Chapter 2

s-BLOCK ELEMENTS

Elements of group IA and IIA are called s-block elements. In electronic configuration of these elements, last electrons goes into s-orbital. The number of s-block elements are 14. (IA, IIA, H and He).

Alkali Metals:

"Elements of group IA except hydrogen are called alkali metals." Alkali metals include lithium, sodium, potassium, rubidium, cesium and francium. They are very reactive metals. When these metals are dissolved in water, they form strong alkaline solution. "The base which is water soluble is called alkali."

The name "alkali" is from Arabic language, which means "the ash". The Arabs used this term for these metals because they found ashes of some plants were composed mainly of sodium and potassium oxides.

Alkaline Earth Metals:

"The elements of IIA group are called alkaline earth metals." Groups IIA includes beryllium, magnesium, calcium strontium, barium and radium. Elements of group IIA are called alkaline earth metals because they produce alkalies in water and are widely distributed in earth's crust in the form of carbonates and silicates.

Electronic Configuration of Alkali Metals:

Alkali and alkaline earth metals are electropositive in nature. They lose electrons very easily. Properties of elements are mainly based upon the electronic configuration of elements. The electronic configuration of alkali metals (group IA) are given below:

Table – Electronic configuration of alkali metals

Elements	Symbol	At. Number	Electronic configuration
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2, 2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$
Cesium	Cs	55	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1$
Francium	Fr	87	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^1$

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.

$$M \longrightarrow M^+ + e^-$$

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

Table – Physical constants of group IA (alkali metals)

Properties	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Melting points °C	187	97.5	62.7	39.0	26.0
Boiling points (°C)	1325	889	774	688	690
Atomic radius (pm)	123	158	203	216	235
Ionic radius of +1 ion (pm)	60	95	133	148	169
Ionization energy (kJ/mole)	520	496	419	400	380
Density gm/cm^3 at (20°C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mole)	505	475	384	345	310
Electron affinity (kJ/mole)	–60	–53	–48	–47	–46
Electronegativity	1.0	0.9	0.8	0.8	0.7

In going down the group, the number of shell increases by one at each step and equal to the number of the period to which the element belongs.

Table – Electronic configuration of alkali earth metals

Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2, 2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2$
Radium	Ra	88	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 60^6, 7s^2$

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

$$M \longrightarrow M^{2+} + 2e^-$$

$$Ca \longrightarrow Ca^{2+} + 2e^-$$

$$Mg \longrightarrow Mg^{2+} + 2e^-$$

Table – Physical constants of group IIA (alkali earth metals)

Properties	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Melting points °C	1289	651	851	771	849
Boiling points (°C)	2970	1107	1448	1384	1640
Atomic radius (pm)	89	136	174	191	198
Ionic radius of +2 ion (pm)	31	65	99	113	135
2^{nd} ionization energy (kJ/mole)	1800	1450	1150	1060	970
Density gm/cm^3 at (20°C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mole)	2337	1897	1619	1455	1250
Electron affinity (kJ/mole)	240	230	156	168	52

OCCURRENCE OF ALKALI METALS (GROUP IA)

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 – Metals in group IA

Element	Name of mineral	Chemical formula
Lithium	Spodumene	$LiAl(SiO_3)_2$
Sodium	Rock salt (halite)	$NaCl$
	Chile salt petre	$NaNO_3$
	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)	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

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

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.

Occurrence of Alkaline Earth Metals (Group IIA):

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.

Table – Common minerals of the alkaline earth metals (Group IIA)

Element	Mineral	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	$CaSO_4.2H_2O$
	Flourite	CaF_2
	Phosphorite	$Ca_3(PO_4)_2$
Strontium	Strontionite	$SrCO_3$
Barium	Barite (heavy spar)	$BaSO_4$
	Whetherite	$BaCO_3$

Magnesium halides are found in sea water. Magnesium is an essential constituent 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.

PECULAR BEHAVIOUR OF LITHIUM FROM OTHER MEMBER OF GROUP IA

In many properties lithium has different behaviour from other members of group IA. The deviation from the regular trend is due to the following reason.

The **atomic radius of lithium is very small** as compared to the other members of group I. The ionic radius of Li^+ is 60 pm while that of Na^+ is 95 pm. Li^+ ion has greater charge density. Charge density is the ratio of charge to volume. The nuclear charge of Li^+ is screened by only two electrons of k-shell. Due to these reasons, lithium is less electropositive than other members of group IA.

