



CONTENTS

S.NO.	TOPIC	PAGE NO.
01.	<i>Hydrogen & It's Compounds</i>	<i>01 - 27</i>
02.	<i>s-Block</i>	<i>28 - 68</i>
03.	<i>p-Block Element</i>	<i>69 - 104</i>

HYDROGEN & IT'S COMPOUNDS

Index

1.0 POSITION OF HYDROGEN IN THE PERIODIC TABLE

2.0 DIHYDROGEN, H_2

- 2.1 Occurrence
- 2.2 Isotopes of Hydrogen
- 2.3 Different forms of Hydrogen
- 2.4 Preparation of dihydrogen, H_2
- 2.5 Properties of Dihydrogen
- 2.6 Uses of Dihydrogen

3.0 HYDRIDES

- 3.1 Ionic or Saline Hydrides
- 3.2 Covalent or Molecular Hydride
- 3.3 Metallic or Non-stoichiometric (or Interstitial) Hydrides

4.0 WATER

- 4.1 Physical Properties of Water
- 4.2 Structure of Water
- 4.3 Structure of Ice
- 4.4 Chemical Properties of Water
- 4.5 Hard and Soft Water
- 4.6 Temporary Hardness
- 4.7 Permanent Hardness

5.0 HYDROGEN PEROXIDE (H_2O_2)

- 5.1 Preparation
- 5.2 Preparation
- 5.3 Tests for H_2O_2

6.0 HEAVY WATER, D_2O

- 6.1 Physical properties
- 6.2 Uses

7.0 DIHYDROGEN AS A FUEL

EXERCISE-1

EXERCISE-2

EXERCISE-3

EXERCISE-4

EXERCISE-5

HYDROGEN & IT'S COMPOUNDS

1.0 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Hydrogen is the first element in the periodic table. However, its placement in the periodic table has been a subject of discussion in the past. As you know by now that the elements in the periodic table are arranged according to their electronic configurations. Hydrogen has electronic configuration $1s^1$. On one hand, its electronic configuration is similar to the outer electronic configuration (ns^1) of alkali metals, which belong to the first group of the periodic table. On the other hand, like halogens (with ns^2np^5 configuration belonging to the seventeenth group of the periodic table), it is short by one electron to the corresponding noble gas configuration, helium ($1s^2$). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form unipositive ions, as well as with halogens, which gain one electron to form uninegative ion. Like alkali metals, hydrogen forms oxides, halides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions. In fact, in terms of ionization enthalpy, hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ mol^{-1} , F is 1680 kJ mol^{-1} and that of H is 1312 kJ mol^{-1} . Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens.

In spite of the fact that hydrogen, to a certain extent resembles both with alkali metals and halogens, it differs from them as well. Now the pertinent question arises as where should it be placed in the periodic table? Loss of the electron from hydrogen atom results in nucleus (H^+) of $\sim 1.510^{-3} \text{ pm}$ size. This is extremely small as compared to normal atomic and ionic sizes of 50 to 200 pm. As a consequence, H^+ does not exist freely and is always associated with other atoms or molecules. Thus, it is unique in behaviour and is, therefore, best placed separately in the periodic table.

2.0 DIHYDROGEN, H_2

2.1 Occurrence

Dihydrogen is the most abundant element in the universe (70% of the total mass of the universe) and is the principal element in the solar atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen. However, due to its light nature, it is much less abundant (0.15% by mass) in the earth's atmosphere. Of course, in the combined form it constitutes 15.4% of the earth's crust and the oceans. In the combined form besides in water, it occurs in plant and animal tissues, carbohydrates, proteins, hydrides including hydrocarbons and many other compounds.

2.2 Isotopes of Hydrogen

Hydrogen has three isotopes: **protium**, ${}^1_1\text{H}$, **deuterium**, ${}^2_1\text{H}$ or D and **tritium**, ${}^3_1\text{H}$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, protium, has no neutrons, deuterium (also known as heavy hydrogen) has one and tritium has two neutrons in the nucleus. In the year 1934, an American scientist, Harold C. Urey, got Nobel Prize for separating hydrogen isotope of mass number 2 by physical methods.

The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD. The tritium concentration is about one atom per 1018 atoms of protium. Of these isotopes, only tritium is radioactive and emits low energy β^- particles.

Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (g mol^{-1})	1.008	2.014	3.016
Melting point / K	13.96	18.73	20.62
Boiling point / K	20.39	23.67	25.0
Density / g L^{-1}	0.09	0.18	0.27
Enthalpy of fusion/ kJ mol^{-1}	0.117	0.197	–
Enthalpy of vaporization/ kJ mol^{-1}	0.904	1.226	–
Enthalpy of bond dissociation/ kJ mol^{-1} at 298.2K	435.88	443.35	–
Internuclear distance/pm	74.14	74.14	–
Ionization enthalpy/ kJ mol^{-1}	1312	–	–
Electron gain enthalpy/ kJ mol^{-1}	–73	–	–
Covalent radius/pm	37	–	–
Ionic radius(H^-)/pm	208		

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation. However, in physical properties these isotopes differ considerably due to their large mass differences.

2.3 Different forms of Hydrogen :

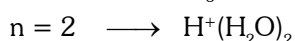
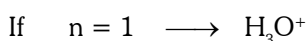
(a) Based on oxidation Number.

There are three types of hydrogen

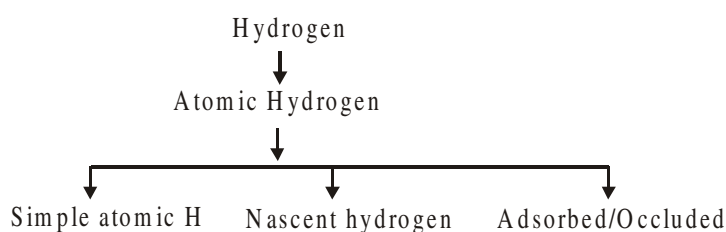
	H^+	H^-	H
	Proton	Hydride	Atomic hydrogen
Number of electron	0	2	1
Oxidation number	+1	–1	0
Formation	$\text{H} \rightarrow \text{H}^+ + \text{e}^-$	$\text{H} + \text{e}^- \rightarrow \text{H}^-$	$\text{H}_2 \xrightarrow{\Delta} 2\text{H}$

Note : In the aqueous state proton (H^+) exist as $\text{H}^+(\text{H}_2\text{O})_n$

Where n is a large number.

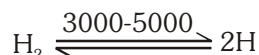


(b) Based on reactivity :



♦ **Atomic hydrogen :**

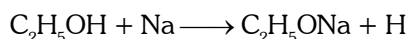
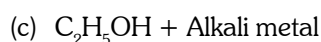
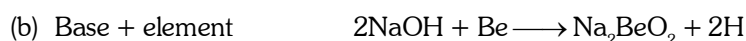
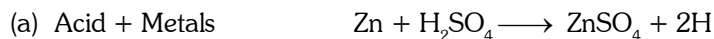
(i) **Simple atomic hydrogen** – It is formed by simple dissociation of hydrogen.



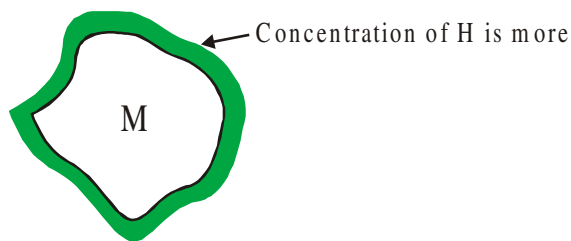
Favourable condition – Favourable condition are high temp & low pressure.

(ii) **Nascent hydrogen** – Hydrogen at the moment of its birth it called nascent hydrogen means which forms at the instant is known as Nascent hydrogen.

It is formed only by some specific chemical reaction.



(iii) **Adsorbed/Occluded hydrogens**



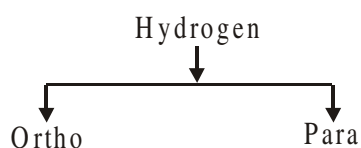
Adsorbed H is hydrogen present at the outer surface of metal.

♦ **Occlusion :** The property of metal to adsorb any gas is called occlusion.

Reactivity order

Atomic hydrogen > Nascent hydrogen > Molecular hydrogen

(iii) **Based on Nuclear spin (Nuclear isomers)**



(a) **Ortho hydrogen** : The molecular form of hydrogen having same spin of nucleus is called ortho hydrogen.

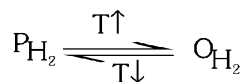
(b) **Para hydrogen** : The molecular form of hydrogen having opposite spin of nucleus is called para hydrogen.

In ortho hydrogen spin of nucleus is same, so they will repel each other & because of this repulsion, internal energy of ortho hydrogen increases. So ortho hydrogen has more internal energy.

♦ **Stability of ortho & Para hydrogen**

Stability of ortho & para hydrogen depends upon temperature condition.

At low temp : para hydrogen is more stable than ortho hydrogen while at high temp ortho hydrogen is more stable than para hydrogen.



	Ortho	Para
At high temperature	75%	25%
At absolute zero temp.	0	100%

♦ **Imp. Note :**

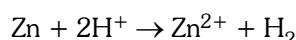
- (i) We can obtain 100% pure para hydrogen at low temp but can't ortho because at high temp parahydrogen will dissociate into atomic hydrogen.
- (ii) Ortho & Para hydrogen differs only in physical properties but have same chemical properties.

2.4 PREPARATION OF DIHYDROGEN, H₂

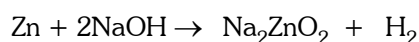
There are a number of methods for preparing dihydrogen from metals and metal hydrides.

♦ **Laboratory Preparation of****Dihydrogen**

- (i) It is usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.



- (ii) It can also be prepared by the reaction of zinc with aqueous alkali.

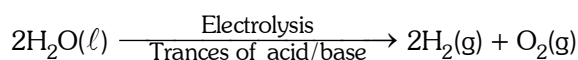


Sodium zincate

♦ **Commercial Production of Dihydrogen**

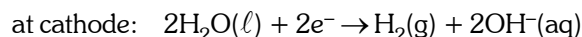
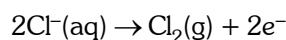
The commonly used processes are outlined below :

- (i) Electrolysis of acidified water using platinum electrodes gives hydrogen.



- (ii) High purity (>99.95%) dihydrogen is obtained by electrolysis of warm aqueous barium hydroxide solution between nickel electrodes.

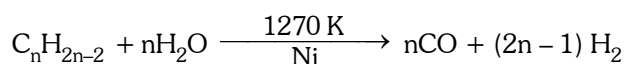
- (iii) It is obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. During electrolysis, the reactions that take place are: at anode:



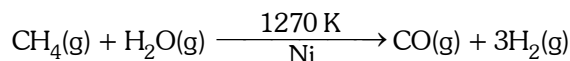
The overall reaction is



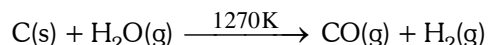
- (iv) Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.



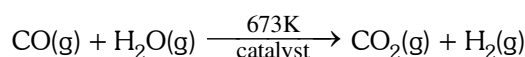
e.g.,



The mixture of CO and H₂ is called *water gas*. As this mixture of CO and H₂ is used for the synthesis of methanol and a number of hydrocarbons, it is also called *synthesis gas* or '**syngas**'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called '*coal gasification*'.



The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst (Fe₂O₃ and Cr₂O₃).



This is called water-gas shift reaction /**Bosch process**. Carbon dioxide is removed by scrubbing with sodium arsenite solution. Presently ~77% of the industrial dihydrogen is produced from petro-chemicals, 18% from coal, 4% from electrolysis of aqueous solutions and 1% from other sources.

2.5 PROPERTIES OF DIHYDROGEN

♦ **Physical Properties**

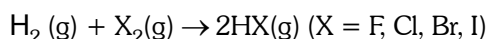
Dihydrogen is a colourless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water. Its other physical properties alongwith those of deuterium are given in Table.

♦ **Chemical Properties**

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond dissociation enthalpy. The H–H bond dissociation enthalpy is the highest for a single bond between two atoms of any element. What inferences would you draw from this fact ? It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H–H bond enthalpy. Thus, the atomic hydrogen is produced at a high temperature in an electric arc or under ultraviolet radiations. Since its orbital is incomplete with $1s^1$ electronic configuration, it does combine with almost all the elements. It accomplishes reactions by (i) loss of the only electron to give H^+ , (ii) gain of an electron to form H^- , and (iii) sharing electrons to form a single covalent bond.

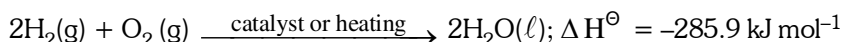
The chemistry of dihydrogen can be illustrated by the following reactions:

- ♦ **Reaction with halogens :** It reacts with halogens, X_2 to give hydrogen halides HX ,

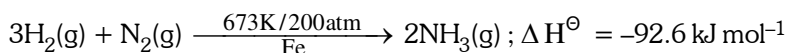


While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst.

- ♦ **Reaction with dioxygen:** It reacts with dioxygen to form water. The reaction is highly exothermic.

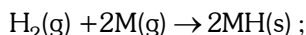


- ♦ **Reaction with dinitrogen:** With dinitrogen it forms ammonia.



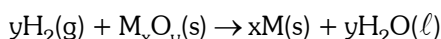
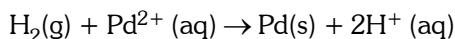
This is the method for the manufacture of ammonia by the Haber process.

- ♦ **Reactions with metals :** With many metals it combines at a high temperature to yield the corresponding hydrides.



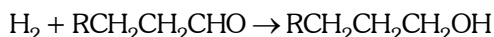
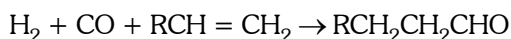
where M is an alkali metal

- ♦ **Reactions with metal ions and metal oxides:** It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.



- ♦ **Reactions with organic compounds:** It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example :

- Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)
- Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.



Problem-1

Comment on the reactions of dihydrogen with (i) chlorine, (ii) sodium, and (iii) copper(II) oxide.

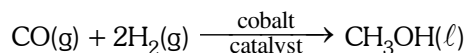
Solution

- Dihydrogen reduces chlorine into chloride (Cl^-) ion and itself gets oxidised to H^+ ion by chlorine to form hydrogen chloride. An electron pair is shared between H and Cl leading to the formation of a covalent molecule.
- Dihydrogen is reduced by sodium to form NaH. An electron is transferred from Na to H leading to the formation of an ionic compound, Na^+H^- .
- Dihydrogen reduces copper(II) oxide to copper in zero oxidation state and itself gets oxidised to H_2O , which is a covalent molecule.

2.6 Uses of Dihydrogen

The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.

- ◆ Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc. . It is used in the manufacture of bulk organic chemicals, particularly methanol.



- ◆ It is widely used for the manufacture of metal hydrides.
- ◆ It is used for the preparation of hydrogen chloride, a highly useful chemical.
- ◆ In metallurgical processes, it is used to reduce heavy metal oxides to metals.
- ◆ Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
- ◆ It is used as a rocket fuel in space research.
- ◆ Dihydrogen is used in fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels and electric power. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

3. HYDRIDES

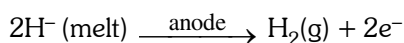
Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as EH_x (e.g., MgH_2) or E_mH_n (e.g., B_2H_6).

The hydrides are classified into three categories :

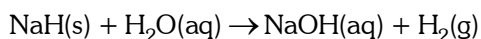
- Ionic or saline or saltlike hydrides
- Covalent or molecular hydrides
- Metallic or non-stoichiometric hydrides

3.1 Ionic or Saline Hydrides

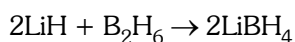
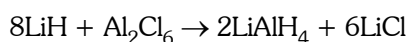
These are stoichiometric compounds of dihydrogen formed with most of the s-block elements which are highly electropositive in character. However, significant covalent character is found in the lighter metal hydrides such as LiH , BeH_2 and MgH_2 . In fact BeH_2 and MgH_2 are polymeric in structure. The ionic hydrides are crystalline, non-volatile and nonconducting in solid state. However, their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode, which confirms the existence of H^- ion.



Saline hydrides react violently with water producing dihydrogen gas.



Lithium hydride is rather unreactive at moderate temperatures with O_2 or Cl_2 . It is, therefore, used in the synthesis of other useful hydrides, e.g.,



3.2 Covalent or Molecular Hydride

Dihydrogen forms molecular compounds with most of the p-block elements. Most familiar examples are CH_4 , NH_3 , H_2O and HF . For convenience hydrogen compounds of nonmetals have also been considered as hydrides. Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative numbers of electrons and bonds in their Lewis structure into :

(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

An electron-deficient hydride, as the name suggests, has too few electrons for writing its conventional Lewis structure. Diborane (B_2H_6) is an example. In fact all elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

Electron-precise compounds have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds (e.g., CH_4) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. (NH_3 has 1- lone pair, H_2O – 2 and HF –3 lone pairs). They will behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N, O and F in hydrides results in hydrogen bond formation between the molecules. This leads to the association of molecules.

Problem -2

Would you expect the hydrides of N, O and F to have lower boiling points than the hydrides of their subsequent group members? Give reasons.

Solution

On the basis of molecular masses of NH_3 , H_2O and HF , their boiling points are expected to be lower than those of the subsequent group member hydrides. However, due to higher electronegativity of N, O and F, the magnitude of hydrogen bonding in their hydrides will be quite appreciable. Hence, the boiling points NH_3 , H_2O and HF will be higher than the hydrides of their subsequent group members.

3.3 Metallic or Non-stoichiometric (or Interstitial) Hydrides

These are formed by many *d*-block and *f*-block elements. However, the metals of group 7, 8 and 9 do not form hydride. Even from group 6, only chromium forms CrH . These hydrides conduct heat and electricity though not as efficiently as their parent metals do. Unlike saline hydrides, they are almost always nonstoichiometric, being deficient in hydrogen. For example, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $ZrH_{1.3-1.75}$, $VH_{0.56}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$ etc. In such hydrides, the law of constant composition does not hold good.

Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides. However, recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have lattice different from that of the parent metal. The property of absorption of hydrogen on transition metals is widely used in catalytic reduction / hydrogenation reactions for the preparation of large number of compounds. Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for **hydrogen storage** and as a **source of energy**.

Problem-3

Can phosphorus with outer electronic configuration $3s^2 3p^3$ form PH_5 ?

