



17

HYDROGEN AND s-BLOCK ELEMENTS

Hydrogen, alkali metals (like sodium and potassium) and alkaline earth metals (like magnesium and calcium) are the essential parts of the world we live in. For example, hydrogen is used in making vanaspati. Yellow glow of street light is due to sodium. Sodium chloride, potassium chloride and compounds of alkali metals are essential for life. Sodium hydroxide sold under the name of caustic soda is used in the manufacture of soap. Plaster of paris, a compound of calcium is used as a building material as well as by doctors in setting of fractured bone.

In this lesson we shall study occurrence, physical and chemical properties and uses of hydrogen and s-block elements (alkali metals and alkaline earth metals).



OBJECTIVES

After reading this lesson, you will be able to:

- explain the unique position of hydrogen in the periodic table;
- list the sources of hydrogen;
- compare and contrast the properties of different isotopes of hydrogen;
- recall the various physical and chemical properties and uses of hydrogen with chemical reactions;
- explain the structure of water molecule and ice;
- list the uses of heavy water;
- list the different methods of preparation of hydrogen peroxide;
- list oxidizing and reducing properties of hydrogen peroxide with at least two examples of each;
- list the uses of hydrogen peroxide;
- explain the different types of hydrides;

- describe the use of hydrogen as fuel;
- recall the names and formulae of some common ores of alkali and alkaline earth metals;
- recall the electronic configuration of alkali and alkaline earth metals;
- write reactions of alkali and alkaline earth metals with oxygen, hydrogen, halogens and water;
- explain the trend of basic nature of oxides and hydroxides;
- explain the solubility and thermal stability of their carbonates and sulphates.
- explain diagonal relationship between Li and Mg;
- describe the biological importance of sodium and potassium;
- explain anomalous nature of beryllium;
- explain the digonal relationship between Be and Al;
- describe the biological role of Mg^{2+} and Ca^{2+} ; and
- describe the manufacturing processes for NaOH, Na_2CO_3 and $NaHCO_3$.



Notes

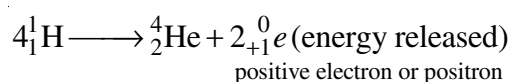
17.1 HYDROGEN

Hydrogen is the first element of the periodic table. Hydrogen has the simplest atomic structure and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$.

17.1.1 History and Occurrence of Hydrogen

Turquet de Mayerne (1655) and Boyle (1672) collected an inflammable gas by reacting iron with sulphuric acid. A century later Cavendish investigated the properties of this gas and called it 'inflammable air', but it was Lavoisier who called it by its present name, hydrogen.

Hydrogen occurs in the free state in some volcanic gases and in the outer atmosphere of the sun; other stars are composed almost entirely of hydrogen. The extremely high temperatures that are common place in stars (10^6 — 10^7 °C) enable nuclear fusion of hydrogen atoms to occur, resulting in a colossal liberation of energy; several reaction schemes have been put forward for this process which ultimately results in the formation of helium



The hydrogen liberated during chemical reactions is lost very readily, since the mass of the hydrogen molecule is so small and its speed so high that it can escape from the earth's gravitational field. The main sources of hydrogen are water, and petroleum and natural gas, where it occurs in combination with carbon. The element is an essential ingredient in all living matter, being found in proteins and fats.

17.1.2 Position in the Periodic Table

Where is hydrogen placed in the periodic table?

Elements are placed in the periodic table according to their outermost electronic configuration. So hydrogen ($1s^1$) may be placed with alkali metals (ns^1). But hydrogen attains noble gas configuration of helium atom ($1s^2$) by gaining one electron. It forms the hydride ion H^- ($1s^2$) like halogens (ns^2np^5) by gaining one electron. On electrolysis of used alkali hydride, hydrogen is liberated at anode just as chlorine is liberated at anode during electrolysis of sodium chloride. Thus hydrogen ought to be placed in group 17 along with halogens. Hydrogen also resembles group 14 elements, since both have a half filled shell of electrons. So where should hydrogen be placed? This problem is solved by placing hydrogen neither with alkali metals nor with halogens. It has been given a unique position in the periodic table (see Periodic Table in lesson 4).

17.1.3 Isotopes of hydrogen

If atoms of the same element have different mass numbers they are called isotopes. This difference in mass number arises because the nucleus contains a different number of neutrons.

Naturally occurring hydrogen contains three isotopes: protium 1_1H or H, deuterium 2_1H or D and tritium 3_1H or T. These three isotopes contain one proton and 0, 1 and 2 neutrons, respectively in the nucleus (Fig 17.1). Protium is by far the most abundant.

Naturally occurring hydrogen contains 99.986% of the 1_1H isotope, 0.014% of D and $7 \times 10^{-16}\%$ of T, therefore the properties of hydrogen are essentially those of the lightest isotope. Tritium is radioactive and emits low energy β particles ($t_{1/2} = 12.33\text{yrs}$).

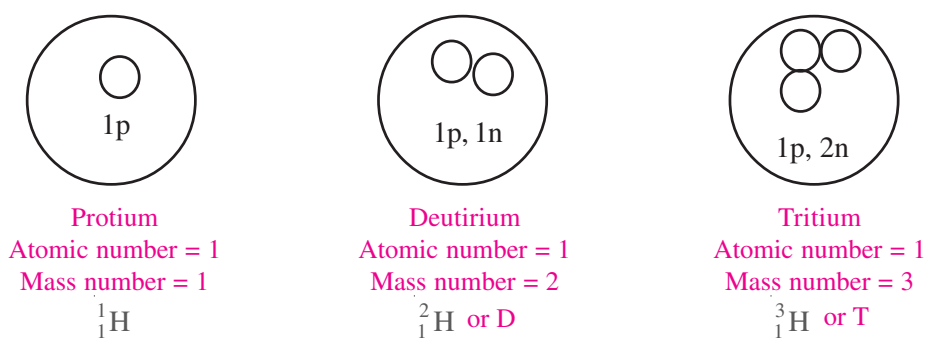


Fig 17.1: Isotopes of hydrogen

Due to difference in mass of different isotopes, there arise a few differences in their properties. For example:

1. H_2 is more rapidly adsorbed on the metal surface than D_2 .
2. H_2 reacts over 13-times faster with Cl_2 than does D_2 .



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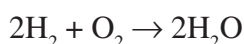
Difference in properties that arises from the difference in mass is called *isotope effect*. Since the percentage difference in the mass of isotopes of hydrogen is very large. The difference in properties of isotopes of hydrogen is very large the difference in properties of compounds containing these isotopes is also large.