Some important differences of lithium from other metals are given below:

(1) Lithium is much harder and lighter than the other alkali metals.

(2) The lithium salts of anions with high density are generally less soluble in water than those of the other alkali metals. e.g., LiOH, LiF, Li_3PO_4, Li_2CO_3 are not soluble in water.

(3) Lithium forms stable complex compounds, although 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.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

(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 super oxides.

$$4Li + O_2 \longrightarrow 2Li_2O \qquad \text{(Lithium oxide)}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \qquad \text{(Sodium peroxide)}$$

(7) Lithium hydride (LiH) 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 alkals and aryls of lithium are more stable than those of other alkali metals.

(9) Lithium is the latest 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.

$$2Na + C_2H_2 \longrightarrow Na^+C^- \equiv C^-Na^+ + H_2$$

(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 nitrate of other alkali metals.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

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

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O + H_2O$$

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

$$6Li + N_2 \longrightarrow 2Li_3N$$

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

(*The amount of heat evolved or absorbed when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change is called heat of solution*).

(15) Lithium carbide Li_4C, is the only alkali metal carbide formed readily by direct reaction of carbon with lithium.

$$4Li + C \longrightarrow Li_4C$$

Peculiar behaviour of Beryllium from other member of groups IIA:

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 alkali earth metals.

(3) As reducing agents, the group IIA metals are all powerful enough to reduce water. However, with water, beryllium forms insoluble oxide (BeO) coating that protects it from further attack.

(4) Complete oxidation of Beryllium does not occur in the presence of an acid. It forms a protective layer which stops the further attack of an acid.

(5) Beryllium reacts with alkali NaOH to form sodium beryllate while other members do not react with alkali NaOH.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

CHEMICAL PROPERTIES OF ALKALI METALS

Good Reducing Agents:

Alkali metals are **good reducing agents**. Reducing property of an element depends upon the ionization energy value. Elements with **low ionization energy** value, are good reducing agents. Reducing agent is a substance which can lose electrons and its oxidation increases during a chemical reaction. Alkali metals have low I.E value and are good reducing agents. They are highly electropositive. They react readily with halogens and alkali metal halides.

$$Na + \frac{1}{2}Cl_2 \longrightarrow NaCl$$

Some other properties are given below:

(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 is not found in alkali metals.

(3) The cations of alkali metals e.g., Na^+, K^+, Rb^+ have low charge and large radii than the radius of any cation from the same period, so the lattice energies of their salts are realtively low. Consequently, most of the simple salts of the alkali metals are water-soluble. Most of the salts 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. In normal oxides, oxidation state of oxygen is -2.

$$4Li + O_2 \longrightarrow 2Li_2O$$

White solid (Lithium oxide)

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.

$$Li_2O + CO_2 \longrightarrow Li_2CO_3$$

Lithium oxide Lithium carbonate

Sodium will undergo a similar reaction, but only if the supply of oxygen is limited.

$$4Na + O_2 \longrightarrow 2Na_2O$$

Limited

In the presence of excess of oxygen, sodium forms the pale yellow peroxide. In peroxide, oxidation state of oxygen is -1.

$$2Na + O_2 \longrightarrow Na_2O_2$$

Excess Sodium peroxide (Pale yellow)

The reaction of sodium metal with oxygen produces a crust of sodium peroxide that hinders further reaction even though sodium metal is still present.

Potassium, rubidium and cesium react with oxygen to form super oxides.

In super oxide, oxidation state of oxygen is $-1/2$.

$$K + O_2 \longrightarrow KO_2$$

Potassium super oxide (Orange yellow)

Caesium explodes spontaneously when it is in contact with air or oxygen.

(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 energy produced by the reaction may even ignite the hydrogen.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

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. In ionic hydrides, oxidation state of hydrogen is -1.

$$2M + H_2 \longrightarrow 2M^+H^-$$

$$2Na + H_2 \longrightarrow 2NaH$$

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

$$LiH + H_2O \longrightarrow LiOH + H_2$$

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.

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

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

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

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Potassium, rubidium and caesium react vigorously with all the halogens, forming metal halides.

