CHAPTER

2

s-BLOCK ELEMENTS

Animation 2.1 : s block elements
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IN THIS CHAPTER YOU WILL LEARN

1. To write the electronic configuration of s-block elements in sequence.
2. The occurrence of group IA and IIA elements and the peculiar behaviours of lithium and beryllium.
3. The difference in the physical properties of group IA and IIA elements as well as the differences in the chemical behaviour of their compounds.
4. The commercial preparation of sodium.
5. How sodium hydroxide is commercially prepared.
6. The role of gypsum and lime in agriculture and industry.

2.1 INTRODUCTION

The s-block elements are the metals in Group IA and Group IIA of the periodic table.They are called the s-block elements because s-orbitals are being filled, in their outer most shells.The elements of group IA except hydrogen are called “Alkali metals” while those of IIA are named “Alkaline-earth metals”.

The name alkali came from Arabic, which means ‘The Ashes’. The Arabs used this term for these metals because they found that the ashes of plants were composed chiefly of sodium and potassium. Alkali metals include the elements, lithium, sodium, potassium, rubidium, caesium and francium. These are very reactive metals, produce strong alkaline solutions with water.The alkaline-earth metals are beryllium, magnesium, calcium, strontium, barium and radium.They are called alkaline-earth because they produce alkalies in water and are widely distributed in earth’s crust.

The alkali and alkaline-earth metals include the most reactive electropositive elements and a study of their electronic configurations will help in understanding their properties.

Animation 2.2 : Haloform_reaction
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2.1.1 Electronic Configurations of s-Block Elements.

Alkali Meta1

Alkali metals have only one electron in 's' orbital of their valence shell. All alkali metals lose their one electron of the valence shell to form monopositive ions M^+ because their ionization energy values are very low. They form ionic compounds and show +1 oxidation state. The electronic configurations and some physical constants of alkali metals are given in Table2.1

Table 2.1 Electronic Configurations and Physical Constants of Alkali Metals

Properties	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configurations	$1s^2 2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Ionization energy (kJ/ mol)	520	496	419	403	376
Electron affinity (kJ/mol)	60	53	48	47	48
Electronagetivity	1.0	0.9	0.8	0.8	0.7
Atomic radius	123	158	203	216	235
Ionic radius of 1+ion (pm)	60	95	133	148	169
Melting points (°C)	187.0	97.5	63.6	39.0	28.5
Boiling points (°C)	1325	889	774	688	690
Density gm/cm^3 at (20°C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mol)	505	475	384	345	310

Alkaline-Earth Metals

Alkaline earth metals have two electrons in 's' orbital of their valence shell. All alkaline earth metals lose their two electrons to form dipositive ions M^{2+}, because their ionization energy values are low. They form ionic compounds and show + 2 oxidation state.

The electronic configurations and some physical constants of alkaline earth metals are given in Table 2.2.

Table 2.2 Electronic Configurations and Physical Constants of Alkaline-Earth Metals

Properties	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electronic configurations	$1s^2 2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$
Ionization energy (kJ/ mol)	899	738	590	549	503
Electron affinity (kJ/mol)	240	230	156	168	52
Electronagetivity	1.5	1.2	1.0	1.0	0.9
Atomic radius	89	136	174	191	198
Ionic radius of 2+ion (pm)	31	65	99	113	135
Melting points (°C)	1289	649	839	769	725
Boiling points (°C)	2970	1107	1484	1384	1640
Density gm/cm^3 at (20°C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mol)	2337	1897	1619	1455	1250

In going down a group the number of shells increase by one at each step and equal to the number of the period to which the element belongs.

Animation 2.3 : s-block elements
Source and credit: Crescen

2.1.2 Occurrence of Alkali Metals

Due to high reactivity, the alkali metals occur in nature in the combined state. None of the alkali metals is found free in nature. Sodium and potassium are abundant alkali metals and each constitute about 2.4 percent of earth's crust. Most of the earth's crust is composed of insoluble alumino-silicates of alkali metals.

Table 2.3 Common Minerals of The Most Important Alkali Metals

Name of Mineral	Chemical Formula
Lithium	
Spodumene	$LiAl(SiO_3)_2$
Sodium	
Rock Salt (Halite)	$NaCl$
Chile saltpetre	$NaNO_3$
Natron	$Na_2CO_3.H_2O$
Trona	$Na_2CO_3.2NaHCO_3.2H_2O$
Borax	$Na_2B_4O_7.10H_2O$
Potassium	
Carnallite	$KCl.MgCl_2.6H_2O$
Sylvite	KCl
Alunite(Alum Stone)!	$K_2SO_4, Al_2(SO_4)_3.4Al(OH)_3$

Animation 2.4 : Metals
Source and credit: wordpress

Lithium deposits, usually in the form of complex minerals, are widely scattered over the earth. An important commercial source of lithium is the mineral spodumene, $LiAl(SiO_3)_2$.

Small amounts of rubidium and caesium are found in potassium salts deposits. Francium has not been found in nature. It has been prepared artificially in the laboratory and is very unstable, so that a very little is known about this metal.

2.1.3 Occurrence of Alkalme-Earth Metals

Being very reactive, alkaline earth metals also do not occur in free state. The compounds of these metals occur widely in nature.

Magnesium and calcium are very abundant in earth's crust. The outer portion of the earth was originally in the form of silicates and alumino-silicates of alkaline-earth metals. Magnesium and calcium, with sodium and potassium are present in the rocks as cations.Magnesium halides are found in sea water. Magnesium is an essential constitutent of chlorophyll. Calcium phosphate, $Ca_3(PO_4)_2$ and calcium fluoride, CaF_2 are also found as minerals.Calcium is an essential constituent of many living organisms. It occurs as skeletal material in bones, teeth, sea-shells and egg shells.Radium is a rare element. It is of great interest because of its radioactive nature.

