### 2.2 GENERAL BEHAVIOUR OF ALKALI METALS

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

They react readily with halogens giving alkali metal halides.

2.2.1 Trends in Chemical Properties of Alkali Metals

1. Low ionization energies make the alkali metals, the most reactive family of metals.
2. Very high second ionization energies indicate that oxidation number higher than 1, are ruled out for the alkali metals.
3. The cations of alkali metals have low charge and large radii than the radius of any cation from the same period, so the lattice energies of their salts are relatively low. Consequently, most of the simple salts of the alkali metals are water-soluble. Most of the salts are dissociated completely in aqueous solution and the hydroxides are among the strongest bases available.
4. They react with oxygen and the surface is tarnished due to the oxides formed. Only lithium burns in air to form the normal oxide, Li2O (white solid).

4 Li(s) + O2(g) → 2 Li O2 (s)

#### Lithium oxide

The exposed metals are oxidized almost immediately by oxygen in air, and in the presence of moisture. The oxides formed react with CO2 in the atmosphere to form carbonates. Li O2 (s) + CO2(g) → Li CO2 3(s)

#### Lithium oxide Lithium carbonate

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

### 2Na(s) + O2(g) → Na O2 2(s) Sodium peroxide

Potassium, rubidium and caesium react with oxygen to form superoxides (orange yellow). Caesium explodes spontaneously when it is in contact with air or oxygen. K(s) + O2(g) → KO2(s)

Potassium superoxide

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

#### 2Na(s) + 2H O2 ( ) ¾¾® 2NaOH(aq) + H2(g)

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

6. Alkali metals form ionic hydrides with hydrogen.

2M(s) + H2(g) → 2M H+ −(s)

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

### LiH(s) + H O2 ( ) → LiOH(aq) + H2(g)

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

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

6Li(s) + N2(g) → 2Li N3 (s)

Lithium nitride

#### 4Li(s) + C(s) → Li C4 (s)

Lithium carbide

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

### 2Na(s) + Cl2(g) → 2NaCl(s)

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

2M(s) + S(s) → M S2 (s)

2.2.2 Trends in Chemical Properties of Alkaline-Earth Metals

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

#### 2Be(s) + O2(g) →800C 2BeO(s)

When exposed to air magnesium quickly becomes coated with the layer of MgO.

This layer protects the surface from further corrosion at ordinary temperature.

#### 2Mg(s) + O2(g) → 2MgO(s)

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

Ba(s) + O2(g) →500 600− C BaO2(s)

Barium peroxide

1. Hydrides are produced by treating the molten alkaline earth metals with hydrogen, usually under high pressures. Magnesium reacts with hydrogen at high pressure and in the presence of a catalyst (Mgl2) forming magnesium hydride.

Mg(s) + H2(g) →Pressure(MgI2) MgH2(g) similarly Ca(s) + H2(g) → CaH2(g)

1. All Group II-A elements react with nitrogen on heating giving nitrides.

For example, magnesium reacts with nitrogen to give magnesium nitride.

##### 3Mg(s) + N2(g) → Mg N3 2(g)

###### Magnesium nitride

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

###### Mg N3 2(s) + 6H O2 ( ) → 2NH3(g) + 3Mg(OH)2(s)

4. With sulphur, magnesium gives magnesium sulphide, MgS. The other

Group II-A metals also react similarly.

### Mg + S → MgS

#### Magnesium sulphide

5. All group II-A elements react directly with halogens giving halides of the type MX2  e.g.

## Ca(s) + Cl2(g) → CaCl2(g)

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

### Mg(s) + H O2 (g) →100C MgO(s) + H2(g)

Steam

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

#### M(s) + 2H O2 (l) →100C M(OH)2(s) + H2(s)

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

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

For example:

#### Li O(s) + H O(2 2 l) → 2LiOH (aq) 2Na O (s) + 2H O( 2 2 2 l) → 4NaOH (aq) + O (g)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.

## O2−(aq) + H O2 (l) → 2OH−(aq)

The basic character of alkali metal oxides increases down the group. Potassium superoxide (K02) 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.

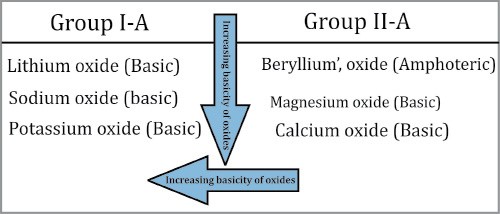
4KO (s) + 2CO (g) 2 2 → 2K CO (s) + 3O (g)2 3 2

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

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

Animation 2.6 : [Reaction with acids](http://learnthings.co.za/content/secondary/Home/Lessons/Science/Chemistry/Grade10/metals/metalsrea/thereacti/reacti_01/default.htm)

Source and Credit: [Learn](http://learnthings.co.za/content/secondary/Home/Lessons/Science/Chemistry/Grade10/metals/metalsrea/thereacti/reacti_01/default.htm)



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

BeO(s) + H SO2 4(aq) → BeSO4(s) + H O2 ( )

BeO(s) + 2NaOH(aq) → Na BeO2 2(aq) + H O2 ( )

Sodium beryllate

ii) Hydroxides

The alkali metal hydroxides are all crystalline solids, very soluble in water except LiOH, which is slightly soluble.They are generally hygrsocopic and are very strong bases, execpt LiOH. The solubility of alkaline earth metal hydroxides in water increases down the group. Be(OH)2 is quite insoluble. Mg(OH)2 is sparingly soluble while Ba (OH)2 is more soluble.This increase in solubility is due to low lattice energy of hydroxides which is, in turn, due to higher ionic size.

Alkali metal hydroxides are stable to heat except LiOH, while alkaline earth metal hydroxides like Mg(OH)2 and Ca(OH)2 decompose on heating.

2LiOH(s) → Li O(s) + H O2 2 ( )

Mg(OH) (s) 2 → MgO(s) + H O2 ( )

A saturated solution of Ca(OH)2 in water is called lime water and is used as a test for CO2. A suspension of Mg(OH)2 in water is called milk of magnesia and it is used for treatment of acidity in stomach. iii) Carbonates

The carbonates of alkali metals are all soluble in water and are stable towards heat except Li2CO3 which is not only insoluble but also decompose on heating to lithium oxide. The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable. In case of large cation like K+ in K2CO3, the gain in electrostatic attraction is relatively much less and the decomposition is difficult. Sodium carbonate is very important industrial chemical. At temperature below 35.2°C, Na2CO3 crystallizes out from water as Na2CO3.10H2O, which is called washing soda. Above this temperature it crystallizes as Na2CO3. H2O. On standing in air, Na2CO3.10H2O slowly loses water and converted to a white powder Na2CO3.H20. The solution of Na2CO3 in water is basic due to hydrolysis of carbonate ion.

