

# **Descriptive Chemistry of Elements**

## **s-Block**

**Department of Chemistry**  
The Open University of Sri Lanka

# 1. The Group 1 elements

Li

Na

K

Rb

Cs

Fr

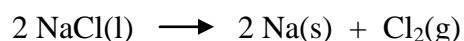
## Introduction

The elements in the Groups 1 and 2 are called *s*-block elements. The Group 1 elements (formerly Group I or IA) include **lithium** (Li), **sodium** (Na), **potassium** (K), **rubidium** (Rb), **caesium** (Cs) and **francium** (Fr). They are also called “alkali metals”. In some Periodic Tables, hydrogen is placed just above Li though its properties are somewhat different to other elements in Group 1. The chemistry of hydrogen will be discussed separately.

## 1.1 Occurrence and isolation

Alkali metals are reactive and they are not found in nature as free metals. Sodium and potassium are relatively more abundant than the other metals in this group. Na is present as a salt (*e.g.* Sodium chloride, NaCl) in huge quantities in underground deposits (salt mines), in seawater and other natural waters. Potassium salts are found naturally in seawater, and as carnalite,  $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  or potash (KOH). The concentrations of  $\text{Na}^+$  and  $\text{K}^+$  ions in seawater are 10,800 and 590 ppm, respectively.

Sodium and lithium are obtained by electrolysis of their molten chloride. For example,



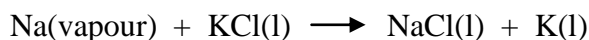
During electrolysis  $\text{Na}^+$  ions are reduced to Na metal and chloride ions are oxidized to chlorine gas.



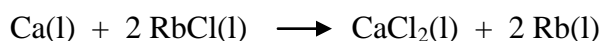
## Activity

1. Can we obtain Na metal by electrolyzing a concentrated aqueous solution of NaCl?

Potassium is made by the reaction of sodium vapor with molten/fused KCl at 850°C.



Rb and Cs are made by the reduction of their chlorides with calcium metal at 800°C.



All isotopes of francium are radioactive.

## 1.2 Some properties of alkali metals

In this lesson, we will mainly concentrate on the chemistry of Na, K and Li. The elements of Group 1 are soft metals and they conduct electricity and heat. Table 1 provides you with some of the physical data of Group 1 elements. As one would expect the ionic radius,  $r(\text{M}^+)$ , increases as you go down the group. The melting point (m.p.) decreases from Li to Cs. Alkali metals have low densities and the densities ( $d$ ) of Li, Na and K are less than that of water; thus these metals float on water.

*Table 1: Some properties of Group 1 elements*

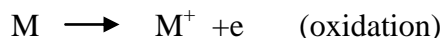
Element	$r(\text{M}^+)$ / pm	Electron configuration	m.p./ °C	$d/\text{gcm}^{-3}$	$E^\circ/\text{V}$	$\text{IE}_1/$ $\text{kJmol}^{-1}$	$\text{IE}_2/$ $\text{kJmol}^{-1}$
<b>Li</b> (Lithium)	60	[He] $2s^1$	181	0.53	-3.04	520	7590
<b>Na</b> (Sodium)	95	[Ne] $3s^1$	98	0.97	-2.71	496	4560
<b>K</b> (Potassium)	133	[Ar] $4s^1$	63	0.86	-2.94	418	3060
<b>Rb</b> (Rubidium)	148	[Kr] $5s^1$	39	1.53	-2.94	401	2630
<b>Cs</b> (Caesium)	169	[Xe] $6s^1$	29	1.90	-3.03	376	2430



## Activity

2. Why are alkali metals soft and have low melting points?

The *valence electron configuration* of these elements can be written as  $ns^1$  and they have a tendency to lose the single *s*-electron and attain a noble gas electron configuration.



Therefore, these alkali metals are the most reactive and *electropositive* elements known. This is due to the *low* first ionization energy ( $IE_1$ ) shown by each element. They all form only  $M^+$  ions as the second ionization energy ( $IE_2$ ) is very high when compared to  $IE_1$  (see Table 1).

Q : Write the electron configuration of Na,  $Na^+$  and Ne.

A :

Electron configuration of Na	$1s^2, 2s^2, 2p^6, 3s^1$	(11 electrons)
Electron configuration of $Na^+$	$1s^2, 2s^2, 2p^6$	(10 electrons)
Electron configuration of Ne	$1s^2, 2s^2, 2p^6$	= [Ne] (10 electrons)
Electron configuration of Na	$1s^2, 2s^2, 2p^6, 3s^1$	= [Ne] $3s^1$



### Activity

3. Cs has the lowest first ionization energy (see Table 1), explain. Comment on the electropositivity of the cations as you go down the Group.

Group 1 elements form *colorless ionic salts* with common simple anions and the *oxidation state/number* of the metal is always +1. Almost all derivatives of alkali metals are ionic except some lithium compounds. The Group 1 metal ions ( $M^+$ ) are quite stable towards reduction to its free elements (M), for example  $Na^+$  is more stable than free Na metal.

*Standard reduction electrode potentials* ( $E^\circ$ ) of the Group 1 metals are given in Table 1. The negative values indicate that these elements are *good reducing agents*. Li has a more negative  $E^\circ$  value than Na because of its high hydration energy. Simple salts of alkali metals tend to be very

soluble in water, but LiF and Li<sub>2</sub>CO<sub>3</sub> are partially soluble in water. Free alkali metals are normally stored in dry hydrocarbon solvents (paraffin oil) to prevent them from reacting with atmospheric oxygen or moisture.

### 1.3 Compounds of alkali metals

In this section, we will consider some reactions and properties of simple salts of alkali metals: *metal oxides*, *metal hydroxides* and *metal halides*.

#### Alkali metal oxides

The product(s) obtained due to combustion of Group 1 elements in oxygen vary with the alkali metal and the amount of oxygen used: three different oxygen containing anions (*e.g.* **oxide**, **peroxide** and **superoxide**) are formed (Table 2). Hydrolysis (reaction with water) of *lithiummonoxide* gives LiOH. Hydrolysis of *sodium peroxide* at 0 °C gives NaOH and H<sub>2</sub>O<sub>2</sub>, but H<sub>2</sub>O<sub>2</sub> is unstable at room temperature and liberates O<sub>2</sub> as the temperature is raised. The corresponding metal hydroxide, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> are produced when *superoxides* of K, Rb and Cs are hydrolysed. K, Rb and Cs form all three oxides.

**Table 2:** Stable oxides (main product) obtained by reacting alkali metals with oxygen, and the product(s) due to hydrolysis of the corresponding salt

Metal	Product isolated	Anion type	Product/s due to hydrolysis
Li	Li <sub>2</sub> O	O <sup>2-</sup> (oxide)	OH <sup>-</sup>
Na	Na <sub>2</sub> O <sub>2</sub>	O <sub>2</sub> <sup>2-</sup> (peroxide)	OH <sup>-</sup> , H <sub>2</sub> O <sub>2</sub>
K, Rb, Cs	MO <sub>2</sub>	O <sub>2</sub> <sup>-</sup> (superoxide)	OH <sup>-</sup> , H <sub>2</sub> O <sub>2</sub> , O <sub>2</sub>

Lithium forms only the monoxide (Li<sub>2</sub>O). Superoxide of sodium is unstable. The superoxide becomes more stable as you go down the group. K, Na and Cs are known to form all three oxides. Large alkali metals form stable superoxides MO<sub>2</sub> (M = K, Rb, Cs), which are ionic and *paramagnetic*. Note that paramagnetic compounds contain *unpaired electrons*, like in the oxygen molecule.