Table 2.4 Common Minerals of the Alkaline-Earth Metals

Name of Mineral	Chemical Formula
Beryllium	
Beryl	$Be_3Al_2(SiO_3)_6$
Chrysoberyl	Al_2BeO_4
Magnesium	
Magnesite	$MgCO_3$
Dolomite	$MgCO_3 . CaCO_3$
Carnallite	$KCl.MgCl_2.6H_2O$
Epsom salt	$MgSO_4.7H_2O$
Soap stone (talc)	$H_2Mg_3(SiO_3)_4$
Asbestos	$CaMg_3(SiO_3)_4$
Calcium	
Calcite (Lime Stone)	$CaCO_3$
Gypsum	$CaSO_4.2H_2O$
Fluorite	CaF_2
Phosphorite	$Ca_3(PO_4)_2$
Strontium	
Strontionite	$SrCO_3$
Barium	
Barite	$BaSO_4$

2.1.4 Peculiar Behaviour of Lithium

In many of its properties, lithium is quite different from the other alkali metals.This behaviour is not unusual, because the first member of each main group of the periodic table shows marked deviation from the regular trends of the group as a whole.

The deviation shown by lithium can be explained on the basis of its small radius and high charge density. The nuclear charge of Li^+ ion is screened only by a shell of two electrons. The so-called 'anomalous' properties of lithium are due to the fact that lithium is unexpectedly far less electropositive than sodium. Some of the more important differences of lithium from other alkali metals are listed below:

1. Lithium is much harder and lighter than the other alkali metals.
2. The lithium salts of anions with high charge density are generally less soluble in water than those of the other alkali metals, e.g. LiOH, LiF, Li_3PO_4, Li_2CO_3.

3. Lithium forms stable complex compounds, althongh complex formation generally is not a property of alkali metals. One of the stable complexes formed by lithium is $[Li(NH_3)_4]^+$
4. Lithium reacts very slowly with water, while other alkali metals react violently.
5. Lithium salts of large polarizable anions are less stable than those of other alkali metals. Unlike other alkali metals lithium does not form bicarbonate, tri-iodide or hydrogen sulphide at room temperature.

6. When burnt in air lithium forms only normal oxide, whereas the others form peroxides or superoxides.
7. Lithium hydride is more stable than the hydrides of other alkali metals.
8. Lithium compounds are more covalent, that is why its halides are more soluble in organic solvents and the alkyls and aryls of lithium are more stable than those of other alkali metals.
9. Lithium is the least reactive metal of all the alkali metals.

Animation 2.5 : ALKALI METALS
Source and Credit: Docbrown

10. When acetylene is passed over strongly heated lithium, it does not produce lithium acetylide, but other alkali metals form the corresponding metallic acetylides.

$$2Na_{(s)} + C_2H_{2(g)} \longrightarrow Na^+C^- \equiv C^-Na^+ + H_{2(g)}$$

Sodium acetylide

11.Lithium has low electropositive character, thus its carbonate and nitrate are not so stable and therefore decompose giving lithium oxide. Carbonates of other alkali metals do not decompose.Decomposition of lithium nitrate gives different products than the nitrates of other alkali metals.

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

$$4LiNO_3(s) \longrightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

12. Lithium hydroxide when strongly heated , forms lithium oxide but the other alkali metal hydroxides do not show this behaviour.

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O(s) + H_2O(l)$$

13. Lithium reacts with nitrogen to form nitride, while the other members of the group do not give this reaction.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

14. Lithium chloride has an exothermic heat of solution, whereas chlorides of sodium and potassium have endothermic heats of solution.

15. Lithium carbide is the only alkali metal carbide formed readily by the direct reaction.

2.1.5 Peculiar Behaviour of Beryllium

Beryllium is the lightest member of the series and differs from the other group IIA elements in many ways.This is due to its small atomic size and comparatively high electronegativity value. The main points of difference are:

1. Beryllium metal is almost as hard as iron and hard enough to scratch glass. The other alkaline earth metals are much softer than beryllium but still harder than the alkali metals.
2. The melting and boiling points of beryllium are higher than other alkaline earth metals. (Table 2.2)
3. As reducing agents, the group IIA metals are all powerful enough to reduce water, at least in principle. However, with water, beryllium forms insoluble oxide coating that protects it from further attack.

4. Beryllium in particular is quite resistant towards complete oxidation, even by acids, because of its BeO coating.
5. Beryllium is the only member of its group which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

$$Be_{(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_{2(aq)}} + H_{2(g)}$$

2.2 GENERAL BEHAVIOUR OF ALKALI METALS

The reducing property of an element depends on the magnitude of its ionization energy. Reducing agent is a substance which can lose electrons. Since alkali metals have got low ionization energies, so they are strong reducing agents. They are highly electropositive. They react readily with halogens giving alkali metal halides.

2.2.1 Trends in Chemical Properties of Alkali Metals

1. Low ionization energies make the alkali metals, the most reactive family of metals.
2. Very high second ionization energies indicate that oxidation number higher than 1, are ruled out for the alkali metals.
3. The cations of alkali metals have low charge and large radii than the radius of any cation from the same period, so the lattice energies of their salts are relatively low. Consequently, most of the simple salts of the alkali metals are water-soluble. Most of the salts are dissociated completely in aqueous solution and the hydroxides are among the strongest bases available.