### Na CO2 3(s) + 2H O2 ( ) → 2NaOH(aq) + H CO2 3(aq)

Unlike the alkali metal carbonates, the alkaline earth metal carbonates are only very slightly soluble in water, with the solublity decreasing down the group. They also decompose on heating and the ease of decomposition decreases down the group. CaCO (s) 3 → CaO(s) + CO (g)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.

iv) Nitrates

Nitrates of both alkali and alkaline-earth metals are soluble in water. Nitrates of Li, Mg , Ca and Ba decompose on heating to give O2, NO2and the metallic oxide whereas nitrates of Na and K decompose to give different products.

### 4LiNO (s) 3 → 2Li O (s) + 4NO (s) + O (g)2 2 2 2Mg(NO ) (s) 3 2 → 2MgO (s) + 4NO (g) + O (g)2 2 2Ca(NO ) (s) 3 2 → 2CaO (s) + 4NO (g) + O (g)2 2 2NaNO (s) 3 → 2NaNO (s) + O (g)2 2

v) Sulphates

All the alkali metals give sulphates and they are all soluble in water. The solubilities of sulphates of alkaline earth metals, gradually decrease down the group. BeSO4 and MgSO4 are fairly soluble in water. CaSO4 is slightly soluble, while SrSO4 and BaSO4 are almost insoluble.

Calcium sulphate occurs in nature as gypsum CaSO4.2H2O. When it is heated above 100°C, it loses three quarters of its water of crystallization, giving a white powder called’ Plaster of Paris.

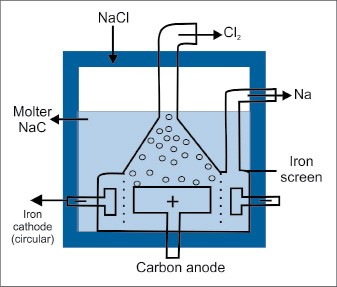
### 2CaSO . 2H O 4 2 → (CaSO ) . H O + 3H O4 2 2 2

Gypsum Plaster of Paris

#### 2.3 COMMERCIAL PREPARATION OF SODIUM BY DOWNS CELL

Most of sodium metal is produced by the electrolysis of fused sodium chloride. Since the melting point of sodium chloride is 801°C, some calcium chloride is added to lower its melting point and to permit the furnace to operate at about 6000C.

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



Molten

Nacl

Fig.2.1 Down’s Cell

Animation 2.7 DOWN’S CELL

Source and Credit: eLearn.Punjab

Sodium metal rises in a special compartment from which it is taken out at intervals.

The cell produces dry chlorine and 99.9 percent pure sodium. The process is carried out at 600°C and it has the following advantages.

1. The metallic fog is not produced.
2. Liquid sodium can easily be collected at 600°C.
3. Material of the cell is not attacked by the products formed during the electrolysis.

During the process the following reactions take place:

NaCl Na→ + +Cl-

|  |  |
| --- | --- |
| At cathode  At anode | Na+ +e- →Na  Cl- 1/2Cl→+1e- |

2

#### 2.4 COMMERCIAL PREPARATION OF SODIUM HYDROXIDE BY THE DIAPHRAGM CELL

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

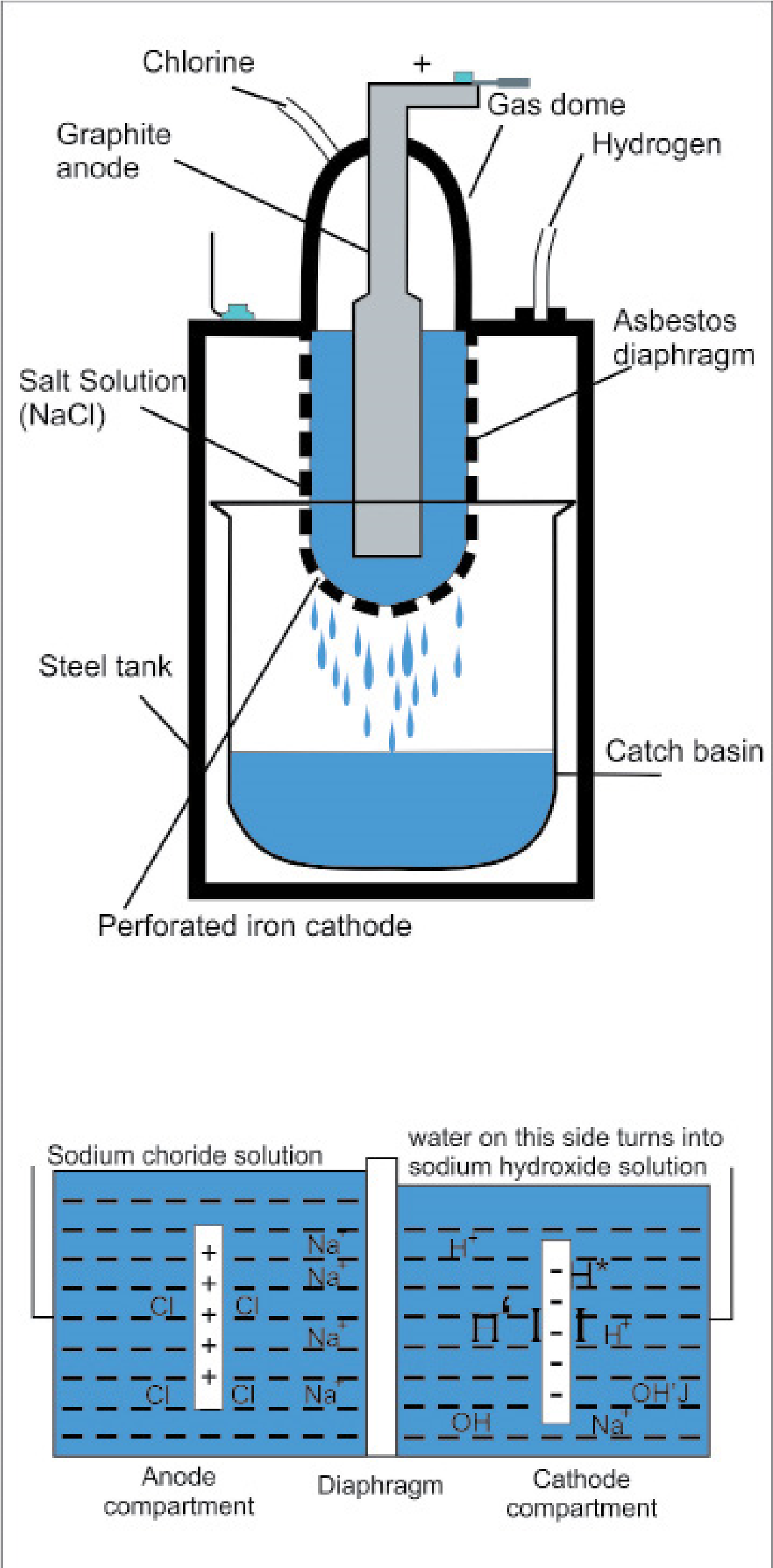


Fig.2.2(a) Nelson Cell for the

Production of NaOH

Fig.2.2(b)