17.1.4 Physical properties

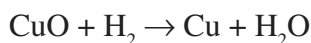
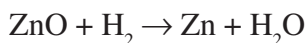
Hydrogen is a diatomic gas, H_2 . It is colourless and has no smell. It is lightest of all the gases known. It is insoluble in water, acids and most of the organic solvents. It is adsorbed when passed over platinum and palladium.

17.1.5 Chemical properties

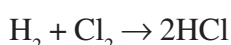
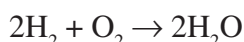
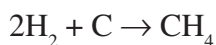
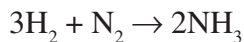
1. Combustion: Hydrogen is combustible and burns in air with pale blue flame.



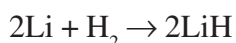
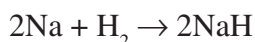
2. Reducing property: Hydrogen reduces heated metal oxides to metals.



3. Reaction with non-metals: Hydrogen combines with nitrogen, carbon, oxygen and chlorine under appropriate conditions to form ammonia, methane, water and hydrogen chloride, respectively.



Reaction with metals: Hydrogen reacts with highly electropositive metals to form the corresponding hydrides.



17.1.6 Uses

Hydrogen is used:

1. for conversion of coal into synthetic petroleum.
2. in the manufacture of bulk organic chemicals, particularly methanol.
3. in the hydrogenation of oils. Vegetable oils change in to vegetable ghee when hydrogen is passed through the oils at 443K in presence of nickel as catalyst.
4. in the manufacture of ammonia, which is used in the production of fertilizers.
5. as primary fuel for heavy rockets.
6. for filling balloons.



Notes



INTEXT QUESTIONS 17.1

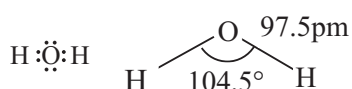
1. Name the isotopes of hydrogen.
2. Name the isotope of hydrogen which is radioactive?
3. Why is hydrogen used for filling balloons?
4. Which gas is produced, when hydrogen combines with carbon?
5. Name the gas which is used for the production of fertilizers.
6. How are vegetable oils changed into vegetable ghee?

17.2 COMPOUNDS OF HYDROGEN

Hydrogen forms a large number of compounds: here we will consider only two of them, namely water (H_2O) and hydrogen peroxide (H_2O_2).

17.2.1 Water (H_2O)

This oxide of hydrogen is essential to all life. It occurs in the form of snow, as water in rivers, lakes, sea etc. and as vapour in the atmosphere. Water is a covalent compound made up of two hydrogen atoms linked with one oxygen atom through covalent bonds. Its Lewis structure and molecular structure are shown below.



Because of the large electronegativity of oxygen, water molecule is highly polar. It has partial negative charge (δ^-) on the oxygen atom and partial positive charge (δ^+) on the hydrogen atom. An electrostatic attraction between H of one molecule with O of other molecule results in the formation of intermolecular hydrogen bonds.

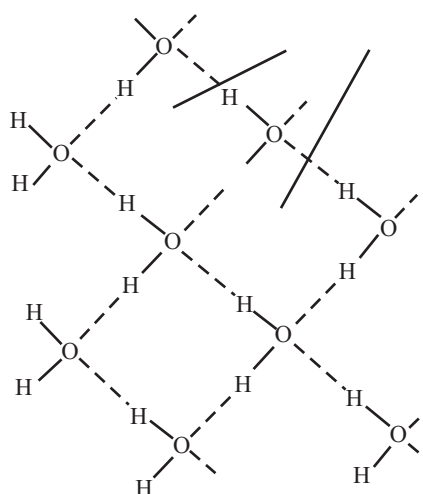
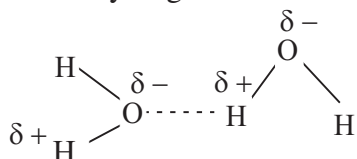


Fig. 17.2: Tetrahedral arrangement of oxygen atoms in ice.

Structure of ice:

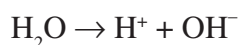
The remarkable characteristic of water is that in solid form, it is less dense than liquid form. Consequently an ice cube floats on water. Water molecules are joined together in an extensive three dimensional network in which oxygen atom is bonded to four hydrogen atoms, two by hydrogen bonds and two by normal covalent bonds, in a near tetrahedral hydrogen bonded structure (Fig. 17.2), which has got open spaces. This is responsible for low density.



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17.2.2 Heavy water and its applications

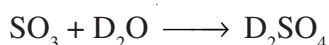
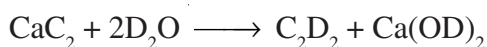
Water containing deuterium in place of ordinary hydrogen (protium) is termed as heavy water (D_2O). Heavy water is separated from water by electrolysis. The equilibrium constant for the dissociation of water containing protium is very high (1.0×10^{-14}) as compared to water containing deuterium (3.0×10^{-15}) e.g.



O–H bonds are broken more rapidly than O–D bonds. Thus when water is electrolyzed, H_2 is liberated much faster than D_2 , and the remaining water thus becomes enriched in heavy water D_2O . In order to obtain one litre of almost pure D_2O , we have to electrolyze about 30000 litres of ordinary water.

Uses:

1. Heavy water is used as a moderator in nuclear reactors. In this process the high speed neutrons are passed through heavy water in order to slow down their speed.
2. It is used in the study of mechanism of chemical reactions involving hydrogen.
3. It is used as the starting material for the preparation of a number of deuterium compounds, for example:

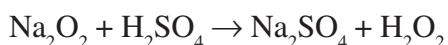
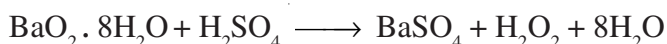
**17.2.3 Hydrogen peroxide (H_2O_2)**

Hydrogen peroxide is an important compound of hydrogen. Its chemical formula is H_2O_2 .

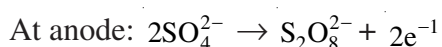
Methods of preparation:

Two methods of preparation of hydrogen peroxide are given below:

1. By the action of dilute mineral acids (H_2SO_4) on metallic peroxides (barium peroxide, sodium peroxide)

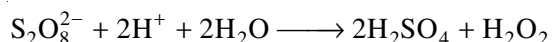


2. By the electrolysis of H_2SO_4 (50% W/W) followed by distillation



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The anodic solution which contains persulphate ions $(S_2O_8)^{2-}$ is distilled with sulphuric acid at reduced pressure yielding H_2O_2 :

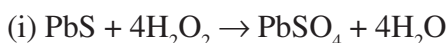


Properties:

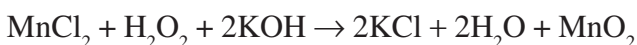
Hydrogen peroxide is a colourless syrupy liquid and has sharp odour. It has a boiling point of 423K. It is miscible in all proportions with water, alcohol and ether. The oxidation state of oxygen in hydrogen peroxide is -1 , a value, which lies between the oxidation state of oxygen in O_2 (zero) and water (-2). Therefore, hydrogen peroxide acts as an oxidizing agent as well as a reducing agent in acidic and alkaline media.