4. They react with oxygen and the surface is tarnished due to the oxides formed. Only lithium burns in air to form the normal oxide, Li_2O (white solid).

$$4\,Li(s) + O_2(g) \longrightarrow \underset{\text{Lithium oxide}}{2\,Li_2O(s)}$$

The exposed metals are oxidized almost immediately by oxygen in air, and in the presence of moisture. The oxides formed react with CO_2 in the atmosphere to form carbonates.

$$\underset{\text{Lithium oxide}}{Li_2O(s)} + CO_2(g) \longrightarrow \underset{\text{Lithium carbonate}}{Li_2CO_3(s)}$$

Sodium will undergo a similar reaction, but only if the supply of oxygen is limited. In the presence of excess of oxygen, sodium forms the pale yellow peroxide.

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2(s)}$$

Potassium, rubidium and caesium react with oxygen to form superoxides (orange yellow). Caesium explodes spontaneously when it is in contact with air or oxygen.

$$K(s) + O_2(g) \longrightarrow \underset{\text{Potassium superoxide}}{KO_2(s)}$$

5. Very rapid reactions occur when alkali metals react with water. A small piece of sodium (potassium or lithium) floated on water reacts vigorously to liberate hydrogen and produce metal hydroxide. The reaction is highly exothermic. The energy produced by the reaction may even ignite the hydrogen.

$$2Na(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2(g)$$

The reaction becomes increasingly vigorous from lithium to caesium. Potassium, rubidium and caesium are so highly reactive that they react with ice even at -100°C.

6. Alkali metals form ionic hydrides with hydrogen.

$$2M(s) + H_2(g) \longrightarrow 2M^{+}H^{-}(s)$$

Rubidium and caesium react violently with hydrogen at room temperature. The other three metals require elevated temperature in order to form the hydride. Lithium and sodium hydrides are useful sources of hydrogen when treated with water.

$$LiH(s) + H_2O(\ell) \longrightarrow LiOH(aq) + H_2(g)$$

Due to the presence of hydride ion (H), the ionic hydrides are used as powerful reducing agents.

7. Lithium is the only Group IA metal that combines with nitrogen and carbon to form nitride and carbide, respectively.

$$6Li(s) + N_2(g) \longrightarrow \underset{\text{Lithium nitride}}{2Li_3N(s)}$$

$$4Li(s) + C(s) \longrightarrow \underset{\text{Lithium carbide}}{Li_4C(s)}$$

Alkali metals react easily with halogens to give halides. Lithium and sodium, for example, react slowly with chlorine at room temperature. Molten sodium burns with a brilliant yellow flame in a chlorine atmosphere to form sodium chloride.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Potassium, rubidium and caesium react vigorously with all the halogens, forming metal halides. All alkali metals form their sulphides when treated with molten sulphur. The general reaction is:

$$2M(s) + S(s) \longrightarrow M_2S(s)$$

2.2.2 Trends in Chemical Properties of Alkaline-Earth Metals

1. The alkaline-earth metals burn in oxygen to form oxides or in the case of barium, the peroxide. Beryllium is the least reactive metal in the group. It is resistant to complete oxidation and stable in air at ordinary temperature but oxidizes rapidly at about 800“C. Therefore beryllium is not tarnished by atmospheric attack but the metal soon loses the silvery appearance.

$$2Be(s) + O_2(g) \xrightarrow{800^\circ C} 2BeO(s)$$

When exposed to air magnesium quickly becomes coated with the layer of MgO.
This layer protects the surface from further corrosion at ordinary temperature.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

When magnesium is burnt in air a small amount of nitride is also formed along with magnesium oxide: When barium is heated in air or oxygen at 500 - 600°C, its peroxide is formed.

$$Ba(s) + O_2(g) \xrightarrow{500-600^\circ C} \underset{\text{Barium peroxide}}{BaO_2(s)}$$

2. Hydrides are produced by treating the molten alkaline earth metals with hydrogen, usually under high pressures. Magnesium reacts with hydrogen at high pressure and in the presence of a catalyst (MgI_2) forming magnesium hydride.

$$Mg(s) + H_2(g) \xrightarrow[(MgI_2)]{Pressure} MgH_2(g)$$

similarly $$Ca(s) + H_2(g) \longrightarrow CaH_2(g)$$

3. All Group II-A elements react with nitrogen on heating giving nitrides. For example, magnesium reacts with nitrogen to give magnesium nitride.

$$3Mg(s) + N_2(g) \longrightarrow \underset{\text{Magnesium nitride}}{Mg_3N_2(g)}$$

The nitrides hydrolyse vigorously when treated with water, giving ammonia and the respective hydroxides.

$$Mg_3N_2(s) + 6H_2O(\ell) \longrightarrow 2NH_3(g) + 3Mg(OH)_2(s)$$

4. With sulphur, magnesium gives magnesium sulphide, MgS. The other Group II-A metals also react similarly.

$$Mg + S \longrightarrow \underset{\text{Magnesium sulphide}}{MgS}$$

5. All group II-A elements react directly with halogens giving halides of the type MX_2 e.g.

$$Ca(s) + Cl_2(g) \longrightarrow CaCl_2(g)$$

6. Magnesium is more reactive than beryllium, even though it is not attacked by cold water. Magnesium reacts slowly with boiling water and quite rapidly with steam to liberate hydrogen.

$$\underset{\text{Steam}}{Mg(s) + H_2O(g)} \xrightarrow{100^\circ C} MgO(s) + H_2(g)$$

Beryllium does not react with water even at red hot temperature but remaining alkaline earth metals produce hydroxides with water.

$$M(s) + 2H_2O(l) \xrightarrow{100^\circ C} M(OH)_2(s) + H_2(s)$$

2.2.3 General Trends in Properties of Compounds of Alkali and Alkaline Earth metals

i) Oxides

Alkali metal oxides dissolve in water to give strong alkaline solutions. For example:

$$Li_2O(s) + H_2O(l) \longrightarrow 2LiOH\ (aq)$$

$$2Na_2O_2(s) + 2H_2O(l) \longrightarrow 4NaOH\ (aq) + O_2(g)$$

The reaction of an alkali metal oxide with water is an acid-base reaction and not an oxidation reduction reaction since no element undergoes a change in its oxidation number. The reaction simply involves the decomposition of water molecule by an oxide ion.