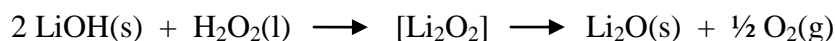


## Activity

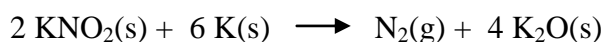
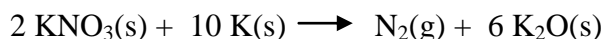
4. Write the balanced equations for the reaction of Na with O<sub>2</sub>.

### Preparation of metal oxides

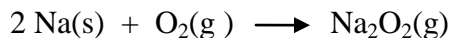
The reaction of LiOH with H<sub>2</sub>O<sub>2</sub>, generates unstable lithium peroxide [Li<sub>2</sub>O<sub>2</sub>], which decomposes to Li<sub>2</sub>O and O<sub>2</sub>.



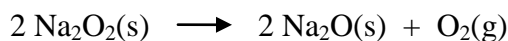
K<sub>2</sub>O is prepared by reducing KNO<sub>2</sub> or KNO<sub>3</sub> with free metal.



Sodium peroxide is produced by passing carbon dioxide free dry air over heated Na.



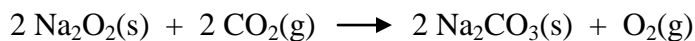
Upon heating, sodium peroxide decomposes to sodium monoxide and oxygen.



These peroxides (M<sub>2</sub>O<sub>2</sub>) have ionic structures and they react with cold water (0°C) to give H<sub>2</sub>O<sub>2</sub>. (M = Li, Na, K and Cs)



Alkali metal peroxides are powerful oxidizing agents and they oxidize sulfides to sulfates. Na<sub>2</sub>O<sub>2</sub> absorbs CO<sub>2</sub> and gives out O<sub>2</sub>.



These peroxides are used to purify air (by removing CO<sub>2</sub>) in closed spaces such as submarines.

## Alkali metal hydroxides

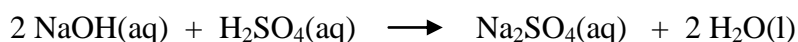
Alkali metals react with water to give an alkaline solution with hydrogen evolution.



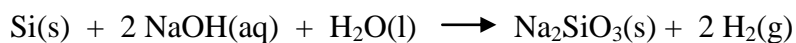
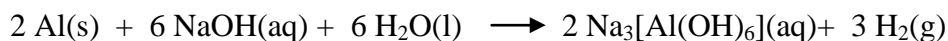
Li, Na and K all float on water, Li reacts *steadily*, Na reacts *vigorously* and K reacts *violently*.

NaOH is a very deliquescent white solid. On exposure to air it absorbs moisture. A solid sample of NaOH could combine with CO<sub>2</sub> in air to form a layer of Na<sub>2</sub>CO<sub>3</sub>. This layer protects NaOH from reacting further with moisture and CO<sub>2</sub>. Due to these reactions NaOH cannot be used as a **primary standard** for the standardization of acid solutions. NaOH is produced by electrolyzing NaCl.

Alkali metal hydroxides are used in various acid-base titrations. For example, NaOH can neutralize dilute sulfuric acid giving a salt and water.



Nonmetals such as carbon, nitrogen and oxygen do not react with aqueous NaOH but many other elements do react with NaOH. For example,



## Alkali metal halides

Alkali halides (MX) of sodium and potassium are ionic compounds and readily dissolve in water (a polar solvent). But LiCl, LiBr and LiI have some covalent character and are more soluble in alcohol (a less polar solvent than water). The *covalent* character of lithium compounds is due to the strong *polarizing power* of the Li<sup>+</sup> ion. Large anions are polarized by the Li<sup>+</sup> ion by attracting outermost electrons of the anion and at the same time repelling the positively charged nucleus of the anion. This distortion or polarization of the anion by the cation results in a certain degree of sharing of electrons between ions, *i.e.* the bond would become partially covalent in character. The small fluoride ion resists polarization by the lithium ion thus LiF has more ionic *character*.

The degree of polarization/polarizing power increases as the

- (i) charge of the cation increases,
- (ii) charge of the anion increases,
- (iii) size of the cation decreases, and
- (iv) size of the anion increases.

Q : List the halides in the order of increasing degree of polarization.

A :  $F^- < Cl^- < Br^- < I^-$

Q : List the cations of alkali metals in the order of increasing polarizing power.

A :  $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$

## Summary

- Group 1 elements are soft, reactive metals with low melting points; low densities; low first ionization energies; very high second ionization energies; very negative standard reduction potentials. Most simple salts of alkali metals are soluble in water.
- Valence electron configuration of alkali metals (M) is  $ns^1$  and they readily form  $M^+$  ions. Therefore, they are strong reducing agents.
- Na and Li are obtained by electrolyzing of their molten chloride; K is made by reacting molten KCl with sodium vapor.
- They form three types of oxides: monoxide, peroxide and superoxide.
- Alkali metal hydroxides are used in acid-base titrations.





## Learning Outcomes

At the end of this lesson you should be able to

- give the sources and methods used to isolate alkali metals, particularly, Na and K.
- compare the variation in properties of alkali metals such as ionic radius, melting points, density, ionization energies, and standard electrode potentials as you go down the Group.
- write the electron configuration of a Group 1 element or ion.
- mention preparation methods of alkali metal oxides, peroxides and superoxides.
- explain reactions of alkali metal oxides and metal hydroxides.

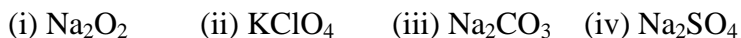


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### Activity

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5. Determine the oxidation states of the non-metals in the following substances.



6. Draw the structures of the following anions  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^{2-}$   
(Hint: Think about the valency and possible oxidation state(s) of atoms/ions)

7. What is the order of reactivity of alkali metals towards water?

8. Give two organometallic reagents of alkali metals, *i.e.* organic derivatives of alkali metals?

9. Which alkali metals form stable superoxides when it is reacted with oxygen?

10. Which alkali metals do not form stable superoxides?

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## 2. The Group 2 elements

Be

Mg

Ca

Sr

Ba

Ra

### Introduction

Here we will discuss the properties and chemistry of Group 2 elements and their compounds. The Group 2 (formerly Group II or IIA) elements include **beryllium** (Be), **magnesium** (Mg), **calcium** (Ca), **strontium** (Sr), **barium** (Ba) and **radium** (Ra). They are also called “alkaline earth metals”. We will also make an attempt to compare the chemical properties of Group 2 elements with the Group 1 elements.