Oxidizing Properties:

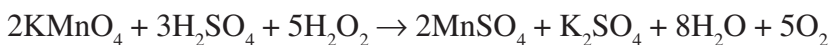
(a) Oxidizing action in acid solution:



(b) Oxidizing action in alkaline solution:



(c) Reducing action in acid solution:



(d) Reducing action in alkaline solution:



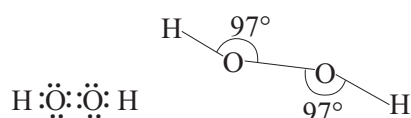
Uses:

Hydrogen peroxide is used:

1. for bleaching hair, leather and wool etc.
2. as a germicide and disinfectant.
3. as an explosive when mixed with alcohol.
4. in the preparation of foam rubber.
5. in pollution control e.g. treatment of drainage and sewage water for dechlorination.

Structure:

The Lewis structure and molecular structure of hydrogen peroxide are shown below:



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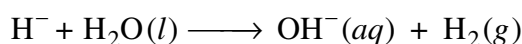
17.2.4 Hydrides

Hydrogen reacts with metals and nonmetals to form hydrides. Hydrides can be classified as:

(1) Ionic hydrides

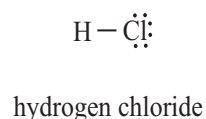
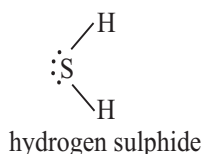
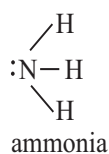
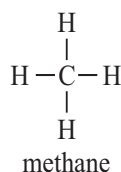
Only the Group 1 and 2 metals are sufficiently electropositive to force the hydrogen atom to accept an electron. These hydrides, which are white crystalline solids, are formed by heating the metal in hydrogen at temperatures up to 700°C. The Group 1 hydrides, e.g. Na^+H^- , have the sodium chloride structure, i.e. each cation is surrounded by six equidistant hydride ions and vice versa; the structures of the Group 2 hydrides, e.g. $\text{Ca}^{2+}(\text{H}^-)_2$, are more complex.

Except for lithium hydride they decompose before their melting points are reached, and the fact that they contain the hydride ion is proved by electrolysis in fused alkali halides, when hydrogen is evolved at the anode. The hydride ion is a very reactive entity and all ionic hydrides are decomposed by water and air (probably initiated by traces of water vapour in the air)



(2) Covalent Hydrides

By far the greatest number of hydrides come under this classification and, except for a few, they are gaseous at ordinary temperature. They are formed by the elements from Group 13 to Group 17 in the Periodic Table.



The stability of the hydrides of the elements of a particular periodic group decreases with increasing atomic number (as the element becomes more 'metallic'); thus hydrogen chloride is stable to heat while hydrogen iodide is easily decomposed into its elements. Some are so unstable in the presence of small traces of air, e.g. stannane, SnH_4 , that special methods are necessary for their preparation.

In the covalent hydrides, hydrogen is showing its natural tendency to acquire the stable electronic configuration of helium by electron sharing.

(3) Interstitial hydrides

These are ill-defined compounds formed by a number of transition metals in which hydrogen is accommodated in the lattice of the transition element. Some expansion of the metal lattice occurs, since the density of the hydride is less



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than that of the parent metal. No definite chemical formula can be allocated to these substances, i.e. they are non-stoichiometric. Although the composition can be varied by changes in temperature and pressure, formulae such as $\text{TiH}_{1.73}$ and $\text{ZrH}_{1.92}$ have been reported. The uptake of hydrogen is reversible and can in all cases be removed by pumping at a sufficiently high temperature. The use of finely divided palladium for making extremely pure hydrogen depends on this reversibility.

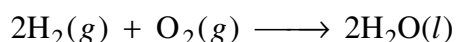


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17.2.5 The Hydrogen Economy (Hydrogen as Fuel)

The total volume of ocean water is about 1×10^{21} L. Thus, the ocean contains an almost inexhaustible supply of hydrogen.

The world's fossil fuel reserves are being depleted at an alarmingly fast rate. Faced with this dilemma, scientists have made intensive efforts in recent years to develop a method of obtaining hydrogen gas as an alternative energy source. Hydrogen gas could replace gasoline to power automobiles (after considerable modification of the engine, of course) or be used with oxygen gas in fuel cells to generate electricity. One major advantage of using hydrogen gas in these ways is that the reactions are essentially free of pollutants; the end product formed in a hydrogen-powered engine or in a fuel cell would be water, just as in the burning of hydrogen gas in air:



Of course, success of a hydrogen economy would depend on how cheaply we could produce hydrogen gas and how easily we could store it.

Although electrolysis of water consumes too much energy for large-scale application, if scientists can devise a more practical method of “splitting” water molecules, we could obtain vast amounts of hydrogen from seawater. One approach that is currently in the early stages of development would use solar energy. In this scheme a catalyst (a complex molecule containing one or more transition metal atoms, such as ruthenium) absorbs a photon from solar radiation and becomes energetically excited. In its excited state the catalyst is capable of reducing water to molecular hydrogen.



INTEXT QUESTIONS 17.2

1. Why does ice float on water?
2. What is heavy water? Write its important uses.
3. Give one method of preparation of hydrogen peroxide.
4. Give two uses of hydrogen peroxide.

- How does hydrogen peroxide decolorize potassium permanganate?
- Name the types of hydrides
- NaH is covalent or ionic hydride?

17.3 s-BLOCK ELEMENTS

The *s*-block elements have an outer electronic configuration ns^1 or ns^2 and are placed in the group 1 and 2 of the periodic table. Group 1 consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals after the Arabic word *al-qis* meaning plant ashes. These ashes are particularly rich in carbonates of calcium, strontium, barium and radium. The elements beryllium, magnesium, calcium, strontium, barium and radium belong to group 2 and are known as alkaline earth metals.

17.3.1 The alkali metals

In this group all the elements are electropositive metals and there exists resemblance between the elements owing to their similar outer electron configuration. The occurrence and properties of alkali metals are discussed below:

17.3.1.1 Occurrence

Sodium and potassium are abundant. Sodium is found as sodium chloride in the sea water and as sodium nitrate (Chile saltpeter) in the deserts of Chile. Potassium too, is found in sea water, and also as carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). Lithium, rubidium and caesium occur in a few rare aluminosilicates. Francium is radioactive; its longest-lived isotope ^{223}Fr has a half life of only 21 minutes.