(9) All alkali metals form their sulphides when treated with molten sulphur.

$$2M + S \longrightarrow M_2S$$

$$2Na + S \longrightarrow Na_2S$$

$$2K + S \longrightarrow K_2S$$

CHEMICAL PROPERTIES OF ALKALINE EARTH METALS

(1) Reaction with Air:

The alkaline earth metals burn in oxygen to form normal oxides except barium which forms perioxide. 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.

$$2Be + O_2 \xrightarrow{800°C} 2BeO$$

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

$$2Mg + O_2 \longrightarrow 2MgO$$

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.

$$Ba + O_2 \xrightarrow{500–600°C} BaO_2$$

Barium peroxide

(2) Reaction with Hydrogen:

Hydrides are produced by treating the molten alkaline earth metals with hydrogen, usually under high pressure.

Magnesium reacts with hydrogen at high pressure and in the presence of a catalyst (MgI_2) forming magnesium hydride.

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

Similarly $Ca + H_2 \xrightarrow[(MgI_2)]{\text{Pressure}} CaH_2$

(3) Reaction with Nitrogen:

All group II-A elements react with nitrogen on heating giving nitrides. For example:

$$3Mg + N_2 \longrightarrow Mg_3N_2 \quad \text{(Magnesium nitride)}$$

$$3Ca + N_2 \longrightarrow Ca_3N_2 \quad \text{(Calcium nitride)}$$

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

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

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$$

(4) Reaction with Sulphur:

Elements of group II-A react with sulphur, to form metal sulphides. e.g.,

$$Mg + S \longrightarrow MgS \quad \text{(Magnesium sulphide)}$$

(5) Reaction with Halogens:

All group IIA elements react directly with halogens giving halides of the type MX_2. e.g.,

$$Ca + Cl_2 \longrightarrow CaCl_2$$

(6) Reaction with Water:

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.

$$Mg_{(s)} + H_2O_{(g)} \xrightarrow{100°C} MgO_{(s)} + H_{2(g)}$$

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

$$M + 2H_2O \xrightarrow{100°C} M(OH)_2 + H_2$$

GENERAL TREND IN PROPERTIES OF COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS

(1) Oxides:

(a) Solubility of Group IA Oxides:

Normal oxide of group IA and IIA reacts with water to form hydroxides. Peroxide and superoxides on dissolving in water forms hydroxide and oxygen gas.

$$Li_2O_{(s)} + H_2O_{(l)} \longrightarrow 2LiOH_{(aq)}$$

$$2Na_2O_{2(s)} + 2H_2O_{(l)} \longrightarrow 4NaOH_{(aq)} + O_{2(g)}$$

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

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.

$$O^{2-} + H_2O \longrightarrow 2OH^-$$

The basic character of alkali metal oxides increases down the group.

Potassium super oxide (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.

$$4KO_{2(s)} + 2CO_{2(g)} \longrightarrow 2K_2CO_{3(s)} + 3O_{2(g)}$$

(b) Solubility of Group IIA:

The basic characters of alkali metal oxides and alkaline earth metal oxides increase downward in a group. Due to smaller ionic radii, the elements of group IIA are less basic as compared to elements of group IA.

Group IA	Group IIA
Li_2O (Basic)	BeO (Amphoteric)
Na_2O (Basic)	MgO (Basic)
K_2O (Basic)	CaO (Basic)
Rb_2O (Basic)	SrO (Basic)
CsO_2 (Basic)	BaO (Basic)

Along the group from top to bottom, basic characters of oxides increase. Along the period from left to right, basic characters decrease.

All basic oxides react with acids to form salt and water.

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

BeO is amphoteric oxides, it reacts with acids as well as bases to form salt and water.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

Base Acid Salt Water

$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

Acid Base Sodium beryllate (Salt)

(2) Hydroxides:

(a) Solubility of Hydroxides:

Alkali metal hydroxides are crystalline solids and highly soluble in water except LiOH. LiOH is slightly soluble in water. Hydroxides of group IA are strong bases except LiOH and hygroscopic in nature.

(The substance which **absorbs moisture** from the atmosphere is called **hygroscopic** substance). The solubility of alkaline earth metal increases downward in a group $Be(OH)_2$ is insoluble in water. $Mg(OH)_2$ is sparingly or slightly soluble while $Ba(OH)_2$ is highly soluble.