### 2.1 Occurrence and isolation

The Group 2 elements are too reactive to occur as free elements in nature. Mg is the second most abundant element in seawater and it occurs as  $\text{MgCl}_2$  (0.3%),  $\text{MgBr}_2$  (0.04%) and  $\text{MgSO}_4$  (0.18%). Magnesium also occurs in *carналite* deposits,  $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ . Dolomite ( $\text{CaCO}_3\cdot\text{MgCO}_3$ ) is found in Digana (Kandy District) and Rattota (Matale District) which is used in the manufacture of Porcelain and Fertilizer. Limestone, chalk and marble contain  $\text{CaCO}_3$ . Calcium also occurs as a sulfate,  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  in *gypsum*. *Apatite*,  $\text{Ca}_3(\text{PO}_4)_2$  is found in Eppawala (Anuradhapura District). Seawater also contains  $\text{CaSO}_4$ . Sr and Ba are rare and Be is even rarer and found as beryl, an aluminosilicate,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ . The most important source of calcium is the deposits of  $\text{CaCO}_3$ , which are the fossilized remains of dead shellfish. Dolomite is the major constituent of the mountain range, the Dolomite Alps in Italy. Ca and Mg are the fifth and sixth most abundant element in the earth’s crust. From an Industrial standpoint, Mg is the most important metal.

Group 2 elements are normally prepared by electrolysis of the corresponding fused chlorides. Electrolysis of anhydrous  $\text{MgCl}_2$  using a graphite anode and a steel cathode produces Mg at the

cathode. Anhydrous carnalite can be directly used for electrolysis; usually NaCl is added to lower the melting point of MgCl<sub>2</sub>.

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### Activity

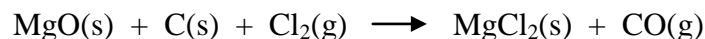
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11. Write the half-cell reactions for the above process - electrolysis of anhydrous MgCl<sub>2</sub>.

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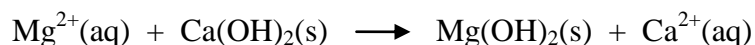
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The anhydrous MgCl<sub>2</sub> can also be prepared by heating magnesite (MgCO<sub>3</sub>) with coke (carbon) and passing chlorine over the mixture.

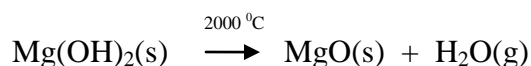


Magnesium can also be obtained from seawater as shown below.

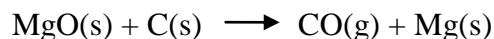
(i) Mg(OH)<sub>2</sub> is precipitated by adding Ca(OH)<sub>2</sub>.



(ii) MgO is obtained by heating Mg(OH)<sub>2</sub>.



(iii) MgO is reduced to Mg by heating with carbon (coke).



Calcium metal is also obtained by electrolysis of a mixture of CaCl<sub>2</sub> and CaF<sub>2</sub>. CaF<sub>2</sub> is added to lower the melting point of the mixture.

## 2.2 Some properties of Group 2 elements

All Group 2 elements are metals and all are powerful reducing agents. Table 3 provides you with some physical properties of Group 2 elements. The *valence electron configuration* of these elements can be written as  $ns^2$  and they have the tendency to lose both s-electrons and attain a noble gas electron configuration.

**Table 3:** Some properties of Group 2 elements  
(E.Con. = Electron configuration; 100 pm (picometres) = 1Å)

Element (name)		E.Con	IE <sub>1</sub> kJmol <sup>-1</sup>	IE <sub>2</sub> kJmol <sup>-1</sup>	IE <sub>3</sub> kJmol <sup>-1</sup>	r(M <sup>2+</sup> ) pm
<b>Be</b>	(Beryllium)	[He] 2s <sup>2</sup>	899	1757	14848	59
<b>Mg</b>	(Magnesium)	[Ne] 3s <sup>2</sup>	738	1451	7733	86
<b>Ca</b>	(Calcium)	[Ar] 4s <sup>2</sup>	590	1145	4912	114
<b>Sr</b>	(Strontium)	[Kr] 5s <sup>2</sup>	549	1064	4207	132
<b>Ba</b>	(Barium)	[Xe] 6s <sup>2</sup>	503	965	3500	149
<b>Ra</b>	(Radium)	[Rn] 7s <sup>2</sup>	-	-	-	-

As seen in the Table 3, the ionic radius of the divalent ions increases as you go down the group. Each free atom has two valence s-electrons (when compared to Group 1 elements) which results in atoms being held together much more strongly in the free metal. Hence ***the Group 2 elements are harder, denser and have a much higher melting point than the corresponding alkali metals*** (see Table 4).

**Table 4:** Densities and melting points of the elements of Groups 1 and 2

Metal	Li	Be	Na	Mg	K	Ca	Rb	Sr	Cs	Ba
<b>Density (gcm<sup>-3</sup>)</b>	0.53	1.85	0.97	1.75	0.86	1.55	1.53	2.63	1.90	3.62
<b>Melting Point (°C)</b>	181	1287	98	649	63	839	39	768	29	727

Group 2 elements form colorless largely *ionic compounds* in the solid state in which the oxidation state of the metal is always +2. No stable compounds containing  $M^+$  ions are known. All Group 2 metals form only  $M^{2+}$  ions. The *high charge density* of  $Be^{2+}$  means that the free ions cannot exist, and all its compounds are either covalent or exist as solvated ions such as  $[Be(H_2O)_4]^{2+}$ .

Beryllium thus shows properties markedly different from the other elements in Group 2. The higher charge density of  $M^{2+}$  ions of the Group 2 elements (when compared to  $M^+$  ions of the Group 1 elements) results in

- (i) smaller  $M^{2+}$  ions; e.g.  $r(Ca^{2+})$  is 114 pm and  $r(K^+)$  is 133 pm.
- (ii) strongly hydrated complexes than Group 1 elements
- (iii) higher lattice energies
- (iv) salts which are less soluble in water.



### Activity

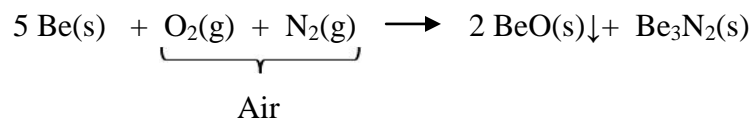
12. Group 2 elements do not form  $M^{3+}$  ion. Explain.
13. Why is  $IE_3$  for Magnesium very large, when compared to its  $IE_2$ ?

## 2.3 Compounds of Group 2 elements

In this section, we will discuss the preparation and reactions of Group 2 metal oxides (MO), hydroxides  $M(OH)_2$ , peroxides ( $MO_2$ ), halides ( $MX_2$ ), hydrides ( $MH_2$ ), nitrates  $[M(NO_3)_2]$ , sulfates ( $MSO_4$ ) and carbonates ( $MCO_3$ ).

### Oxides

Let us consider preparation of metal oxides. There are three methods to prepare metal oxides: (i) direct reaction with oxygen, (ii) decomposition of metal carbonates, and (iii) direct reaction with water at high temperature.

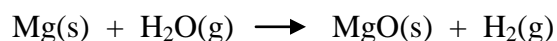


Similar reactions do occur with Mg, Ca, Sr and Ba. Metal oxides are essentially ionic solids with a divalent cation and an anion ( $M^{2+}O^{2-}$ ). Beryllium oxide (BeO) may have some covalent character. This may be due to higher polarizing power of  $Be^{2+}$  ion.