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

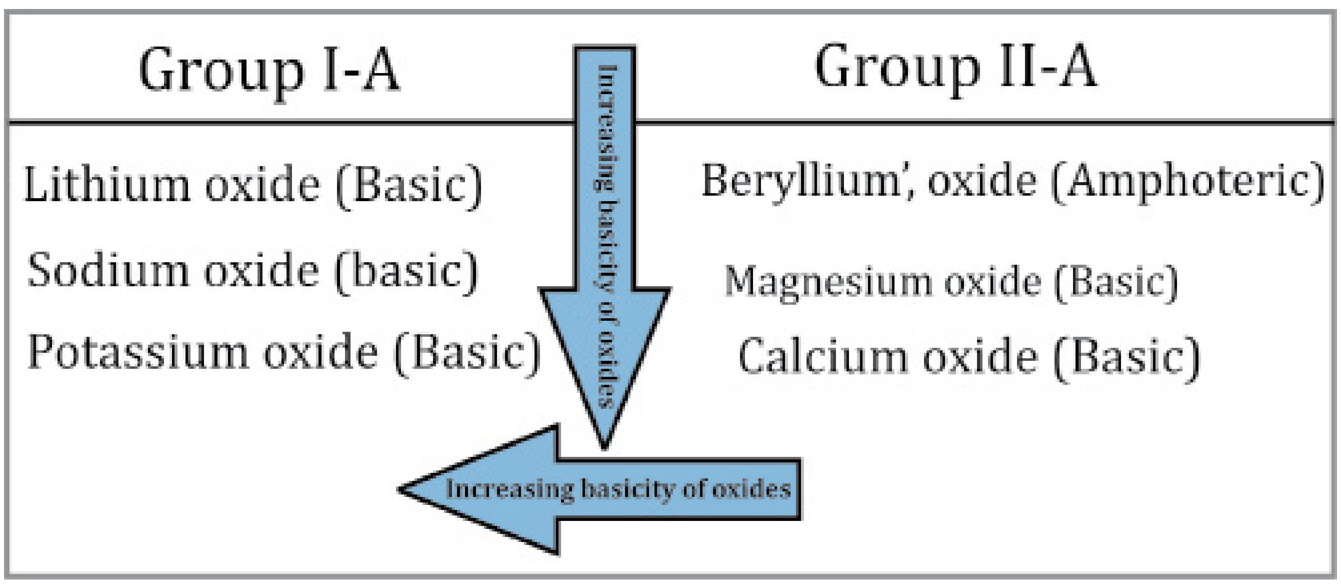
The basic character of alkali metal oxides increases down the group. Potassium superoxide ($K0_2$) has a very interesting use in breathing equipments for mountaineers and in space craft. It has the ability to absorb carbon dioxide while giving out oxygen at the same time.

$$4KO_2(s) + 2CO_2(g) \longrightarrow 2K_2CO_3(s) + 3O_2(g)$$

The solubility of alkaline earth metal oxides in water increases down the group. BeO and MgO are insoluble but CaO, SrO and BaO are soluble and react with water to form the corresponding hydroxides.

The basic character of the oxides of alkaline earth metals increases down the group. The tendency for group IIA oxides to form alkaline solution is relatively less than that of alkali metals .

Animation 2.6 : Reaction with acids
Source and Credit: Learn



BeO is amphoteric in nature since it reacts with both acids and bases.

$$BeO(s) + H_2SO_4(aq) \longrightarrow BeSO_4(s) + H_2O(\ell)$$

$$BeO(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2(aq)} + H_2O(\ell)$$

ii) Hydroxides

The alkali metal hydroxides are all crystalline solids, very soluble in water except LiOH, which is slightly soluble.They are generally hygrsocopic and are very strong bases, execpt LiOH. The solubility of alkaline earth metal hydroxides in water increases down the group. $Be(OH)_2$ is quite insoluble. $Mg(OH)_2$ is sparingly soluble while Ba $(OH)_2$ is more soluble.This increase in solubility is due to low lattice energy of hydroxides which is, in turn, due to higher ionic size.

Alkali metal hydroxides are stable to heat except LiOH, while alkaline earth metal hydroxides like $Mg(OH)_2$ and $Ca(OH)_2$ decompose on heating.

$$2LiOH(s) \longrightarrow Li_2O(s) + H_2O(\ell)$$

$$Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(\ell)$$

A saturated solution of $Ca(OH)_2$ in water is called lime water and is used as a test for CO_2. A suspension of $Mg(OH)_2$ in water is called milk of magnesia and it is used for treatment of acidity in stomach.

iii) Carbonates

The carbonates of alkali metals are all soluble in water and are stable towards heat except Li_2CO_3 which is not only insoluble but also decompose on heating to lithium oxide. The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable. In case of large cation like K^+ in K_2CO_3, the gain in electrostatic attraction is relatively much less and the decomposition is difficult. Sodium carbonate is very important industrial chemical. At temperature below 35.2°C, Na_2CO_3 crystallizes out from water as $Na_2CO_3.10H_2O$, which is called washing soda. Above this temperature it crystallizes as $Na_2CO_3.\ H_2O$. On standing in air, $Na_2CO_3.10H_2O$ slowly loses water and converted to a white powder $Na_2CO_3.H_20$. The solution of Na_2CO_3 in water is basic due to hydrolysis of carbonate ion.