Solution

Although phosphorus exhibits +3 and +5 oxidation states, it cannot form PH_5 . Besides some other considerations, high $\Delta_a H$ value of dihydrogen and $\Delta_{eg} H$ value of hydrogen do not favour to exhibit the highest oxidation state of P, and consequently the formation of PH_5 .

BEGINNER'S BOX-1

1. Ionization energy and electron gain enthalpy of H-atom have sign :

- (A) $\Delta H_{IE} = +ve$, ; $\Delta H_{EGE} = +ve$ (B) $\Delta H_{IE} = +ve$, ; $\Delta H_{EGE} = -ve$
 (C) $\Delta H_{IE} = -ve$, ; $\Delta H_{EGE} = +ve$ (D) $\Delta H_{IE} = -ve$, ; $\Delta H_{EGE} = -ve$

2. Which reaction is called water gas shift reaction?

- (A) $CH_4 + H_2O(g) \xrightarrow{1000^\circ C} CO + 3H_2$
 (B) $C + H_2O(g) \xrightarrow{1000^\circ C} CO + H_2$
 (C) $CO + H_2O(g) \xrightarrow{\text{Catalyst}} CO_2 + H_2$
 (D) All of the above

3. Binary hydrogen compounds of electropositive metals are regarded as :
 (A) saline hydride (B) covalent hydride
 (C) metallic hydride (D) hydra acid
4. Which reaction does not produce hydrogen gas ?
 (A) Electrolysis of Aq. NaCl (B) Reaction of KH with C_2H_5OH
 (C) Boiling of temporary hard water (D) Treating Na metals with benzoic acid
5. Which of the following pair is also called spin isomers ?
 (A) H_2 and D_2 (B) D_2 and T_2
 (C) H_2 and T_2 (D) ortho H_2 and para H_2
6. Select CORRECT option
 (A) para hydrogen has lower energy
 (B) ortho hydrogen has lower energy
 (C) At absolute zero the gas contain 100% ortho form
 (D) All are correct
7. Select correct for the ionization energy of atomic hydrogen and molecular hydrogen.
 (A) $H > H_2$ (B) $H_2 > H$
 (C) $H = H_2$ (D) Not possible to compare
8. Which reaction does not produce hydrogen gas ?
 (A) Sodium-amalgam + Water (B) Calcium + Water
 (C) Calcium oxide + Water (D) Zinc + Dil. hydrochloric acid
9. Which of the following is/are saline hydride?
 (A) AsH_3 (B) H_2Se
 (C) $ZrH_{1.30}$ (D) BaH_2
10. A molecular hydride have absence of lone pair on central atom and all the bonds are two-center, two-electron bonds are categorized as:
 (A) electron deficient hydride (B) electron rich hydride
 (C) electron precise hydride. (D) none of these

4.0 WATER

A major part of all living organisms is made up of water. Human body has about 65% and some plants have as much as 95% water. It is a crucial compound for the survival of all life forms. It is a solvent of great importance. The distribution of water over the earth's surface is not uniform. The estimated world water supply is given in Table.

Estimated World Water Supply

Source	% of total
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.001

4.1 Physical Properties of Water

It is a colourless and tasteless liquid. Its physical properties are given in Table along with the physical properties of heavy water. The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules. This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H_2S and H_2Se . In comparison to other liquids, water has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc. These properties allow water to play a key role in the biosphere.

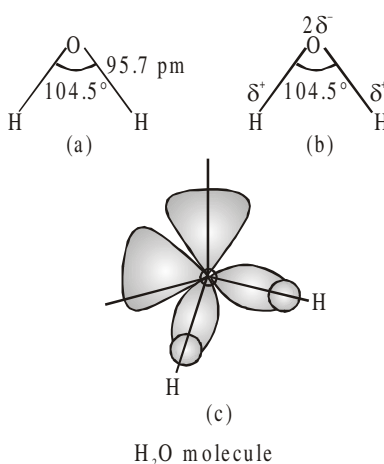
Physical Properties of H_2O and D_2O

Property	H_2O	D_2O
Molecular mass (g mol^{-1})	18.0151	20.0276
Melting point/K	273.0	276.8
Boiling point/K	373.0	374.4
Enthalpy of formation/ kJ mol^{-1}	-285.9	-294.6
Enthalpy of vaporisation (373K)/ kJ mol^{-1}	40.66	41.61
Enthalpy of fusion/ kJ mol^{-1}	6.01	-
Temp of max. density/K	276.98	284.2
Density(298K)/ g cm^{-3}	1.0000	1.1059
Viscosity/centipoise	0.8903	1.107
Dielectric constant/ $\text{C}^2/\text{N.m}^2$	78.39	78.06
Electrical conductivity (293K/ $\text{ohm}^{-1} \text{ cm}^{-1}$)	5.7×10^{-8}	-

The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings. It is an excellent solvent for transportation of ions and molecules required for plant and animal metabolism. Due to hydrogen bonding with polar molecules, even covalent compounds like alcohol and carbohydrates dissolve in water.

4.2 Structure of Water

In the gas phase water is a bent molecule with a bond angle of 104.5° and O-H bond length of 95.7 pm as shown in Fig (a).



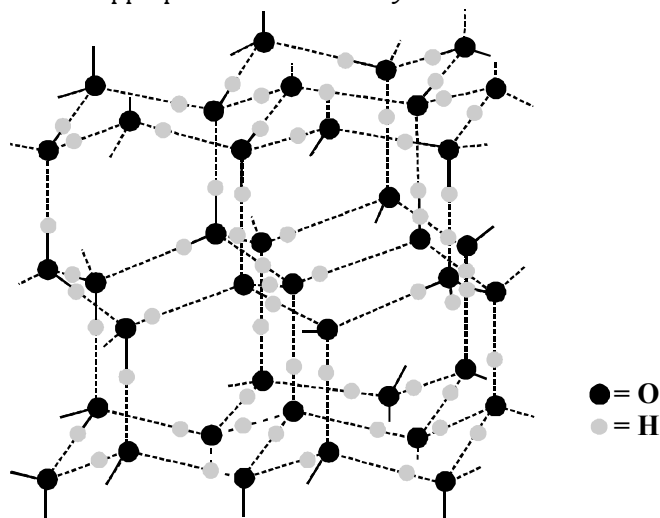
(a) The bent structure of water; (b) the water molecule as a dipole and (c) the orbital overlap picture in water molecule.

It is a highly polar molecule, (Fig (b)). Its orbital overlap picture is shown in Fig. (c). In the liquid phase water molecules are associated together by hydrogen bonds.

The crystalline form of water is ice. At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to cubic form. Density of ice is less than that of water. Therefore, an ice cube floats on water. In winter season ice formed on the surface of a lake provides thermal insulation which ensures the survival of the aquatic life. This fact is of great ecological significance.

4.3 Structure of Ice

Ice has a highly ordered three dimensional hydrogen bonded structure as shown in Fig. Examination of ice crystals with X-rays shows that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm. Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially.



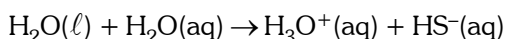
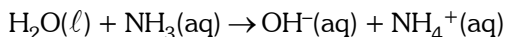
The Structure of Ice

4.4 Chemical Properties of Water

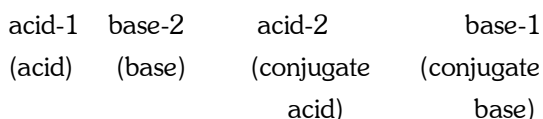
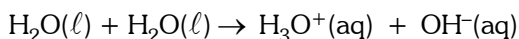
Water reacts with a large number of substances. Some of the important reactions are given below.

(1) Amphoteric Nature :

It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Brønsted sense it acts as an acid with NH_3 and a base with H_2S .

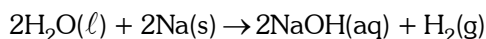


The auto-protolysis (self-ionization) of water takes place as follows :



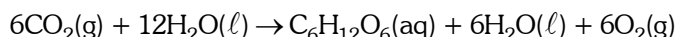
(2) Redox Reactions Involving Water:

Water can be easily reduced to dihydrogen by highly electropositive metals.

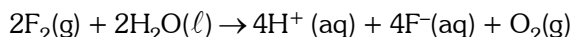


Thus, it is a great source of dihydrogen.

Water is oxidised to O_2 during photosynthesis.

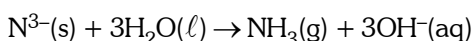
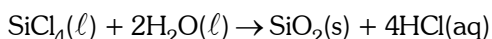
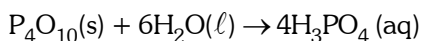


With fluorine also it is oxidised to O_2 .



(3) Hydrolysis Reaction:

Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water.



(4) Hydrates Formation:

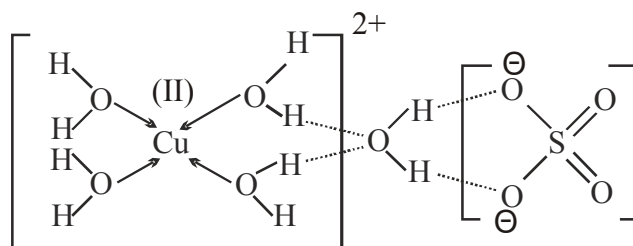
From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

- (i) coordinated water e.g.,
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$
- (ii) interstitial water e.g., $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
- (iii) hydrogen-bonded water e.g.,
 $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$ in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Problem -4

The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is - **[JEE 2009]**

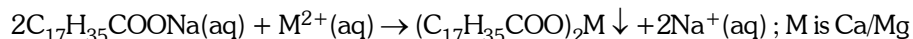
Solution. 4,



4.5 Hard and Soft Water

Rain water is almost pure (may contain some dissolved gases from the atmosphere). Being a good solvent, when it flows on the surface of the earth, it dissolves many salts. Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes water '**hard**'. **Hard water** does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COONa}$) reacts with hard water to precipitate out Ca/Mg stearate.



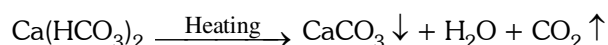
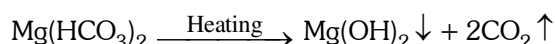
It is, therefore, unsuitable for laundry. It is harmful for boilers as well, because of deposition of salts in the form of scale. This reduces the efficiency of the boiler. The hardness of water is of two types:

- (i) temporary hardness, and (ii) permanent hardness.

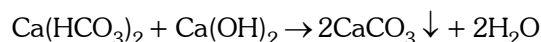
4.6 Temporary Hardness :

Temporary hardness is due to the presence of magnesium and calcium hydrogencarbonates. It can be removed by:

- (i) **Boiling** : During boiling, the soluble $\text{Mg}(\text{HCO}_3)_2$ is converted into insoluble $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{HCO}_3)_2$ is changed to insoluble CaCO_3 . It is because of high solubility product of $\text{Mg}(\text{OH})_2$ as compared to that of MgCO_3 , that $\text{Mg}(\text{OH})_2$ is precipitated. These precipitates can be removed by filtration. Filtrate thus obtained will be soft water.



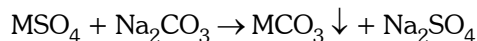
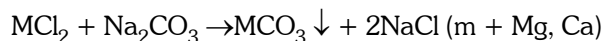
- (ii) **Clark's method** : In this method calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off.



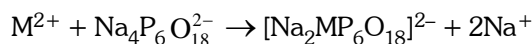
4.7 Permanent Hardness

It is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water. Permanent hardness is not removed by boiling. It can be removed by the following methods:

- (i) **Treatment with washing soda (sodium carbonate)** : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

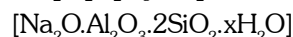
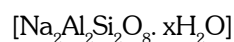


- (ii) **Calgon's method** : Sodium hexametaphosphate ($\text{Na}_6\text{P}_6\text{O}_{18}$), commercially called 'calgon', when added to hard water, the following reactions take place.

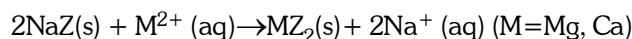


The complex anion keeps the Mg^{2+} and Ca^{2+} ions in solution.

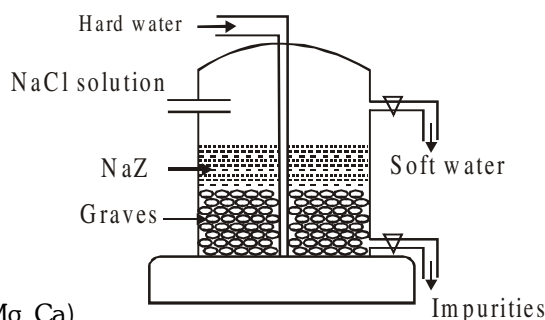
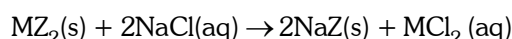
- (iii) **Ion-exchange method (By Zeolite)** : This method is also called zeolite / permutit process.



Hydrated sodium aluminium silicate is zeolite/permutit. For the sake of simplicity, sodium aluminium silicate (NaAlSiO_4) can be written as NaZ . When this is added in hard water, exchange reactions take place.

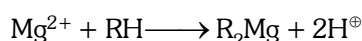
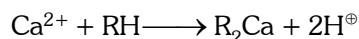


Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.

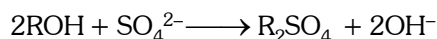
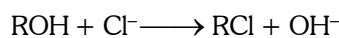


- (iv) **Ion exchange method (By synthetic resins)** : Ion exchanges resins are the most popular water softener these days. These resins are synthetic substance. The **cation exchanger** consists of granular insoluble organic acid resins having giant molecules with $-\text{SO}_3\text{H}$ or $-\text{COOH}$ groups (represented as RH) while the **anion exchanger** contains giant organic molecules with basic groups derived from amine (represented as ROH). Ion exchange resins remove all soluble mineral from water.

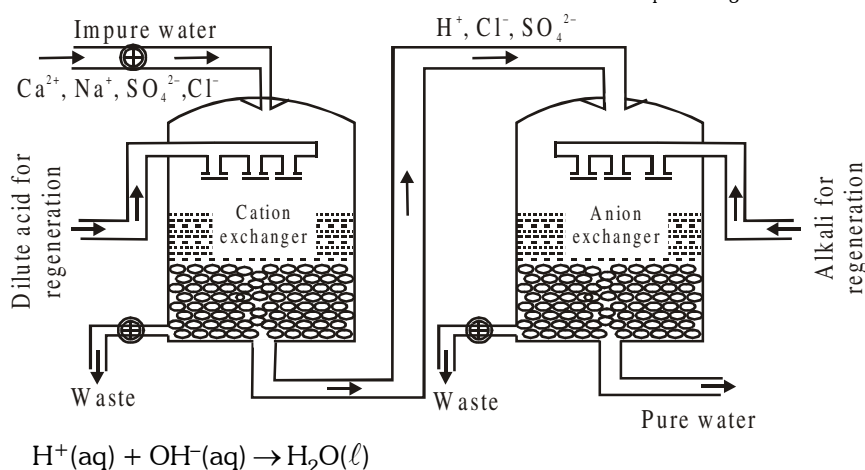
Reaction at Cation exchanger



Reaction at Anion exchanger



The water coming from cation exchanger is acidic due to H^+ . This water is then passed through another bed containing anion exchanger. This exchanger removes anion like Cl^- , SO_4^{2-} , NO_3^- by exchanging with OH^- ions.

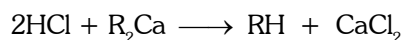


This water is free from impurities & can be used for drinking purpose.

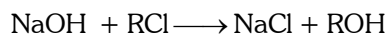
After some times when both resin gets exhausted process is stopped.

Regeneration of resin :

- (i) Cation exchange resin : We use dil acid.



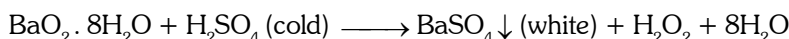
- (ii) Anion exchange resin : We use dil NaOH solution



5.0 HYDROGEN PEROXIDE (H_2O_2)

5.1 Preparation :

- (i) **Laboratory method:**



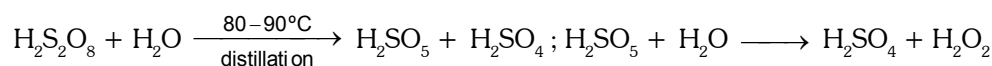
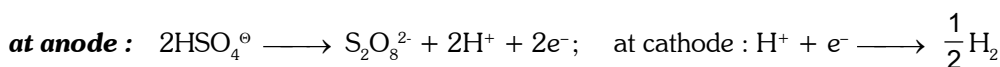
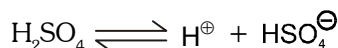
BaSO_4 is filtered to get aqueous hydrogen peroxide.

Since H_2SO_4 can decompose H_2O_2 at a higher temperature, therefore, the reaction should be carried out at low temperature or H_3PO_4 can be used in place of H_2SO_4

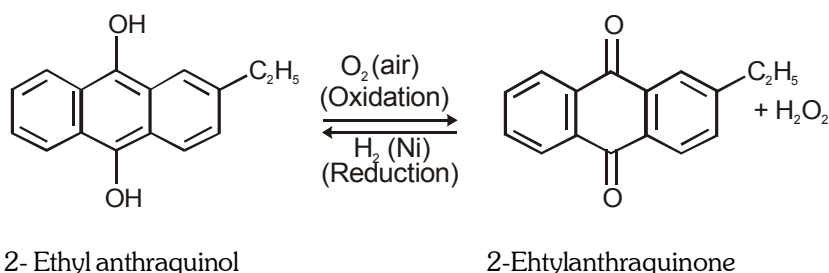


H_3PO_4 can again be used.

- (ii) By electrolysis of concentrated H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ at a high current density to form peroxosulphates, which then hydrolysed.

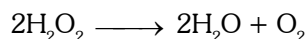


- (iii) **Industrial method (Auto oxidation) :**



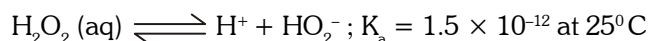
5.2 Properties :

- (i) Colourless viscous liquid which appears blue in the larger quantity and is soluble in water (due to H-bonding) in all proportions and form a hydrate $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ (melting point 221 K).
- (ii) Its boiling point 423 K is more than water but freezing point (-4°C) is less than water. Density and dielectric constant are also higher than H_2O
- (iii) Its aqueous solution is more stable than the anhydrous liquid where it decomposes into water and O_2 slowly on exposure to light.