Group 2 metal oxides are normally prepared by thermal decomposition of the corresponding metal carbonate.

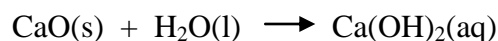


Magnesium reacts with steam to produce MgO and hydrogen.

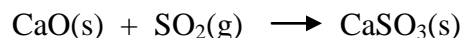


Some of the reactions of metal oxides are given below.

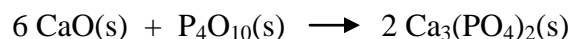
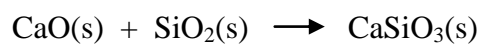
- (i) Group 2 metal oxides have high lattice energies and are less soluble in water compared to those of Group 1 metal oxides. BeO and MgO are quite insoluble in water whilst CaO, SrO and BaO readily react with water giving ionic hydroxides. For example, CaO is a basic oxide and it reacts with water to give  $Ca(OH)_2$ .



- (ii) CaO reacts with gaseous acidic oxides such as  $SO_2$  to give sulphite.



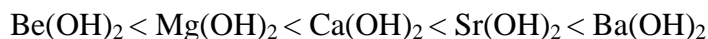
- (iii) At higher temperatures, CaO reacts with solid acidic oxides such as silica and  $P_4O_{10}$  to give silicate and phosphate, respectively.



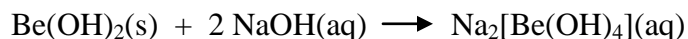
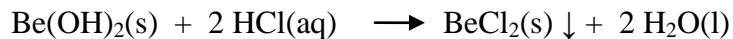
CaO is used in the laboratory as a drying agent in desiccators for drying organic solvent (*e.g.* ethyl alcohol). During this process  $Ca(OH)_2$  is produced.

## Hydroxides

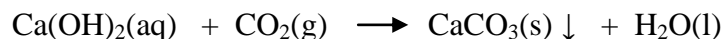
We know that metal hydroxides can be prepared by hydrating the corresponding metal oxide. The basic character of metal hydroxide increases with the size of the cation, thus basicity increases as shown below.



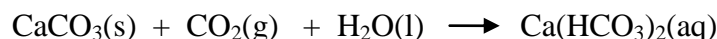
Be(OH)<sub>2</sub> shows amphoteric properties; it dissolves in mineral acid (HX) to form the corresponding halide (BeX<sub>2</sub>); in alkaline solutions (*e.g.* NaOH), it produces beryllates, Na<sub>2</sub>[Be(OH)<sub>4</sub>].



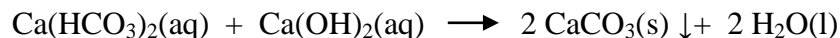
An aqueous solution of calcium hydroxide is called limewater; which is used to test for carbon dioxide. When carbon dioxide is passed into limewater, a precipitate of calcium carbonate is formed first.



Addition of more CO<sub>2</sub> converts the carbonate into more water soluble calcium bicarbonate so that CaCO<sub>3</sub> precipitate dissolves up giving a clear solution.



If more limewater is added, CaCO<sub>3</sub> re-precipitates.

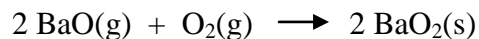


CaCO<sub>3</sub> can be precipitated by boiling a solution of Ca(HCO<sub>3</sub>)<sub>2</sub>



## Peroxides

The formation of metal peroxides (MO<sub>2</sub>) is observed with larger cations. BaO<sub>2</sub> is readily formed when BaO is heated in air or oxygen.

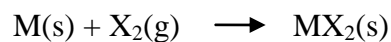


SrO<sub>2</sub> is obtained in a low yield by heating SrO in oxygen under pressure at 400°C.

Hydrated peroxides of the type MO<sub>2</sub>·8H<sub>2</sub>O can be obtained by adding H<sub>2</sub>O<sub>2</sub> to a concentrated solution of metal salts.

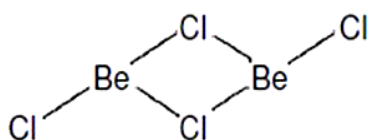
## Halides

Group 2 metals react directly with halogen to give metal dihalides,  $\text{MX}_2$ .  $\text{M} = \text{Be}, \text{Mg}, \text{Ca}$  and  $\text{Sr}$ ;  $\text{X} = \text{Cl}$  and  $\text{Br}$ .

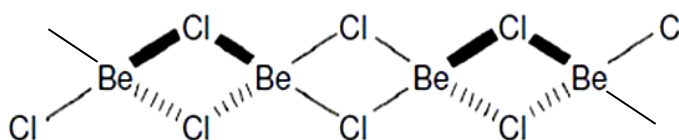


The reaction with bromine takes place at higher temperatures. Calcium can react with  $\text{F}_2$  and  $\text{I}_2$  to give  $\text{CaF}_2$  and  $\text{CaI}_2$ , respectively.

Beryllium chloride ( $\text{BeCl}_2$ ) is a *covalent polymer* in the solid state containing Be-Cl-Be bridges. In the vapor phase, the polymer  $[\text{BeCl}_2]_n$  is broken into a mixture of the monomer  $\text{BeCl}_2$  and the dimer  $\text{Be}_2\text{Cl}_4$ .



Coordination number = 3



Coordination number = 4

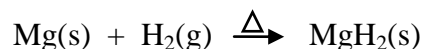
Some hydrated chlorides are  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ . Hydrated magnesium chloride decomposes on heating to give a basic chloride.



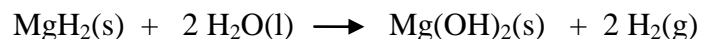
Calcium chloride crystallizes as  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . Anhydrous  $\text{CaCl}_2$  is used as a drying agent for organic solvents. It also absorbs ammonia and alcohols giving compounds such as  $\text{CaCl}_2 \cdot 8\text{NH}_3$  and  $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$ .

## Hydrides

Magnesium hydride is formed when Mg powder is reacted with hydrogen under pressure at a high temperature.  $\text{MgI}_2$  acts as a catalyst.



$\text{MgH}_2$  reacts with water to give  $\text{Mg(OH)}_2$  and hydrogen.





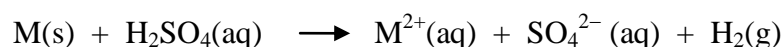
Group 2 metal hydrides are thermally more stable than the alkali metal hydrides.  $\text{CaH}_2$  is used as a reducing agent and also as a drying agent.

### Nitrates

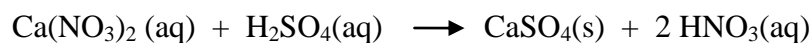
The reaction of nitric acid with metal oxides, hydroxides or carbonates gives Group 2 metal nitrates.  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Ca}(\text{NO}_3)_2$  are very soluble in water. Unlike Group 1 metal nitrates, nitrates of Group 2 metals can be decomposed to their oxides by heating. The thermal stability increases from  $\text{Mg}(\text{NO}_3)_2$  to  $\text{Ba}(\text{NO}_3)_2$ .