$$Na_2CO_3(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2CO_3(aq)$$

Unlike the alkali metal carbonates, the alkaline earth metal carbonates are only very slightly soluble in water, with the solublity decreasing down the group. They also decompose on heating and the ease of decomposition decreases down the group.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The ease of decomposition can be related to the size of the metal ion, the smaller the ion, the more is the lattice energy of the resulting oxide and hence higher the stability of the product.

iv) Nitrates

Nitrates of both alkali and alkaline-earth metals are soluble in water. Nitrates of Li, Mg , Ca and Ba decompose on heating to give O_2, $NO_2$and the metallic oxide whereas nitrates of Na and K decompose to give different products.

$$4LiNO_3(s) \longrightarrow 2Li_2O\,(s) + 4NO_2(s) + O_2(g)$$

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

$$2Ca(NO_3)_2(s) \longrightarrow 2CaO\,(s) + 4NO_2(g) + O_2(g)$$

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

v) Sulphates

All the alkali metals give sulphates and they are all soluble in water. The solubilities of sulphates of alkaline earth metals, gradually decrease down the group. $BeSO_4$ and $MgSO_4$ are fairly soluble in water. $CaSO_4$ is slightly soluble, while $SrSO_4$ and $BaSO_4$ are almost insoluble.

Calcium sulphate occurs in nature as gypsum $CaSO_4.2H_2O$. When it is heated above 100°C, it loses three quarters of its water of crystallization, giving a white powder called' Plaster of Paris.

$$\underset{\text{Gypsum}}{2CaSO_4\,.\,2H_2O} \longrightarrow \underset{\text{Plaster of Paris}}{(CaSO_4)_2\,.\,H_2O} + 3H_2O$$

2.3 COMMERCIAL PREPARATION OF SODIUM BY DOWNS CELL

Most of sodium metal is produced by the electrolysis of fused sodium chloride. Since the melting point of sodium chloride is 801°C, some calcium chloride is added to lower its melting point and to permit the furnace to operate at about 600^0C.

In the electrolytic cell, the large block of graphite at the centre is the anode, above which there is a dome for the collection of chlorine. The cathode is a circular bar of copper or iron which surrounds the anode but is separated from it by an iron screen, which terminated in a gauze. The arrangement permits the electric current to pass freely but prevents sodium and chlorine from mixing after they have been set free at the electrodes, Fig. 2.1

