CHAPTER

2

S-BLOCK ELEMENTS

Animation 2.1 : s block elements Source and Credit: eLearn.Punjab

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.

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

Animation 2.2 : Haloform_reaction Source and Credit: wiki

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 metals lose their one electron of the valence shell alkali form M⁺ because monopositive ions their ionization values energy are very low. They form ionic compounds and show +1 oxidation state. electronic configurations physical The of alkali and some constants metals are given in Table 2.1

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/cm³ 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

have two Alkaline earth metals electrons in 's' orbital of their shell. All alkaline earth metals lose valence their two electrons to M^{2+} , because form ions ionization energy dipositive their 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		Ca		Ва
Atomic number	4	12	20	38	56
Electronic configurations	1s ² 2s ²	[Ne]3s²	[Ar]4s ²	[Kr]5s ²	[Xe]6s²
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/cm³ 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 ₂ CO ₃ .2NaHCO ₃ .2H ₂ O			
Borax	$Na_{2}B_{4}O_{7}.10H_{2}O$			
Pot	assium			
Carnallite	KCl.MgCl ₂ .6H ₂ O			
Sylvite	KCI			
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 aluminosilicates 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 Chrysoberyl	Be ₃ Al ₂ (SiO ₃) ₆ Al ₂ BeO ₄			
Ma	ngnesium			
Magnesite Dolomite Carnallite Epsom salt Soap stone (talc) Asbestos	MgCO ₃ MgCO ₃ . CaCO ₃ KCl.MgCl ₂ .6H ₂ O MgSO ₄ .7H ₂ O H ₂ Mg ₃ (SiO ₃) ₄ CaMg ₃ (SiO ₃) ₄			
	Calcium			
Calcite (Lime Stone) Gypsum Fluorite Phosphorite	CaCO ₃ CaSO _{4.} 2H ₂ O CaF ₂ 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, Li₃PO₄, Li₅CO₃.
- 3. forms stable compounds, Lithium complex although complex formation generally is not property of alkali metals. a stable complexes of formed by $[Li(NH_3)_4]^+$ One the lithium is 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 lithium forms burnt in air only normal oxide, whereas others form the peroxides or superoxides.
- 7. Lithium hydride is more stable than the hydrides of other alkali metals.
- compounds 8. Lithium more covalent, that is why its halides are organic and aryls soluble solvents the alkyls are more in of of lithium more stable than those other alkali metals. are
- 9. Lithium is the least reactive metal of all the alkali metals.

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.

$$\begin{array}{cccc} \text{Li}_2\text{CO}_3(s) & \longrightarrow & \text{Li}_2\text{O}(s) + \text{CO}_2(g) \\ & & 4\text{LiNO}_3(s) & \longrightarrow & 2\text{Li}_2\text{O}(s) + 4\text{NO}_2(g) + \text{O}_2(g) \\ & & 2\text{NaNO}_3(s) & \longrightarrow & 2\text{NaN O}_2(s) + \text{O}_2(g) \end{array}$$

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

$$2\text{LiOH} \xrightarrow{\text{Red hot}} \text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l)$$

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

lightest member the of Beryllium is the series and differs from other group IIA elements in ways.This many is due its comparatively high small atomic size and 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 reduce water, at least in principle. However, with water, beryllium protects forms insoluble oxide that from further attack. coating it
- 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.

$$Be(s) + 2NaOH(aq) \longrightarrow Na_2BeO_2(aq) + H_2(g)$$

Sodium beryllate

2.2 GENERAL BEHAVIOUR OF ALKALI METALS

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

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, Li₂O (white solid).

$$4 \operatorname{Li}(s) + O_2(g) \longrightarrow 2 \operatorname{Li}_2O(s)$$

Lithium oxide

oxidized The exposed almost immediately metals are the of moisture. The oxides in air. and in presence oxygen in the atmosphere carbonates. formed react with CO₃ to form

$$\text{Li}_2\text{O}(s) + \text{CO}_2(g) \longrightarrow \text{Li}_2\text{CO}_3(s)$$

Lithium oxide

Lithium carbonate

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.

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$
Sodium peroxide

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

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

Potassium superoxide

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.

$$2Na(s) + 2H_2O(\ell)$$
 3/4 39 $2NaOH(aq) + H_2(g)$

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

6. Alkali metals form ionic hydrides with hydrogen.

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

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

2. s-Block Elements

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

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.