### Sulfates

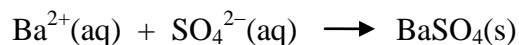
Be (powdered) and Mg dissolve in dilute  $\text{H}_2\text{SO}_4$  to give  $\text{BeSO}_4$  and  $\text{MgSO}_4$ , respectively.



$\text{CaSO}_4$  can be precipitated by adding dilute  $\text{H}_2\text{SO}_4$  to a solution of calcium salt.

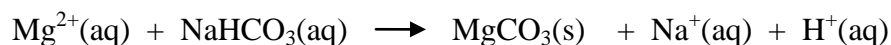


The solubility of sulfates decreases as you go down the group.  $\text{MgSO}_4$  is soluble in water but  $\text{BaSO}_4$  is insoluble. Thus  $\text{BaCl}_2$  is used as a reagent to determine sulfate ions in inorganic analysis,



### Carbonates

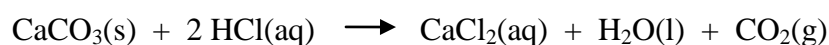
When magnesium salts are treated with a  $\text{Na}_2\text{CO}_3$  solution, a precipitate of the basic carbonate,  $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  is formed. The composition of the precipitate varies. The normal carbonate ( $\text{MgCO}_3$ ) can be obtained by adding a solution of  $\text{NaHCO}_3$  to a solution of  $\text{Mg}^{2+}$  ions.



$\text{MgCO}_3$  is fairly insoluble in water but if  $\text{CO}_2$  is bubbled through a suspension of  $\text{MgCO}_3$  in water, the soluble bicarbonate is formed.



Group 2 metal carbonates react with acids to give the corresponding salt and  $\text{CO}_2$ .



Thermal stability of metal carbonates increases with the size of the cation as indicated by their decomposition temperature ( $T_D$ ).

Compound	MgCO <sub>3</sub>	CaCO <sub>3</sub>	SrCO <sub>3</sub>	BaCO <sub>3</sub>
$T_D / ^\circ\text{C}$	540	900	1290	1360

### Summary

- Group 2 elements are shiny and reactive. They do not occur as free elements in nature.
- Valence electron configuration of alkali earth metal (M) is  $ns^2$  and they readily form  $M^{2+}$  ions. Therefore, they are strong reducing agents.
- All elements can be obtained by electrolysis of their molten salts.
- The Group 2 elements are harder, denser and have a much higher melting point than the corresponding alkali metals.
- $M^{2+}$  ions of the Group 2 elements are (i) smaller (ii) strongly hydrated and (iii) less soluble in water than the  $M^+$  ions of Group 1 elements.
- Metal oxides can be prepared by (i) direct reaction with oxygen, (ii) decomposition of metal carbonates and (iii) direct reaction with water at high temperatures.
- The basic character of metal hydroxide increases with the size of the cation, thus basicity increases from  $\text{Be}(\text{OH})_2$  to  $\text{Ba}(\text{OH})_2$ .
- Group 2 metals react directly with halogen to give metal dihalides,  $\text{MX}_2$ .  $M = \text{Be, Mg, Ca}$  and  $\text{Sr}$  and  $X = \text{Cl}$  and  $\text{Br}$ .
- Group 2 metal hydrides are thermally more stable than the alkali metal hydrides.



## Learning Outcomes

At the end of this session you should be able to

- give the sources and methods used to isolate alkali earth metals, particularly, magnesium.
- compare the variation in properties of alkali earth metals such as ionic radius, melting points, density, and ionization energies, as you go down the Group.
- write the electron configuration of a Group 2 element or ion.
- explain the properties and reactions of alkaline earth metals and their compounds.

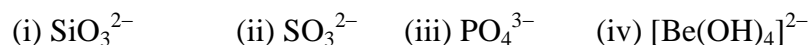


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### Activity

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14. Determine the oxidation states of the non-metals in the following substances:



15. Draw the structures of the following anions:  $\text{SiO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $[\text{Be}(\text{OH})_4]^{2-}$   
(Hint: Think about the valency & possible oxidation state(s) of atoms/ions)

16. What do you think about the relative solubility of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  in water?

17. What is the alkaline earth metal which does not react with water?

18. Write a balanced equation for the reaction between strontium and bromine.

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## *3. Uses and some industries of s-block elements*

### Introduction

In this lesson, we consider uses and some industries based on *s*-block elements. The chloralkali industry refers to the industries that produce chlorine ( $\text{Cl}_2$ ), sodium hydroxide ( $\text{NaOH}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). These three chemicals are used in a large number of chemical processes; for example, production of paper, glass, soap, alkaline cleaners and polymers. In industry,  $\text{Na}_2\text{CO}_3$  is known as soda ash. In USA, there are deposits called 'trona' which are mixtures of sodium carbonate and bicarbonate,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ . Na, Li and Mg are obtained by the electrolysis of their molten chlorides. Methods for preparation of calcium salts such as  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_3$  and  $\text{CaSO}_4$  were discussed in the previous lesson.

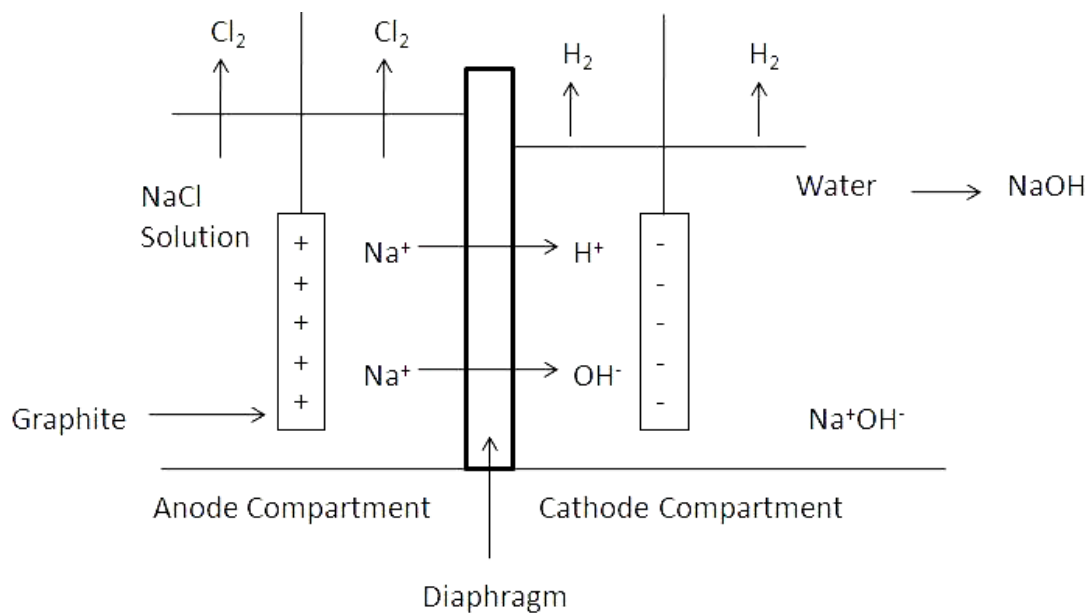
### 3.1 Production of chlorine and NaOH

Chlorine and NaOH are both made by the electrolysis of brine (salt water). There are two types of cells used for this process.