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

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

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

2Cl (aq) −  Cl (g) + 2e−

→ 2

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

### 2H O + 2e − 2OH (aq) + H (g)− (Cathode)

2 → 2

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

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

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

Cl (g) + 2OH (aq) −  OCl (aq) + Cl (aq) + H O− −

2 → 2

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

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

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

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

#### 2.5 ROLE OF GYPSUM IN AGRICULTURE AND INDUSTRY

1. Role of Gypsum in Agriculture

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

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

1. Role of Gypsum in Industries

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

‘Dead burnt’.

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

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

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

Two varieties of plasters are made.

1. Cement Plaster.

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

1. Hard Finish Plasters

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

form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions. Gypsum is also used as a filler in paper industries.

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

#### 2.6 ROLE OF LIME IN AGRICULTURE AND INDUSTRY

Lime, (CaO) is a soft, white compound which is obtained by the thermal decomposition of CaCO3.

(a) Role of Lime in Agriculture

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

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

Calcium oxide is also used in large amounts for making lime-sulphur sprays which have a strong fungicidal action. The hydroxide of calcium is obtained when the oxide of the calcium is allowed to react with water. The process is called slaking of lime and it is an exothermic reaction.

CaO + H O 2 → Ca(OH)2

#### Slaked lime

Functions of Calcium in Plant-Growth

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

(b) Role of Lime in Industries

1. Large quantities of lime are used in the extraction and refining of metals.
2. Lime is also used in paper, cement and leather industries
3. The ability of lime to react with sand at high temperature forming calcium silicate

(CaSiO3) serves as an important basis for glass manufacture.

1. Lime is used in ceramic industry for producing different types of sanitary materials.
2. Ordinary mortar, also called lime mortar, is prepared by mixing freshly prepared slaked lime (one volume) with sand (three or four volumes) and water to form a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the blocks firmly together. The equations for the chemical reactions which take place when mortar hardens are:

##### CaO + H O 2 → Ca(OH)2 Ca(OH) + CO 2 2 → CaCO + H O3 2 Ca(OH) + SiO 2 2 → CaSiO + H O3 2

1. Lime is also used in refining of sugar and other food products.
2. Lime is used in the manufacturing of bleaching powder, which is used for the bleaching of the fabric and paper pulp.
3. A suspension of the calcium hydroxide is called milk of lime and is used as a white-wash.
4. When lime is heated with coke at about 2800°C in an electric furnace, calcium carbide is produced, which on hydrolysis yields acetylene (C2H2).

#### CaO + 3C → CaC + CO2 Calcium carbide

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

Animation 2.8 : [Gals(The most radio active alkali metal 2)](http://www.targeticse.co.in/articles/objectivechemistry)

Source and Credit: [Targeticse](http://www.targeticse.co.in/)

##### Key Points

1. The elements of group IA except hydrogen are called ‘alkali metals’ while those of group IIA are named as alkaline earth metals.
2. Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions.
3. Alkaline earth metals have two electrons in s-orbital of their valence shell. They lose two electrons forming dipositive ions M2+.
4. Spodumene, Chile saltpetre, trona, borax, carnallite, sylvite, alunite, halite, natron, are the common minerals of alkali metals.
5. Beryl, magnesite, dolomite, epsom salt, asbestos, calcite, gypsum, strontionite and barite are the important minerals of alkaline earth metals.
6. Lithium behaves different from the other alkali metals.
7. Lithium forms only normal oxide, whereas the others form higher oxides like peroxides and superoxides.
8. Beryllium is the only member of group II, which reacts with alkalies to give hydrogen. The other member do not react with alkalies.
9. Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
10. When gypsum is heated above 100°C, it loses three quarters of its water of crystallization, giving white powder of CaSO4.1/2H2O which is called Plaster of

Paris.

1. Sodium is prepared by the electrolysis of molten sodium chloride in Down’s cell.
2. Calcium is necessary for development of leaves and it tends to accumulate in leaves and bark. An adequate quantity of calcium is essential for the optimum activity of microorganisms that produce nitrates.
3. Lime is used in paper and glass industries. It is also used for refining sugar and other food products.

|  |  |  |
| --- | --- | --- |
|  | EXERCISE |  |

Q1. Fill in the blanks:

1. Alkali metals are reactive than alkaline-earth metals.
2. Alkali metals decompose water vigorously producing\_\_\_\_\_\_\_\_ and hydrogen.
3. When heated in a current of dry hydrogen, alkaline earth metals form white crystalline of the type MH2.
4. The beryllium hydroxide, like the hydroxide of aluminium is amphoteric, while the hydroxides of the other members of the group IIA are\_\_\_\_\_\_\_\_ . (v) The elements of the group IA are termed as alkali metals, because their\_\_\_\_\_\_\_\_are alkaline.
5. Spodumene is an ore of\_\_\_\_\_\_\_ metal.
6. Alkali metal nitrates on heating give the corresponding\_\_\_\_\_\_\_ and oxygen.
7. Na2CO3.H2O is the chemical formula of a mineral of sodium which is known as\_\_\_\_\_\_ .
8. Metallic bicarbonates are decomposed on heating into their carbonates, along with\_\_\_\_\_\_\_\_ and\_\_\_\_\_\_\_\_ .
9. Metal nitrates other than the alkali metals on heating decompose into the

corresponding metal\_\_\_\_\_\_\_\_\_\_along with the evolution of nitrogen peroxide and oxygen.

Q2. Indicate True or False.