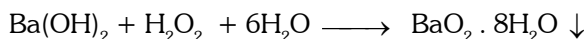
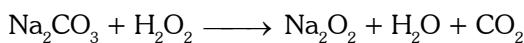


H_2O_2 is not kept in glass containers because traces of alkali metal ions from the glass can catalyse the explosive decomposition of H_2O_2 . Therefore, aqueous solution is stored in plastic or wax-lined glass containers and some urea or phosphoric acid or glycerol is added to that solution because these compounds have been found to behave as negative catalyst for the decomposition of H_2O_2

(iv) **Acidic nature :** Behaves as a weak acid according to the following equation

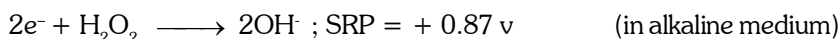
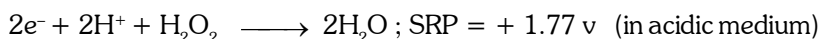


Aqueous solution of H_2O_2 turns blue litmus red which is then bleached by the oxidising property of H_2O_2



A 30% H_2O_2 solution has $\text{pH} = 4.0$

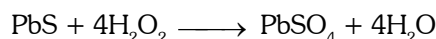
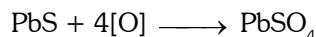
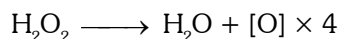
(v) **Oxidising Agent :**



On the basis of the above potentials, we can say that H_2O_2 is strong oxidising agent in acidic medium but kinetically it is found that reactions are faster in basic medium.

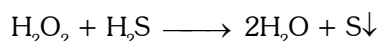
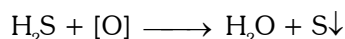
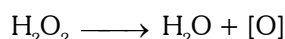
(a) **In acidic medium :**

- It oxidises PbS to PbSO_4 .

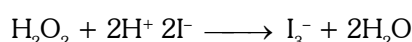


This property is utilised in restoring the white colour in old paintings which turns black due to the formation of PbS by the action of atmospheric H_2S .

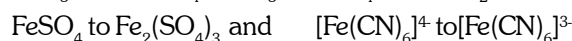
- H_2O_2 oxidises H_2S to sulphur.



Potassium iodide and starch produces deeper blue colour with acidified H_2O_2 .



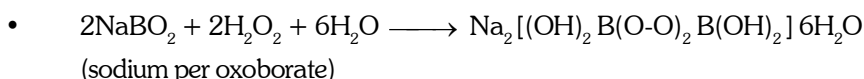
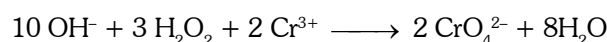
H_2O_2 in acidic medium also oxidises



(b) **In alkaline medium :**

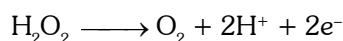


or

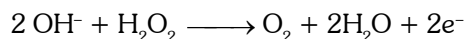


Used as a brightener in washing powder.

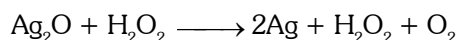
(vi) **Reducing Agent :** It acts as a reducing agent towards powerful oxidising agent.



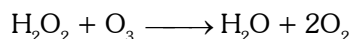
In alkaline solution, its reducing character is more than in acidic medium.



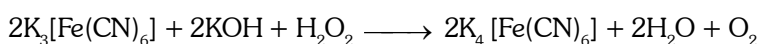
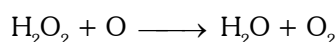
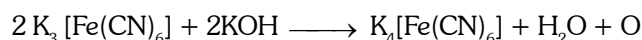
(a) Ag_2O is reduced to Ag .



(b) It reduces O_3 to O_2 .



(c) It reduces ferric cyanide to ferrous cyanide (basic medium).



5.3 Tests for H_2O_2

(i) With $\text{K}_2\text{Cr}_2\text{O}_7$: $\text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ + 4\text{H}_2\text{O}_2 \xrightarrow{\text{amyl alcohol}} 2\text{CrO}_5 + 5\text{H}_2\text{O}$

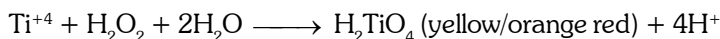
CrO_5 bright blue coloured compound soluble in diethyl ether, amyl alcohol and amyl acetate.



(ii) $2 \text{HCHO} + \text{H}_2\text{O}_2 \xrightarrow[\text{pyrogallol}]{\text{OH}^-} 2 \text{HCOOH} + \text{H}_2$

When this reaction is carried out in dark, it is accompanied by emission of light (yellow coloured). It is an example of chemiluminescence.

(iii) An acidified solution of titanium salt gives yellow or orange colour with H_2O_2 .



Orange red coloured in slightly acid solution and yellow colour with very dilute solution.

Uses :

- In bleaching of delicate materials such as silk, wool, cotton, ivory etc.
- As a valuable antiseptic and germicide for washing wounds, teeth and ears under the name perhydrol.
- As 'antichlor' to remove traces of chlorine and hypochlorite.
- As oxidising agent in rocket fuels.

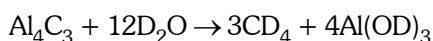
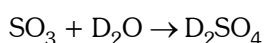
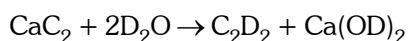
6.0 HEAVY WATER, D_2O :

It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

6.1 Physical properties :

(a) Heavy water is a colourless, odourless and tasteless mobile liquid, (b) Nearly all the physical constants are higher than the corresponding values of ordinary water.

It is used for the preparation of other deuterium compounds, for example:



6.2 Uses : It is extensively used as a moderator & coolant in nuclear reactors and in exchange reactions for the study of reaction mechanisms. **As a neutron moderator :** Fission in uranium-235 is brought by slow speed neutrons. The substances which are used for slowing down the speed of neutrons are called moderators. Heavy water is used for this purpose in nuclear reactors.

7.0 DIHYDROGEN AS A FUEL

Dihydrogen releases large quantities of heat on combustion. The data on energy released by combustion of fuels like dihydrogen, methane, LPG etc. are compared in terms of the same amounts in mole, mass and volume, are shown in Table.

From this table it is clear that on a mass for mass basis dihydrogen can release more energy than petrol (about three times). Moreover, pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen).

This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place. However, the mass of the containers in which dihydrogen will be kept must be taken into consideration. A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Also, dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like NaNi_5 , Ti-TiH_2 , Mg-MgH_2 etc. are in use for storage of dihydrogen in small quantities. These limitations have prompted researchers to search for alternative techniques to use dihydrogen in an efficient way.

In this view Hydrogen Economy is an alternative. The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Advantage of hydrogen economy is that energy is transmitted in the form of dihydrogen and not as electric power. It is for the first time in the history of India that a pilot project using dihydrogen as fuel was launched in October 2005 for running automobiles. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. The percentage of dihydrogen would be gradually increased to reach the optimum level.

Nowadays, it is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy.

The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume

Energy released on Combustion in kJ state)	Dihydrogen in gaseous state)	Dihydrogen (in liuqid)	LPG	CH ₄ gas	Octance (in liuqid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

BEGINNER'S BOX-2

- Which one of the following processes will produce hard water ?
 (A) Saturation of water with CaSO_4 (B) Addition of Na_2SO_4 to water
 (C) Saturation of water with CaCO_3 (D) Saturation of water with MgCO_3
- In which of the following reaction H_2O_2 acts as a reducing agent ?
 (i) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (ii) $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
 (iii) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$ (iv) $\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^-$
 (A) (i), (iii) (B) (ii), (iv) (C) (i), (ii) (D) (iii), (iv)
- Select CORRECT statement.
 (A) Protium water (H_2O) dissociate at higher extent that of D_2O
 (B) Heavy water (D_2O) dissociate at higher extent that of H_2O
 (C) Both H_2O and D_2O have same extent of dissociation
 (D) None of the above

4. Polyphosphates are used as water softening agent because they :
 (A) Form soluble complexes with anionic species (B) Precipitate anionic species
 (C) Form soluble complexes with cationic species (D) Precipitate cationic species

5. Sodium hexameta phosphates are used as water softening agent in :
 (A) Clark's method (B) Permutit method
 (C) Calgon method (P) Synthetic resin method

6. H_2O_2 is slowly decomposed on exposure of light and reaction is' catalysed by :
 (A) metal surface (B) alkali
 (C) glass containers (D) all of these

7. H_2O_2 is required to store in :
 (A) dark to prevent from light (B) plastic vessels
 (C) wax-lined glass (D) all are correct

8. Very pure H_2 is prepared by electrolysis of aq. solution of NaOH or KOH. Reaction completed at anode in this process :
 (A) $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$ (B) $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$
 (C) $H_2O \longrightarrow \frac{1}{2}O_2 + 2e^- + 2H^+$ (D) $H_2O \longrightarrow H_2 + \frac{1}{2}O^2$

ANSWERS

BEGINNER'S BOX-1

1. (B) 2. (C) 3. (A) 4. (C) 5. (D) 6. (A) 7. (B) 8. (C)
9. (D) 10. (C)

BEGINNER'S BOX-2

1. (A) 2. (B) 3. (D) 4. (D) 5. (C) 6. (D) 7. (D) 8. (B)

EXERCISE – 1**MCQ (SINGLE CHOICE CORRECT)**

- The sum number of neutrons and protons in one of the isotopes of hydrogen is :-
 (A) 3 (B) 4 (C) 5 (D) 6
- The most abundant isotope of hydrogen is :-
 (A) Tritium (B) Deuterium (C) Protium (D) Para hydrogen
- Ordinary hydrogen at high temperature is a mixture of :-
 (A) 75% o-Hydrogen + 25% p-Hydrogen (B) 25% o-Hydrogen + 75% p-Hydrogen
 (C) 50% o-Hydrogen + 50% p-Hydrogen (D) 1% o-Hydrogen + 99% p-Hydrogen
- Hydrogen is behave as :-
 (A) Electropositive
 (B) Electronegative
 (C) Both electropositive as well as electro-negative
 (D) Neither electropositive nor electronegative
- The lightest gas is :-
 (A) Nitrogen (B) Helium (C) Oxygen (D) Hydrogen
- The ratio of electron, proton and neutron in tritium is :-
 (A) 1 : 1 : 1 (B) 1 : 1 : 2 (C) 2 : 1 : 1 (D) 1 : 2 : 1
- The nuclei of tritium (H^3) atom would contain neutrons :-
 (A) 1 (B) 2 (C) 3 (D) 4
- The adsorption of hydrogen by metals is called :-
 (A) Dehydrogenation (B) Hydrogenation (C) Occlusion (D) Adsorption
- Only temporary hardness in water is removed by :-
 (A) Boiling (B) Filtration (C) Calgon's process (D) None of these
- Both temporary and permanent hardness is removed on boiling water with :-
 (A) $Ca(OH)_2$ (B) Na_2CO_3 (C) $CaCO_3$ (D) CaO
- Calgon is an industrial name given to :-
 (A) Normal sodium phosphate (B) Sodium meta-aluminate
 (C) Sodium hexametaphosphate (D) Hydrated sodium aluminium silicate
- Heavy water has found application in atomic reactor as :-
 (A) Coolant (B) Moderator
 (C) Both coolant and moderator (D) Neither coolant nor moderator
- Calgon (a water softener) is :-
 (A) $Na_2[Na_4(PO_3)_6]$ (B) $Na_4[Na_2(PO_3)_6]$ (C) $Na_2[Na_4(PO_4)_6]$ (D) $Na_4[Na_2(PO_4)_6]$

- 14.** The hardness of water is due to.....metal ions
(A) Ca^{2+} and Na^+ (B) Mg^{2+} and K^+ (C) Ca^{2+} and Mg^{2+} (D) Zn^{2+} and Ba^{2+}
- 15.** The formula of heavy water is :-
(A) H_2O^{18} (B) D_2O (C) T_2O (D) H_2O^{17}
- 16.** The bleaching properties of H_2O_2 are due to its :-
(A) Reducing properties (B) Oxidising properties
(C) Unstable nature (D) Acidic nature
- 17.** Hydrogen peroxide has a :-
(A) Linear structure (B) Pyramidal structure
(C) Closed book type structure (D) Half open book type structure
- 18.** Hydrogen peroxide is a :-
(A) Liquid (B) Gas (C) Solid (D) Semi-solid
- 19.** Which of the following is a true structure of H_2O_2
(A) $\text{H}-\overset{180^\circ}{\text{O}}-\text{O}-\text{H}$ (B) $\text{H}-\overset{94.8^\circ}{\text{O}}-\text{O}-\text{H}$ (C) $\begin{array}{c} \text{H} \\ \diagdown \\ \text{O} \end{array} \rightarrow \text{O}$ (D) $\begin{array}{c} \text{H} \\ \diagdown \\ \text{O} \end{array} = \text{O}$
- 20.** Decomposition of H_2O_2 is retarded by :-
 $2\text{H}_2\text{O}_2(\ell) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$
(A) Acetanilide (B) MnO_2
(C) Zinc (D) Finely divided metals
- 21.** H_2O_2 is :-
(A) An oxidising agent (B) Both oxidising and reducing agent
(C) Reducing agent (D) None of the above
- 22.** H_2O_2 is always stored in black bottles because :-
(A) It is highly unstable
(B) Its enthalpy of decomposition is high
(C) It undergoes auto-oxidation on prolonged standing
(D) None of these
- 23.** H_2O_2 restores the colour of old lead paintings, blackened by the action of H_2S gas by :-
(A) Converting PbO_2 to Pb (B) By oxidising PbS to PbSO_4
(C) Converting PbCO_3 to Pb (D) Oxidising PbSO_3 to PbSO_4
- 24.** The reaction, $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \longrightarrow \text{S} + 2\text{H}_2\text{O}$ manifests:
(A) Acidic nature of H_2O_2 (B) Alkaline nature of H_2O_2
(C) Oxidising nature of H_2O_2 (D) Reducing nature of H_2O_2

EXERCISE - 2**MCQ (ONE OR MORE CHOICE CORRECT)**

- Which of the following is / are same for Ortho and Para hydrogen :-
 (A) In the number of protons (B) In the molecular mass
 (C) In the nature of spins of nucleus (D) In the nature of spins of electrons
- In Bosch's process which gas is **NOT** utilised for the production of hydrogen :-
 (A) Producer gas (B) Water gas (C) Coal gas (D) Natural gas
- The gas(es) used in the hydrogenation of oils in presence of nickel as a catalyst is / are :-
 (A) Methane (B) Ethane (C) Ozone (D) Hydrogen
- Water softening by Clarke's process does **NOT** uses :-
 (A) Calcium bicarbonate (B) Sodium bicarbonate
 (C) Potash alum (D) Calcium hydroxide
- Which of the following produces hydrolith with dihydrogen :-
 (A) Mg (B) Al (C) Cu (D) Ca
- Which process is/are used to remove permanent hardness :-
 (A) Boiling (B) Clark's method
 (C) On reaction with NaOH (D) Permutit process
- Ionic hydrides is/are usually :-
 (A) Good electrically conductors when solid (B) Easily reduced
 (C) Good reducing agents (D) Liquid at room temperature
- Which of the following will produce hydrogen gas :-
 (A) Reaction between Fe and dil. HCl (B) Reaction between Zn and conc. H_2SO_4
 (C) Reaction between Zn and NaOH (D) Electrolysis of NaCl (aq.) in Nelson's cell
- Ortho-hydrogen and para-hydrogen resembles in which of the following property :-
 (A) Thermal conductivity (B) Magnetic properties
 (C) Chemical properties (D) Heat capacity
- Which of the following statements concerning protium, deuterium and tritium is / are true :-
 (A) They are isotopes of each other (B) They have similar electronic configurations
 (C) They exist in the nature in the ratio of 1 : 2 : 3 (D) Their mass numbers are in the ratio of 1 : 2 : 3
- Ionic hydrides are formed by :-
 (A) Transition metals (B) Elements of very high electropositivity
 (C) Elements of very low electropositivity (D) Metalloids
- Which of the following statements is/are correct :
 (A) Atomic hydrogen is obtained by passing hydrogen gas through an electric arc
 (B) 30% (w/v) or 100V H_2O_2 solution is not called perhydrol.
 (C) Finely divided palladium absorbs large volume of hydrogen gas.
 (D) Ortho and para hydrogen have same physical properties.

- 13.** Which hydride is/are an ionic hydride :-
 (A) NH_3 (B) H_2S (C) $\text{TiH}_{1.73}$ (D) NaH
- 14.** Which of the following hydride is/are 'electron-precise' type ?
 (A) HF (B) H_2O (C) SiH_4 (D) PH_3
- 15.** Hydrogen peroxide can act as a :-
 (A) A reducing agent (B) An oxidising agent
 (C) A dehydrating agent (D) A bleaching agent

Matrix Match Type

- 16.** Match List I with List II and select the correct answer using the codes given below the lists :-

List - I

P. Heavy water
 Q. Temporary hard
 R. Soft water
 S. Permanent hard

List II

1. Bicarbonates of Mg and Ca in water
 2. No foreign ions in water
 3. D_2O
 4. Sulphates and chlorides of Mg and Ca in water

Code :

P	Q	R	S
(A) 3	1	2	4
(B) 3	4	2	3
(C) 3	2	1	4
(D) 2	3	1	4

- 17.** Match List I with List II and select the correct answer using the codes given below the lists :-

List - I

P. Calgon
 Q. Non-stoichiometric compound
 R. Covalent hydride
 S. Salt-like hydride

List II

1. Metallic hydride
 2. Polymetaphosphate of sodium
 3. Hydrolith
 4. Hydrogen compounds of non-metals

Code :

P	Q	R	S
(A) 2	1	3	4
(B) 3	4	2	3
(C) 2	1	4	3
(D) 2	3	1	4

Comprehension Type :

Passage for Q.3 to Q.5

Hydrogen accounts for approximately 75% of the mass of the universe. Hydrogen serves as the nuclear fuel of our Sun and other stars, and these are mainly composed of hydrogen.

Hydrogen has three isotopes : hydrogen or protium (^1_1H), deuterium or heavy hydrogen (D or ^2_1H), tritium (T or ^3_1H).

- 18.** Which of the following is radioactive in nature ?
 (A) hydrogen only (B) deuterium only
 (C) tritium only (D) deuterium and tritium

19. Hydrogen, H_2 , is very less abundant in the atmosphere due to -
 (A) inflammable nature of H_2
 (B) weak earth's gravity which is not able to hold light H_2 molecules
 (C) diatomic nature of hydrogen
 (D) very rapid reaction between hydrogen and atmospheric oxygen
20. Liquid H_2 has been used as rocket fuel as
 (A) its reaction with oxygen is highly exothermic
 (B) it occupies small space
 (C) it has high thrust
 (D) all of the above

Answer Q.21, Q.22 and Q.23 by appropriately matching the information given in the three columns of the following table.