1. The diaphragm cell
2. The mercury cell

#### The diaphragm cell method

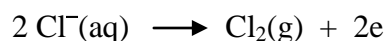
In Sri Lanka at Paranthan, NaOH is produced by the **diaphragm cell** method. In the diaphragm cell the anode (graphite) and the cathode (steel) are separated into two compartments by a diaphragm made of asbestos. A NaCl solution is electrolyzed to produce chlorine, hydrogen and NaOH as shown below.



*Figure 1: Diagram of a diaphragm cell*

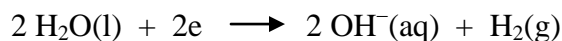
### Anode reaction

At the anode, Cl<sup>-</sup> ions are oxidized to chlorine gas.

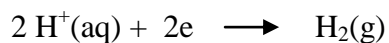


### Cathode reaction

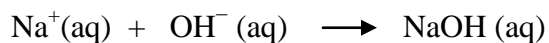
At the cathode, H<sup>+</sup> ions (from water) are reduced to hydrogen gas.



or



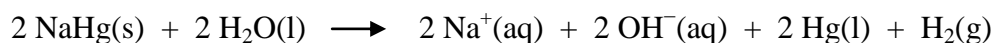
During electrolysis, OH<sup>-</sup> ions are produced, therefore the solution becomes increasingly alkaline. Na<sup>+</sup> ions can pass through the diaphragm into the cathode compartment. These Na<sup>+</sup> ions combine with OH<sup>-</sup> ions to form an aqueous solution of NaOH.



It is important to maintain the liquid level in the anode compartment higher than that in the cathode compartment. This allows continuous flow of sodium ions into the cathode compartment. Otherwise  $\text{OH}^-$  ions may reach the anode and get oxidized to give  $\text{O}_2$ .

### The mercury cell method

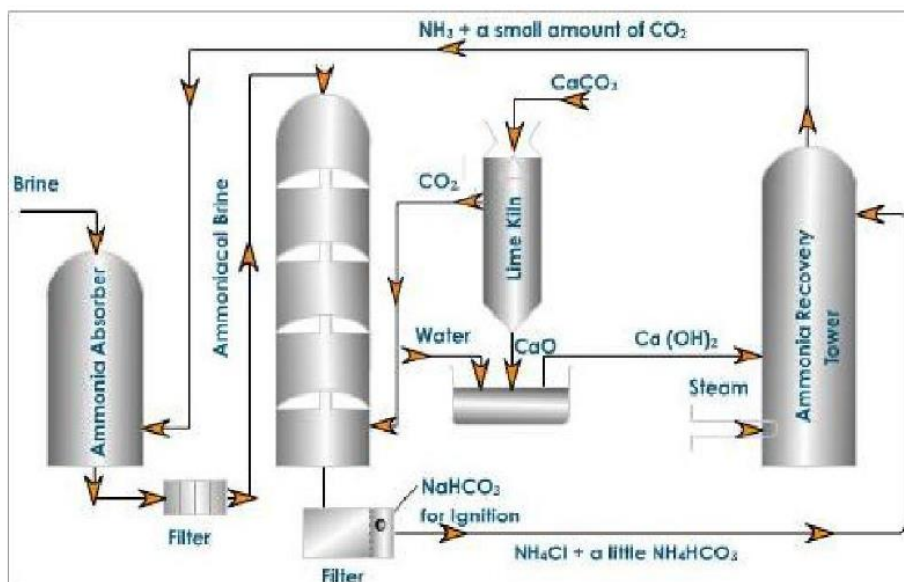
In the **mercury cell** method, brine is continuously passed into a cell that has graphite anodes and a moving layer of mercury as the cathode. As usual,  $\text{Cl}^-$  ions are oxidized to give  $\text{Cl}_2$ . In contrast to the **diaphragm cell** method, here  $\text{Na}^+$  ions are reduced to form sodium amalgam ( $\text{NaHg}$ ) which with unused mercury travels out of the cell into a chamber containing water. In this chamber,  $\text{NaHg}$  reacts with water to give  $\text{NaOH}$ ,  $\text{Hg}$  and  $\text{H}_2$  as given below.



## 3.2 Production of $\text{Na}_2\text{CO}_3$

Large scale production of  $\text{Na}_2\text{CO}_3$  is achieved by the Ammonia-soda or **Solvay** process (see figures 2 and 3). Limestone ( $\text{CaCO}_3$ ) and  $\text{NaCl}$  are the starting materials, and the production process consists of the following steps.

- (1) Production of saturated brine solution
- (2) Saturation of brine solution with ammonia
- (3) Production of carbon dioxide by roasting of limestone
- (4) Production of  $\text{NaHCO}_3$
- (5) Conversion of  $\text{NaHCO}_3$  to  $\text{Na}_2\text{CO}_3$ .



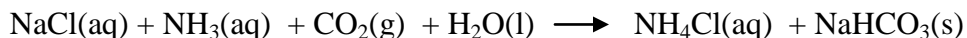
**Figure 2:** Production of  $\text{Na}_2\text{CO}_3$  by the Solvay process (from reference 7)

Saturated brine solution is made by dissolving  $\text{NaCl}$  in water (**Step 1**). It is important to have the brine solution free from magnesium and calcium ions; otherwise the final product ( $\text{Na}_2\text{CO}_3$ ) gets contaminated with  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Then, this brine solution is treated with ammonia to saturate the brine with ammonia (**Step 2**).

$\text{CO}_2$  is produced by heating limestone in the column (**Step 3**).



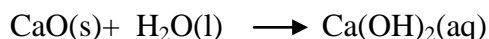
Now, the solution containing brine and ammonia is passed down a tower, against an upward moving current of  $\text{CO}_2$  which precipitates  $\text{NaHCO}_3$  (**Step 4**). The reaction can be summarized as given below.



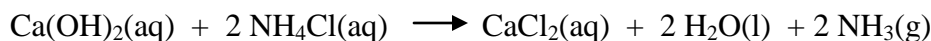
The resulting  $\text{NaHCO}_3$  precipitate is separated and heated in a rotary drier to obtain  $\text{Na}_2\text{CO}_3$  (**Step 5**)



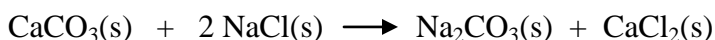
The resulting  $\text{CaO}$  (**in Step 3**) is converted into  $\text{Ca}(\text{OH})_2$  by adding water.