17.3.1.2 Electronic configuration

The alkali metals with their symbols, atomic numbers and electronic configurations are listed below in Table 17.1:

Table 17.1: Electronic configuration of alkali metals

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	$1s^2, 2s^1$
Sodium	Na	11	$1s^2, 2s^2p^6, 3s^1$
Potassium	K	19	$1s^2, 2s^2p^6, 3s^2p^6, 4s^1$
Rubidium	Rb	37	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Caesium	Cs	55	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^1$



Notes

17.3.1.3 Physical properties of Alkali Metals

Alkali metals are placed in group 1 of periodic table. They readily form unipositive ions. As we go down the group the alkali metals show steady increase in size due to the addition of a new shell at each step. The increase in size of the atoms or ions, directly influences the physical and chemical properties of the alkali metals. Some physical properties are given in Table 17.2.

Table 17.2: Physical properties of alkali metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol ⁻¹)	Electro negativity	Density (g cm ⁻³)	M.P. K	Electrode Potential (E° volts)
Li	76	520.1	1.0	0.54	454	-3.05
Na	102	495.7	0.9	0.97	371	-2.71
K	138	418.6	0.8	0.86	336	-2.83
Rb	152	402.9	0.8	1.53	312	-2.89
Cs	167	375.6	0.7	1.90	302	-2.93

The trends in physical properties are listed in Table 17.3.

Table 17.3: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +1 oxidation state
2.	Atomic/ionic radii	Li < Na < K < Rb < Cs Atomic and ionic radii increases since number of shells increase as we go down the group.
3.	Ionization energy	Li > Na > K > Rb > Cs As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	Li > Na > K > Rb > Cs The electropositive character increases due to decrease in ionization enthalpy therefore electronegativity decreases.
5.	Metallic character	Li < Na < K < Rb < Cs Metallic character increases as we go down the group due to increase in electropositive character.



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6.	Density	Li < Na > K < Rb < Cs Generally density increases from Li to Cs as the atomic mass increases (exception K).										
7.	Melting point & boiling points	Li > Na > K > Rb > Cs Decreases down the group because of increasing size and weak intermetallic bond.										
8.	Flame coloration	They show characteristic colors in the flame. The outermost electron absorbs energy and is excited to a higher energy level. This absorbed energy is remitted when the electron comes back to ground state. The difference in energy falls in the visible range of radiation hence the colors are seen.										
		<table style="width: 100%; border: none;"> <tbody> <tr> <td style="text-align: center;">Li</td> <td style="text-align: center;">Na</td> <td style="text-align: center;">K</td> <td style="text-align: center;">Rb</td> <td style="text-align: center;">Cs</td> </tr> <tr> <td style="text-align: center;">Crimson red</td> <td style="text-align: center;">Yellow</td> <td style="text-align: center;">Pale violet</td> <td style="text-align: center;">Violet</td> <td style="text-align: center;">Violet</td> </tr> </tbody> </table>	Li	Na	K	Rb	Cs	Crimson red	Yellow	Pale violet	Violet	Violet
Li	Na	K	Rb	Cs								
Crimson red	Yellow	Pale violet	Violet	Violet								

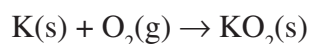
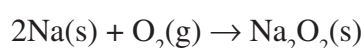
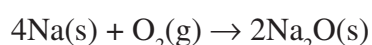


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17.3.1.4 Chemical Properties

Alkali metals are the most reactive metals in the whole periodic table due to their ease in losing outermost electron hence getting oxidized easily. As the ease of losing electrons increases, the reactivity increases down the group.

(i) Oxides: All alkali metals form oxides, which are basic in nature. Lithium forms only one type of oxide, lithium monoxide Li_2O . Sodium peroxide Na_2O_2 is formed when sodium is heated with oxygen. Other metals of this group also form superoxides MO_2 on reaction with oxygen.



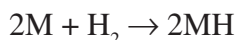
The formation of a particular oxide is determined by the size of the metal ion. Tiny lithium ion is not able to come in contact with sufficient number of peroxo ions. However, the ions of potassium, rubidium, caesium are large enough to come in close contact with peroxo ions and form stable structures as superoxides.

(ii) Reactivity towards water: Although lithium has the most negative E° , its reaction with water is considerably less vigorous than that of sodium which has the least negative E° among the alkali metals (Table 17.2). The low reactivity of lithium is due to small size and high ionization enthalpy. All the metals of the group react with water explosively to form hydroxide and liberate hydrogen.

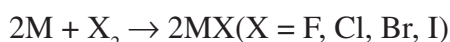


Basic character of oxides and hydroxides: The basic character of oxides and hydroxides of alkali metals increases with the increase in size of metal ion. So, lithium oxide and hydroxide are least basic whereas, caesium oxide and hydroxide are most basic in nature.

(iii) Hydrides: The alkali metals react with hydrogen at about 637K to form hydrides (MH), where M stands for alkali metals.



(iv) Halides: Alkali metals react with halogens to form halides:



17.3.1.5 Diagonal Relationship between Lithium and Magnesium

The similarity between first member of one group and the second member of succeeding group is called diagonal relationship. Thus lithium shows properties similar to magnesium. Likewise Beryllium and aluminium have similar characteristics.

The closeness of the diagonal elements arises due to their comparable polarizing power. Mathematically,

$$\text{Polarizing power} \propto \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

On going from lithium to sodium, the ionic charge remains the same, the ionic radius increases and, therefore, the polarizing power decreases. On going from lithium to beryllium, the ionic charge increases, the ionic radius decreases and, therefore, the polarizing power increases.

On going from beryllium to magnesium, the polarizing power decreases—and becomes comparable to that of lithium.

In other words, the ratio between ionic charge to the square of ionic radius is nearly the same for lithium and magnesium. So are their physical and chemical properties, as shown in the following examples.

1. Both elements have nearly the same values of electronegativities.
2. The melting and boiling points of the two elements are comparable.
3. Lithium and magnesium possess nearly the same degree of hardness.
4. Both the elements form nitrides when heated directly with nitrogen.
5. Both the elements form carbides when heated directly with carbon.
6. Both the elements form normal oxides when heated in air.
7. The carbonates, nitrates and hydroxides of both the elements undergo thermal decomposition to their respective oxides.



Notes

- The halides of both the elements are appreciably soluble in organic solvents.
- Oxyacid salts of both the elements are sparingly soluble in water.

17.3.1.6 Anomalous behaviour of Lithium

- Lithium salts of large polarizable anions are less stable than those of other alkali metals, as expected



In each case, the more stable salts of the heavier alkali metals decompose at a temperature higher than that normally obtainable in the laboratory. Lithium forms no solid bicarbonate, triiodide, hydrosulphide, or superoxide. These are unstable at room temperature, whereas those of the other alkali metals require a higher temperature to effect their decomposition.