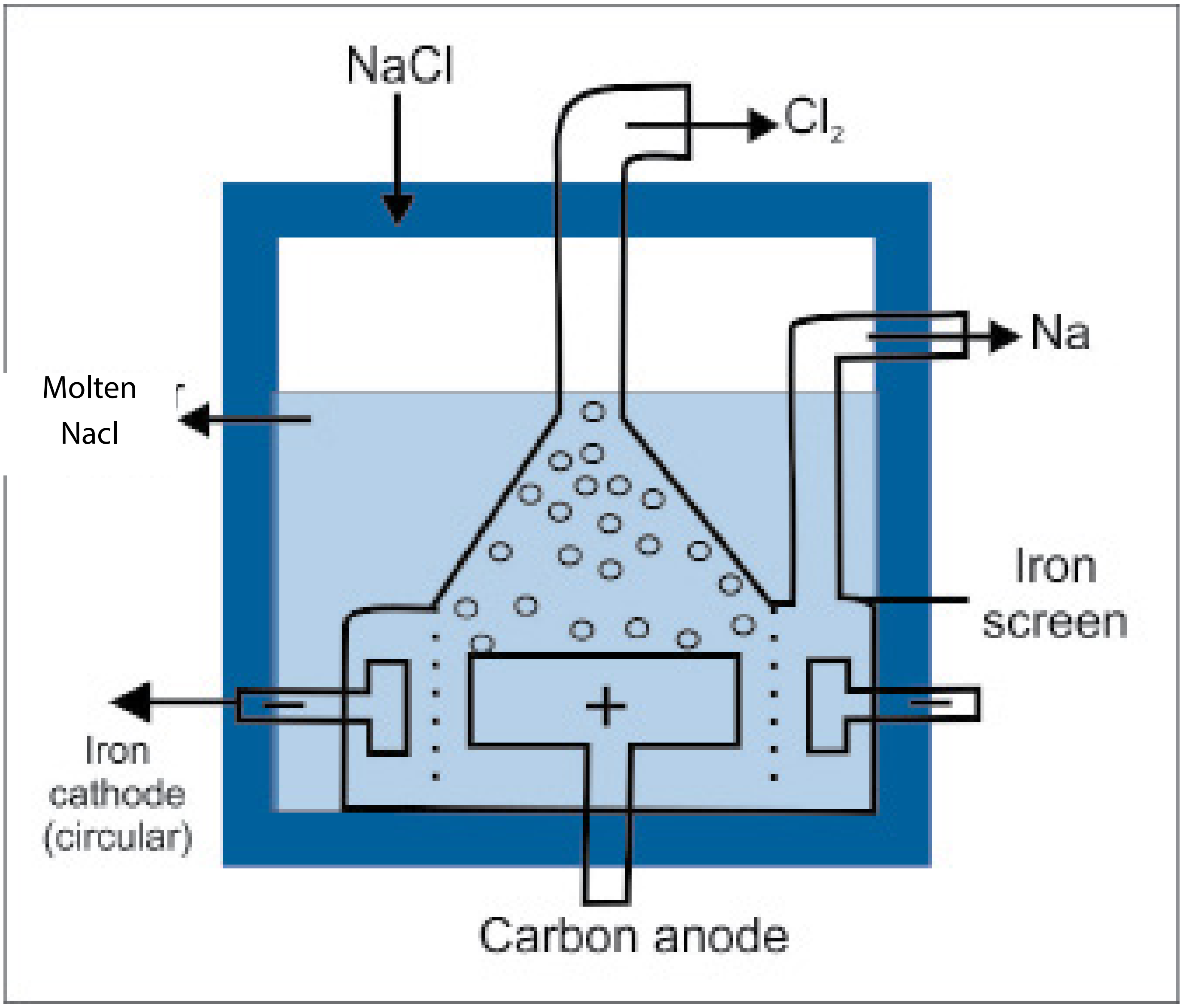


Fig.2.1 Down's Cell

Animation 2.7 DOWN'S CELL
Source and Credit: eLearn.Punjab

Sodium metal rises in a special compartment from which it is taken out at intervals.
The cell produces dry chlorine and 99.9 percent pure sodium. The process is carried out at 600°C and it has the following advantages.

(a) The metallic fog is not produced.
(b) Liquid sodium can easily be collected at 600°C.
(c) Material of the cell is not attacked by the products formed during the electrolysis.
During the process the following reactions take place:

$$NaCl \longrightarrow Na^+ + Cl^-$$

At cathode $$Na^+ + e^- \longrightarrow Na$$

At anode $$Cl^- \longrightarrow 1/2Cl_2 + 1e^-$$

2.4 COMMERCIAL PREPARATION OF SODIUM HYDROXIDE BY THE DIAPHRAGM CELL

Sodium hydroxide is manufactured on a large scale by the electrolysis of aqueous solution of common salt in a diaphragm cell Fig. 2.2 (a)

The cell is made of steel tank. An oblong perforated steel vessel lined inside with asbestos diaphragm serves as a cathode. It is provided with a constant level device to keep the vessel filled to the specified level with brine. A graphite anode is held within the U shaped diaphragm and it projects into the salt solution. The steam is blown during the process which keeps the electrolyte warm and helps to keep the perforations clear.

The chlorine released at the anode, rises into the dome at the top while hydrogen released at the cathode, escapes through a pipe. The sodium hydroxide solution slowly percholates into a catch basin.

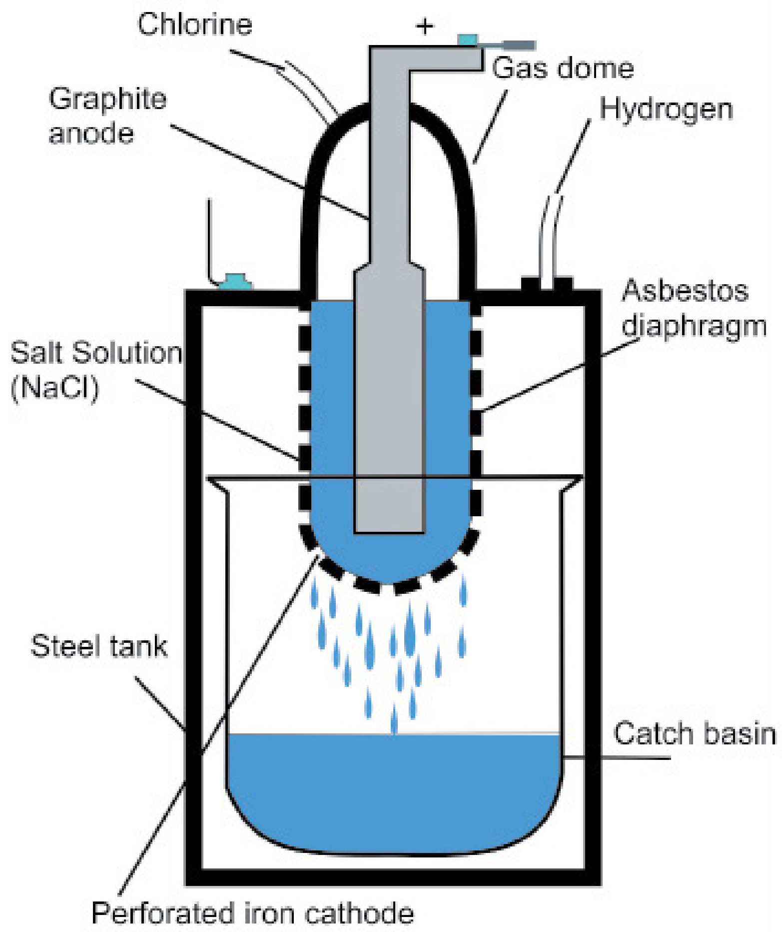


Fig.2.2(a) Nelson Cell for the Production of NaOH

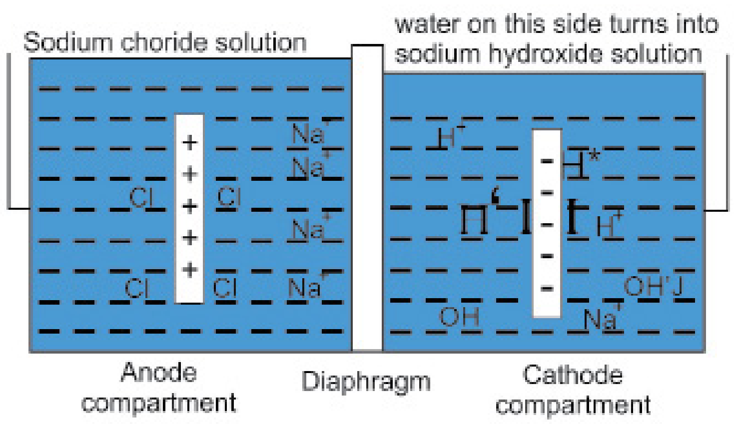


Fig.2.2(b)

The Fig. 2.6 (b) shows a simplified version of the cell in order to understand the purpose of diaphragm. When the electrolysis takes place, chlorine is given off at the anode according to the following reaction.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$$

At the cathode hydrogen is discharged by the reduction of water.

$$2H_2O + 2e^- \longrightarrow 2OH^-(aq) + H_2(g) \quad \text{(Cathode)}$$

The overall result of the above reactions is that the brine loses its chloride ions and the solution turns increasingly alkaline in cathode compartment.