1. Group IA elements are called alkali metals because their chlorides are alkaline in

nature

1. Alkali metals are very good conductor of electricity.
2. The hydroxides of alkali metals and alkaline-earth metals are soluble in water.
3. Plaster of Paris is a hemihydrate.
4. Alkali metals have low melting and boiling points as compared to those of alkaline earth metals.
5. Lithium carbonate is decomposed to its oxide, but the carbonates of the other alkali metals are stable towards heat.
6. All alkali metal sulphates are insoluble in water.
7. Lithium combines with nitrogen to form lithium nitride but other alkali metals do not react with nitrogen.
8. Trona is a mineral of lithium.
9. Alkaline earth metals are stronger reducing agents than alkali metals.Q 4. (a) Give the names, electronic configurations and occurrence of s-block elements.

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

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

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

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

(b) Why the aqueous solution of Na2CO3 is alkaline in nature?

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

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

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

(b) What happens when:

* 1. Lithium carbonate is heated.
  2. Lithium hydroxide is heated to red hot.
  3. Beryllium is treated with sodium hydroxide.
  4. Lithium hydride is treated with water.

Q10.Give formulas of the following minerals.

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

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

Q.11. Answer the following questions briefly.

* + 1. Why alkali and alkaline earth metals are among the reactive elements of the periodic table?
    2. Why line water turns milky with CO2but becomes clear with excess CO2?

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

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

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

* 1. How lime and sand are used to make glass?
  2. How lime mortar is prepared?

CHAPTER

# GROUP IIIA AND GROUP IVA ELEMENTS

3

[Animation 3.1 : Periodic Table](http://elearn.punjab.gov.pk/animations/chemistry/index.html)

Source and Credit: [eLearn.Punjab](http://elearn.punjab.gov.pk/animations/chemistry/index.html)

|  |
| --- |
| IN THIS CHAPTER YOU WILL LEARN |
| 1. The names, electronic configurations and occurrence of IIIA and IVA group elements. 2. The peculiar properties of boron and carbon in their respective groups. 3. The preparation and properties of borax and orthoboric acid. 4. The reactions of aluminium. 5. Structures and properties of oxides of carbon and silicon, silicates, silicones and their uses. 6. The uses of silicon and germanium in semi-conductor industries and lead in paints. |

## 3.1 GROUP IIIA ELEMENTS

The Group IIIA of the Periodic Table comprises the elements boron, aluminium, gallium, indium and thallium.Electronic configurations and some physical properties of group IIIA elements are shown in Table 3.1.

Table 3.1 Electronic Configurations and Physical Properties of Group IIIA Elements

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Properties | B | Al | Ga | In | Tl |
| Atomic number | 5 | 13 | 31 | 49 | 81 |
| Electronic configurations | [He]2s22p1 | [Ne]3s23p1 | [Ar] 3d104s24p1 | [Kr]4d105s25p1 | [Xe]4f14 5d106s26p1 |
| Ionization energy (kJ/ mol) | 801 | 577 | 579 | 558 | 589 |
| Electron affinity (kJ/mol) | -27 | -45 | -29 | -29 | -30 |
| Electronagetivity | 2.0 | 1.5 | 1.6 | 1.7 | 1.8 |
| Atomic radius (pm) | 80 | 125 | 126 | 144 | 148 |
| Ionic radius of 1+ion (pm) | 20 | 52 | 60 | 81 | 95 |
| Melting points (°C) | 2300 | 660 | 30 | 157 | 304 |
| Boiling points (°C) | 2550 | 2467 | 2403 | 2080 | 1457 |
| Density (g/cm3) | 2.33 | 2.7 | 5.93 | 7.3 | 11.85 |

The small size and high nuclear charge make boron non-metallic while all the other elements of this group are metals. The abrupt increase in metallic character from B to Al is associated with the increased size of aluminium atom. The increase in the atomic size is not regular in this group. This is due to the presence of d electrons in heavier members which have poor shielding effect than s and p electrons.

3.1.1 Occurrence (Boron and Aluminium)

Boron is not an abundant element. It occurs in traces in most soils and has been found to be essential in very small amounts for the proper growth of many plants.

Boron is always found in nature combined with oxygen, usually as oxyborate ions. Boron occurs principally as salts of various polyboric acids.

Table 3.2 Common Minerals of Boron

|  |  |
| --- | --- |
| Name of Minerals of Boron | Chemical Formula |
| Borax or Tincal | Na2B4O7.10H2O |
| Colemanite | Ca2B6O11.5H2O |
| Orthoboric Acid | H BO |

3 3

Aluminium is the third most abundant element in the earth’s crust (after oxygen and silicon)

### Table 3.3 Common Minerals of Aluminium

|  |  |
| --- | --- |
| Name of Minerals of Aluminium | Chemical Formula |
| Feldspar | KAlSi3O8 or K2O.  Al2O3.6SiO2 |
| Mica (Muscovite) | KH2Al3(SiO4)3 |
| Kaolin (Clay) | H2Al2(SiO4)2.H2O or Al2O3 .2SiO2.2H2O |
| Corundum | Al2O3 |
| Emerald | AIF2SiO4 |
| Gibbsite | (Al2O3.3H2Oor AlO (OH)3) |
| Bauxite | Al2O3.2H2O |
| Cryolite | Na3AIF6 |
| Diaspore | (Al2O3.H2Oor AlO (OH) |

It occurs primarily as alumino-silicate minerals found in the rocks of the outer portion of the earth.

The other elements of group IIIA gallium, indium and thallium are relatively rare and are obtained as by-products during the processing of other metals.

#### 3.1.2 Peculiar Behaviour of Boron

Boron is the first member of the Group IIIA, it shows many dissimilarities with the members of its own group.The difference in the properties of boron and those of the other members of the series is mainly due to the large difference in their sizes and ionization energies.

1. Boron is the only elementinGroupIIIAwhichisnon-metallic in behaviour
2. It is the only element with less than four electrons in the outermost shell which is not a metal.
3. Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states are + 3 and -3.
4. One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.
5. Boron does not form ionic compounds with sulphate, nitrate or other anions because boron does not from a stable cation.

## 3.2 COMPOUNDS OF BORON

3.2.1 Borax (Sodium Tetraborate Na2B4O7.lOH2O)

Borax is the sodium salt of tetraboric acid. It is the most important of all borates.

Occurrence:

Borax occurs as a natural deposit called tincal in the dried up lakes of Tibet and California.