- Solubility differences: The lithium salts of anions of high charge density are less soluble than those of the other alkali metals, for example LiOH, LiF, Li_3PO_4 , Li_2CO_3 . The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.
- Complex formation: Lithium forms more stable covalent bonds than the other alkali metals and therefore forms more stable complex compounds (Section 20.4) not only with oxygen donor ligands, but also with nitrogen donors. For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of $\text{Li}(\text{NH}_3)_4$.
- Lithium reacts only very slowly with water.
- Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air lithium forms the normal oxide, whereas the others form higher oxides such as peroxides and superoxides. Lithium reacts with nitrogen to form the nitride, Li_3N ; the others do not react. Lithium hydride is more stable than the other hydrides, and lithium carbide forms more easily (with acetylene).
- Lithium compounds are more covalent. Thus the halides are more soluble in organic solvent and the alkyls and aryls are more stable than those of the other alkali metals.

The so-called “anomalous” properties of lithium occur because lithium is “unexpectedly” much less electropositive than sodium.



Notes

17.3.1.7 Sodium Hydroxide

Manufacture of sodium hydroxide by the Castner-Kellner process

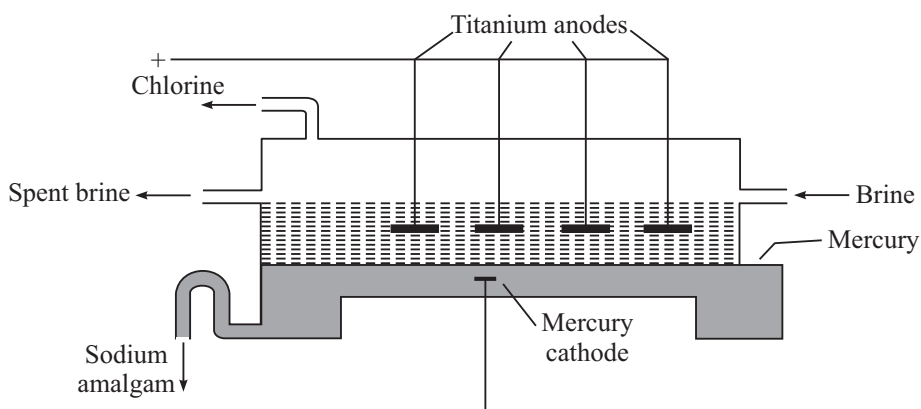


Fig. 17.3 The Castner-Kellner cell

In this process a saturated solution of sodium chloride (brine) flows through the cell (Fig. 17.3) in the same direction as a shallow stream of mercury which constitutes the cathode; the anode consists of a number of titanium blocks. On electrolysis chlorine is discharged at the anode and sodium at the cathode, where it dissolves in the mercury and is removed from the cell. The sodium amalgam is passed through water where the sodium reacts to form 50 per cent sodium hydroxide solution of high purity, the reaction being catalysed by the presence of iron grids. The mercury is then returned to the cell. The products are thus sodium hydroxide, chlorine and hydrogen.

Cathode	Anode
Na^+ discharged	Cl^- discharged
$2\text{Na}^+ + 2e^- \rightarrow 2\text{Na}$	$2\text{Cl}^- \rightarrow 2\text{Cl}\cdot + 2e^-$
$\text{Na} + \text{Hg} \rightarrow \text{Na}/\text{Hg}$	$2\text{Cl}\cdot \rightarrow \text{Cl}_2$
$2\text{Na}/\text{Hg} + 2\text{H}_2\text{O} \longrightarrow 2\text{Na}^+\text{OH}^- + \text{H}_2 + 2\text{Hg}$	

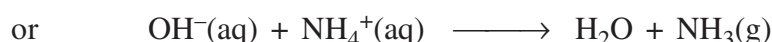
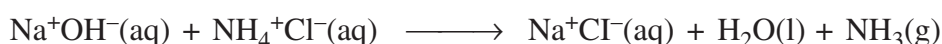
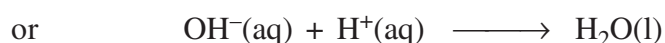
Sodium is discharged in preference to hydrogen in the cell, since hydrogen has a high overvoltage at a mercury electrode. This amounts to saying that the discharge of hydrogen ions or the combination of hydrogen atoms to give molecules is difficult to achieve at a mercury surface, i.e. mercury is a poor catalyst for either or both of these processes. Since sodium dissolves in mercury which is circulated through the cell, the formation of sodium hydroxide and hydrogen in the electrolytic cell itself is prevented.



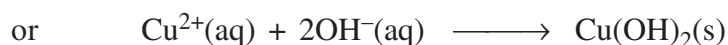
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Reactions of sodium hydroxide

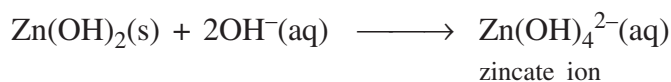
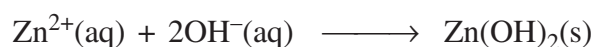
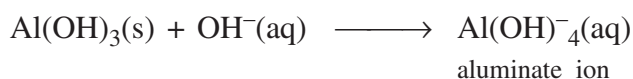
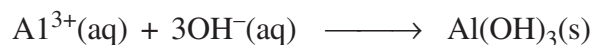
Sodium hydroxide is a white deliquescent solid which is caustic and slimy to touch: it dissolves readily in water with vigorous evolution of heat. In aqueous solution this is completely dissociated and its reactions are essentially those of the hydroxide ion which is a strong base, i.e. it will neutralise acids and displace ammonia from ammonium salts when heated :



In aqueous solution it reacts with many salts and precipitates the corresponding basic hydroxide, e.g.



The hydroxides of the less electropositive metals are amphoteric and dissolve in an excess of alkali, e.g. the hydroxides of aluminium (III), lead (II), tin (II) and zinc(II):



Sodium reacts with a variety of non-metals, e.g. the halogens, silicon, sulphur, white phosphorus; sodium salts are formed in which the non-metal is incorporated into the anion.

Uses of Sodium hydroxide

Sodium hydroxide is used in the laboratory for absorbing carbon dioxide and other acidic gases, in a number of organic reactions involving hydrolysis and in volumetric analysis. Industrially it is used in the manufacture of soap (essentially sodium stearate) and sodium formate (obtained by heating sodium hydroxide with carbon monoxide under pressure).