Solubility of alkaline earth metals **increases downward** due to increase in the size of cations. Due to greater ionic radii of group IIA cations, the lattice energy of hydroxide decreases. *"Lattice energy is the amount of energy required to break ionic solid into its gaseous ions."*

(b) Thermal Stability:

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.

$$2LiOH_{(s)} \longrightarrow Li_2O_{(s)} + H_2O_{(l)}$$

$$Mg(OH)_{2(s)} \longrightarrow MgO_{(s)} + H_2O_{(l)}$$

$Be(OH)_2$ is amphoteric in character.

$$Be(OH)_2 + H_2SO_4 \longrightarrow BeSO_4 + 2H_2O$$

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$

Note: NaOH is called caustic soda and KOH is called caustic potash. A saturated solution of $Ca(OH)_2$ is called **milk of lime** and is used to identify CO_2. A saturated solution of $Mg(OH)_2$ is called **milk of magnesia**. Milk of magnesia is used to reduce the acidity of stomach.

(3) (i) Carbonates of Alkali Metals:

(a) Effect of Heat:

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.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$

The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable. In case of large cation like K^+ ion K_2CO_3 (pearl ash), the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

(b) Sodium carbonate is very important industrial chemical. At temperature below 35.2°C, Na_2CO_3 crystalizes out from water as $Na_2CO_3.10H_2O$ which is called washing soda. Above this temperature it crystallizes out from water as

$Na_2CO_3.H_2O$. On standing in air, $Na_2CO_3.10H_2O$ slowly loses water and converted to a white powder $Na_2CO_3.H_2O$. *"The substance which loses water of crystallization in atmosphere at room temperature is called efflorescent."*

(c) The aqueous solution of Na_2CO_3 is base due to hydrolysis of the salt. Na_2CO_3 is salt of strong base and weak acid.

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3$$

(ii) Carbonates of Alkaline Earth Metals:

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

$$MgCO_3 \xrightarrow{450^\circ} MgO + CO_2$$

$$CaCO_3 \xrightarrow{900^\circ} CaO + CO_2$$

$$SrCO_3 \longrightarrow SrO + CO_2$$

$$BaCO_3 \longrightarrow BaO + CO_2$$

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.

(4) Nitrates of Group IA and IIA:

Nitrates of both alkali and alkaline earth metals are soluble in water.

Nitrate of Li, and alkaline earth metals decompose on heating to give O_2, NO_2 and the metallic oxide whereas nitrates of alkali metals decomposes to give alkali metal nitrite and oxygen except lithium.

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

$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$

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

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

(5) Sulphates of Group IA and IIA:

(a) Al the alkali metals sulphates are soluble in water.

(b) The **solubility of sulphates** of alkaline earth metals gradually **decreases** down the group. $BeSO_4$ and $MgSO_4$ are fairly soluble in water. $CaSO_4$ is slightly soluble and $SrSO_4$ 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.

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

MANUFACTURE OF SODIUM METAL BY DOWN'S 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 amount of **calcium chloride** is added to lower its melting point and to permit the furnace to operate at about 600°C.

Construction of Cell (J.C. Down designed this cell):

In the electrolytic cell, the large block of **graphite** at the centre acts as 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 it separated from it by an iron screen, which terminates in 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.