Manufacture:

1. Formally borax was manufactured by treating a hot solution of boric acid with the proper amount of soda ash.

### 4H BO3 3(s) + Na CO2 3(s) → Na B O2 4 7 (s) + 6H O2 ( )l + CO2 (g)

Boric acid Borax

1. Now-a-days borax is almost exclusively obtained from calcium borate. Finely powdered colemanite is boiled with Na2CO3 solution, when CaCO3 precipitates out and a mixture of borax and sodium metaborate is formed.

Ca B O2 6 11(s) + 2Na CO2 3(s) → 2CaCO3(s) + Na B O2 4 7(s) + 2NaBO2(s)

Colemanite

The clear solution from the top is taken off and is then allowed to crystallize, when crystals of borax separate out. To get more borax, CO2 is blown through the mother-liquor, the sodium metaborate is decomposed into borax, which separates out in the form of fine crystals.

4NaBO2(s) + CO2(g) → Na CO2 3(s) + Na B O2 4 7(s)

Sodium metaborate Borax

1. Borax may also be obtained from tincal (Na2B4O7.10H2O) by treating tincal with water and subsequently evaporating the clear solution, when crystals of borax separate out.

Properties:

1. Borax is a white, crystalline solid. It is sparingly soluble in cold water but is more soluble in hot water: 100 grams of water dissolve 3 grams of decahydrate at 10°C and 99.3 grams at 100°C. If a saturated solution be allowed to crystallize above 62°C, octahedral crystals of the pentahydrate, Na2B4O7.5H2Oseparate out, if the temperature is below 62°C, the decahydrate is formed. Its aqueous solution is alkaline in nature due to hydrolysis.

## Na B O2 4 7(s) + 7H O2 ( )l → 2NaOH(aq) + 4H BO3 3(s)

Strong alkali Weak acid

The hydrolysis is prevented in the presence of glycerine.

2. When heated, borax loses water and swells up into a white porous mass due to the expulsion of water: on further heating it melts into a clear transparent glass, which dissolves many metallic oxides forming coloured beads. This reaction forms the basis of borax bead test.

## Na B O .10H O2 4 7 2 (s) →∆ Na B O2 4 7(s) + 2NaBO2(s) + B O2 3(s)

Glassy mass

3. Its aqueous solution reacts with HCl or H2SO4 to form boric acid:

NA B O2 4 7(s) + 2HCI(aq) + 5H O 2 → 2NaCl(aq) + 4H BO3 3(s)

Borax Boric acid

### NA B O2 4 7(s) + H SO2 4(aq) + 5H O2 ( )l → Na SO2 4(s) + 4H BO3 3(s)

4. When borax is heated with ammonium chloride, boron nitride is produced:

#### Na B O2 4 7(s) + 2NH Cl4 (aq) → 2NaCl(s) + 2BN(s) + B O2 3(s) + 4H O2 ( )l

5. Borax when dissolved in water ionizes as:

Na B O2 4 7(s) → 2Na+(s) + B O4 72-(s)

Hydrolysis of B4O7-2 occurs as follows:

## B O4 72-(s) + 7H O2 ( )l → 4H BO3 3(s) + 2OH-( )l

So, a strong alkali (NaOH) is formed which is highly ionized. On the other hand, boric acid (H3BO3) is ionized to a little extent, because it is a weak acid. Hence, solution of borax as a whole is alkaliine in nature.

6. Borax Bead Test

Prepare a loop at the end of a platinum wire. Heat the wire and take a little powdered borax on the hot loop. Heat again, borax first swells up and then melts into colourless, glasslike bead on the loop. Now put a few grains of the substance, under examination, on the beads and re-heat it first in the oxidizing flame and then in the reducing flame.

Chemistry of the Borax-bead Test:

Borax, when fused, is decomposed into sodium metaborate and boric anhydride.

Na B O2 4 7(s) → 2NaBO2(s)+ B O2 3(s)

The metallic oxide formed from the substance, under examination, combines with B2O3 giving the coloured metallic borates. With cupric oxide, the beads are coloured blue in the oxidizing flame because cupric borates are blue in colour.

CuO(s) + B O2 3(s) → Cu (BO )2 2(s)

Uses of Borax:

1. It is used to prepare borate glass, which is heat resistant.
2. It is used in softening of water.
3. It is employed in borax bead test, for the detection of metallic cations.
4. It is used in metallurgical operations.
5. It is used as a flux in welding and in metallurgy.
6. It is employed in making washing powders.
7. It is used in leather industry for tanning and dyeing.
8. It is used in cosmetics, soaps, textiles, paints, medicine, match industry and as a preservative.

3.2.2 Boric Acids

There are four important boric acids.Out of these orthoboric acid is the most important and the stable one. The remaining acids are stable in solid state and change into orthoboric acid in solution:

1. Orthoboric Acid, H3BO3
2. Metaboric Acid, HBO2
3. Tetraboric Acid, H2B4O7
4. Pyroboric Acid, H6B4O9

HBO2(s) + H O2 (l ) → H BO3 3(s)

Metaboric acid Boric acid

H B O2 4 7(s) + 5H O2 (l ) → 4H BO3 3(s)

Tetraboric acid Boric acid

## H B O6 4 9(s) + 3H O2 (l ) → 4H BO3 3(s)

Pyroboric acid Boric acid

Orthoboric Acid or Boric acid (H3BO3)

It is a white crystalline chemical substance (triclinic), sparingly soluble in cold water (2.6% at 40 0C) but dissolves readily in hot water (37% at 107°C). This temperature variation in solubility forms the basis for its separation and purification.

Preparation of Boric acid on Commercial Scale

1. From Colemanite

On commercial scale, boric acid is prepared from a natural calcium borate called colemanite (Ca2B6O11. 5H2O) by suspending it in boiling water while, sulphur dioxide is passed through it. Boric acid crystallizes out from the solution while, the other product CaSO3 remains in the solution.

### Ca B O .5H O2 6 11 2 (s) + 2SO2 (g) + 4H O2 ( )l → 2CaSO3(aq) + 6H BO3 3(s)

Colemanite

From Borax:

A hot concentrated solution of borax is treated with a calculated quantity of conc. H2SO4. On cooling, crystals of boric acid formed separate out.

### Na B O2 4 7(s) + H SO2 4(aq) + 5H O2 ( )l → Na SO2 4(s) + 4H BO3 3(s)

Borax Boric acid

Properties of Boric Acid

1. Boric acid is a white lustrous crystalline solid having a soft soapy touch, very slightly soluble in cold water but fairly soluble in hot.
2. It is volatile in steam.
3. It reacts with ethyl alcohol forming ethyl borate.