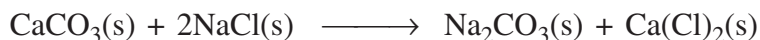


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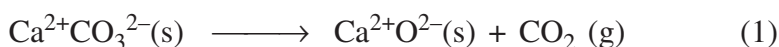
17.3.1.8 Sodium Carbonate

The manufacture of sodium carbonate – the Solvay process

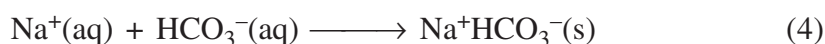
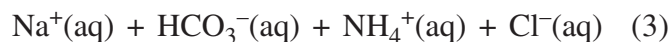
It is manufactured by the ammonia-soda or Solvay process. In theory the process involves the reaction between sodium chloride and calcium carbonate to produce sodium carbonate and calcium chloride, but in practice other chemicals are required, since the reaction as given below does not take place:



The raw materials are sodium chloride, calcium carbonate, a fuel and ammonia. The calcium carbonate is strongly heated to give quicklime and carbon dioxide:



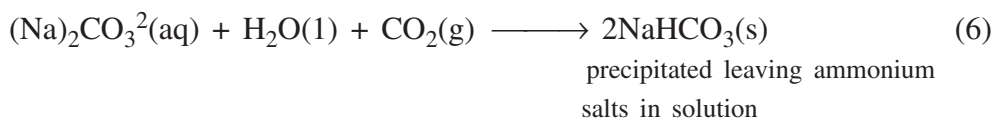
The carbon dioxide is now passed up a large tower, fitted with perforated plates, down which a concentrated aqueous solution of sodium chloride saturated with ammonia trickles. The reactions taking place in the tower can be represented by the equations:



Sodium hydrogen carbonate, which is not very soluble in sodium chloride solution, due to the common ion effect is filtered and heated to produce sodium carbonate:



The sodium carbonate at this stage is contaminated with ammonium salts. If required pure, it is dissolved in water and carbon dioxide is blown through the solution. The precipitate of sodium hydrogen carbonate is filtered and heated to produce pure sodium carbonate; recrystallisation from water produces washing soda, $(\text{Na}^+)_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.



The Solvay process is a very economical process since:

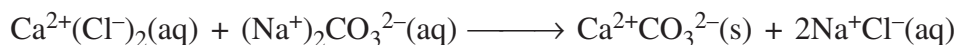
- sodium chloride and calcium carbonate are cheap;
- quicklime and ammonium chloride formed in reactions (1) and (3) respectively are reacted together to produce ammonia so that, apart from making up small losses, no additional ammonia is required;
- carbon dioxide formed in reactions (5) is reintroduced into the Solvay tower.



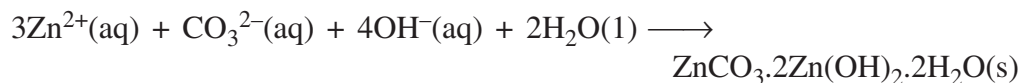
Notes

Properties and uses of sodium carbonate

Sodium carbonate is freely soluble in water and gives an alkaline reaction. It reacts with some salts in solution and precipitate the corresponding carbonates, e.g.



Because of its alkaline reaction in solution, sodium carbonate frequently precipitate basic carbonates, e.g.



In these instances the normal carbonate can usually be obtained by using sodium hydrogen carbonate solution.

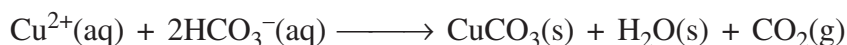
Sodium carbonate is often used in the laboratory as a volumetric reagent. Industrially it is used in a wide variety of ways, including the manufacture of glass, in the preparation of sodium salts, in the treatment of hard water, for the manufacture of soap, and in paper making.

17.3.1.9 Sodium hydrogen carbonate

This can be obtained by passing carbon dioxide through a cold concentrated solution of the corresponding carbonate, e.g.



Because sodium hydrogen carbonate solution is less alkaline than sodium carbonate solution, the former is often used to precipitate normal carbonates which would otherwise be formed as basic carbonates, e.g.

**17.3.1.10 Biological Importance of Sodium and Potassium**

1. To keep normal osmotic pressure of body matter and to save many matter from loss
2. To increase nanomuscular
3. Sodium and potassium salt combine weak acid to give respective extracellular and intracellular matter. They form buffer.

17.3.1.11 Stability and Solubility of Carbonates and Sulphates:

The carbonates and sulphates of alkali metals are generally soluble in water and thermally stable. The carbonates are highly stable to heat and melt without decomposing. As the electropositive character increases down the group, the stability of the carbonates increases. Carbonate of lithium is not so stable to heat due to the small size of lithium.



Notes



INTEXT QUESTIONS 17.3

1. Name the important ores of sodium.
2. Arrange the alkali metals in order of increasing ionization enthalpy.
3. Which of the alkali metals forms only monoxide?
4. Write down the chemical equation for the reaction of sodium with water.
5. What type of bond exists in the hydrides of alkali metals?
6. Name the element which forms (i) peroxide, (ii) superoxide.
7. Write chemical equation when NaHCO_3 is heated.
8. Li^+ resembles Mg^{2+} . Why?
9. Name the common ore of Mg.
10. Arrange the alkaline earth metals in order of increasing reactivity.
11. Name an amphoteric oxide of alkaline earth metals.
12. Arrange the carbonates of alkaline earth metals in order of thermal stability.
13. What is the biological role of Ca^{2+} .

17.3.2 The Alkaline Earth Metals

You have seen a gradual increase in the size of the alkali metals as we move down the group 1 of the periodic table. Identical observations may be made in the case of alkaline earth metals placed in group 2 of the periodic table. Some physical properties of the alkaline earth metals are given in Table 17.4.

Table 17.4: Physical properties of the alkaline earth metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (g cm^{-3})	M.P. K	Electrode Potential (E°) volts
Be	89	899	1.5	1.85	1562	-1.70
Mg	136	737	1.2	1.74	924	-2.38
Ca	174	590	1.0	1.55	1124	-2.76
Sr	191	549	1.0	2.63	1062	-2.89
Ba	198	503	0.9	3.59	1002	-2.90

An alkaline earth metal atom is smaller in size compared to its adjacent alkali metal. This is due to the added proton in the nucleus, which exerts a pull on the electrons in an atom resulting in squeezing of the atom. This reduction in size shows higher control of the nucleus on the electrons in the shells.

The ease of losing electrons makes the alkaline earth metals good reducing agents. But this property is less prominent as compared to the corresponding alkali metals.



Notes

17.3.2.1 Occurrence

The alkaline earth metals are too reactive to occur native. Magnesium is the second most abundant metallic element in the sea, and it also occurs as carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in earth crust. Calcium occurs as calcium carbonate (marble, chalk etc) and with magnesium as dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$). Other ores of calcium are anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Strontium and barium are rare and are found as carbonates and sulphates. Beryllium too is rare and is found as beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$).