We can face two major problems during the working of the cell.

1. Chlorine produced can react with hydroxide ions in cold giving hypochlorite ions.

$$Cl_2(g) + 2OH^-(aq) \longrightarrow OCl^-(aq) + Cl^-(aq) + H_2O$$

2. Hydroxide ions may be attracted towards anode, where they can be discharged releasing oxygen gas. This oxygen gas may contaminate the chlorine and renders it impure.

The first problem is solved by using asbestos diaphragm. This keeps the two solutions separate while allowing sodium ions to move towards the cathode. This movement of ions keep the current following through the external current.

The second problem is solved keeping the level of brine in anode compartment slightly higher, this keeps the direction of flow of liquid toward the cathode and thus preventing the possibility of hydroxides ions to reach the anode.

The solution that flows out of the cathode compatment contains 11% NaOH and 16% NaCl. Evaporation of this solution crystallizes the less soluble NaCl which is filtered off, the liquid left contains about 50% NaOH and only 1% NaCl as an impurity. For commercial purposes this small impurity is not important.

2.5 ROLE OF GYPSUM IN AGRICULTURE AND INDUSTRY

(a) Role of Gypsum in Agriculture

Gypsum, a hydrated calcium sulphate, is a mineral that occurs in large deposits throughout the world.Gypsum is applied to the soil as a source of calcium and sulphur. The calcium supplied by gypsum in fertilizers is of importance in crop production in area where soils are subject to extensive leaching.

Sulphur has been recognised as an essential constituent of plants. For centuries, sulphur compounds had been applied to soils because of their observed beneficial effect on plant growth. Aside from serving as a constituent of protein and various other compounds in plants, sulphur has an influence on chlorophyll development in plant leaves. Although not a constituent of chlorophyll, plants deficient in sulphur exhibits a pale green colour. The root system of several plants have been observed to be greatly enlarged by the application of sulphur. It has been reported that good crops are produced by the application of sulphur containing materials such as gypsum.

(b) Role of Gypsum in Industries

When gypsum is heated under carefully controlled conditions, it loses three quarters of water of crystallization. The resulting product is called Plaster of Paris. Gypsum must not be heated too strongly as the anhydrous salt is then formed which absorbs water slowly. Such plaster is called 'Dead burnt'.

Plaster of Paris when mixed with half of its weight of water, it forms a plastic type viscous mass and then sets to a hard porous mass. This process is completed within 10 to 15 minutes. During the process expansion about 1% in volume also occurs, which fills the moulds completely and thus a sharp impression is achieved Plaster of Paris is used for making plaster walls, casts of statuary,coins, etc.

It is used in surgery, Plaster of Paris bandages are used for holding in place fractured bones after they have been set.

Special plasters contain plaster of Paris and other ingredients which vary with the demands of the use to which they are to be put. Two varieties of plasters are made.

(1) Cement Plaster.

It is plaster of Paris to which usually glue or other oils have been added as retarders to prolong the time of setting.

(2) Hard Finish Plasters

These are made by the calcination of the anhydrous sulphate with alum or borax.These plasters are set very slowly but give a hard finish. When mixed with wood pulp and allowed to set in the form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions. Gypsum is also used as a filler in paper industries.

Portland cement is made by strongly heating a finely powdered mixture of clay and limestone. The final product, known as clinker, is cooled and then ground into a very fine powder. During the grinding there is added about 2% of gypsum which prevents the cement from hardening too rapidly.The addition of gypsum increases the setting time of cement.

2.6 ROLE OF LIME IN AGRICULTURE AND INDUSTRY

Lime, (CaO) is a soft, white compound which is obtained by the thermal decomposition of $CaCO_3$.

(a) Role of Lime in Agriculture

Large quantities of calcium oxide are used in agriculture for neutralizing acidic soils.

It has been found that application of lime to acidic soils increases the amount of readily soluble phosphorus. Calcium oxide is also used in large amounts for making lime-sulphur sprays which have a strong fungicidal action. The hydroxide of calcium is obtained when the oxide of the calcium is allowed to react with water. The process is called slaking of lime and it is an exothermic reaction.

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

Functions of Calcium in Plant-Growth

The presence of calcium is essential for the normal development of plants. The quantity of calcium required by different plants varies considerably. An adequate supply of calcium appears to stimulate the development of root hairs and, in fact, the entire root system. Calcium is also necessary for normal leave development and tends to accumulate in leaves as well as in bark. An adequate supply of calcium is also essential for the optimum activity of microorganisms that produce nitrates. The effect of calcium on the supply of available phosphorus in the soil is of special significance. Soils containing sufficient calcium are slightly alkaline in nature. When a deficiency of calcium exists various substances such as aluminium and manganese may accumulate in plants in harmful concentrations.

(b) Role of Lime in Industries

1. Large quantities of lime are used in the extraction and refining of metals.
2. Lime is also used in paper, cement and leather industries
3. The ability of lime to react with sand at high temperature forming calcium silicate
($CaSiO_3$) serves as an important basis for glass manufacture.
4. Lime is used in ceramic industry for producing different types of sanitary materials.