Column - I Name	Column - II Formula	Column - III Specification
(1) Calogen	(P) $Na_6P_6O_{18}$	(i) Used to Remove temporary Hardness
(2) Permutit	(Q) $Na_2Al_2Si_2O_8 \cdot xH_2O$	(ii) Used to remove permanent hardness
(3) Perhydrol	(R) '100 V' H_2O_2	(iii) Used in Rocket propellant
(4) Washing Soda	(S) $Na_2CO_3 \cdot 10H_2O$	(iv) Also named as zeolite

21. Which combination is **NOT** related to removal of Ca^{+2}/Mg^{+2} from the sample of water
 (A) (1)-(P)-(i)(ii) (B) (2)-(Q)-(i)(ii)(iv) (C) (3)-(R)-(i)(ii) (D) (4)-(S)-(i)(ii)
22. Which of the following is **INCORRECT** between column I & II
 (A) 1-P (B) 2-Q (C) 3-R (D) 2-S
23. Which of the following is **INCORRECT** matching between column III & column II
 (A) (iii) - R (B) (iv) - Q (C) (iv) - P (D) none of these

EXERCISE - 3

SUBJECTIVE

Integer Type

1. Find out the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen.
2. Find out the number of following orders which are correct against the mentioned properties :
 - (i) $H_2 < D_2 < T_2$ (Number of protons)
 - (ii) $H_2 < D_2$ (Bond energy)
 - (iii) $H_2 < D_2 < T_2$ (Boiling point)
 - (iv) $H_2 < D_2 < T_2$ (No. of neutrons)
3. Find out the number of following orders which are **NOT** correct against the mentioned properties :
 - (i) $CaH_2 < BeH_2$ (Electrical conductance in molten condition)
 - (ii) $LiH < NaH < CsH$ (Ionic character)
 - (iii) $H_2 < D_2 < F_2$ (Bond dissociation enthalpy)
 - (iv) $NaH < MgH_2 < H_2O$ (Reducing property)
4. What is the oxidation state of oxygen of H_2O_2 in the final product when it reacts with ClO_3^- .
5. Find out the value of 'x' in ion $[H_xO_4]^+$:

EXERCISE - 4**RECAP OF AIEEE/JEE (MAIN)**

- Which one of the following processes will produce hard water :- [AIEEE 2003]
 (A) Saturation of water with CaSO_4 (B) Addition of Na_2SO_4 to water
 (C) Saturation of water with CaCO_3 (D) Saturation of water with MgCO_3
- Very pure hydrogen (99.9%) can be made by which of the following processes? [AIEEE 2012]
 (A) Reaction of salt like hydrides with water
 (B) Reaction of methane with steam
 (C) Mixing natural hydrocarbons of high molecular weight
 (D) Electrolysis of water
- In which of the following reaction H_2O_2 acts as a reducing agent ? [JEE MAIN-2014]
 (a) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (b) $\text{H}_2\text{O}_2 - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$
 (c) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$ (d) $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$
 (A) (a), (c) (B) (b), (d) (C) (a), (b) (D) (c), (d)
- Which of the following statements about Na_2O_2 is **not** correct ? [JEE MAIN-2014]
 (A) Na_2O_2 oxidises Cr^{3+} to CrO_4^{2-} in acid medium (B) It is diamagnetic in nature
 (C) It is the super oxide of sodium (D) It is a derivative of H_2O_2
- Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases H_2O_2 acts as a reducing agent in acid medium ? [JEE MAIN-2014]
 (A) MnO_4^- (B) SO_3^{2-} (C) KI (D) $\text{Cr}_2\text{O}_7^{2-}$
- Permanent hardness in water cannot be cured by: [JEE MAIN-2015]
 (A) Treatment with washing soda (B) Calgon's method
 (C) Boiling (D) Ion exchange method
- From the following statements regarding H_2O_2 , choose the incorrect statement : [JEE MAIN-2015]
 (A) It has to be stored in plastic or wax lined glass bottles in dark
 (B) It has to be kept away from dust
 (C) It can act only as an oxidizing agent
 (D) It decomposes on exposure to light
- In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ? [JEE MAIN-2017]
 (A) $\text{I}_2 + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2$
 (B) $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- + \text{O}_2$
 (C) $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
 (D) $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \rightarrow 2\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} + 2\text{OH}^-$
- The temporary hardness of water is due to :- [JEE MAIN-2019]
 (A) $\text{Ca}(\text{HCO}_3)_2$ (B) NaCl (C) Na_2SO_4 (D) CaCl_2
- The hardness of a water sample (in terms of equivalents of CaCO_3) containing 10^{-3} M CaSO_4 is : [JEE MAIN-2019]
 (molar mass of $\text{CaSO}_4 = 136 \text{ g mol}^{-1}$)
 (A) 100 ppm (B) 50 ppm (C) 10 ppm (D) 90 ppm

- 11.** The isotopes of hydrogen are : **[JEE MAIN-2019]**
 (A) Tritium and protium only (B) Deuterium and tritium only
 (C) Protium and deuterium only (D) Protium, deuterium and tritium
- 12.** Among the following reactions of hydrogen with halogens, the one that requires a catalyst is : **[JEE MAIN-2019]**
 (A) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ (B) $\text{H}_2 + \text{F}_2 \rightarrow 2\text{HF}$ (C) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ (D) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
- 13.** The chemical nature of hydrogen peroxide is : **[JEE MAIN-2019]**
 (A) Oxidising and reducing agent in acidic medium, but not in basic medium.
 (B) Oxidising and reducing agent in both acidic and basic medium
 (C) Reducing agent in basic medium, but not in acidic medium
 (D) Oxidising agent in acidic medium, but not in basic medium.
- 14.** The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are : **[JEE MAIN-2019]**
 (A) 2 and 0 (B) 3 and 2 (C) 3 and 1 (D) 2 and 1
- 15.** The hydride that is NOT electron deficient is : **[JEE MAIN-2019]**
 (A) B_2H_6 (B) AlH_3 (C) SiH_4 (D) GaH_3
- 16.** The correct statements among (a) to (d) regarding H_2 as a fuel are : **[JEE MAIN-2019]**
 (a) It produces less pollutants than petrol
 (b) A cylinder of compressed dihydrogen weighs ~30 times more than a petrol tank producing the same amount of energy
 (c) Dihydrogen is stored in tanks of metal alloys like NaNi_5
 (d) On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively
 (A) b and d only (B) a, b and c only (C) b, c and d only (D) a and c only
- 17.** NaH is an example of : **[JEE MAIN-2019]**
 (A) Electron-rich hydride (B) Molecular hydride (C) Saline hydride (D) Metallic hydride
- 18.** The synonym for water gas when used in the production of methanol is :- **[JEE MAIN-2019]**
 (A) natural gas (B) laughing gas (C) syn gas (D) fuel gas
- 19.** The metal that gives hydrogen gas upon treatment with both acid as well as base is : **[JEE MAIN-2019]**
 (A) zinc (B) iron (C) magnesium (D) mercury
- 20.** The temporary hardness of a water sample is due to compound X. Boiling this sample converts X to compound Y. X and Y, respectively, are : **[JEE MAIN-2019]**
 (A) $\text{Ca}(\text{HCO}_3)_2$ and CaO (B) $\text{Mg}(\text{HCO}_3)_2$ and MgCO_3
 (C) $\text{Mg}(\text{HCO}_3)_2$ and $\text{Mg}(\text{OH})_2$ (D) $\text{Ca}(\text{HCO}_3)_2$ and $\text{Ca}(\text{OH})_2$

EXERCISE - 5**RECAP OF IIT-JEE/JEE (ADVANCED)**

1. When zeolite (hydrated sodium aluminium silicate) is treated with hard water, the sodium ions are exchanged with :- **[IIT 1990]**
(A) H^+ ions (B) Ca^{2+} ions (C) SO_4^{2-} ions (D) OH^- ions
2. Which of the following statement is correct :-
(A) Hydrogen has same ionisation potential as sodium
(B) H has same electronegativity as halogens
(C) It will not be liberated at anode
(D) H has oxidation state +1, zero and -1
3. Polyphosphates are used as water softening agent because they :- **[IIT 2002]**
(A) Form soluble complexes with anionic species
(B) Precipitate anionic species
(C) Form soluble complexes with cationic species
(D) Precipitate cationic species.
4. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a **[JEE Adv. 2014]**
(A) reducing agent, oxidising agent (B) reducing agent, reducing agent
(C) oxidising agent, oxidising agent (D) oxidising agent, reducing agent
5. Which of the following combination will produce H_2 gas? **[JEE Adv. 2017]**
(A) Zn metal and $NaOH(aq.)$ (B) Au metal and $NaCN(aq.)$ in the presence of air
(C) Cu metal and conc. HNO_3 (D) Fe metal and conc. HNO_3

ANSWERS KEY

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	C	A	C	D	B	B	C	A	B	C	C	A	C	B
Que.	16	17	18	19	20	21	22	23	24						
Ans.	B	D	A	B	A	B	C	B	C						

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A,B,D	A,C,D	D	A,B,C	D	D	C	A,C,D	C	A,B,D	B	A,C	D	C	A,B,D
Que.	16	17	18	19	20	21	22	23							
Ans.	A	C	C	B	D	C	D	C							

EXERCISE-3

Que.	1	2	3	4	5
Ans.	D	C	C	0	9

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	D	B	C	A	C	C	C	A	A	D	A	B	C	C
Que.	16	17	18	19	20										
Ans.	B	C	C	A	C										

EXERCISE-5

Que.	1	2	3	4	5
Ans.	B	D	C	A	A

s-BLOCK

Recap of Early Classes

So far we have studied ionic eq. (acid, base, titration & solubility). Now we will study s-block elements, which includes alkali metals & alkaline earth metals.

Index

ALKALI METAL

1.0 PROPERTIES

- 1.1 Physical State
- 1.2 Atomic Size
- 1.3 Softness
- 1.4 Melting Point and Boiling Point
- 1.5 Electro Positive Character or Metallic Character
- 1.6 Flame Test
- 1.7 Reaction with NH_3
- 1.8 Photo Electric Effect
- 1.9 Standard Oxidation Potential
- 1.10 Hydration Energy (Heat of Hydration)
- 1.11 Reducing Property
- 1.12 Reaction with Air
- 1.13 Reaction with Oxygen
- 1.14 Reaction with Water
- 1.15 Halides
- 1.16 Carbonates
- 1.17 Nitrates
- 1.18 Nitrides
- 1.19 Formation of Amalgam
- 1.20 Sulphates
- 1.21 Reaction with acids

2.0 COMPOUNDS OF ALKALI METALS

- 2.1 Sodium (Na), Natrium
- 2.2 Sodium Chloride NaCl
- 2.3 Sodium Hydroxide (NaOH), Caustic Soda
- 2.4 Sodium Bicarbonate or Baking soda (NaHCO_3)
- 2.5 Sodium carbonate or washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)
- 2.6 Sodium Peroxide Na_2O_2
- 2.7 Potassium Hydroxide KOH
- 2.8 Potassium Carbonate
- 2.9 Potassium Chloride
- 2.10 Oxides of Potassium

ALKALINE EARTH METAL

3.0 PROPERTIES

- 3.1 Physical State
- 3.2 Atomic Size
- 3.3 Softness
- 3.4 Melting point and Boiling point
- 3.5 Electro Positive Character or Metallic Character
- 3.6 Flame Test
- 3.7 Reaction with NH_3
- 3.8 Photo Electric Effect
- 3.9 Standard Oxidation Potential
- 3.10 Hydration Energy (Heat of hydration)
- 3.11 Reducing Property
- 3.12 Reaction with Air
- 3.13 Reaction with Oxygen
- 3.14 Reaction with Water
- 3.15 Halides
- 3.16 Carbonates
- 3.17 Nitrates
- 3.18 Nitrides
- 3.19 Formation of Amalgam
- 3.20 Sulphates
- 3.21 Reaction with Acids

4.0 COMPOUNDS OF ALKALINE EARTH METALS

- 4.1 Magnesium
 - 4.2 Magnesium Chloride MgCl_2
 - 4.3 Magnesium Sulphate MgSO_4
 - 4.4 Calcium
 - 4.5 Calcium Oxide (CaO) Quick lime
 - 4.6 Calcium Hydroxide Ca(OH)_2 Slaked lime
 - 4.7 Calcium Carbonate (CaCO_3)
 - 4.8 Calcium Sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum)
 - 4.9 Plaster of Paris ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$)
 - 4.10 Similarities between lithium and Magnesium
 - 4.11 Diagonal Similarity between Beryllium and Aluminium
- EXERCISE-1
EXERCISE-2
EXERCISE-3
EXERCISE-4
EXERCISE-5

ALKALI METAL

1.0 PROPERTIES

1.1 Physical State

SL AL

- (a) One electron in outermost shell & **General formula ns^1** .
- (b) Francium is radioactive element.
- (c) All are silvery white
- (d) Light soft, malleable and ductile metals with metallic lustre.
- (e) Alkali metals are paramagnetic, diamagnetic and colourless in form of ions.

1.2 Atomic Size

SL AL

- (a) Biggest in their respective period
(except noble gas element)
- (b) Size increases from Li to Fr due to addition of an extra shell.
 $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{Fr}$
- (c) order of ionic radius
 $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Fr}^+$

1.3 Softness

SL AL

- (a) Alkali metals are soft because of -
 - (i) Large atomic size
 - (ii) BCC crystal structure (HCP in Li)
 - (iii) Loose packing (68% packing efficiency)
 - (iv) Weak metallic bond
- (b) Cs is the softest metal in s-block

$\text{Atomic size} \propto \frac{1}{\text{strength of metallic bond}} \propto \text{softness} \propto \frac{1}{\text{Melting \& Boiling point}}$

1.4 Melting Point and Boiling Point

SL AL

- (a) Weak interatomic bonds are due to their large atomic radii and presence of only one valence electron hence melting point and boiling point are low.
- (b) Decreasing order of melting point and boiling point is
 $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$
- (c) With the increase in the size of metal atom, the repulsion of the non-bonding electrons increases and therefore melting point and boiling point decreases from Li to Cs.

1.5 Electro Positive Character or Metallic Character

SL AL

Electropositivity $\propto 1/\text{Ionisation Potential}$

Due to their larger size electron can easily be removed to form M^+ ion. Electro positive property increases from Li to Cs.

1.6 Flame Test

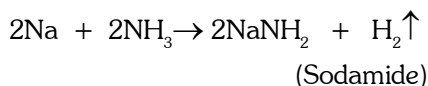
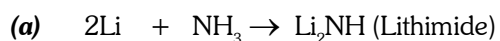
SL AL

Alkali metals and their salts give characteristic colour to Bunsen flame. The flame energy causes an excitation of the outer most electron which on dropping back to ground state emits absorbed energy as visible light

Ex. Li-Crimson red Na-Golden yellow K-Violet
Rb-Red violet Cs-Blue

1.7 Reaction with NH_3

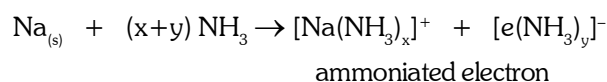
SL AL



(b) Solubility in liquid ammonia

(i) All the alkali metals dissolve in NH_3 (liq.) and produce blue solution.

(ii) This blue solution conducts electricity and possesses strong reducing power, due to the presence of ammoniated electrons.



(iii) This dilute solution is paramagnetic in nature.

1.8 Photo Electric Effect

SL AL

(a) Atomic size of K, Rb and Cs is quite large, so their ionisation potential is very low

(b) Due to very low ionisation potential their valence shell electrons get excited even by absorbing visible light. That's why Cs is used in photo cells.

1.9 Standard Oxidation Potential

SL AL

(a) All the alkali metals have high +ve values of standard oxidation potential (tendency of releasing electrons in water or self ionic solutions)

(b) So these are good reducing agents, having upper most positions in the electrochemical series.

(c) Li has highest standard oxidation potential (+3.05 eV) due to its high hydration energy. Such that it converts into Li^+ ion by losing one electron.

1.10 Hydration Energy (Heat of Hydration)

SL AL

(a) Alkali metal salts are generally soluble in water due to hydration of cations by water molecules.

(b) Smaller the cation, greater is the degree of its hydration.

1.11 Reducing Property

SL AL

(a) Since alkali metals have high standard oxidation potential, so these are strongest reductants.

(b) Reducing property increases down the group in gaseous or molten state



(c) But in aqueous solution order is -

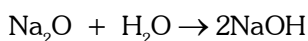
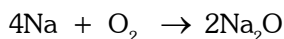


1.12 Reaction with Air

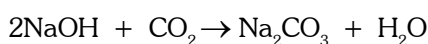
SL AL

(a) Alkali metals get tarnish in air due to the formation of oxide at their surface hence they are kept in kerosene or paraffin oil.

(b) These elements react with moist air to form carbonates



(moist)



(in air)

In dry air only Li gives nitride and oxide both while other elements give only oxides.

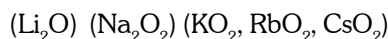
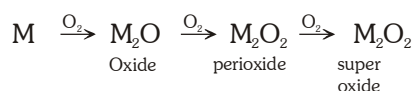
1.13 Reaction with Oxygen

SL AL

Oxide ion $[\text{O}^{2-}]$: Li forms only Li_2O (Lithium oxide).

Peroxide $[\text{O}_2]^{-2}$: Na reacts with O_2 to form peroxide (Na_2O_2).

Super oxide $[\text{O}_2^-]$: K, Rb and Cs form MO_2 type oxides (super oxides) in excess of O_2 . So super oxides are paramagnetic and coloured.



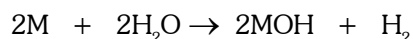
Their stability order is –

Normal oxide > Peroxide > Superoxide

1.14 Reaction with Water

SL AL

(a) Alkali metals react vigorously with water forming hydroxides with the liberation of H_2 .



(b) Reactivity with water increases from Li to Cs.

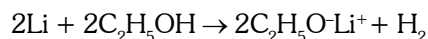
Li → least reactive towards water

Na → reacts vigorously

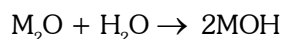
K → reacts producing a flame

Rb, Cs → reacts explosively.

(c) These metals also react with alcohol giving alkoxide and H_2 .