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

Lithium nitride

$$4\text{Li}(s) + C(s) \longrightarrow \text{Li}_{4}C(s)$$

Lithium carbide

react easily with halogens to give Alkali metals halides. Lithium for example, react slowly with sodium, chlorine and room temperature. Molten sodium with yellow burns a brilliant atmosphere flame in a chlorine 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 burnt in air a small nitride magnesium is amount of is When also formed along with magnesium oxide: barium is or oxygen 500 - 600°C, its heated peroxide formed. in air at is

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

Barium peroxide

produced by treating alkaline 2. **Hydrides** the molten are usually earth metals with hydrogen, under high pressures. with hydrogen high pressure Magnesium at and in the reacts catalyst (Mgl_2) forming magnesium hydride. presence of a

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

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(g)$$

Magnesium nitride

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.

$$Mg + S \longrightarrow MgS$$

Magnesium sulphide

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

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

2. s-Block Elements

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.

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

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:

$$\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow 2\text{LiOH (aq)}$$

 $2\text{Na}_2\text{O}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{NaOH (aq)} + \text{O}_2(g)$

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.

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

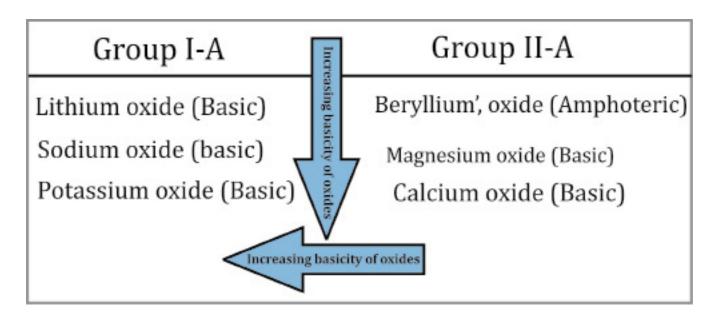
The basic character of alkali metal oxides increases down the group. Potassium superoxide (KO_2) has a very interesting use in breathing equipments for mountaineers and in space craft. It has the ability to absorb carbon dioxide while giving out oxygen at the same time.

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

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.

2. s-Block Elements

ii) Hydroxides

hydroxides are The alkali metal all crystalline solids, very except LiOH, which slightly soluble.They in water is soluble are are very strong bases, generally hygrsocopic and execpt LiOH. The solubility of alkaline earth metal hydroxides in water increases down the group. Be(OH), is quite insoluble. Mg(OH), is sparingly soluble while Ba (OH), 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 ${\rm Mg(OH)}_2$ and ${\rm Ca(OH)}_2$ decompose on heating.

$$2\text{LiOH(s)} \longrightarrow \text{Li}_2\text{O(s)} + \text{H}_2\text{O}(\ell)$$

$$\text{Mg(OH)}_2(s) \longrightarrow \text{MgO(s)} + \text{H}_2\text{O}(\ell)$$

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 Li₂CO₃ 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 K₂CO₃, 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, Na₂CO₃ crystallizes out from water as Na₂CO₃.10H₂O, which is called washing soda. Above this temperature it crystallizes as Na₂CO₃. H₂O. On standing in air, Na₂CO₃.10H₂O slowly loses water and converted to a white powder Na₂CO₃.H₂O. The solution of Na₂CO₃ in water is basic due to hydrolysis of carbonate ion.

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

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

2. s-Block Elements

$$4LiNO_{3}(s) \longrightarrow 2Li_{2}O(s) + 4NO_{2}(s) + O_{2}(g)$$

$$2Mg(NO_{3})_{2}(s) \longrightarrow 2MgO(s) + 4NO_{2}(g) + O_{2}(g)$$

$$2Ca(NO_{3})_{2}(s) \longrightarrow 2CaO(s) + 4NO_{2}(g) + O_{2}(g)$$

$$2NaNO_{3}(s) \longrightarrow 2NaNO_{2}(s) + O_{2}(g)$$

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.

$$2CaSO_4 \cdot 2H_2O \longrightarrow (CaSO_4)_2 \cdot H_2O + 3H_2O$$
Gypsum Plaster of Paris