H BO3 3(s) + 3C H OH2 5 ( )l → (C H ) BO2 5 3 3( )l + 3H O2 ( )l

4. When heated strongly, it swells to frothy mass losing water molecules.

It is first converted into metaboric acid, thep to tetra boric acid and finally to boric anhydride.

H BO3 3(s) →100o C HBO2 (s) + H O2 ( )l

Metaboric Acid

4HBO(s) →140o C H B O2 4 7 (s) + H O2 ( )l

#### Tetraboric acid

Red

H B O2 4 7 (s) →hot 2B O2 3(s) + H O2 ( )l

#### Boric anhydride

5. It is a very weak acid and ionizes to a very limited extent mainly as a monobasic acid.

### H BO3 3(s) + H O2 ( )l → [B(OH) ]4 -(s) + H+

1. Its solution has no effect on methyl orange, although it turns blue litmus red.
2. It is partially neutralised by caustic soda to give borax.

### 4H BO3 3(aq) + 2NaOH(aq) → Na B O2 4 7(aq) + 7H O2 ( )l

8. When boric acid is neutralized by soda ash (Na2CO3), borax is obtained.

#### 4H BO3 3(aq) + Na CO2 3(aq) → Na B O2 4 7(s) + 6H O2 ( )l + CO2(g)

Borax

9. Boric acid being a weak acid, cannot be titrated with alkalies in the usual manner. In the presence of glycerol, however, it can be titrated against a standard alkali using phenolphthalein as an indicator.

Uses of Boric Acid

1. Boric acid is used in medicines as an antiseptic, e.g. dusting powder, boric ointment and boric solution is used as an eye-wash.
2. It is used in pottery as a glaze because borate glazes are more fusible than silicate glazes and possess a higher coefficient of expansion.
3. It is also used in candle industry for stiffening of wicks.

3.3 REACTIONS OF ALUMINIUM

1. Reaction with Air

When a piece of aluminium sheet is exposed to moist air it acquires a thin, continuous coating of aluminium oxide, which prevents further attack on the metal by atmospheric oxygen and water under normal conditions. Because of this aluminium sheets are said to be corrosion-free. However, if the aluminium powder is heated to 800°C and above, the metal will react with air to form aluminium oxide, Al2O3, and aluminium nitride, AIN. The reaction is accompanied by the evolution of heat and intense white light.

This property of aluminium is made use of in flash light photography.

### 4Al(s) + 3O2 (g) → 2Al O2 3(s) 2Al(s) + N2 (g) → 2AlN(s)

Because of its ability to combine with both oxygen and nitrogen, the metal is often used to remove air bubbles from molten metals. Salt solutions corrode aluminium badly so aluminium and aluminium alloys are not suitable for marine use.

2. Reaction with Non-Metals

Heated aluminium combines with the halogens, sulphur, nitrogen, phosphorus and carbon, accompanied by the evolution of heat.

#### 2Al(s) + 3Cl2(g) → 2AlCl3 (S)

Aluminium on heating with hydrogen forms aluminium hydride.

2Al(s) + 3H2(g) → 2AlH3(s)

3. Reaction with Acids and Alkalies

Aluminium is amphoteric. It dissolves in both acids and bases with the liberation of hydrogen gas. Aluminium reacts slowly with dilute acid and more rapidly with concentrated hydrochloric acid to displace hydrogen.

## 2Al(s) + 6HCl(aq) → 2AlCl3 (aq) + 3H2 (g)

Aluminium does not react with dilute sulphuric acid. However, it is oxidized by hot concentrated sulphuric acid to liberate sulphur dioxide gas.

### 2Al(s) + 6H SO2 4(aq) → Al (SO )2 4 3 (aq) + 6H O2 ( ) + 3SO2(g)

Aluminium does not react with nitric acid at any concentration, probably because of the formation of protective layer of aluminium oxide. The acid is said to render the aluminium passive. Nitric acid is, therefore, frequently transported in aluminium containers.Aluminium dissolves in both sodium and potassium hydroxides to form a soluble aluminate, with the evolution of hydrogen.

2Al(s) + 2NaOH(aq) + 6H O2 ( ) → 2NaAl(OH)4 (aq) + 3H2 (g)

USES

1. Aluminium is very-light (nearly three times less dense than iron) but posseses high tensile strength. These properties account for its extensive use in the transport industries, in the construction of aircrafts, ships and cars.
2. It is an excellent conductor of both electricity and heat. Thus, it is used as heat exchanger in chemical, oil and other industries. Heavy duty electrical cables are made of aluminium metal.
3. Aluminium is an excellent reflector of radiant energy. For this reason, it is commonly used to insulate buildings. Aluminium foil is also used to jam radar.
4. It is non-magnetic and is thus used in navigational equipment.
5. It is a good reducing agent and can thus be used for this purpose in the chemical and steel industries.
6. It is non-toxic and can be used for making food and brewing equipments and in packaging.
7. Aluminium readily forms alloys with other metals like copper, magnesium, nickel and zinc.
8. At homes, aluminium is found in the form of cooking utensils, window frames and kitchen foil.
9. Aluminium is used for making petrol and milk storage tanks because it reflects heat and prevents them of being over heated in the sun.

#### 3.4 GROUP IVA ELEMENTS

Group IVA of the periodic table comprises elements, carbon, silicon, germanium, tin and lead.

Table 3.4 Electronic Configurations and Physical Properties of Group IVA Elements

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Properties | C | Si Ge | | Sn | Pb |
| Atomic number | 6 | 14 | 32 | 50 | 82 |
| Electronic configurations | [He]2s22p2 | [Ne]3s23p2 | [Ar]3d104s24p2 | [Kr]4d105s25p2 | [Xe]4f145d106s26p2 |
| Ionization energy (kj/ mol) | 1086 | 736 | 760 | 707 | 715 |
| Electron affinity (kj/mol) | -122.5 | -120 | -116 | -121 | -101 |
| Electronagetivity | 2.5 | 1.8 | 1.8 | 1.8 | 1.8 |
| Atomic radius (pm) | 77 | 117 | 122 | 140 | 154 |
| Ionic radius of 2+ion (pm) | 60 | 71 | 73 | 93 | 121 |
| Melting points (°C) | 3570 | 1410 | 937 | 232 | 328 |
| Boiling points (°C) | sublimes | 2355 | 2830 | 2270 | 1750 |
| Density gm/cm3 at (20°C) | 2.33 | 2.7 | 5.93 | 7.3 | 11.85 |

There is a marked change of properties from carbon to lead.This gradation is of such nature, however, that there are very few similarities between

|  |  |  |  |
| --- | --- | --- | --- |
| the extreme members.Thus carbon  far more, for example, | and | lead differ very | considerably; |
| than do lithium and caesium in | group | IA. The electronic | configurations |
| of IVA group elements along with  Table 3.4. | their | physical properties | are given in |

Carbon and silicon are the only non-metals in Group IVA. Carbon has the peculiar property of forming long carbon chains, silicon forms long chains of alternating silicon and oxygen atoms.