(d) Monoxides give strongly alkaline solution with water



1.15 Halides

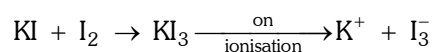
SL AL

(a) Alkali metals react directly with halogen to form MX

(M – alkali metal, X – Halide ion)

(b) Ionic properties of MX increase from LiCl to CsCl

- (c) LiCl is covalent in nature (due to polarisation of Cl^- ion by small Li^+ ion). hence it hydrolyses with water while rest are ionic so do not hydrolyse.
- (d) K, Rb and Cs halides reacts with more halogens to gives polyhalides.



1.16 Carbonates

SL AL

- (a) All the alkali metals forms M_2CO_3 type carbonates.
- (b) Except Li_2CO_3 , all the carbonates are stable towards heat



- (c) Thermal stability of carbonates $\propto 1/\phi$ (Ionic potential)

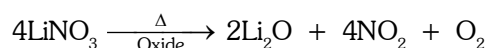
Order of stability is–



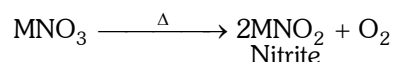
1.17 Nitrates

SL AL

- (a) Alkali metals forms MNO_3 type nitrates (M – alkali metal)
- (b) Stability increases from LiNO_3 to CsNO_3 . LiNO_3 decomposes into Li_2O , NO_2 and O_2 on heating.



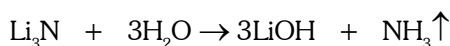
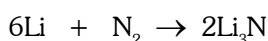
- (c) Other nitrates, on heating to give nitrite and oxygen.



1.18 Nitrides

SL AL

Only Li reacts directly with N_2 to form nitride which gives NH_3 on reacting with water.



1.19 Formation of Amalgam

SL AL

- (a) Alkali metals gives amalgam with Hg.
- (b) These metals reacts with other metals to give mixed metals (alloys)

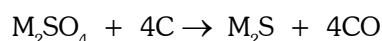
1.20 Sulphates

SL AL

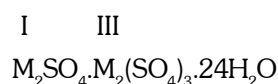
- (a) Alkali metals forms M_2SO_4 type sulphates.
- (b) All alkali metal sulphates are ionic. Ionic properties increases from Li to Cs.



- (c) Li_2SO_4 Least soluble in water.
- (d) These sulphates on burning with C forms sulphides

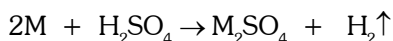


- (e) Except lithium, sulphates of IA group reacts with sulphates of trivalent metals like Fe^{+3} , Cr^{+3} , Al^{+3} etc. gives double salts called alum.



1.21 Reaction with acids

Reacts vigorously with acids.



2.0 COMPOUNDS OF ALKALI METALS

2.1 Sodium (Na), Natrium

SL AL

(a) Extraction : Down's Process

By Electrolysis of fused $NaCl + CaCl_2 + NaF$

At cathode (Iron Vessel) : $Na^+ + e^- \longrightarrow Na(s)$

At Anode (Graphite) : $2Cl^- \longrightarrow Cl_2 + 2e^-$

(i) $(CaCl_2 + NaF)$ is used to lower Melting point ($800^\circ C$) of $NaCl$ to about $600^\circ C$.

(ii) Aqueous sodium chloride cannot be used for preparing sodium by electrolysis. Because instead of metallic sodium, hydrogen gas will be liberated at cathode.

(b) Properties

(i) It is a crystalline soft metal.

(ii) Highly reactive, so kept in kerosene.

(iii) Na dissolves in liquid NH_3 to give blue solution.

(c) Uses

(i) In the preparation of sodium amalgam (used as reducing agent)

(ii) In sodium vapour lamp, which emits monochromatic yellow light.

(iii) As heat transfer medium in nuclear reactors.

2.2 Sodium Chloride NaCl

SL AL

(a) **Occurrence** : Sea water is the main source and also found in salt lakes.

(b) Preparation

(i) Sea water $NaCl(2.7 - 2.9\%) \xrightarrow[\text{by solar heat}]{\text{Evaporation}}$ crude $NaCl$

(ii) It contains impurities – Na_2SO_4 , $MgCl_2$, $CaCl_2$ etc.

(iii) Insoluble impurities removed by filtration.

(iv) Filtrate $\xrightarrow{\text{HCl gas passed}}$ Pure $NaCl$ precipitation (Common ion effect)



Ionic product of $[Na^+][Cl^-] >$ solubility product of $NaCl$ hence it precipitates out.

(v) $MgCl_2$ and $CaCl_2$ are more soluble in water so left in solution.

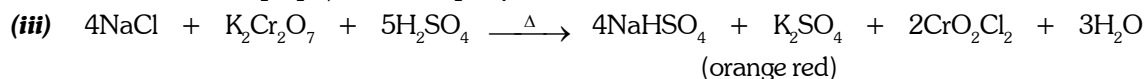
(c) Properties

(i) Table salt is slightly hygroscopic due to the presence of magnesium and calcium chlorides in small amounts.

(ii) Reaction with $AgNO_3$



Reaction with $K_2Cr_2O_7 + \text{conc. } H_2SO_4$



(d) Uses

(i) As a preservative for pickles, meat and fish.

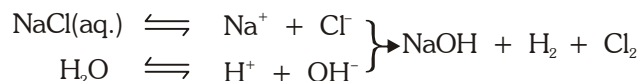
(ii) For making freezing mixture with Ice.

2.3 Sodium Hydroxide (NaOH), Caustic Soda

SL AL

(a) **Manufacture** : By electrolysis of NaCl.

(b) **Nelson Cell or Diaphragm Cell** : The following reactions takes place –



At cathode (Perforated steel) : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ At anode (Carbon) : $2\text{Cl}^-(\text{aq.}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

(c) **Castner – Kellner Cell** : (Hg – Cathode Process)

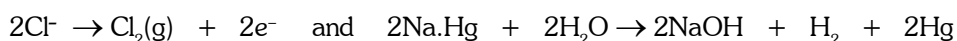
Electrolyte (Brine) $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

On electrolysis –

At Cathode (Hg)



At anode (Graphite)

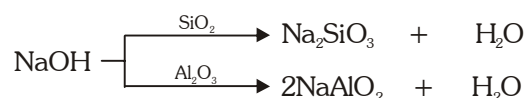


(d) **Properties**

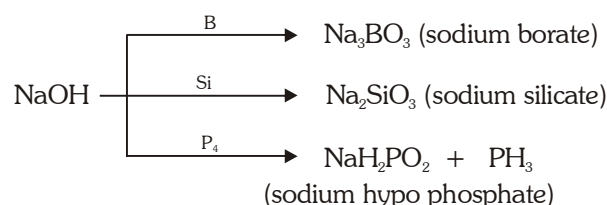
(i) It is deliquescent white crystalline solid.

(ii) It absorbs CO_2 from air forming Na_2CO_3 .

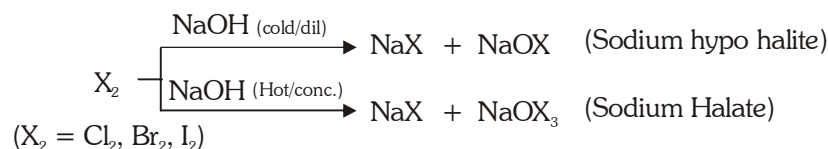
(iii) NaOH is **strong base**



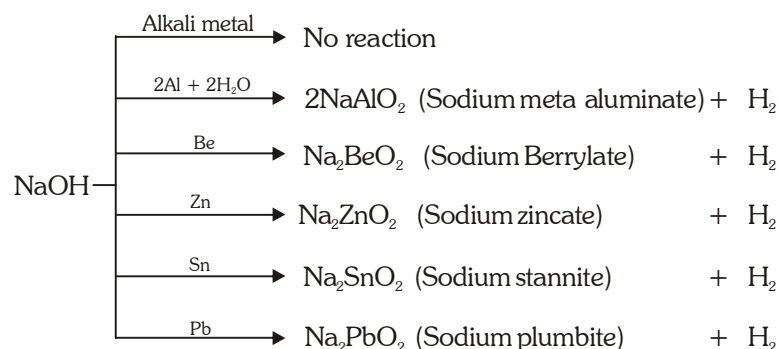
(iv) **Reaction with non metals** : no reaction with H_2 , N_2 and C

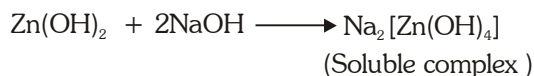


(v) **Reaction with halogens**



(vi) **Reaction with Metal** :

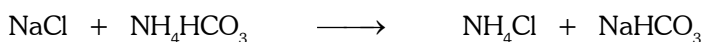
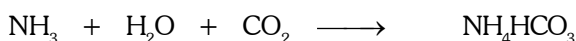
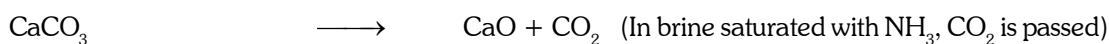
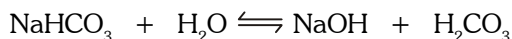


(vii) Reaction with ZnCl_2 or ZnSO_4 

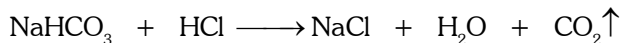
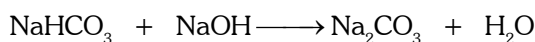
(viii) The hydroxides of aluminium, zinc, lead and tin, however, dissolve in excess of sodium hydroxide giving clear solution which can also be obtained when these metals are acted upon by the concentrated solution of sodium hydroxide.

**(e) Uses**

- (i)** In the manufacture of soap, rayon, dyes, paper and drugs.
- (ii)** In petroleum refining.

2.4 Sodium Bicarbonate or Baking soda (NaHCO_3)**SL AL****(a) Preparation : Solvay process** (Commercial Scale)**(b) Properties****Hydrolysis****Effect of heat** (temp. $> 100^\circ\text{C}$)

(Process occurs during preparation of cake)

Reaction with acids – gives CO_2 **Reaction with base****(c) Uses**

- (i)** In the preparation of baking powder.
- (ii)** In the preparation of effervescent drinks.
- (iii)** In the fire extinguishers.
- (iv)** As antacid medicine (removing acidity)

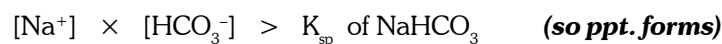
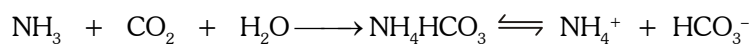
2.5 Sodium carbonate or washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$)**SL AL****(a) Occurrence :** Na_2CO_3 – Soda ash.

(b) Manufacture : By solvay process

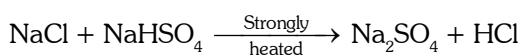
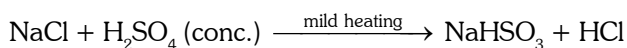
(i) Concentrated aqueous solution of NaCl is saturated with NH_3 .

(ii) Current of CO_2 passed through the solution.

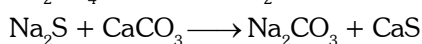
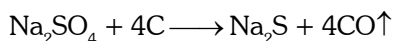
(iii) NaHCO_3 precipitated –



(iv) Potassium bicarbonate (KHCO_3) cannot be prepared by solvay process as it is soluble in water.

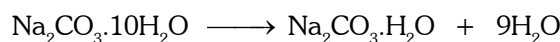
(c) Leblanc Process


(Salt Cake)


(d) Properties

(i) **Efflorescence :**

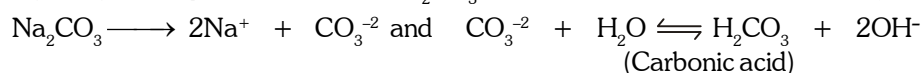
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ when exposed to air it gives out nine out of ten H_2O molecules.



(Monohydrate)

This process is called efflorescence. Hence washing soda losses weight on exposure to air.

(ii) **Hydrolysis :** Aqueous solution of Na_2CO_3 is alkaline in nature due to anionic hydrolysis.


(e) Uses

(i) For making fusion mixture ($\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$)

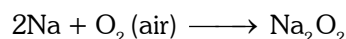
(ii) In the manufacture of glass, caustic soda, soap powders etc.

(iii) In laundries and softening of water.

2.6 Sodium Peroxide Na_2O_2

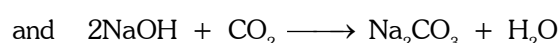
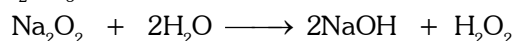
SL AL

(a) Sodium peroxide is manufactured by heating sodium metal on aluminium trays in air (free from CO_2)

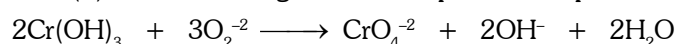


(i) When pure it is colourless, and the faint yellow colour of the usual product arises from the presence of a small amount of NaO_2 .

(ii) When it is exposed, it comes in contact with moist air and turns white due to formation of NaOH and Na_2CO_3 . Thus



(iii) Sodium peroxide is a powerful oxidizing agent and oxidizes chromium (III) hydroxide to sodium chromate, manganese (II) to sodium manganate and sulphides to sulphates.



(b) Uses

- (i) Sodium peroxide is widely used as an oxidizing agent yielding in inorganic chemistry; its reaction with organic compounds are dangerously violent.
- (ii) Sodium readily combines with carbon dioxide, sodium carbonate and oxygen, it may be used for the purification of air in confined spaces such as submarines.
- (iii) It is also used as a bleaching agent because of its oxidizing property.
- (iv) Sodium peroxide is used in the manufacture of dyes, and many other chemicals such as benzoyl peroxide, sodium perborate etc.

2.7 Potassium Hydroxide KOH**SL AL****(a) Preparation:** Electrolysis of KCl aqueous solution.**(b) Properties:** Same as NaOH

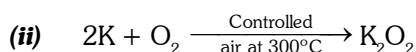
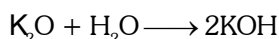
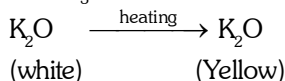
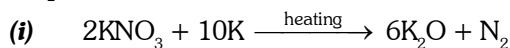
- (i) It is stronger base compared to NaOH.
- (ii) Solubility in water is more compared to NaOH.
- (iii) In alcohol, NaOH is sparingly soluble but KOH is highly soluble.
- (iv) As a reagent KOH is less frequently used but in absorption of CO_2 , KOH is preferable used compared to NaOH. Because KHCO_3 formed is soluble whereas NaHCO_3 is insoluble and may therefore choke the tubes of apparatus used.

2.8 Potassium Carbonate**SL AL**

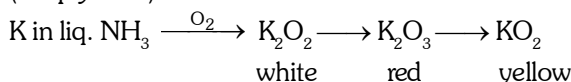
- (a) By leblanc process, it can be prepared but by solvay process it cannot be prepared because KHCO_3 is soluble in water.
- (b) **Properties:** It resembles with Na_2CO_3 , m.p. is 900°C but a mixture of Na_2CO_3 and K_2CO_3 melts at 712°C .
- (c) **Uses:** It is used in glass manufacturing.

2.9 Potassium Chloride**SL AL**It also occurs in nature and sylvinite (KCl) or carnalite ($2\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)**Uses:** It is used as fertiliser.**2.10 Oxides of Potassium****SL AL**

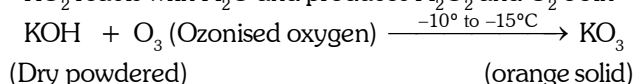
	K_2O	K_2O_2	K_2O_3	KO_2	KO_3
Colours	White	White	Red	Bright yellow	Reddish brown needles

Preparation :

(iii) Passage of O_2 through a blue solution of K in liquid NH_3 yields oxides K_2O_2 (white), K_2O_3 (red) and KO_2 (deep yellow) i.e.



KO_2 reacts with H_2O and produces H_2O_2 and O_2 both



BEGINNER'S BOX-1
General characteristics of Alkali Metals

1. Alkali metals possess metallic lustre when freshly cut because :
 (A) they have a hard surface and light is reflected back.
 (B) their crystal structure contains ordered arrangement of constituent atoms.
 (C) they contain loosely bound electrons which absorb the photons and then re-emit.
 (D) they are obtained from the minerals on which light has been falling for years.
2. When mixture of slaked lime and sodium peroxide is compressed :
 (A) Na_2O , CaO and H_2O are formed. (B) NaO_2 , H_2O and CaO are formed.
 (C) NaOH and CaO_2 are formed. (D) NaOH and CaO are formed.
3. Potassium carbonate is not prepared by :
 (A) Solvay process (B) Le-Blanc process (C) Prechts process (D) None of these
- 4*. If NaOH is added to an aqueous solution of Al^{3+} ions, a white precipitate appears and on adding excess of NaOH , the precipitate dissolves. In the solution, aluminium exists in the :
 (A) anionic part (B) cationic part
 (C) both in anionic and cationic part (D) colloidal form
5. Zinc reacts with excess of caustic soda to form :
 (A) $\text{Zn}(\text{OH})_2$ (B) ZnO (C) Na_2ZnO_2 (D) $\text{Zn}(\text{OH})_2 \cdot \text{ZnCO}_3$
- 6*. Which one of the following products is formed when a mixture of steam, sulphur dioxide gas and oxygen gas (from air) is passed over dry lumps of common salt, the sodium chloride ?
 (A) Na_2SO_3 (B) Cl_2 (C) NaHSO_3 (D) Na_2SO_4

Chemical Properties of Alkali Metals

7. A solution of sodium in liquid ammonia is strongly reducing and highly conducting due to the presence of
 (A) sodium atoms (B) sodium hydride (C) sodium amide (D) solvated electrons
- 8*. Colourless solid NaNO_3 on heating gives :
 (A) A white solid (B) A black solid (C) Colourful gas (D) A green solid
- 9*. Which of the following is commercially known as oxone ?
 (A) $\text{Na}_2\text{O}_2 + \text{HCl}$ (B) $\text{Na}_2\text{O} + \text{HCl}$ (C) $\text{Na}_2\text{O}_2 + \text{Na}_2\text{O}$ (D) None of these
10. Own's cell (for production of sodium), graphite is used as anode because :
 (A) Graphite does not react with Na (B) Graphite does not react with Cl_2
 (C) Graphite can easily be fashioned in circular form (D) None of these
- 11*. An aqueous solution of salt "R" when treated with dil. HCl , a colourless gas is liberated. The gas so evolved when passed through acidified KMnO_4 decolorizes KMnO_4 solution. The salt R is :
 (A) Na_2CO_3 (B) NaClO_3 (C) NaNO_2 (D) NaSO_3
- 12*. Which of the following is called black ash ?
 (A) Na_2CO_3 (B) K_2CO_3 (C) $\text{Na}_2\text{CO}_3 + \text{CaS}$ (D) $\text{K}_2\text{CO}_3 + \text{CaS}$

ALKALINE EARTH METAL

3.0 PROPERTIES

3.1 Physical State

SL AL

- (a) Two electrons in outer most shell & General formula ns^2 .
- (b) Radium is radioactive element.
- (c) All are greyish white.
- (d) These metals are harder than alkali metals.
- (e) These are diamagnetic and colourless in form of ions or in metal states.

