

Table 10.1 Atomic and Physical Properties of the Alkali Metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass (g mol <sup>-1</sup> )	6.94	22.99	39.10	85.47	132.91	(223)
Electronic configuration	[He] 2s <sup>1</sup>	[Ne] 3s <sup>1</sup>	[Ar] 4s <sup>1</sup>	[Kr] 5s <sup>1</sup>	[Xe] 6s <sup>1</sup>	[Rn] 7s <sup>1</sup>
Ionization enthalpy / kJ mol <sup>-1</sup>	520	496	419	403	376	~375
Hydration enthalpy/kJ mol <sup>-1</sup>	-506	-406	-330	-310	-276	-
Metallic radius / pm	152	186	227	248	265	-
Ionic radius M <sup>+</sup> / pm	76	102	138	152	167	(180)
m.p. / K	454	371	336	312	302	-
b.p / K	1615	1156	1032	961	944	-
Density / g cm <sup>-3</sup>	0.53	0.97	0.86	1.53	1.90	-
Standard potentials E <sup>o</sup> / V for (M <sup>+</sup> / M)	-3.04	-2.714	-2.925	-2.930	-2.927	-
Occurrence in lithosphere <sup>†</sup>	18*	2.27**	1.84**	78-12*	2-6*	~ 10 <sup>-18</sup> *

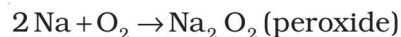
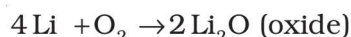
\*ppm (part per million), \*\* percentage by weight; † Lithosphere: The Earth's outer layer: its crust and part of the upper mantle

This property makes caesium and potassium useful as electrodes in photoelectric cells.

### 10.1.6 Chemical Properties

The alkali metals are highly reactive due to their large size and low ionization enthalpy. The reactivity of these metals increases down the group.

**(i) Reactivity towards air:** The alkali metals tarnish in dry air due to the formation of their oxides which in turn react with moisture to form hydroxides. They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxides. The superoxide O<sub>2</sub><sup>-</sup> ion is stable only in the presence of large cations such as K, Rb, Cs.



(M = K, Rb, Cs)

In all these oxides the oxidation state of the alkali metal is +1. Lithium shows exceptional behaviour in reacting directly with nitrogen of air to form the nitride, Li<sub>3</sub>N as well. Because of their high reactivity towards air and water, alkali metals are normally kept in kerosene oil.

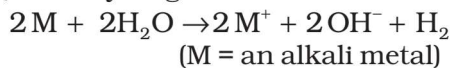
#### Problem 10.1

What is the oxidation state of K in KO<sub>2</sub>?

#### Solution

The superoxide species is represented as O<sub>2</sub><sup>-</sup>; since the compound is neutral, therefore, the oxidation state of potassium is +1.

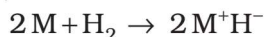
**(ii) Reactivity towards water:** The alkali metals react with water to form hydroxide and dihydrogen.



It may be noted that although lithium has most negative  $E^\ominus$  value (Table 10.1), its reaction with water is less vigorous than that of sodium which has the least negative  $E^\ominus$  value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

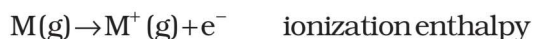
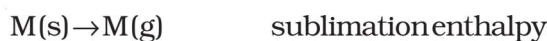
They also react with proton donors such as alcohol, gaseous ammonia and alkynes.

**(iii) Reactivity towards dihydrogen:** The alkali metals react with dihydrogen at about 673K (lithium at 1073K) to form hydrides. All the alkali metal hydrides are ionic solids with high melting points.



**(iv) Reactivity towards halogens:** The alkali metals readily react vigorously with halogens to form ionic halides,  $M^+X^-$ . However, lithium halides are somewhat covalent. It is because of the high polarisation capability of lithium ion (The distortion of electron cloud of the anion by the cation is called polarisation). The  $Li^+$  ion is very small in size and has high tendency to distort electron cloud around the negative halide ion. Since anion with large size can be easily distorted, among halides, lithium iodide is the most covalent in nature.