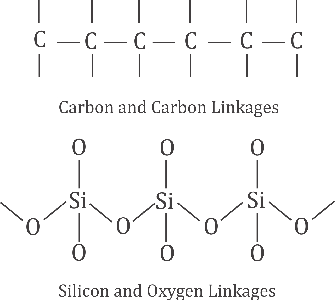
1. Carbon and silicon both form acidic oxides, whereas the oxides of germanium, tin and lead are amphoteric in nature.
2. Both carbon and silicon form covalent bonds. Their oxides are acidic and both form hydrides and chlorides.

The elements of group IVA are characterized by a set of four valence electrons, which form two pairs.

In the first three elements of IVA group, carbon, silicon and germanium, all the four outermost electrons are used as valency electrons, while in tin and lead either all four (stannic and plumbic compounds) or only one of the pairs of electrons (stannous and plumbous compound) is used for bonding.

The pair of valence electrons that do not readily take part in chemical combination is termed as inert pair. As in other groups, the inert pair effect is most marked in the element of highest atomic mass, namely lead.

The increase in electropositive character from carbon through silicon, tin, and lead is pronounced. This trend is shown also by the. increase in the metallic character of the elements with increased atomic mass.



The Following are the Common Properties of Group IVA Elements:

1. All the elements of this group show a valency of four.
2. All of them form hydrides, MH4.
3. They form tetrachlorides, MCI4.
4. They also form the dioxides, MO2

3.4.1 Occurrence of Carbon

|  |  |
| --- | --- |
| Minerals of Carbon | Chemical Formula |
| Limestone  (calcite) | CaCO3 |
| Dolomite | MgCO3.CaCO3 |
| Magnesite | Mg CO |

Carbon occurs naturally in the two states. One is crystallline (graphite, diamond) form and the other is amourphous

(coal, charcoal) form. 3

3.4.2 Occurrence of Silicon

Silicon is very abundant, about 25% of the mass of the Earth’s crust being due to this element. Silicon, unlike carbon, is not found in free state.

|  |  |
| --- | --- |
| Minerals of Silicon | Chemical Formula |
| Analcite (a zeolite) | NaAl(SiO3)2.H2O |
| Asbestos | CaMg3(SiO3)4 |
| Kaolin (pottery clay) | H2Al(SiO4)2.H2O |
| Zircon | ZrSiO4 |
| Talc (or soapstone) | H Mg (SiO ) |

2 3 3 4

Silicon is found as a major constituent of rocks either in the form of silica or silicates. Most minerals other than sulphides, sulphates, phosphates, and carbonates contain a high proportion of silicon.

As oxide, it is found as quartz in the following forms:

Rock crystal, amethyst quartz, smoky quartz, rose quartz and milky quartz. Sand is largely silicon dioxide (silica). Opal is a hydrated variety of quartz.

3.4.3 Peculiar Behaviour of Carbon

Carbon differs from the remaining members of Group IV-A in the following respects:

1. Carbon and silicon are nonmetals while the other members of the family are metalloids or metals.
2. Catenation or self linkage. Carbon has a tendency to form long chains of identical atoms. The type of linkage of identical atoms with each other is called catenation or self-linkage. The property of catenation decreases on moving down the group from carbon to lead. The maximum tendency of catenation associated with carbon forms the basis of the carbon compounds which constitute organic chemistry.

#### 3.5 COMPOUNDS OF CARBON AND SILICON

3.5.1 Structure of Oxides of Carbon

Three oxides of carbon are known:

(i) Carbon monoxide, CO (ii) Carbon dioxide, CO2 (iii) Carbon suboxide, C3O2 Out of these, the last one is of little importance. Structure of Carbon Monoxide (CO)

Carbon monoxide is diatomic molecule having triple bond between the two atoms. It is very slightly polar. The electronic structure of carbon monoxide can be represented as xxC xx O It is usually written as: xxC O .

→

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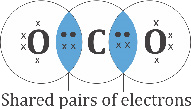
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It might appear from the above structure that the molecule should have a large dipole moment, but in fact the molecule has a small dipole moment

(0.112D). d- d+

### C O

Structure of the Carbon Dioxide

Carbon dioxide exists in the gaseous state as linear molecules. The observed C-O bond distance is 115 pm and is in agreement with the Structure shown. Solid CO2 has a face-centered cubic structure. Being linear its dipole moment is zero.

3.5.2 Oxides of Silicon Silicon Dioxide

Silicon dioxide, SiO2 called silica, is probably the most common and the most important compound of silicon. In silica every silicon atom is attached tetrahedrally to four oxygen atoms and each oxygen atom has two close silicon neighbours.

Vitreous silica possesses the following interesting and useful properties.

1. High transparency to light.
2. Very refractory, does not soften below 1500 to 1600°C.
3. Very low thermal expansion.
4. Excellent insulator.
5. Hard, brittle and elastic.
6. Insoluble in water and inert toward many reagents.
7. It is resistant towards all acids except HF.

Quartz, the common crystalline form of silicon dioxide, is a hard, brittle, refractor, colourless solid which differs very markedly from carbon dioxide.

Both carbon and silicon have four electrons in their valence shells and both also form four covalent bonds. So, why should there be a big difference between CO2 and SiO2 ?

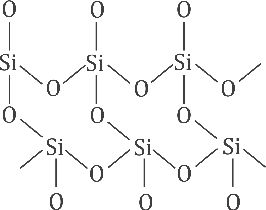
The answer lies in the fact that silicon atoms are much larger than carbon atoms and thus tend to surround themselves with more oxygen neighbours; silicon forms only single bonds to oxygen atoms whereas carbon may form double bonds. Carbon, in fact, forms double bonds to each of the two oxygen atoms to produce a small, symmetrical, linear molecule CO2,which is volatile and reasonably reactive.

The silicon atom can be approached closely by four oxygen atoms and forms a single bond to each at tetrahedral angles. This structure can be continued in three dimensions to produce a continuous giant silicon oxygen network extending out to give the massive silicon dioxide crystal.