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

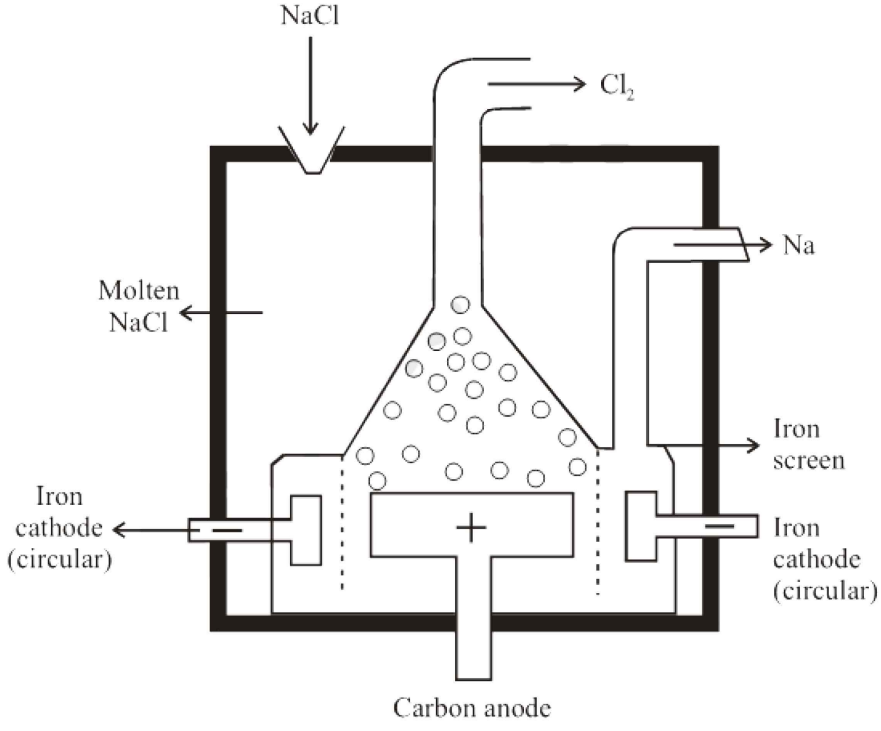


Fig. Down's cell

Reactions:

When sodium chloride is heated at high temperature, it ionizes as follows:

$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(l)} + Cl^{-}_{(l)}$$

Na^+ ions move towards cathode and Cl^- ions move towards anode.

At cathode: $Na^+ + e^- \longrightarrow Na$ (Reduction)

At anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ (Oxidation)

Not cell reaction: $NaCl \longrightarrow Na + \frac{1}{2}Cl_2$

Advantages of Process:

(i) The metallic fog is not produced.

(ii) Liquid sodium can easily be collected at 600°C.

(iii) Material of the cell is not attacked by the products formed during the electrolysis.

MANUFACTURE OF SODIUM HYDROXIDE

Sodium hydroxide NaOH, is also called caustic soda or lye.

"Caustic" means "to corrode the skin."

On large scale, sodium hydroxide is prepared by the Nelson cell method (diaphragm cell) or Castner-Kellner's cell (Hg-cell).

Construction of Nelson Cell:

The cell is made of steel tank provided with a constant level device to keep the inner part of the tank filled the specified level with brine. Saturated solution of NaCl is called brine.

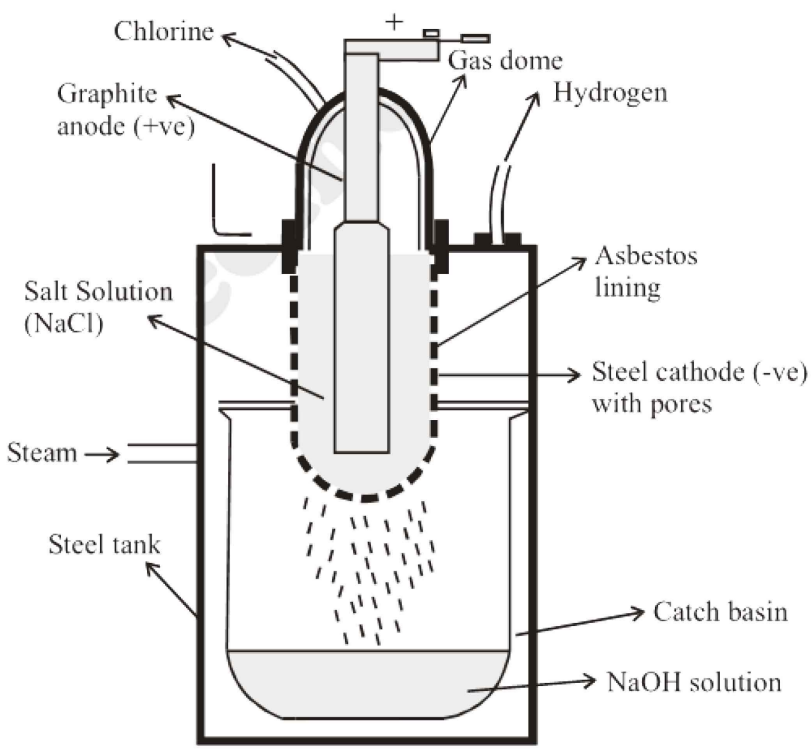
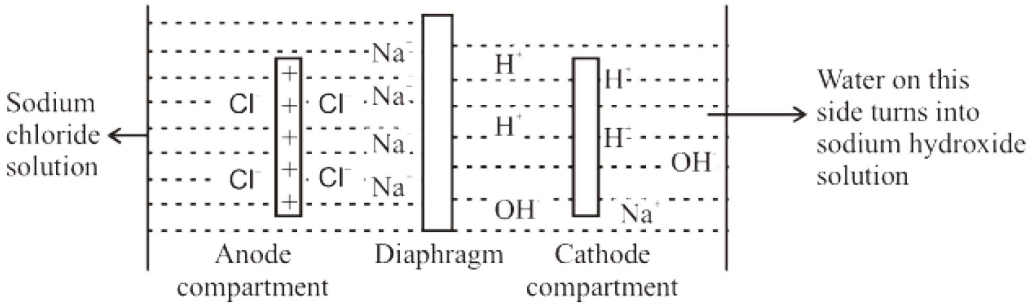