3.2 Atomic Size

SL AL

Smaller than IA group elements, since extra charge on nucleus attracts the electron cloud.

- (a) Size increases gradually from Be to Ba
 $Be < Mg < Ca < Sr < Ba$
- (b) In s-block elements
 Be is the smallest, Cs is the biggest

3.3 Softness

SL AL

- (a) These metals are slightly harder than IA group because of -
 - (i) Smaller atomic size
 - (ii) FCC, HCP crystal structures
 - (iii) Packing capacity 74%
 - (iv) Stronger metallic bond due to presence of two electrons in valence shell.
- (b) Be is the hardest metal in s-block.

3.4 Melting point and Boiling point

SL AL

- (a) Metallic bond is stronger than IA group due to smaller atomic size and two electrons in valence shell hence melting point and boiling point are higher.
- (b) Decreasing order of melting point and boiling point is
 $Be > Ca > Sr > Ba > Mg$
- (c) Melting point and Boiling point of Ca, Sr and Ba is higher than Mg because of presence of d-orbitals in the outer most shell, which forms stronger metallic bond.

3.5 Electro Positive Character or Metallic Character

SL AL

Their atomic size is smaller than IA group so these are lesser electro positive than IA group. Electropositivity increases from Be to Ba

3.6 Flame Test

SL AL

- (a) Be and Mg atoms, due to small size, bind their electrons more strongly, so are not excited to higher level, hence no flame test.
- (b) Other elements gives characteristic colour to flame
Ca-Brick red **Sr-crimson red**
Ba-Apple green

3.7 Reaction with NH_3

SL AL

- (a) On increasing metal ion concentration solution converts into bronze colour due to cluster formation of metal ions.
- (b) Solubility in liquid ammonia
 - (i) Only Ca, Sr and Ba gives blue solution of ammoniated electron.
 - (ii) Be and Mg are small in size and have high ionisation potential so do not dissolve in liquid NH_3 .
 - (iii) Dark blue colour of solution becomes faded if it is allowed to stand for a long time, it is because of metal amide formation.
 - (iv) Blue colour of solution disappears on addition of ammonium salt, due to NH_3 formation.



3.8 Photo Electric Effect

SL AL

These elements do not show this property as their atomic size is small hence ionisation potential is higher than IA group.

3.9 Standard Oxidation Potential

SL AL

- (a) They have lower values of standard oxidation potential due to their small size.
- (b) Increasing order of standard oxidation potential is -

$$\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$$

$$\xrightarrow{\hspace{10em}}$$
- (c) Tendency of losing electron increases

3.10 Hydration Energy (Heat of hydration)

SL AL

- (a) Due to smaller ionic size and higher charge density their hydration energy is high.
- (b) Its decreasing order is

$$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$$
- (c) Hydration energy $\propto 1/\text{cation size}$

3.11 Reducing Property

SL AL

- (a) Less reductant than alkali metals
- (b) Order of reducing property in aqueous and gaseous medium is

$$\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$$

3.12 Reaction with Air

SL AL

- (a) Except Be, these metals are easily tarnished in air, as a layer of oxide is formed on the surface.
- (b) Barium in powdered form, bursts into flame on exposure to air.
- (c) In moist air, except Be all the elements convert into carbonates.
- (d) In dry air Be and Mg give nitride and oxide both while others give only oxides.

3.13 Reaction with Oxygen

SL AL

- (a) Alkaline earth metals reacts with O_2 to form 'MO' type oxides
(M = Be, Mg, Ca, Sr, Ba)
- (b) But Ca, Sr and Ba due to low ionisation potential and more reactivity, forms MO_2 (peroxides) at low temperature.
- Ex.** CaO_2 , SrO_2 , BaO_2
- (c) Peroxides are coloured due to Lattice defect.
- (d) BeO shows amphoteric property.
- $MgO \rightarrow$ weak base
- CaO , SrO & $BaO \rightarrow$ Strong base
- (e) Basic properties increases from Be to Ba
- (f) Its stability order general oxide > peroxide > super oxide

3.14 Reaction with Water

SL AL

- (a) These metals reacts slowly with water gives H_2 and metals hydroxides.
- $$M + 2H_2O \rightarrow M(OH)_2 + H_2$$
- (b) Be does not reacts with water
- (c) Mg reacts only with hot water
- (d) Ca, Sr, Ba reacts with cold water but not as energetically as alkali metals. order of reactivity
 $Ba > Sr > Ca > Mg > Be$
- (e) from $Be(OH)_2$ to $Ba(OH)_2$ basic property and stability increases.

3.15 Halides

SL AL

- (a) Alkaline metals reacts with X (Halogen) to form MX_2 .
- Ex.** ($BeCl_2$, $MgCl_2$, $CaCl_2$ etc.)
- (b) Ionic nature of MX_2 increases from $BeCl_2$ to $BaCl_2$
- (c) Ba burns in contact with Cl_2
- (d) Hydrolytic nature of these halides decreases from $BeCl_2$ to $BaCl_2$
- (e) $BeCl_2$ and $MgCl_2$ are covalent in nature. Order of ionic nature –
 $BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$
 Solubility in water
 $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$

3.16 Carbonates

SL AL

- (a) All the alkaline metals forms MCO_3 type carbonates.
- (b) Except $BeCO_3$, all the carbonates are stable towards heat
- $$BeCO_3 \xrightarrow{\Delta} BeO + CO_2$$
- (c) Order of decreasing stability -
 $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

3.17 Nitrates

SL AL

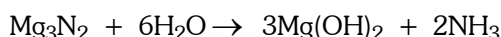
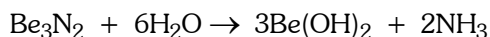
- (a) Alkaline earth metals forms $M(NO_3)_2$ type nitrates. (M –Alkaline earth metal).

- (b) Stability increases from $\text{Be}(\text{NO}_3)_2$ to $\text{Ba}(\text{NO}_3)_2$ but these are less stable than IA group, due to smaller atomic size.
- (c) All alkaline metals nitrates on heating gives oxides and $\text{NO}_2 + \text{O}_2$
- $$\text{M}(\text{NO}_3)_2 \xrightarrow{\Delta} \text{Oxides} + \text{NO}_2 + \text{O}_2$$
- (d) $\text{Be}(\text{NO}_3)_2$ forms a layer of BeO on its surface so reaction stops.

3.18 Nitrides

SL AL

Only Be and Mg burns in N_2 to give M_3N_2 ($\text{Be}_3\text{N}_2, \text{Mg}_3\text{N}_2$)



3.19 Formation of Amalgam

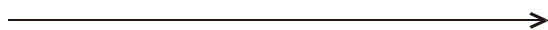
SL AL

Shows same properties as alkali metals.

3.20 Sulphates

SL AL

- (a) Alkaline earth metals forms MSO_4 type sulphates.
- (b) Ionic nature of alkaline metal sulphat is increases from Be to Ba
 $\text{BeSO}_4 < \text{MgSO}_4 < \text{CaSO}_4 < \text{SrSO}_4 < \text{BaSO}_4$
- (c) Solubility decreases from BeSO_4 to BaSO_4 as Be^{+2} and Mg^{+2} are of small size so their hydration energy is high Hydration Energy > Lattice energy.
- (d) Order of solubility –
 $\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$
- (e) Order of thermal stability –
 $\text{BeSO}_4, \text{MgSO}_4, \text{CaSO}_4, \text{SrSO}_4, \text{BaSO}_4$

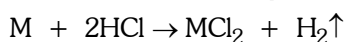


Ionic nature increases, Thermal stability increases

3.21 Reaction with Acids

SL AL

Freely reacts with acids and displaces hydrogen



4.0 COMPOUNDS OF ALKALINE EARTH METALS

4.1 Magnesium

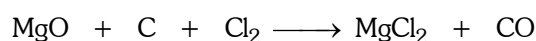
SL AL

(a) **Preparation :**

(i) **From Magnesite or Dolomite :** The ore is first calcined to form the oxide



(ii) **From MgO :** The oxide is mixed with carbon and heated in a current of chlorine gas

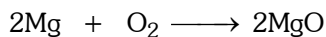


The chloride thus obtained is subjected to electrolysis.

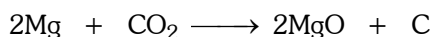
- (iii) The mixed oxides (CaO.MgO) obtained from calcination of dolomite (CaCO₃ MgCO₃) are reduced by ferrosilicon under reduced pressure above 1273 K.
- (iv) It is prepared by the electrolysis of fused magnesium chloride.

(b) Properties

- (i) Magnesium burns in air with dazzling light.



- (ii) Burning Mg continues to burn in CO₂ forming MgO because reducing nature $\text{Mg} > \text{C}$

**(c) Uses**

- (i) In preparation of alloy

Electron : 95% Mg + 5% Zn, air craft

Magnalium : 1 – 15% Mg + 85 – 99% Al, used in aeroplanes, balance beams, light instruments.

- (ii) In photographic flash light.

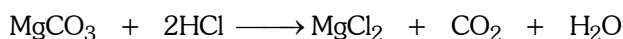
- (iii) In preparation of Grignard's reagent.

4.2 Magnesium Chloride MgCl₂**SL AL**

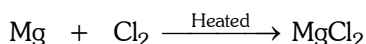
- (a) **Occurrence** : It is mainly found in sea water and carnallite KCl.MgCl₂.6H₂O.

(b) Preparation :

- (i) By reaction of dil HCl on MgCO₃



- (ii) MgCl₂ is obtained by burning Mg metal in chlorine

**(c) Properties**

On heating MgCl₂.6H₂O, it gets hydrolysed by its own water of crystallization to an oxy chlorides.

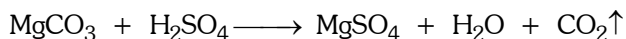
**(d) Uses**

- (i) For preparation of metallic magnesium.
- (ii) In manufacture of magnesia cement.
- (iii) Used for dressing cotton threads.

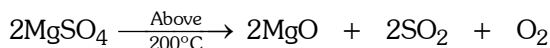
4.3 Magnesium Sulphate MgSO₄**SL AL**

- (a) **Occurrence** : It occurs naturally as kiserite (MgSO₄.H₂O) and epsomite (MgSO₄.7H₂O).

- (b) **Preparation** : By dissolving magnesite in dil. H₂SO₄



- (c) **Properties** : On heating above 200°C



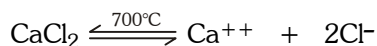
Note : It is used in medicine as purgative.

4.4 Calcium

SL AL

(a) *Extraction*

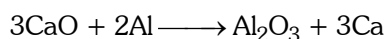
- (i) It is obtained by the electrolysis of fused CaCl_2 . By adding CaF_2 melting point of CaCl_2 (780°C) decreased.



At Cathode (Iron)



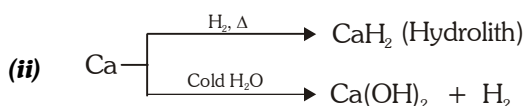
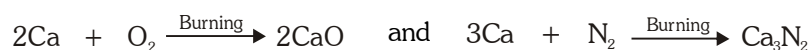
(ii) Goldschmidt (thermite) Process



CaO is reduced by Al because it has greater affinity for oxygen than Ca.

(b) *Properties*

(i) With air



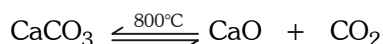
(c) Uses

- (i) For removal of sulphur from petroleum
- (ii) As a dehydrating agent in preparation of absolute alcohol
- (iii) It is used as a deoxidiser for copper, cast Iron and steel

4.5 Calcium Oxide (CaO) Quick lime

SL AL

- (a) **Preparation :** By heating limestones at 800°C .

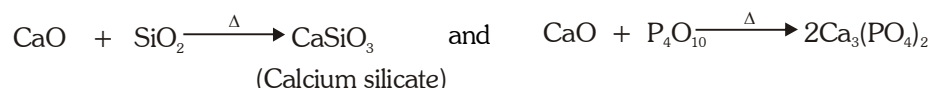


(b) *Properties*

- (i) **Action of water :** $\text{CaO} + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2$
(quick lime) (Slaked lime)

Ca(OH)_2 paste in water called milk of lime.

(ii) Basic Nature :



- (iii) Reaction with carbon : $\text{CaO} + 3\text{C} \xrightarrow{2000^\circ\text{C}} \text{CaC}_2 + \text{CO}\uparrow$

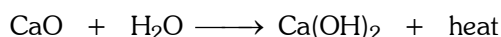
(c) Uses

- (i) In the manufacture of bleaching powder, cement, glass, calcium carbide etc.
- (ii) In the purification of sugar
- (iii) As a drying agent for NH_3 and $\text{C}_2\text{H}_5\text{OH}$
- (iv) As basic lining in furnaces
- (v) For making Soda lime

4.6 Calcium Hydroxide Ca(OH)_2 Slaked lime

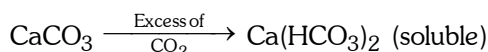
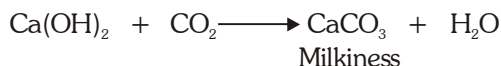
SL AL

(a) **Preparation :** By the action of water on quick lime

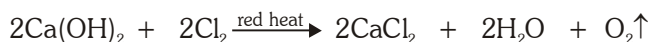
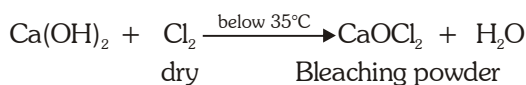


(b) **Properties**

(i) **Action of CO_2 :** Lime water turns milky on passing CO_2 gas.



(ii) **Action of Chlorine :**



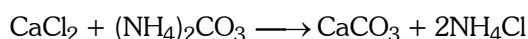
(c) **Uses**

- (i) For softening of hard water.
- (ii) For purification of sugar and Coal gas.
- (iii) In the manufacture of bleaching powder, Caustic soda and soda lime
- (iv) In preparation of mortar, plaster and white washing.

4.7 Calcium Carbonate (CaCO_3)

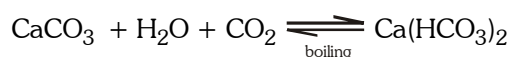
SL AL

(a) It occurs in nature as marble, limestone, chalk, coral, calcite etc. It is prepared by dissolving marble or limestone in HCl and removing iron and aluminium present, by precipitating with NH_3 and then adding $(\text{NH}_4)_2\text{CO}_3$ to the solution.



(b) **Properties**

- (i) It dissociates above 1000°C as follows: $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
- (ii) It dissolves in water containing CO_2 forming $\text{Ca(HCO}_3)_2$ but is precipitated from the solution by boiling



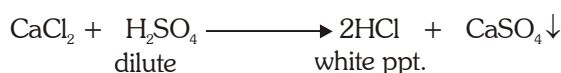
(c) **Uses**

- (i) In the preparation tooth pastes, cosmetics face powder and medicine for indigestion.
- (ii) In the preparation of Quick lime.
- (iii) As a building material.
- (iv) In manufacture of cement, glass, washing soad etc.

4.8 Calcium Sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum)

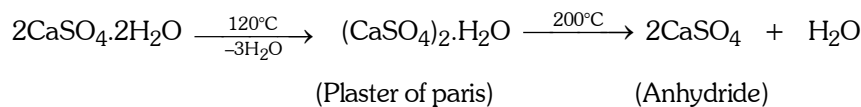
SL AL

(a) **Preparation :** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is naturally occurring calcium sulphate. It can be obtained by the action of dil. H_2SO_4 on a soluble calcium salt below 60°C .

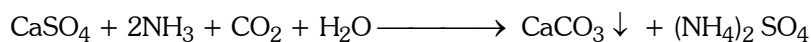


(b) Properties

(i) Action of heat



(ii) It forms an important fertilizer $(\text{NH}_4)_2\text{SO}_4$



(c) Uses

(i) In the preparation of plaster of paris

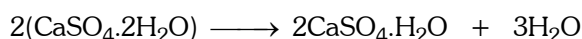
(ii) Anhydrous CaSO_4 used as drying agent.

(iii) Anhydride (CaSO_4) is used for manufacture of sulphuric acid, ammonium sulphate.

4.9 Plaster of Paris ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$)

SL AL

(a) Preparation : It obtained when gypsum is heated at 120°C



(b) Properties

(i) It is a white powder.

(ii) It has the property of setting to a hard mass when a paste with water is allowed to stand aside for sometime.

(iii) When it heated at 200°C , anhydrous CaSO_4 is formed.

(c) Uses

(i) In surgery for setting broken bones

(ii) In making casts for toys, statues etc.

(iii) In making blackboard chalks.

4.10 Similarities between lithium and Magnesium

SL AL

(a) Both lithium and magnesium are harder and lighter than other elements in the respective groups.

(b) Lithium and magnesium react slowly with cold water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride by direct combination with nitrogen, Li_3N and Mg_3N_2 .

(c) The oxides, Li_2O and MgO do not combine with excess oxygen to give a peroxide or a superoxide.

(d) The carbonates of lithium and magnesium decompose easily on heating to form the oxide and CO_2 . Solid bicarbonates are not formed by lithium and magnesium.

(e) Both LiCl and MgCl_2 are soluble in ethanol.

(f) Both LiCl and MgCl_2 are deliquescent and crystallise from aqueous solution as hydrates, $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$.

4.11 Diagonal Similarity between Beryllium and Aluminium

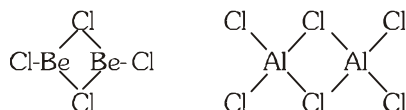
SL AL

In many of its properties, beryllium resembles aluminium. Thus –

(a) The two elements have same electronegativity and their charge/ radius ratios.