17.3.2.2 Electronic Configuration

The electronic configurations of the alkaline earth metals are listed in Table 17.5.

Table 17.5: Electronic configuration

Element	Symbol	Atomic number	Electronic configuration
Beryllium	Be	4	$1s^2, 2s^2$
Magnesium	Mg	12	$1s^2, 2s^2p^6, 3s^2$
Calcium	Ca	20	$1s^2, 2s^2p^6, 3s^2p^6, 4s^2$
Strontium	Sr	38	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^2$
Barium	Ba	56	$1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^2$

17.3.2.3 Physical properties of alkaline earth metals

Alkaline earth metals are less electropositive than alkali metals. The electropositive character of alkaline earth metals increases down the group. They achieve an inert gas configuration by the loss of two electrons. Some physical properties and their trends are given in Table 17.6.

Table 17.6: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +2 oxidation state
2.	Atomic/ionic radii	$\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ Size of alkaline earth metals increases from top to bottom due to increase in the number of shells.
3.	Ionization enthalpy	$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$ As the size increases it becomes easier to remove an electron from the outermost shell.
4.	Electronegativity	$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$ As the electropositive character increases from top to bottom due to decrease in ionization energy, electronegativity decreases from top to bottom.



Notes

5.	Metallic character	Be < Mg < Ca < Sr < Ba Metallic character increases as we go down the group due to increase in electropositive character.
6.	Density	Generally density increases from top to bottom as the atomic mass increases.
7.	Melting point & boiling point	They show higher values of melting and boiling points as compared to alkali metals because of the smaller size and stronger metallic bonds. There is no regular trend down the group. It depends upon packing.
8.	Flame coloration	Except Be and Mg (due to small size and higher ionization enthalpy) all other alkaline earth metals impart characteristic colours to the Bunsen flame. <div style="display: flex; justify-content: space-around; text-align: center;"> <div>Ca Brick red</div> <div>Sr Crimson red</div> <div>Ba Sea green</div> </div>

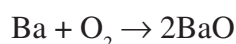
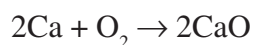
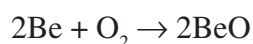
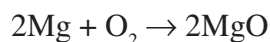


Notes

17.3.2.4 Chemical Properties of Alkaline Earth Metals

The alkaline earth metals are reactive metals, though less reactive than alkali metals. The reactivity increases from top to bottom in a group due to increase in electropositive character.

- (i) **Reactivity and E° values:** The near constancy of the $E^\circ (M^{2+}/M)$ values for group 2 metals (Table 17.4) is somewhat similar to that for group 1 metals. Therefore, these metals are electropositive and are strong reducing agents. The less negative value for Be arises from, the large hydration energy associated with the small size of Be^{2+} being countered by relatively large value of the enthalpy of atomization of beryllium
- (ii) **Oxides:** The alkaline earth metals burn in oxygen forming the ionic oxides of the type MO where M stands for alkaline earth metals except Sr, Ba, and Ra which form peroxides. Peroxides are formed with increasing ease and increasing stability as the metal ions become larger.

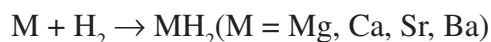


Basic character of the oxides increases gradually from BeO to BaO. Beryllium oxide is amphoteric, MgO is weakly basic while CaO is more basic.

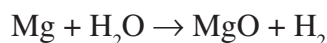


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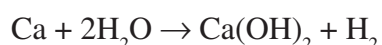
(iii) **Hydrides:** The alkaline earth metals combine with hydrogen to form hydrides of general formula MH_2



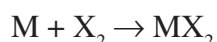
(iv) **Reaction with water:** Usually the alkaline earth metals react with water to liberate hydrogen. Be does not react with water or steam even at red heat and does not get oxidized in air below 837K.



Ca, Sr, and Ba react with cold water with increasing vigour.



(v) **Halides:** All the alkaline earth metals combine directly with the halogens at appropriate temperature forming halides, MX_2 where M stands for alkaline earth metals.



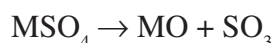
(vi) **Solubility and stability of carbonates and sulphates:**

Carbonates: The carbonates of alkaline earth metals are sparingly soluble in water. They decompose if heated strongly. Their thermal stability increases with increase in the size of the cation. Decomposition temperatures of carbonates are given below:

BeCO₃	MgCO₃	CaCO₃	SrCO₃	BaCO₃
<373K	813K	1173K	1563K	1633K

Sulphates: The sulphates of alkaline earth metals are white solids, stable to heat. The sulphates, $BeSO_4$ and $MgSO_4$ are readily soluble and the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration energies of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore, their sulphates are soluble.

The sulphates decompose on heating, giving the oxides.



The thermal stability of sulphates increases with the increase in the size of cation.

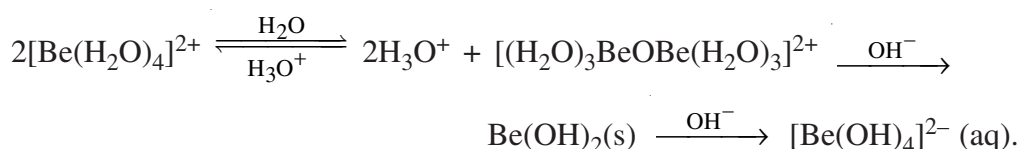
This is shown by the temperature at which decomposition occurs:

BeSO₄	MgSO₄	CaSO₄	SrSO₄
773K	1168K	1422K	1647K

(vii) **Complex compounds:** Smaller ions of the group 2 elements form complexes. For example chlorophyll is a complex compound of magnesium. Beryllium forms complexes like $[BeF_4]^{2-}$.

17.3.2.5 Anomalous Nature of Beryllium: Diagonal Relationship to Aluminium

Beryllium, the first member of the group, appears to be very different from the other members, in the same way as lithium differs from the other alkali metals, and for the same reasons. In fact, the anomalous nature of the first member of the s- and p-block groups becomes more pronounced towards the middle of the table: beryllium differs more from magnesium than lithium does from sodium. Also, beryllium shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium; and the properties in which beryllium differs from magnesium, it shares with aluminium (in general). The cohesive properties of beryllium are much greater than those of magnesium: beryllium has higher melting and boiling points, enthalpy of fusion, etc., and density, and it is much harder. Similarly its attraction for outer electrons is greater than that of magnesium, leading to much lower atomic radii, higher electron affinity and ionization energy, etc. Its higher polarizing power leads to all its compounds being largely covalent, with lower melting and boiling points, enthalpies of formation etc., and with greater solubility in organic solvents than the corresponding magnesium compounds. The hydration enthalpy of the small Be^{2+} ion is very high and its salts are among the most soluble known. Despite this, its electrode potential is not high, because of its very high second ionization enthalpy. Nevertheless, it would be expected to react with water, and react vigorously with acids ($E^\ominus = -1.70$). In fact, it does not react with water, and is resistant to acid. This must be a kinetic effect: perhaps an oxide film protects the metal. Certainly this is one of the metals rendered passive by concentrated nitric acid. The halides are hygroscopic and fume in air, and all soluble salts are largely hydrolysed and polymerized in water except in strong acid or strong alkali solutions (beryllium is amphoteric, unlike magnesium, etc.):

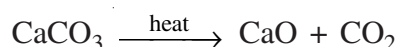


Beryllium is a poor reducing agent, and does not dissolve in ammonia to give blue reducing solutions.