Fig. Nelson cell for production of NaOH

An oblong perforated steel vessel linked inside with asbestos diaphragm serves as a cathode. A graphite anode is held within the U shape 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 percolates into a catch basin.



The figure 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.

Reaction at Anode: $2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$

Reaction at Cathode: At the cathode, hydrogen is discharged by the reduction of water. Reduction potential of H_2O is greater than Na^+ ions.

$$2H_2O + 2e^- \longrightarrow 2OH^-_{(aq)} + H_{2(g)}$$

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

$$2Cl^- + 2H_2O \longrightarrow 2OH^- + H_2 + Cl_2$$

$$2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$$

Na^+ ions are not oxidized or reduced in this cell. The ions which do not undergo oxidation or reduction are called spectator ions.

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

(1) Chlorine produced can react with hydroxide ions in cold giving hypo-chlorite 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.

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

Solution of the two Problems:

(1) 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 flowing through the external circuit.

(2) 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 hydroxide ions to reach the anode.

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

GYPSUM

Its chemical name is calcium sulphate di-hydrate and chemical formula $CaSO_4.2H_2O$. It is a mineral that occurs in large deposits throughout the world.

Uses of Gypsum:

(1) Role in Agriculture:

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 recognized 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 it is not a constituent of chlorophyll but plants deficient in sulphur exhibits a pale green colour.

The **root system** of several plants has 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.

(2) Role in Industry:

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 about 2–5% of gypsum is added which prevents the cement from hardening too rapidly. The addition of gypsum increases the setting time of cement and increases interlocking property.

PLASTER OF PARIS

Plaster of Paris is also called calcium sulphate hemihydrates or half hydrate. Its chemical formula is $CaSO_4 . \frac{1}{2}H_2O$. Plaster of Paris can be prepared by careful heating of gypsum at 100°C.

$$2CaSO_4.2H_2O \longrightarrow (CaSO_4)_2.H_2O + 3H_2O$$

Plaster of Paris

When gypsum is strongly heated at 400°C, it changes to a anhydrous calcium sulphate. Anhydrous salt absorb water very slowly and called "dead burnt gypsum".

$$CaSO_4.2H_2O \xrightarrow{Heat} CaSO_4 + 2H_2O$$ (Dead burnt gypsum)

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 casting is obtained.

Uses of Plaster of Paris:

(i) It is used for making plaster walls and roots.

(ii) Plaster of Paris bandages are used for holding in place fractured bones after they have been set.

(iii) It is used to make casts for statuary and coins etc.

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 to prolong the time of setting.

(2) Hard Finish Plaster:

These are made by the calcinations 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.

LIME

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

(1) Role of Lime in Agriculture:

Large quantities of calcium oxide are used in agriculture for **neutralizing acidic soil and** for preparing sprays. It increase the pH and increases the amount of readily soluble phosphorus in soil.

Calcium oxide is 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.

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

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

(2) Function 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 micro-organisms that produce nitrates.

The effect of calcium on the supply of available phosphorus in the soil is a 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.

Uses of Lime:

(1) Large quantities of lime are used in the extraction and refining of metals.

(2) Lime is also used in paper 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.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

(4) Lime is used ceramic industry for producing different types of sanitary materials.

(5) Ordinary mortar, also called lime mortar, is prepared by mixing freshly slaked lime with sand and water to form a thick paste. Mortar is made by mixing slaked lime (one volume) with sand (three or four volumes) and water to make a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the block firmly together. The equations for the chemical reactions that 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 sued in the manufacturing of bleaching powder, which used for the bleaching of the fabric and paper pulp.

$$Ca(OH)_2 + Cl_2 \xrightarrow{40°C} Ca(OCl)Cl + H_2O$$

(8) A suspension of the calcium hydroxide $Ca(OH)_2$ 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.

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

Calcium carbide on hydrolysis produces acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \quad \text{(Acetylene)}$$

(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 form certain gases.