(b) Both metals are fairly resistant to the action of acids due to a protective film of oxide on the surface. Both metals are acted upon by strong alkalis to form soluble complexes, beryllates $[\text{Be}(\text{OH})_4]^{2-}$ and aluminates, $[\text{Al}(\text{OH})_4]^-$.

- (c) The chlorides of both beryllium and aluminium



have bridged chloride structures in vapour phase.

- (d) Salts of these metals form hydrated ions, Ex. $[\text{Be}(\text{OH}_2)_4]^{2+}$ and $[\text{Al}(\text{OH}_2)_6]^{3+}$ in aqueous solutions. Due to similar charge/ radius ratios of beryllium and aluminium ions have strong tendency to form complexes. For example beryllium forms tetrahedral complexes such as BeF_4^{2-} and $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$ and aluminium forms octahedral complexes like AlF_6^{3-} and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$.

BEGINNER'S BOX-2

General characteristics of Alkaline Earth Metals

- 1*. Which of the following statement is incorrect ?
 (A) The atomic radius of Na is greater than that of Mg.
 (B) Metallic bond in Mg is stronger than the metallic bond in Na.
 (C) Melting and boiling points of Mg are greater than those of Ca.
 (D) Mg and Ca both impart characteristic colour to the flame.
2. Which of the following properties of the elements of group 2nd (alkaline earth metals) does not increase with increasing atomic number?
 (A) Stability of carbonate
 (B) Solubility of hydroxide
 (C) Reactivity with water
 (D) First ionization energy
- 3*. Which of the following is different from other three oxides ?
 (A) MgO (B) SnO (C) ZnO (D) PbO
- 4*. Thermal stability of MCO_3 is in order :
 (A) $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$ (B) $\text{MgCO}_3 < \text{BeCO}_3 < \text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3$
 (C) $\text{CaCO}_3 < \text{SrCO}_3 < \text{BaCO}_3 < \text{BeCO}_3 < \text{MgCO}_3$ (D) $\text{BaCO}_3 < \text{SrCO}_3 < \text{CaCO}_3 < \text{MgCO}_3 < \text{BeCO}_3$
5. A chloride dissolves appreciably in cold water. When placed on a platinum wire in Bunsen flame, no distinctive colour is noticed. The cation of chloride is ?
 (A) Mg^{2+} (B) Ba^{2+} (C) Pb^{2+} (D) Ca^{2+}
6. Which of the following is incorrect ?
 (A) Mg burns in air releasing dazzling light rich in UV rays.
 (B) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ when mixed with ice gives freezing mixture.
 (C) Mg cannot form complexes.
 (D) Be can form complexes due to its very small size.
7. White $\text{Mn}(\text{OH})_2$ becomes green coloured compound on reaction with sodium peroxide. It is :
 (A) because of the formation of manganate ions. (B) because of the formation of $\text{MnO}(\text{OH})_2$.
 (C) because of the formation of Mn^{2+} ions. (D) because of the formation of permanganate ions.
- 8*. At high temperature, nitrogen combines with CaC_2 to give :
 (A) calcium cyanide (B) calcium cyanamide (C) Calcium carbonate (D) calcium nitride

Chemical Properties of Alkaline Earth Metals

- 9*.** When magnesium burns in air compounds of magnesium formed are magnesium oxide and :
(A) $\text{Mg}(\text{NO}_2)$ (B) $\text{Mg}(\text{NO}_3)_2$ (C) Mg_3N_2 (D) MgCO_3
- 10.** Bleaching powder slowly loses its activity when it stands in air. This due to :
(A) Loss of CaCl_2 (B) Formation of $\text{Ca}(\text{OH})_2$
(C) Reaction with CO_2 to evolve chlorine (D) Reaction with water to evolve O_2
- 11*.** Pure anhydrous magnesium chloride can be prepared from the hydrated salt by :
(A) Melting the hydrate
(B) Heating the hydrate with water
(C) Heating the hydrate to red heat in an atmosphere of HCl
(D) Heating the hydrate with Mg ribbon
- 12*.** BeO dissolves in strongly basic solutions to form
(A) $\text{Be}(\text{OH})_2$ (B) Be (C) Be_2O_3 (D) BeO_2
- 13.** Which of the following contains two electron–three centre bonds?
(A) $[\text{Be}(\text{CH}_3)_2]_n$ (B) $(\text{BeBr}_2)_n$ (C) $(\text{BeO})_2$ (D) $(\text{BeI}_2)_2$
- 14*.** The compound insoluble in acetic acid is
(A) Calcium oxide (B) Calcium carbonate (C) Calcium oxalate (D) Calcium hydroxide
-

GOLDEN KEY POINTS

Order of standard oxidation potential of s-block element
 $\text{Li} > \text{K} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Na} > \text{Mg} > \text{Be}$

Hydration energy \propto Charge density on ion

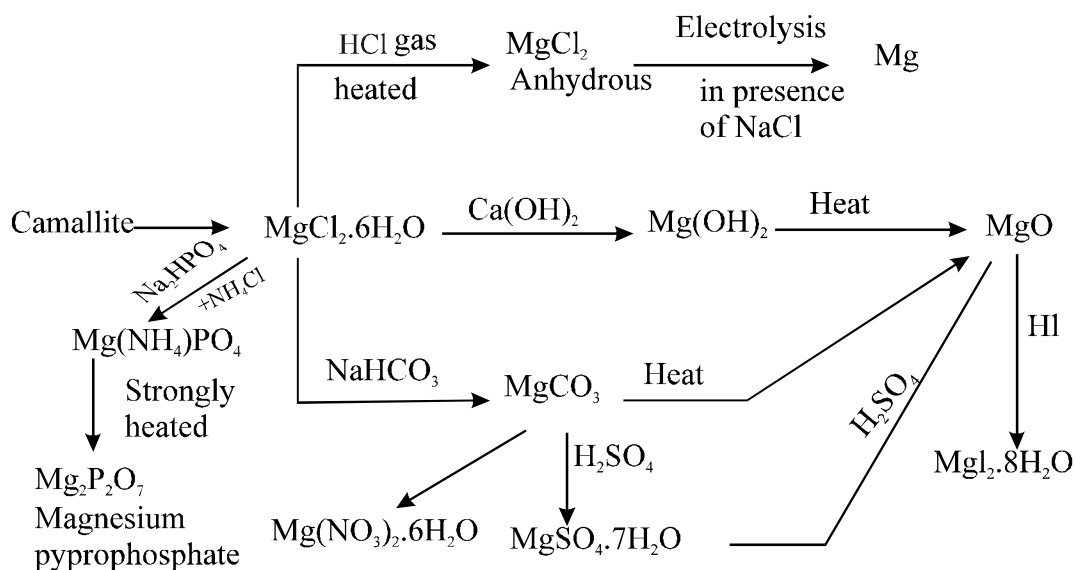
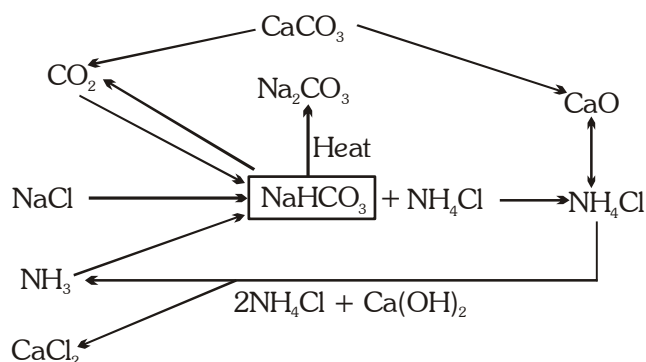
$\text{Li}^+ \quad \text{Na}^+ \quad \text{K}^+ \quad \text{Rb}^+ \quad \text{Cs}^+$

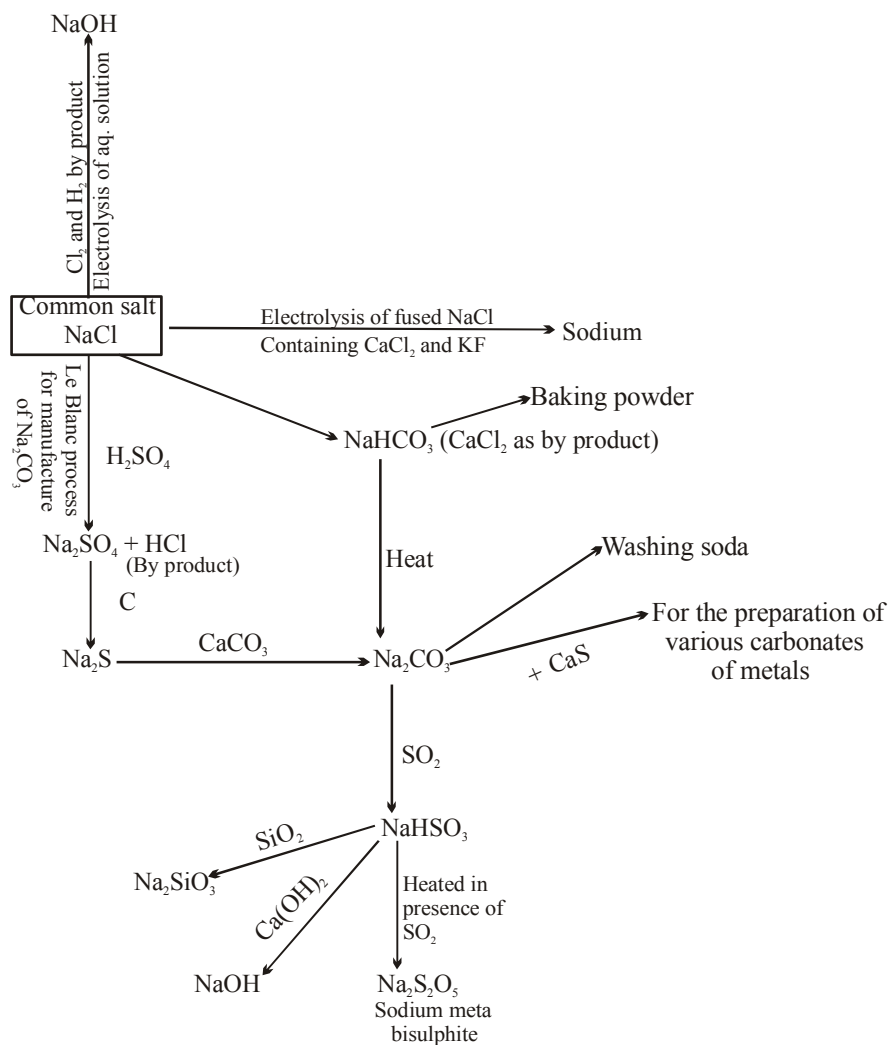
-
- Degree of hydration decreasing
 - Hydration energy decreasing
 - Hydrated ion size decreasing
 - Ionic conductance increasing

On dissolving Metal in NH_3

- $\text{M(s)} \xrightarrow{\text{NH}_3} \text{M}^+ + \text{e}^-$
- $\text{M}^+ + x(\text{NH}_3) \rightarrow [\text{M}(\text{NH}_3)_x]^+$ Ammoniated cation
- $\text{e}^- + y(\text{NH}_3) \rightarrow [\text{e}(\text{NH}_3)_y]^-$ Ammoniated electron
- The blue colour is due to → Ammoniated electron
- The paramagnetic nature is due to → Ammoniated electron
- The conducting nature is due to → Ammoniated M^+ + Ammoniated electron

Flow Sheet of Solvay Process





SOME WORKED OUT EXAMPLES

CORRECT INCREASING ORDER OF SOME PROPERTIES WITH THEIR HINTS/EXPLANATION:

Illustration 1.

$MgO < SrO < K_2O < Cs_2O$ (Basic character).

Solution:

Increasing electropositive nature of the element makes its oxide more basic.

Illustration 2.

$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$ (Ionic radii in water).

Solution:

The smaller size of the ion, the greater extent of hydration, so the size of hydrated ions becomes larger for smaller size ions.

Illustration 3.

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (Molar conductivity in water).

Solution:

Li^+ ion heavily hydrated so lowest mobility while Cs^+ ion less hydrated has the highest mobility.

Illustration 4.

$Li < Na < K < Rb < Cs$ (Reactivity with water).

Solution:

Reactivity increases down the group, due to decrease in ionisation energy.

Illustration 5.

$Cs < Rb < K < Na < Li$ (Reactivity with hydrogen).

Solution:

The ease of formation of hydrides decreases down the group.

Illustration 6.

$Cs < Rb < K < Na < Li$ (Melting point).

Solution:

Melting point decreases down the group due to decrease in strength of metallic bond as size of atom increase.

Illustration 7.

$LiOH < NaOH < KOH < RbOH < CsOH$ (Basic nature of hydroxides).

Solution:

Basic nature of hydroxides increases down the group the strength of as base depends on ionisation of the hydroxide which in turns depends on (a) polarity of bond and internuclear distance between the oxygen of the hydroxide and metal atom.

Illustration 8.

$LiOH < NaOH < KOH < RbOH < CsOH$ (Thermal stability of hydroxides).

Solution:

Thermal stability of hydroxides increases down the group. Bigger cation is stabilised by bigger anion and vice-versa.

Illustration 9.

$LiCl < LiBr < LiI$ (Covalent character).

Solution:

According to Fajan's rule Li^+ ion polarizes the larger anion more, giving larger covalent character.

Illustration 10.

$BeCl_2 < MgCl_2 < CaCl_2 < SrCl_2 < BaCl_2$ (Ionic character).

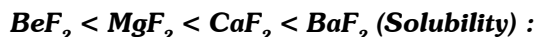
Solution:

According to Fajan's rule.

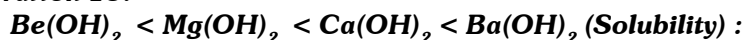
Illustration 11.

Solution:

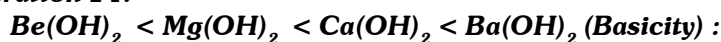
On moving down the group the lattice energy of carbonates do not decrease more while the degree of hydration decreases more so solubility decreases down the group.

Illustration 12.

Solution:

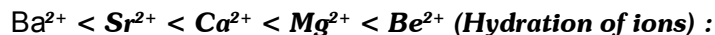
Decrease in lattice energy is more as compared to hydration energy down the group. Also apply Fajan's rule.

Illustration 13.

Solution:

L.E. is dominating factor. (Refer also Hint of 12)

Illustration 14.

Solution:

Basicity of hydroxides increases down the group. (Refer Hint of 7)

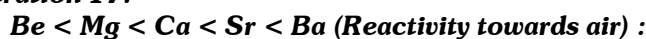
Illustration 15.

Solution:

The extent of hydration of ion decreases with increase in ionic size.

Illustration 16.

Solution:

Reactivity with water increases down the group.

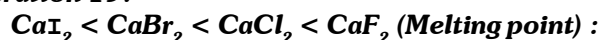
Illustration 17.

Solution:

Reactivity towards air increases down the group.

Illustration 18.

Solution:

Decrease in hydration energy is more as compared to lattice energy down the group.

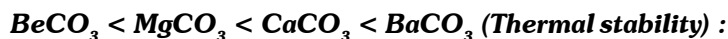
Illustration 19.

Solution

As the size of anion increases, its polarisation by the cation increase, so covalent character increases.

Illustration 20.

Solution

Stability of hydrides decreases down the group due to decrease in lattice energy.

Illustration 21.

Solution:

BeO is more stable than BaO, so BeCO_3 have a greater tendency to decompose to give stable BeO. So BeCO_3 is least stable and BaCO_3 is most stable.

Illustration 22.

Solution:

The larger the difference between the electronegativities, greater the ionic character.

IMPORTANT COMPOUNDS AND THEIR FORMULA

1.	Active nitrogen	:	N(atomic nitrogen)
2.	Alums	:	$M_2'SO_4 \cdot M_2''(SO_4)_3 \cdot 24H_2O$ $M' = K^+, NH_4^+, Na^+ \text{ etc.}$ $M'' = Cr^{+3}, Al^{+3}, Fe^{+3} \text{ etc.}$
3.	Asbestos	:	$CaMg_3(SiO_3)_4$
4.	Arsine	:	AsH_3
5.	Aquaregia	:	Conc. HNO_3 + Conc. HCl (1 : 3 part)
6.	Anhydrone	:	$Mg(ClO_4)_2$
7.	Argentiferous galena	:	$PbS + Ag_2S$
8.	Borax	:	$Na_2B_4O_7 \cdot 10H_2O$
9.	Blue vitriol	:	$CuSO_4 \cdot 5H_2O$
10.	Barytes	:	$BaSO_4$
11.	Baryta water	:	$Ba(OH)_2$ solution
12.	Baryta	:	BaO
13.	Baking soda	:	$NaHCO_3$
14.	Bleaching powder	:	$CaOCl_2$
15.	Boranes	:	Hydride of borone
16.	Brine	:	$NaCl$ solution
17.	Calgon	:	$Na_2[Na_4(PO_3)_6]$
18.	Coinage metals	:	$Cu, Ag \text{ and } Au$
19.	Carborundum	:	SiC
20.	Cementite	:	FeC
21.	Caliche	:	$NaNO_3 + NaIO_3$
22.	Caustic soda	:	$NaOH$
23.	Caustic potash	:	KOH
24.	Calomel	:	Hg_2Cl_2
25.	Corrosive sublimate	:	$HgCl_2$
26.	Deuterium	:	${}_1H^2$ of D
27.	D.D.T.	:	p-dichloro, diphenyl, trichloroethane
28.	Dry ice	:	Solid CO_2
29.	Freon	:	CF_2Cl_2
30.	Ferric Alum	:	$K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
31.	Fenton's reagent	:	H_2O_2 + few drops of $FeSO_4$

32.	Fusion mixutre	:	$\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$
33.	Fluid magnesia	:	12% solution of $\text{Mg}(\text{HCO})_2$
34.	Fehling solution	:	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{NaOH} + \text{Na, K tartarate}$
35.	King of metals	:	Gold
36.	Horn Silver	:	AgCl
37.	Green vitriol	:	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
38.	Graphite	:	An allotrope of carbon
39.	Gun powder	:	$75\% \text{KNO}_3 + 12\% \text{S} + 13\% \text{charcoal (explosive)}$
40.	Glauber salt	:	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
41.	Hydrolith	:	CaH_2
42.	Heavy water	:	D_2O
43.	Hypo (sodium thiosulphate)	:	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
44.	Heavy hydrogen	:	D_2
45.	King of chemicals	:	H_2SO_4
46.	Lime (quick lime or burnt lime)	:	CaO
47.	Lead pencil	:	Graphite
48.	Lime water	:	$\text{Ca}(\text{OH})_2$
49.	Laughing gas	:	N_2O
50.	Lunar Caustic	:	AgNO_3
51.	Litharge (Masscote)	:	PbO
52.	Lithopone	:	$(\text{ZnS} + \text{BaSO}_4)$, a pigment
53.	Mortar	:	Slaked lime + sand (1 : 3 in water)
54.	Mica	:	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
55.	Mohr salt	:	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
56.	Matte	:	$\text{Cu}_2\text{S} + \text{FeS}$
57.	Milk of lime	:	$\text{Ca}(\text{OH})_2$ in water
58.	Minium	:	Pb_3O_4