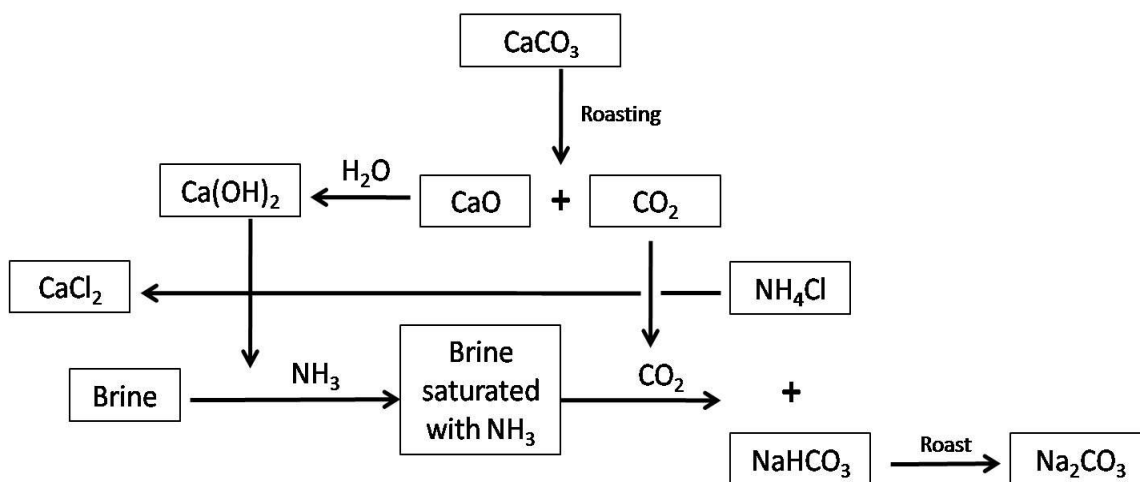
$\text{NH}_4\text{Cl}(\text{aq})$  filtrate obtained in **(Step 4)** is reacted with aqueous  $\text{Ca}(\text{OH})_2$  to regenerate  $\text{NH}_3$  gas. Thus  $\text{NH}_3$  is reused during the ammonia-soda process.



The only by-product of this process is  $\text{CaCl}_2$ , therefore the overall reaction can be summarized as given below.



Sodium carbonate can be crystallized from water as the decahydrate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . An aqueous solution of  $\text{Na}_2\text{CO}_3$  is alkaline. In the laboratory,  $\text{Na}_2\text{CO}_3$  is used as a primary standard to standardize acids. In qualitative analysis,  $\text{Na}_2\text{CO}_3$  is used to precipitate carbonates of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$ . In industry,  $\text{Na}_2\text{CO}_3$  is used to make glass, caustic soda ( $\text{NaOH}$ ) and other salts.



*Figure 3: Flow chart of the key stages of the production of  $\text{Na}_2\text{CO}_3$  by the Solvay process*

### 3.3 Production of NaCl

In Sri Lanka,  $\text{NaCl}$  is produced by concentrating sea water. As the first step, sea water is collected to a tank. Concentration of the solution is achieved by evaporation of water under the hot sun with the help of blowing wind. Precipitation of  $\text{CaCO}_3$  takes place as the concentration of the solution increases.  $\text{CaCO}_3$  precipitate is separated by transferring the concentrated solution into a second tank. Further concentration of the solution leads to the precipitation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Gypsum is removed by transferring the concentrated solution to a third tank.



Upon further concentration, NaCl crystallizes out leaving  $\text{MgCl}_2$ ,  $\text{MgBr}_2$  and  $\text{MgSO}_4$  in the solution, which can be used to extract magnesium. Finally, NaCl crystals are washed with an 8% NaCl solution to get rid of any impurities attached to the solid. A small amount of iodate ( $\text{IO}_3^-$ ) salts is added as a food supplement (source of iodine) before table salt is marketed for human consumption.

### 3.4 Production of salts of Group 2 elements

Methods for preparation of calcium salts such as  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_3$  and  $\text{CaSO}_4$  are given under the topic the Group 2 elements (see section 2.3).

### 3.5 Solubility of salts of s-block elements

Salts of s-block elements are used in every laboratory. Your knowledge in solubility of common salts of s-block elements in water is important in terms of purification and isolation of products from a reaction mixture. Solubility of common salts of s-block elements is given below.

#### Group 1 elements

Almost all the salts (halides, hydroxides, carbonates, bicarbonates, nitrates, nitrites, sulfides, sulphates, sulphites) of Group 1 elements are soluble in water.

#### Group 2 elements

All the halides, sulphides, nitrates, nitrites, and bicarbonates of Group 2 elements are soluble in water.

$\text{Be(OH)}_2$  and  $\text{Mg(OH)}_2$  are insoluble in water,  $\text{Ca(OH)}_2$  and  $\text{Sr(OH)}_2$  are slightly soluble in water and  $\text{Ba(OH)}_2$  is soluble in water.

$\text{BeSO}_3$  and  $\text{MgSO}_3$  are soluble in water,  $\text{CaSO}_3$  is slightly soluble in water,  $\text{SrSO}_3$  and  $\text{BaSO}_3$  are insoluble in water.

$\text{BeSO}_4$  and  $\text{MgSO}_4$  are soluble in water,  $\text{CaSO}_4$  is slightly soluble in water,  $\text{SrSO}_4$  and  $\text{BaSO}_4$  are insoluble in water.

All carbonates of Group 2 elements are insoluble in water.

### 3.6 Uses of s-block elements and their compounds

Some important uses of s-block elements and their compounds are given below.

$\text{Li}_2\text{CO}_3$  is used as an inorganic drug to treat manic-depressive disorders;  $\text{LiAlH}_4$ , butyl lithium (BuLi), methyl lithium (MeLi) are used as reagents in organic chemistry; Li and lithium compounds are used in dry cells and storage batteries.

Compounds of sodium including “common salt” ( $\text{NaCl}$ ), “soda ash” ( $\text{Na}_2\text{CO}_3$ ), “baking soda” ( $\text{NaHCO}_3$ ), “caustic soda” ( $\text{NaOH}$ ) are important to paper, glass, soap, textile and chemical industries.  $\text{NaOCl}$  is a bleaching agent.

$\text{KNO}_3$  and  $\text{KClO}_3$  are used in fireworks;  $\text{KMnO}_4$  is an important oxidizing agent;  $\text{KOH}$  is used in the preparation of potassium phosphate for liquid detergents.

Soap contains sodium salts ( $\text{RCO}_2\text{Na}$ ) of long chain carboxylic acids. Sodium stearate is produced by reacting  $\text{NaOH}$  with stearic acid.

$\text{Mg}(\text{OH})_2$  is used to neutralize acids in the mouth and stomach.

Calcium carbide ( $\text{CaC}_2$ ) is used to generate acetylene ( $\text{C}_2\text{H}_2$ ) which is used to generate oxy-acetylene flame.  $\text{CaO}$  is used for the production of cement.

$\text{BaSO}_4$  is an imaging agent used to detect stomach ulcers.

### Summary

- The chloralkali industry refers to the industries that produce chlorine ( $\text{Cl}_2$ ), sodium hydroxide ( $\text{NaOH}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).
- Chlorine and  $\text{NaOH}$  are both made by the electrolysis of brine (salt water).
- In Sri Lanka at Paranthan,  $\text{NaOH}$  is produced by the diaphragm cell method. In the mercury cell method, brine is continuously passed into a cell that has graphite anodes and a moving layer of mercury as the cathode.
- Large scale production of  $\text{Na}_2\text{CO}_3$  is achieved by the Ammonia-soda or Solvay process.
- Methods for preparation of calcium salts such as  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCl}_2$ ,  $\text{CaSO}_3$  and  $\text{CaSO}_4$  are given in section 2.3.
- Solubility of salts of s-block elements is given in section 3.5.