**(v) Reducing nature:** The alkali metals are strong reducing agents, lithium being the most and sodium the least powerful (Table 10.1). The standard electrode potential ( $E^\ominus$ ) which measures the reducing power represents the overall change :



With the small size of its ion, lithium has

the highest hydration enthalpy which accounts for its high negative  $E^\ominus$  value and its high reducing power.

### Problem 10.2

The  $E^\ominus$  for  $Cl_2/Cl^-$  is +1.36, for  $I_2/I^-$  is +0.53, for  $Ag^+/Ag$  is +0.79,  $Na^+/Na$  is -2.71 and for  $Li^+/Li$  is -3.04. Arrange the following ionic species in decreasing order of reducing strength:

$I^-$ ,  $Ag$ ,  $Cl^-$ ,  $Li$ ,  $Na$

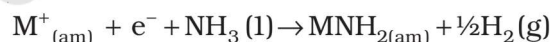
### Solution

The order is  $Li > Na > I^- > Ag > Cl^-$

**(vi) Solutions in liquid ammonia:** The alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.



The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of amide.



(where 'am' denotes solution in ammonia.)

In concentrated solution, the blue colour changes to bronze colour and becomes diamagnetic.

### 10.1.7 Uses

Lithium metal is used to make useful alloys, for example with lead to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions. Lithium is also used to make electrochemical cells. Sodium is used to make a Na/Pb alloy needed to make  $PbEt_4$  and  $PbMe_4$ . These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has

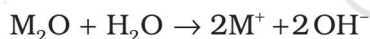
a vital role in biological systems. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide. Caesium is used in devising photoelectric cells.

## 10.2 GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

### 10.2.1 Oxides and Hydroxides

On combustion in excess of air, lithium forms mainly the oxide,  $\text{Li}_2\text{O}$  (plus some peroxide  $\text{Li}_2\text{O}_2$ ), sodium forms the peroxide,  $\text{Na}_2\text{O}_2$  (and some superoxide  $\text{NaO}_2$ ) whilst potassium, rubidium and caesium form the superoxides,  $\text{MO}_2$ . Under appropriate conditions pure compounds  $\text{M}_2\text{O}$ ,  $\text{M}_2\text{O}_2$  and  $\text{MO}_2$  may be prepared. The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions :



The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The superoxides are also paramagnetic. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

#### Problem 10.3

Why is  $\text{KO}_2$  paramagnetic ?

#### Solution

The superoxide  $\text{O}_2^-$  is paramagnetic because of one unpaired electron in  $\pi^*2p$  molecular orbital.

The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of much heat on account of intense hydration.

### 10.2.2 Halides

The alkali metal halides,  $\text{MX}$ , ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are all high melting, colourless crystalline solids. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid ( $\text{HX}$ ). All of these halides have high negative enthalpies of formation; the  $\Delta_f H^\ominus$  values for fluorides become less negative as we go down the group, whilst the reverse is true for  $\Delta_f H^\ominus$  for chlorides, bromides and iodides. For a given metal  $\Delta_f H^\ominus$  always becomes less negative from fluoride to iodide.

The melting and boiling points always follow the trend: fluoride > chloride > bromide > iodide. All these halides are soluble in water. The low solubility of  $\text{LiF}$  in water is due to its high lattice enthalpy whereas the low solubility of  $\text{CsI}$  is due to smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol, acetone and ethylacetate;  $\text{LiCl}$  is soluble in pyridine also.

### 10.2.3 Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid,  $\text{H}_2\text{CO}_3$  ( $\text{OC}(\text{OH})_2$ ); sulphuric acid,  $\text{H}_2\text{SO}_4$  ( $\text{O}_2\text{S}(\text{OH})_2$ ). The alkali metals form salts with all the oxo-acids. They are generally soluble in water and thermally stable. Their carbonates ( $\text{M}_2\text{CO}_3$ ) and in most cases the hydrogencarbonates ( $\text{MHCO}_3$ ) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonates and hydrogencarbonates increases. Lithium carbonate is not so stable to heat; lithium being very small in size polarises a large  $\text{CO}_3^{2-}$  ion leading to the formation of more stable  $\text{Li}_2\text{O}$  and  $\text{CO}_2$ . Its hydrogencarbonate does not exist as a solid.