.

In other words, *the greater strength of lithium as a reducing agent lies in its greater hydration energy*.

14. Characteristic Flame Colouration. All the alkali metals give *characteristic colours* in bunsen flame. The reason is that when an alkali metal or any of its compounds is heated in a bunsen flame, the electrons get excited to higher energy levels. When these electrons return to their original (ground) level, the *excitation energy* which had been absorbed by them, is *released* in the form of light in the visible region of the spectrum. Now for the same excitation energy, the energy level to which the electron in Li rises is lower than that to which the electron in Na rises and this, in turn, is lower than the level to which the electron in K rises and so on. These differences are on account of differences in the forces of attraction between the nucleus and the outermost electron. Consequently, when the electron returns to the ground state, energy released is lowest in Li and increases in the order : Li $\longrightarrow$ Cs. As a result of this, the frequency of the light emitted in the bunsen flame will be minimum in the case of lithium. It increases in the order Li $\longrightarrow$ Cs. Thus, the colour of the flame is crimson red in the case of Li, golden yellow in the case of Na, violet in the case of K and almost the same in the case of Rb and Cs.

... from lithium to iodine atom.

Diagonal Relationship of Lithium with Magnesium. As already mentioned, lithium differs from the rest of its family members in many respects. However, it shows resemblance with magnesium, the second element of Group II. This is a case of **diagonal relationship** *in which the first element of a group shows similarities with the second element in the next higher group in the next period,* as indicated below.



This diagonal relationship is due to *similar polarising powers* of Li^+ and Mg^{2+} ions despite the occurrence of different charges on these ions. This aspect has already been discussed in the last chapter.

Resemblance of Lithium and Magnesium

Because of the diagonal relationship, lithium resembles magnesium in several respects as illustrated below.

1. Atomic radius of lithium is 1·34 Å while that of magnesium, being 1·364 Å, is not very much different.

2. The radii of Li^+ ion (0·60 Å) and Mg^{2+} ion (0·65 Å) are not much different from each other.

3. Polarising powers of Li^+ ion and Mg^{2+} ion are about the same.

4. Electronegativities of Li and Mg, being 1·0 and 1·2, respectively, are not much different from each other.

5. Like magnesium, lithium decomposes water only slowly liberating hydrogen.

6. Like magnesium, lithium hardly reacts with liquid bromine.

7. Lithium reacts with nitrogen to give lithium nitride, Li_3N. Magnesium also reacts with nitrogen to give magnesium nitride, Mg_3N_2

8. Lithium forms only the monoxide, Li_2O. Magnesium also prefers to form only the monoxide, MgO.

9. Lithium hydroxide, like magnesium hydroxide, is very slightly soluble in water.

10. Lithium hydroxide, like magnesium hydroxide, is a weak base.

11. Lithium fluoride, phosphate, oxalate and carbonate, like the corresponding salts of magnesium, are sparingly soluble in water.

12. Lithium chloride, like magnesium chloride, separates out from aqueous solutions as hydrated crystals, $LiCl.2H_2O$.

13. Lithium chloride, like magnesium chloride, is deliquescent.

14. Lithium chloride, like magnesium chloride, undergoes hydrolysis in hot water though to a smaller extent than magnesium chloride.

15. Lithium, nitrate, like magesium nitrate, evolves nitrogen dioxide and oxygen on heating, leaving behind the oxide.

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

$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$