## Learning Outcomes

At the end of this session you should be able to

- describe the production of chlorine, NaOH, NaCl and Na<sub>2</sub>CO<sub>3</sub>
- compare the solubility of salts of *s*-block elements
- list the uses of *s*-block elements and their salts



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### Activity

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19. What is meant by “Chloralkali industry”?
  20. Describe the production of NaOH and chlorine using a diaphragm cell.
  21. What is the starting material used in the production of chlorine in the chemical factory at Paranthan, Sri Lanka. What are the electrodes used for this process?  
Write the equations for the anodic and cathodic reactions.
  22. Identify the electrodes used in the mercury cell method? Describe the chemical process which takes place at the cathode.
  23. How is CO<sub>2</sub> produced for the ammonia soda process?
- 
-

## Abbreviations

(aq)	- Aqueous; dissolved in water
(g)	- Gas state
$\Delta$	- Heat
(l)	- Liquid state
(s)	- Solid state
b.pt./b.p.	- Boiling point
C.N.	- Coordination number
eV	- Electron Volt
$IE_i$	- $i^{\text{th}}$ ionization energy
J	- Joule
L	- Ligand
M	- Metal
M	- Zerovalent metal = $M(0) = M^0$
M(g)	- Element in gas state
m.pt/m.p	- Melting point
$M^+$	- Monovalent metal = $M(I) = M^I$
$M^{2+}$	- Divalent metal = $M(II) = M^{II}$
nm	- nanometres
O.N.	- Oxidation number
pm	- picometres
X	- Halogen
Z	- Atomic number





Brine : Any saline (salt) solution

කරදිය : ලුණු අඩංගු ලවණමය ද්‍රාවණයක්

உப்பு : ஏதாவது உவர்ப்பான (உப்பு) கரைசல்.

Chloralkali Industry : An industrial chemical process based on the electrolysis of brine (aqueous sodium chloride) for the production of caustic soda and chlorine.

ක්ලෝරෝකොර් කර්මාන්ත: කරදිය (NaCl ජලීය ද්‍රාවණය) විද්‍යුත් විච්ඡේදනය කිරීම මගින් කෝස්ටික් සෝඩා සහ ක්ලෝරීන් නිපදවීමේ රසායනික ක්‍රියාවලිය හා බැඳුණු කර්මාන්තයි.

: உப்புக்கரைசலை மின்பகுப்பு செய்வதன் மூலம் எரிசோடாவும், குளோரினும் உற்பத்தி செய்யும் ஒரு தொழிற்சாலை முறை

Coordination number : The number of coordinated atoms surrounding the central metal atom/ion in a complex or crystal.

සංගත අංකය : සංකීර්ණ සංයෝගයක හෝ ස්ඵටිකයක මධ්‍ය ලෝහපරමාණුව/අයනය වටා සංගතව බැඳී පවතින පරමාණු සංඛ්‍යාව

இணைப்பு எண் : ஒரு சிக்கற் சேர்வையில் அல்லது பளிங்கில் உள்ள மைய அணுவை சூழ இணைந்துள்ள அணுக்களின் எண்ணிக்கை

Cracking : The process of breaking down complex chemical compounds by heating them.

බිඳීම : සංකීර්ණ රසායනික සංයෝග රත්කිරීම මගින් බිඳ දැමීමේ ක්‍රියාවලියයි.

உடைதல் : வெப்ப சக்தியை வழங்குவதன் மூலம் இரசாயன சிக்கற்சேர்வையை உடைத்துப் பிரிக்கும் முறை

Degree of polarization : A quantity used to describe the portion of an electromagnetic wave which is polarized.

දූවීකරණ ප්‍රමාණය : විද්‍යුත් චුම්භක තරංගයක් කොපමණ දුරට දූවීකරණය වී ඇතිදී විස්තර කිරීමට භාවිතා කරනු ලබන ප්‍රමාණයයි/මිණුමයි.

முனைவாக்கத்தின் அளவு: முனைவாக்கப்பட்ட மின்காந்த அலையை விபரிப்பதற்கு பிரயோகிக்கப்படும் அளவுப்பிரமாணம்.













Primary standard : A primary standard is a substance from which a standard solution can be prepared by direct weighing of substance and dissolving in a definite volume of a solvent.

ප්‍රාථමික සම්මතය : කෙලින්ම බර කිරීමේදී එය දන්නා ද්‍රාවක පරිමාවක දිය කර ගැනීමෙන් සම්මත ද්‍රාවණයක් සෑදිය හැකි ද්‍රව්‍ය වේ.

முதனியமம் : ஒரு பதார்த்தத்தின் குறித்த நிறையை நேரடியாக நிறுத்து அதை குறிப்பிட்டளவு கனவளவு கரைசலில் கரைப்பதன் மூலம் நியமக்கரைசலை தயாரிக்கப் பயன்படுத்தும் பதார்த்தம்.

Reducing agent : A substance that causes another substance to undergo reduction and that is oxidized in the process.

ඔක්සිහරක ද්‍රව්‍ය : වෙනත් ද්‍රව්‍යයක් ඔක්සිහරණය කරවනු ලබන සහ එම ද්‍රව්‍යයම ඔක්සිකරණය වීම සිදුවන ද්‍රව්‍යයන්

தாழ்த்தும் கருவி : இது தான் ஒட்சியேற்றப்படுவதன் மூலம் ஏனையவற்றை தாழ்த்தும் ஒரு பதார்த்தம்.

Roasting : Cooking (meat or other food) by direct exposure to dry heat, as on a spit.

කර කිරීම : ද්‍රව්‍යයක් කෙලින්ම තාපයට නිරාවරණය කර පිසීම.

வறுத்தல் : நேரடி வெப்பத்திற்குள்ளாக்கப்பட்டு சமைக்கப்படுதல் (இறைச்சி,உணவு)

Steam : Water in the form of an invisible gas or vapor.

හුමාලය : වායුමය හෝ වාෂ්ප ලෙස පවතින ජලය

ஆவி : கண்ணுக்குப் புலனற்ற வாயு அவத்தையிலுள்ள நீர்.

Superoxide : A compound that possesses the superoxide anion with the formula  $O_2^-$ .

සුපර්ඔක්සයිඩ් :  $O_2^-$  යන රසායනික සූත්‍රය සහිත සුපර්ඔක්සයිඩ් ඇනායනය පවතින සංයෝග

மேலொட்சைட்டு :  $O_2^-$  எனும் இரசாயன சூத்திரமுடைய அனயன்.

Tetrahedral molecule : A molecule in which the central atom is coordinated to four groups, located in the four corners of a tetrahedron.

වතුස්තලීය අණුව : වතුස්තලයක කොන් හතරේ පිහිටි කාණ්ඩ 4 ක් මධ්‍ය පරමාණුවකට සංගත ලෙස බැඳී ඇති සංයෝගයකි.

நான்முகிக்குரிய மூலக்கூறு : மைய அணுவானது 4 கூட்டங்களுடன் இணைக்கப்பட்டு அவை நான்முகியின் 4 முனைகளிலும் அமையப்பெற்ற ஒரு மூலக்கூறு.

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