17.3.2.6 Calcium oxide (CaO)

Manufacture of CaO

CaO (quick lime) is manufactured in enormous quantities (126 million tonnes in 1988) by roasting CaCO_3 in lime Kiln.

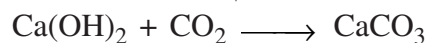


Notes

CaO reacts exothermally with water, forming hydroxide



Ca(OH)₂ is called slaked lime



17.3.2.7 CaCO₃ Calcium Carbonate

CaCO₃ occurs in two different crystalline forms, calcite and aragonite. Both forms occur naturally as minerals. Calcite is the more stable: each Ca²⁺ is surrounded by six oxygen atoms from CO₃²⁻ ions. Aragonite is a metastable form, and its standard enthalpy of formation is about 5 kJ mol⁻¹ higher than that of calcite. In principle aragonite should decompose to calcite, but a high energy of activation prevents this happening. Aragonite can be made in the laboratory by precipitating from a hot solution. Its crystal structure has Ca²⁺ surrounded by nine oxygen atoms. This is a rather unusual coordination number.

Uses of Lime:

1. In steel making to remove phosphates and silicates as slag.
2. By mixing with SiO₂ and alumina or clay to make cement.
3. For making glass.
4. In the lime-soda process, which is part of the chlor-alkali industry, converting Na₂CO₃ to NaOH or vice versa.
5. For 'softening' water.
6. To make CaC₂.
7. To make slaked lime Ca(OH)₂ by treatment with water.

17.3.2.8 Biological Role of Mg²⁺ and Ca²⁺

Mg²⁺ ions are concentrated in animal cells, and Ca²⁺ are concentrated in the body fluids outside the cell. They are also essential for the transmission of impulses along nerve fibres. Mg²⁺ is important in chlorophyll, in the green parts of plants. Ca²⁺ is important in bones and teeth as apatite Ca₃(PO₄)₂, and the enamel on teeth as fluoroapatite [3(Ca₃(PO₄)₂) • CaF₂]. Ca²⁺ ions are important in blood clotting, and to maintain the regular beating of the heart.



WHAT YOU HAVE LEARNT

- Hydrogen can either be placed with alkali metals or with halogens.
- Hydrogen exists in three isotopic forms namely hydrogen, deuterium and tritium.



Notes

- Hydrogen is a combustible gas and has reducing property.
- There are two important oxides of hydrogen: water and hydrogen peroxide.
- Cage-like structure of ice makes it float on water.
- Water containing deuterium in place of ordinary hydrogen is known as heavy water.
- Heavy water can be separated from ordinary water by electrolysis or distillation.
- Heavy water is used as moderator in nuclear reactors.
- Hydrogen peroxide acts both as oxidizing and reducing agent.
- Different types of hydrides i.e. ionic, covalent etc.
- Hydrogen as fuel.
- The alkali and alkaline earth metals show regular variation in various properties along a group and period.
- Alkali metals react with hydrogen, water and halogens to form hydrides, hydroxides and halides respectively.
- Diagonal relationship between Li^+ Mg^{2+}
- Manufacture of NaOH , Na_2CO_3 , NaHCO_3
- Biological role of alkali metals.
- Basic nature of oxides and hydroxides of group 1 and group 2 elements.
- Thermal stability and solubility of carbonates and sulphates.
- Manufacture of CaO and CaCO_3
- Biological role of alkaline earth metals.

**TERMINAL EXERCISE**

1. Write three general characteristics of the s-block elements which distinguish them from the elements of other blocks.
2. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
3. What happens when?
 - (a) sodium metal is dropped in water.
 - (b) sodium metal is heated in free supply of air.
 - (c) sodium peroxide dissolves in water.



Notes

4. Explain why hydrogen is best placed separately in the periodic table of elements.
5. Describe the industrial applications of hydrogen.
6. Discuss the importance of heavy water in nuclear reactor and how is it prepared from normal water?
7. Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen?
8. Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice?
9. Show by proper chemical reactions how hydrogen peroxide can function both as an oxidizing and a reducing agent?
10. Compare the properties of alkali metals and alkaline earth metals with respect to:
 - (a) atomic radii
 - (b) ionization energy
 - (c) melting points
 - (d) reducing behavior
11. Explain the trends of solubility and stability of the carbonates and sulphates of alkaline earth metals.
12. Explain the process involved in the manufacture of NaOH, Na₂CO₃ and NaHCO₃ (Give Chemical equations only)
13. Explain the biological role of Ca²⁺ and Mg²⁺.



Notes



ANSWERS TO INTEXT QUESTIONS

17.1

1. Three isotopes of hydrogen are (a) protium ${}^1_1\text{H}$, deuterium D or ${}^2_1\text{H}$ and (c) tritium T or ${}^3_1\text{H}$.
2. Tritium.
3. It is lightest of all the gases known.
4. Methane (CH₄).
5. Ammonia (NH₃).
6. Vegetable oils + H₂ $\xrightarrow[\text{Ni}]{443\text{K}}$ Vegetable ghee.

17.2

- Ice is less dense as compared to water. It has open spaces in the hydrogen bonded structure.
- D_2O ; Moderator in nuclear reactors.
- $BaO_2 \cdot 8H_2O + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 + 8H_2O$
- (a) as a bleaching agent.
(b) germicide and disinfectant.
- H_2O_2 reduces $KMnO_4$
 $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$
 $Mn(+7)$ is reduced to $Mn(+2)$
- Three types of hydrides : ionic, covalent and interstitial
- Ionic hydride

17.3

- $NaCl$ and $NaNO_3$.
- $Cs < Rb < K < Na < Li$
- Lithium
- $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- Ionic.
- (i) Sodium (ii) potassium
- $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
- Same polarising power.
- Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$).
- $Be < Mg < Ca < Sr < Ba$
- BeO
- $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
- Teeth enamel



Notes