5. Ordinary mortar, also called lime mortar, is prepared by mixing freshly prepared slaked lime (one volume) with sand (three or four volumes) and water to form a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the blocks firmly together. The equations for the chemical reactions which take place when mortar hardens are:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$

6. Lime is also used in refining of sugar and other food products.
7. Lime is used in the manufacturing of bleaching powder, which is used for the bleaching of the fabric and paper pulp.
8. A suspension of the calcium hydroxide is called milk of lime and is used as a white-wash.
9. When lime is heated with coke at about 2800°C in an electric furnace, calcium carbide is produced, which on hydrolysis yields acetylene (C_2H_2).

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

10. Lime is often employed as a dehydrating agent, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium hydroxide (soda lime) is often employed to remove both water and carbon dioxide from certain gases.

Animation 2.8 : Gals(The most radio active alkali metal 2)
Source and Credit: Targeticse

Key Points

1. The elements of group IA except hydrogen are called 'alkali metals' while those of group IIA are named as alkaline earth metals.
2. Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions.
3. Alkaline earth metals have two electrons in s-orbital of their valence shell. They lose two electrons forming dipositive ions M^{2+}.
4. Spodumene, Chile saltpetre, trona, borax, carnallite, sylvite, alunite, halite, natron, are the common minerals of alkali metals.
5. Beryl, magnesite, dolomite, epsom salt, asbestos, calcite, gypsum, strontionite and barite are the important minerals of alkaline earth metals.
6. Lithium behaves different from the other alkali metals.
7. Lithium forms only normal oxide, whereas the others form higher oxides like peroxides and superoxides.
8. Beryllium is the only member of group II, which reacts with alkalies to give hydrogen. The other member do not react with alkalies.
9. Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
10. When gypsum is heated above 100°C, it loses three quarters of its water of crystallization, giving white powder of $CaSO_4.1/2H_2O$ which is called Plaster of Paris.
11. Sodium is prepared by the electrolysis of molten sodium chloride in Down's cell.
12. Calcium is necessary for development of leaves and it tends to accumulate in leaves and bark. An adequate quantity of calcium is essential for the optimum activity of microorganisms that produce nitrates.
13. Lime is used in paper and glass industries. It is also used for refining sugar and other food products.

EXERCISE

Q1. Fill in the blanks:

(i) Alkali metals are reactive than alkaline-earth metals.

(ii) Alkali metals decompose water vigorously producing_________ and hydrogen.

(iii) When heated in a current of dry hydrogen, alkaline earth metals form white crystalline of the type MH_2.

(iv) The beryllium hydroxide, like the hydroxide of aluminium is amphoteric, while the hydroxides of the other members of the group IIA are_________ .

(v) The elements of the group IA are termed as alkali metals, because their_________are alkaline.

(vi) Spodumene is an ore of________ metal.

(vii) Alkali metal nitrates on heating give the corresponding________ and oxygen.

(viii) $Na_2CO_3.H_2O$ is the chemical formula of a mineral of sodium which is known as_______ .

(ix) Metallic bicarbonates are decomposed on heating into their carbonates, along with_________ and_________ .

(x) Metal nitrates other than the alkali metals on heating decompose into the corresponding metal___________along with the evolution of nitrogen peroxide and oxygen.

Q2. Indicate True or False.

(i) Group IA elements are called alkali metals because their chlorides are alkaline in nature

(ii) Alkali metals are very good conductor of electricity.

(iii) The hydroxides of alkali metals and alkaline-earth metals are soluble in water.

(iv) Plaster of Paris is a hemihydrate.

(v) Alkali metals have low melting and boiling points as compared to those of alkaline earth metals.

(vi) Lithium carbonate is decomposed to its oxide, but the carbonates of the other alkali metals are stable towards heat.

(vii) All alkali metal sulphates are insoluble in water.

(viii) Lithium combines with nitrogen to form lithium nitride but other alkali metals do not react with nitrogen.

(ix) Trona is a mineral of lithium.

(x) Alkaline earth metals are stronger reducing agents than alkali metals.

Q 4. (a) Give the names, electronic configurations and occurrence of s-block elements.

(b) Discuss the peculiar behaviour of lithium with respect to the other members of alkali metals.

Q 5. Discuss the trends in chemical properties of compounds like oxides, hydroxides, carbonates, nitrates and sulphates of IA and IIA group elements.

Q 6. Compare the chemical behaviour of lithium with magnesium.

Q 7. (a) Mention the properties of beryllium in which it does not resemble with its own family.

(b) Why the aqueous solution of Na_2CO_3 is alkaline in nature?

Q 8. (a) Describe with diagram the manufacture of sodium by Down's cell.

(b) Point out the three advantages of this process.

Q9. (a) Compare the physical and chemical properties of alkali metals with those of alkaline earth metals.

(b) What happens when:

(i) Lithium carbonate is heated.

(ii) Lithium hydroxide is heated to red hot.

(iii) Beryllium is treated with sodium hydroxide.

(iv) Lithium hydride is treated with water.

Q10.Give formulas of the following minerals.

(a) Dolomite (b) Asbestos (c) Halite (d) Natron

(e) Beryl (f) Sylvite (g) Phosphorite (h) Chile saltpetre

Q.11. Answer the following questions briefly.

(a) Why alkali and alkaline earth metals are among the reactive elements of the periodic table?

(b) Why line water turns milky with CO_2 but becomes clear with excess CO_2?

(c)How gypsum is converted into plaster of paris?

(a) Why 2% gypsum is added in the cement?

(e)Why lime is added to an acidic soil?

(f) How lime and sand are used to make glass?

(g) How lime mortar is prepared?