In the interior of the silica network every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bonded to two silicon atoms. The overall ratio of silicon to oxygen atoms is 1:2 and the simplest formula for silica therefore is SiO2. The silicon oxygen bonds are strong and keep the atoms firmly in place.

Note, however, that it is not the molecular formula for silica but the whole chunk of silica must be considered to be essentially one molecule. The atoms of silicon and oxygen at the surface of the chunk do not have all their valence forces satisfied, as is shown by the high surface activity of silica.

In each of the various crystalline forms of silica, there is a special pattern which is repeated throughout the crystal in a regular definite crystal lattice. The regular tetrahedral arrangement of four oxygen atoms around each silicon persists in each crystalline form but the Si-O-Si bond angles and the rotation about each Si-O bond are different in the different polymorphic species.



*Fig. 3.1 Structure of silicon dioxide*

When crystalline silica is heated sufficiently it melts to give a viscous liquid having a random structure, presumably with the silicon atoms still on the average close to four oxygen atoms and the oxygen atoms close to two silicon atoms. When this liquid silica is cooled it does not crystallize readily, but usually it under supercools tremendously and eventually becomes rigid without having undergone orientation into a regular crystal pattern. This rigid, highly under supercooled liquid is called vitreous silica or silica glass (frequently incorrectly referred to as fused quartz).

3.5.3 Silicates and their Uses

The compounds derived from silicic acids are termed as silicates.

1. Sodium silicate, Na2SiO3

This is a sodium salt of metasilicic acid H2SiO3 It is known as water glass or soluble glass. It is prepared by fusing sodium carbonate with pure sand. The process is carried out in a furnace called reverberatory furnace.

#### Na CO2 3(s) + SiO2(s) → Na SiO2 3(s) + CO2(g)

Sodium silicate

Properties:

Sodium silicate is soluble in water and its solution is strongly alkaline due to the hydrolysis.

|  |
| --- |
| Chemical Garden  When crystals of soluble coloured salts like nickel chloride, ferrous sulphate, copper sulphate or cobalt nitrate, etc. are placed in a solution of sodium silicate, they produce a very beautiful growth, like plant, which is called chemical garden. |

Uses of Sodium Silicate:

1. It is used as a filler for soap in soap industry.
2. It is used in textile as a fire proof.
3. It is used as furniture polish.
4. It is also used in calico printing.

2. Aluminium Silicate

Many important silicate rocks contain aluminium. The weathering of these rocks results in the disintegration of the complex silicates which they contain. The boiling and freezing of water in the rocks, and the chemical action of water and carbon dioxide convert these compounds into potassium carbonate, sand and clay. The following reaction explains the weathering of potassium feldspar.

K O.Al O .6SiO2 2 3 2(s) + H CO2 3(aq) + H O2 ( )l → K CO2 3(s) + 4SiO2(s) + Al O .(SiO ) .2H O2 3 2 2 2 (s)

Pure clay, which has the formula shown above, is white and is called kaolin. It is used to make porcelain and china wares. Ordinary clay contains compounds of iron and other metals and it has a yellow or reddish yellow colour.

Impure clays can be more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily fusiable silicates with sand. Such clays are used to make bricks, tiles, and stonewares. Due to the presence of ferric oxide, the articles of this clay turn reddish when heated in a kiln.

Stoneware is usually glazed to give it a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate and sodium aluminium silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth, waterproof surface. China wares are made from a mixture of kaolin, bone ash, and feldspar; the mixture fuses when heated and fills the pores between the grains of kaolin.

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste. When soaked in water the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated the water of hydration is lost, and a hard rock like mass is formed.

3. Talc or Soapstone

The magnesium silicate, Mg3H2(SiO3)4, is commonly known as talc or soapstone. It is physically greasy to touch. Therefore it is used in making cosmetics. It is also used in making household articles.

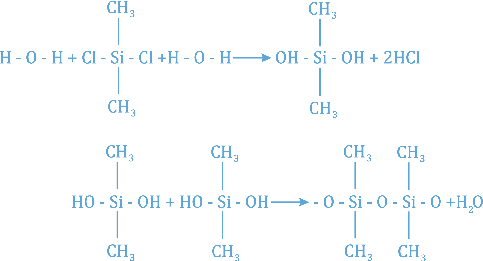
4 . Asbestos

Asbestos is hydrated calcium magnesium silicate CaMg3(SiO3)4. It is commonly used in making incombustible fabrics and hardboard, etc.

##### 3.5.4 Silicones

The chemistry of silicon is, in many respects, very much like the chemistry of carbon. Just as carbon forms the compounds carbon dioxide (CO2), carbon tetrachloride (CCI4), and methane (CH4), similarly silicon forms silicon dioxide (SiO2), silicon tetrachloride (SiCl4), and silane (SiH4).

The silicon atom holds four methyl groups, Si(CH3)4 , just as the carbon atom, C(CH3)4.If a compound of silicon containing chlorine atoms and methyl groups, SiCl2(CH3)2, is allowed to react with water, hydrogen chloride (HCI) comes out, and the silicon atoms join together through oxygen atoms.



By this reaction we can make synthetically the silicon oxygen chains found in the mineral silicates, which we have just been discussing. A difference is that here we have -CH3 groups instead of oxygen atoms joined to silicon as side chains. Such a compound is called a silicone; this particular one is a methyl silicone. Other alkyl groups may also be substituted for the methyl groups and the molecular chain can be made of various lengths.

Properties and Uses of the Silicones

Some of the methyl silicones are oily liquids and they become more viscous as the chain length increases. They are used as lubricants, either incorporated in greases or as oils, in bearings, gears, etc. They are also used in hydraulic brakes and other hydraulic systems. The outstanding physical attribute of silicone oil is its very small change in viscosity with change in temperature, compared with the behaviour of other oils of similar viscosity.

If the temperature is dropped from 100°C to 0°C the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicone oil will increase less than four folds. In the presence of air or oxygen at temperature as high as 300°C, silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.

Silicone molecules can be made in such a way that bridges, or cross linkages bind one long molecule to another at several points along the chain. These compounds have resinous properties and are extensively used in electrical insulation.

Another interesting and important application of silicones is their use in the treatment of various surfaces to make them water repellent. A silicone film covers the surface and repels water like a grease film. Much of the leak of electricity through the moisture film on ceramic electrical insulators can be prevented by a silicone film; cloth, plastics, asbestos, glass, leather, and paper, even filter paper and blotting paper become strongly water repellent when covered with a silicone film.