2.3 COMMERCIAL PREPARATION OF SODIUM BY DOWNS CELL

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

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

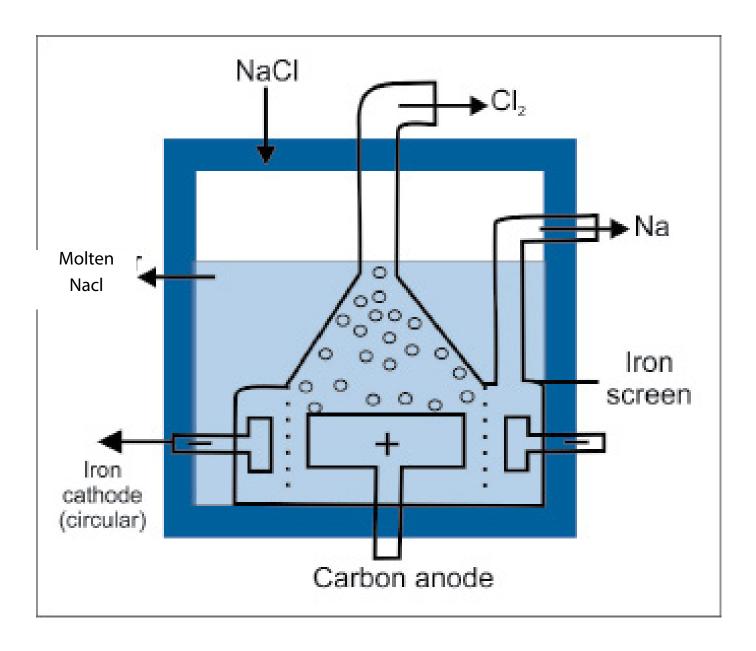


Fig.2.1 Down's Cell

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 la

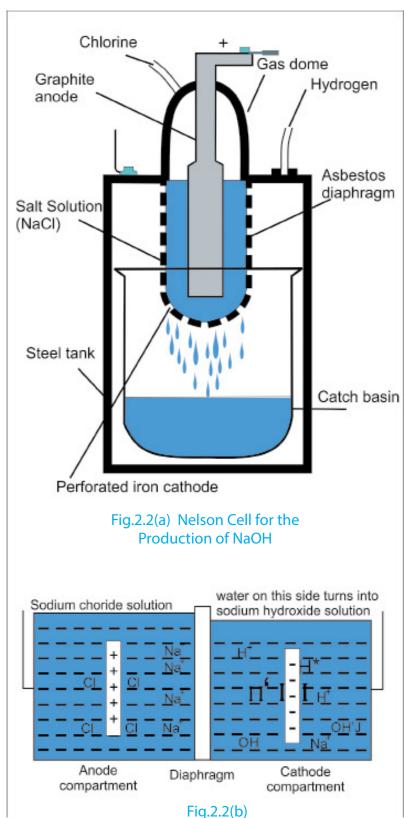
At anode Cl⁻ \longrightarrow 1/2Cl₂+1e⁻

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 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 pipe. through The a solution sodium hydroxide slowly percholates into catch basin. a



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.

$$2H_2O + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$$
 (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.

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

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

The first problem is solved by using asbestos diaphragm. This the while two solutions separate allowing sodium ions This to move towards the cathode. movement of ions following through the the external keep current 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% of NaOH and 16% NaCl. **Evaporation** this solution crystallizes filtered liquid soluble NaCl the less which is off, the left about 50% NaOH only 1% NaCl contains and as an impurity. For commercial this small impurity is important. purposes not

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, chlorophyll influence sulphur has on development an Although plant leaves. not constituent of chlorophyll, a sulphur deficient in exhibits pale colour. plants a green The root of several plants been observed to be system have enlarged application sulphur. greatly by the of lt has good been reported that produced the crops are by such application of sulphur containing materials 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.

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

(2) Hard Finish Plasters

These are made by the calcination of the anhydrous sulphate with alum set very slowly but give a hard finish. or borax.These plasters are pulp When with allowed mixed wood and to set in 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 CaCO₃.

(a) Role of Lime in Agriculture

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

lt been found that application of lime acidic soils has to of phosphorus. the readily soluble increases amount 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.

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

Slaked lime

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 supply of calcium An considerably. adequate 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 may accumulate harmful concentrations. plants in and manganese in

(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

(CaSiO₃) 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_3H_3).

$$CaO + 3C \longrightarrow CaC_2 + CO$$

Calcium carbide

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 M²⁺.
- 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 CaSO₄.1/2H₂O 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
hydro	ogen.
(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
oxyg	en.
(viii)	Na ₂ CO ₃ .H ₂ O is the chemical formula of a mineral of sodium which is
know	n as
(ix)	Metallic bicarbonates are decomposed on heating into their carbonates,
along	
	with and
(x) the	Metal nitrates other than the alkali metals on heating decompose into
	corresponding metalalong with the evolution of nitrogen
perox	kide 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 Na₂CO₃ 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 CO₂but becomes clear with excess CO₂?
 - (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?