59.	Micro cosmic salt	:	$\text{NaNH}_4 \cdot \text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (used in test of silicates)
60.	Milk of magnesia	:	Paste of $\text{Mg}(\text{OH})_2$ in water (Antacid)
61.	Magnesia	:	MgO
62.	Marsh gas	:	CH_4
63.	Nitrolim	:	$\text{CaCN}_2 + \text{C}$ (a fertilizer)
64.	Nascent Hydrogen	:	H at the moment of generation
65.	Nessler's reagent	:	$(\text{K}_2\text{HgI}_4 + \text{KOH})$ aqueous solution
66.	Indian saltpetre, Bengal salt petre	:	KNO_3
67.	Oil of vitriol	:	Conc. H_2SO_4
68.	Ozone	:	O_3
69.	Oleum	:	$\text{H}_2\text{S}_2\text{O}_7$
70.	Permutit (Zeolite)	:	$\text{Na}_2\text{Al}_2\text{SiO}_8 \cdot \text{XH}_2\text{O}$
71.	Pearl ash (Potash)	:	K_2CO_3
72.	Plaster of paris	:	$\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ or $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$
73.	Philosopher's wool (chinese white)	:	ZnO (Zinc white)
74.	Phosgene	:	COCl_2
75.	Phosphine	:	PH_3
76.	Pig iron	:	Impure form of iron
77.	Producer gas	:	A mixture of $\text{CO} + \text{N}_2 + \text{H}_2$
78.	Quartz	:	SiO_2
79.	Refrigerant	:	$\text{CO}_2, \text{NH}_3, \text{CF}_2\text{Cl}_2$ etc.
80.	Red lead	:	Pb_3O_4
81.	Rochelle salt	:	Sodium - potassium tartarate
82.	Rust	:	$\text{Fe}_2\text{O}_3 \cdot \text{xH}_2\text{O}$
83.	Sorel's cement (Magnesia cement)	:	$\text{MgCl}_2 \cdot 5\text{MgO} \cdot \text{XH}_2\text{O}$
84.	Soda - lime	:	$\text{NaOH} + \text{CaO}$
85.	Soda ash	:	Na_2CO_3 (anhydrous)
86.	Slaked lime	:	$\text{Ca}(\text{OH})_2$
87.	Stainless steel	:	An alloy of Fe, Cr and C
88.	Salt cake	:	Na_2SO_4 (anhydrous)
89.	Super phosphate	:	$\text{Ca}(\text{H}_2\text{PO}_4) + 2\text{CaSO}_4$
90.	TNT	:	Trinitro toluene (an explosive)

91.	TNB	:	Trinitro benzene (an explosive)
92.	Tincal	:	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
93.	Talc	:	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ or $\text{Mg}_2(\text{Si}_2\text{O}_3)_2 \cdot \text{Mg}(\text{OH})_2$
94.	Tritium	:	${}_1\text{H}^3$ (an isotope of H)
95.	Water glass	:	Na_2SiO_3
96.	Water gas	:	$\text{CO} + \text{H}_2$
97.	White vitriol	:	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
98.	Wrought iron	:	Pure form of iron
99.	Washing soda	:	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
100.	Willemite \ Zincite	:	ZnO
101.	Zinc white	:	ZnO
102.	Zinc blend	:	ZnS

INDUSTRIALLY IMPORTANT PROCESS

Ammonia Soda process (Solvay process)	:	Manufacture of NaHCO_3 , Na_2CO_3
Birkeland - Eyde process	:	Manufacture of HNO_3
Bosch process	:	Manufacture of H_2
Castner process	:	Manufacture of Na
Caster - Kellner Cell process	:	Manufacture of NaOH
Contact process	:	Manufacture of H_2SO_4
Down process	:	Manufacture of Na
Dow's process	:	Manufacture of phenol
Deacon's process	:	Manufacture of Cl_2
Haber process	:	Manufacture of NH_3
Hasenclever process	:	Manufacture of Bleaching powder
L.D. process	:	Manufacture of steel
Lead chamber process	:	Manufacture of H_2SO_4
Nelson cell process	:	Manufacture of NaOH
Ostwald process	:	Manufacture of HNO_3

ANSWERS

BEGINNER'S BOX-1

- | | | | | |
|-----------------|-----------------|----------------|----------------|----------------|
| 1. (C) | 2. (C) | 3. (A) | 4. (A) | 5. (C) |
| 6. (D) | 7. (D) | 8*. (A) | 9*. (A) | 10. (B) |
| 11*. (D) | 12*. (C) | | | |

BEGINNER'S BOX-2

- | | | | | |
|-----------------|-----------------|----------------|-----------------|----------------|
| 1. (D) | 2. (D) | 3. (A) | 4. (A) | 5. (A) |
| 6. (C) | 7. (A) | 8. (B) | 9*. (C) | 10. (C) |
| 11*. (C) | 12*. (D) | 13. (A) | 14*. (C) | |

EXERCISE – 1
MCQ (SINGLE CHOICE CORRECT)

1. Which is not s-block element ?
 (A) $[\text{Ar}]4s^23d^{10}4p^65s^1$ (B) $1s^22s^22p^1$ (C) $[\text{He}]2s^22p^63s^1$ (D) None of these
2. Alkali metals are not characterised by :
 (A) good conductor of heat and electricity (B) high oxidation potentials
 (C) high melting points (D) solubility in liquid ammonia
- 3*. The metallic lustre exhibited by sodium is explained by :
 (A) diffusion of sodium ions (B) oscillation of mobile valence electrons
 (C) existence of free protons (D) existence of body centered cubic lattice
4. In view of their ionisation energies, the alkali metals are :
 (A) weak oxidising agents (B) strong reducing agents
 (C) strong oxidising agents (D) weak reducing agents
5. Sodium metal can be stored under :
 (A) benzene (B) kerosene (C) alcohol (D) water
- 6*. In certain matters, lithium differs from other alkali metals, the main reason for this is :
 (A) small size of lithium atom and Li^+ ion (B) extremely high electropositivity of Li
 (C) greater hardness of Li (D) hydration of Li^+ ion
- 7*. Alkaline earth metal salts are :
 (A) paramagnetic (B) diamagnetic (C) ferromagnetic (D) all
8. The first ionisation potential (eV) of Be and B respectively are :
 (A) 8.29, 9.32 (B) 9.32, 9.32 (C) 8.29, 8.29 (D) 9.32, 8.29
9. Which of the following has maximum ionisation energy ?
 (A) $\text{Ba} \longrightarrow \text{Ba}^+ + e^-$ (B) $\text{Be} \longrightarrow \text{Be}^+ + e^-$
 (C) $\text{Ca} \longrightarrow \text{Ca}^{2+} + 2e^-$ (D) $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^-$
- 10*. Among the alkaline earth metals, the element forming predominantly covalent compound is :
 (A) Ba (B) Sr (C) Ca (D) Be
11. A piece of magnesium ribbon was heated to redness in an atmosphere of nitrogen and on cooling, water was added, the gas evolved was :
 (A) ammonia (B) hydrogen (C) nitrogen (D) oxygen
12. When magnesium burns in air, compounds of magnesium formed are magnesium oxide and :
 (A) Mg_3N_2 (B) MgCO_3 (C) $\text{Mg}(\text{NO}_3)_2$ (D) $\text{Mg}(\text{NO}_2)_2$
- 13*. The substance X belonging to IA group gives a pale violet colour in flame test, X is :
 (A) NaCl (B) LiCl (C) KCl (D) None of these
14. Which of the following has the highest melting point?
 (A) NaCl (B) NaF (C) NaBr (D) NaI
- 15*. Which does not exist in solid state.
 (A) NaHCO_3 (B) NaHSO_3 (C) LiHCO_3 (D) CaCO_3

- 16.** Sodium burns in dry air to give :
 (A) Na_2O (B) Na_2O_2 (C) NaO_2 (D) Na_3N
- 17.** Which of the following has lowest thermal stability ?
 (A) Li_2CO_3 (B) Na_2CO_3 (C) K_2CO_3 (D) Rb_2CO_3
- 18*.** Sodium carbonate can be manufactured by Solvay's process but potassium carbonate cannot be prepared because:
 (A) K_2CO_3 is more soluble (B) K_2CO_3 is less soluble
 (C) KHCO_3 is more soluble than NaHCO_3 (D) KHCO_3 is less soluble than NaHCO_3
- 19.** When SO_2 gas in excess is passed into an aqueous solution of Na_2CO_3 , product formed is :
 (A) NaHSO_4 (B) Na_2SO_4 (C) NaHSO_3 (D) All
- 20*.** The principal products obtained on heating iodine with concentrated caustic soda solution is :
 (A) $\text{NaIO} + \text{NaI}$ (B) $\text{NaIO} + \text{NaIO}_3$ (C) $\text{NaIO}_3 + \text{NaI}$ (D) $\text{NaIO}_4 + \text{NaI}$
- 21.** Washing soda has the formula :
 (A) Na_2CO_3 (B) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (C) $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ (D) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
- 22.** Sodium carbonate on heating gives :
 (A) CO_2 (B) water vapours
 (C) carbon dioxide + water vapour (D) none of these
- 23.** Sodium carbonate is prepared by:
 (A) Solvay's process (B) Kolbe's process (C) Contact process (D) Nessler's process
- 24*.** Molecular formula of Glauber's salt is :
 (A) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (B) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (C) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (D) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
- 25.** The compound that gives hydrogen peroxide on treatment with a dilute cold acid is :
 (A) PbO_2 (B) Na_2O_2 (C) MnO_2 (D) SnO_2
- 26.** Among LiCl , RbCl , BeCl_2 , MgCl_2 the compounds with greatest and least ionic character respectively are :
 (A) LiCl , RbCl (B) RbCl , BeCl_2 (C) RbCl , MgCl_2 (D) MgCl_2 , BeCl_2
- 27*.** Peroxide ion is present in :
 (A) K_2O_2 (B) CaO (C) Li_2O (D) BaO
- 28*.** Plaster of Paris is :
 (A) CaSO_4 (B) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (C) $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (D) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- 29.** Plaster of Paris hardens by :
 (A) giving off CO_2 (B) utilising water
 (C) changing into CaCO_3 (D) giving out water
- 30.** Identify the correct statement.
 (A) Gypsum contains a lower percentage of calcium than Plaster of Paris.
 (B) Gypsum is obtained by heating Plaster of Paris.
 (C) Plaster of Paris is obtained by hydration of gypsum.
 (D) Plaster of Paris is obtained by partial oxidation of gypsum.

EXERCISE – 2
MCQ (ONE OR MORE CHOICE CORRECT)

1. Which is/are not correct configuration of s-block elements :
 (A) $[\text{Ar}] 3d^{10} 4s^2$ (B) $[\text{Ar}] 3d^{10} 4s^1$ (C) $[\text{Ar}] 4s^2$ (D) $[\text{Ar}] 4s^1$
- 2*. Alkali metals are characterised by their :
 (A) high electropositive character (B) high reduction potentials
 (C) low melting points (D) high solubility in liquid ammonia at -33°C .
- 3*. Which of the following statements is/are true ?
 (A) All alkali metals are soft and can be cut with knife.
 (B) Alkali metals do not occur in free state in nature.
 (C) Alkali metals are highly electropositive elements.
 (D) Alkali metal hydrides are covalent and low melting solids.
4. Select correct statement(s) :
 (A) Li_2CO_3 is only sparingly soluble in water and no LiHCO_3 has been isolated.
 (B) K_2CO_3 cannot be made by a method similar to the ammonia – soda (Solvay) process.
 (C) Li_2CO_3 and MgCO_3 both are thermally stable.
 (D) $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ is a mineral called trona.
- 5*. Select correct statement(s) :
 (A) Stability of peroxides and superoxides of alkali metals increases with increase in size of the cation.
 (B) Increase in stability in (A) is due to stabilisation of large anions by larger cations through lattice energy effects.
 (C) The low solubility of LiF is due to its high lattice energy whereas low solubility of CsI is due to smaller hydration energy
 (D) NaOH does not form hydrated salt.
- 6*. Which of the following statement(s) is/are correct ?
 (A) Sodium bicarbonate is more soluble than sodium carbonate.
 (B) Sodium hydroxide is used in the purification of bauxite.
 (C) Sodium bicarbonate is used as antacid and for making baking powder.
 (D) Potassium hydroxide is used in the manufacture of soft soaps.
7. The pairs of compound which cannot exist together in aqueous solution are :
 (A) NaH_2PO_4 and Na_2HPO_4 (B) Na_2CO_3 and NaHCO_3
 (C) NaOH and NaH_2PO_4 (D) NaHCO_3 and NaOH .
8. Flame test is not given by
 (A) Be (B) Mg (C) Ca (D) Sr
- 9*. Going down in II A group, following properties decrease :
 (A) solubility of sulphates in H_2O (B) hydration energy
 (C) thermal stability of carbonates (D) ionic radius in water.

- 10.** Which is/are true statements ?
- (A) The heats of hydration of the dipositive alkaline earth metal ions decrease with an increase in their ionic size.
- (B) Hydration of alkali metal ion is less than that of II A.
- (C) Alkaline earth metal ions, because of their much larger charge to radius ratio, exert a much stronger electrostatic attraction on the oxygen of water molecule surrounding them.
- (D) None.
- 11.** In water :
- (A) temporary hardness is due to the bicarbonates of Ca^{2+} and Mg^{2+}
- (B) permanent hardness is due to chlorides and sulphates of Ca^{2+} and Mg^{2+}
- (C) hardness can be removed by adding phosphates.
- (D) none is correct.
- 12*.** Sodium sulphate is soluble in water but barium sulphate is sparingly soluble because :
- (A) the hydration energy of Na_2SO_4 is more than its lattice energy
- (B) the lattice energy of BaSO_4 is more than its hydration energy
- (C) the lattice energy has no role to play in solubility
- (D) the lattice energy of Na_2SO_4 is more than its hydration energy
- 13*.** Slaked lime, $\text{Ca}(\text{OH})_2$ is used :
- (A) in the manufacture of sodium hydroxide.
- (B) in the manufacture of bleaching powder.
- (C) in the preparation of ammonia from ammonium salts.
- (D) in the detection of carbon dioxide gas.
- 14.** Nitrate can be converted into metal oxide on heating not above 500°C in case of :
- (A) Li (B) Na (C) Mg (D) None of these.
- 15*.** Be and Al have following resemblance due to diagonal relationship :
- (A) have nearly equal electronegativity (B) form amphoteric oxides
- (C) have same charge/radius ratio (D) both form dimeric halides

Match the Column

16*. **Column-I**

- (A) Hydrolith
- (B) Nitrolium
- (C) Dolomite
- (D) Pearl's ash

Column-II

- (p) Contain Ca
- (q) Used as a fertilizer
- (r) Used to prepare H_2
- (s) Contain potassium

17. **Column-I**

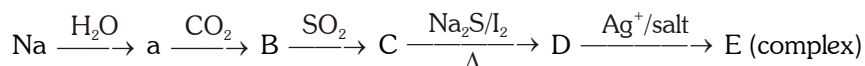
- (A) Solvay process
- (B) Evolve $\text{CO}_2 \uparrow$ on heating
- (C) aq. soln. is neutral towards litmus
- (D) Oxone

Column-II

- (p) NaCl
- (q) Na_2O_2
- (r) NaHCO_3
- (s) Na_2CO_3

Comprehension Based Questions

Comprehension-1



18*. The compound B and C are :

- (A) $\text{Na}_2\text{CO}_3, \text{Na}_2\text{SO}_4$ (B) $\text{NaHCO}_3, \text{Na}_2\text{SO}_4$ (C) $\text{Na}_2\text{CO}_3, \text{Na}_2\text{SO}_3$ (D) None of these

19*. The compound D is :

- (A) Na_2SO_4 (B) $\text{Na}_2\text{S}_4\text{O}_6$ (C) $\text{Na}_2\text{S}_2\text{O}_5$ (D) $\text{Na}_2\text{S}_2\text{O}_3$

20*. Oxidation number of each 'S' atom in compound D :

- (A) + 2, + 2 (B) + 4, 0 (C) + 6, - 2 (D) + 5, - 1

Comprehension-2

Alkali metals readily react with oxyacids forming corresponding salts like M_2CO_3 , MHCO_3 , MNO_3 , M_2SO_4 etc. with evolution of hydrogen. They also dissolve in liquid NH_3 but without the evolution of hydrogen. The colour of its dilute solution is blue but when it is heated and concentrated then its colour becomes bronze.

21*. Among the nitrate of alkali metals which one can be decomposed to its oxide?

- (A) NaNO_3 (B) KNO_3 (C) LiNO_3 (D) All of these

22*. Among the carbonates of alkali metals which one has highest stability?

- (A) Cs_2CO_3 (B) Rb_2CO_3 (C) K_2CO_3 (D) Na_2CO_3

23*. Which of the following statement about the sulphate of alkali metal is correct?

- (A) Except Li_2SO_4 all sulphate of other alkali metals are soluble in water
 (B) All sulphates of alkali metals except lithium sulphate forms alum.
 (C) The sulphates of alkali metals cannot be hydrolysed.
 (D) All of these

24*. Which of the following statement about solution of alkali metals in liquid ammonia is correct?

- (A) The solution have strong oxidizing properties.
 (B) Both the dilute solution as well as concentrated solution are paramagnetic in nature
 (C) Charge transfer is the responsible for the colour of the solution
 (D) None of these

25*. Which metal bicarbonates does not exist in solid state?

- (i) LiHCO_3 (ii) $\text{Ca}(\text{HCO}_3)_2$ (iii) $\text{Zn}(\text{HCO}_3)_2$ (iv) NaHCO_3
 (v) AgHCO_3
 (A) (ii), (iii), (v) (B) (i), (ii), (iii) (C) (i), (ii), (v) (D) (ii), (iii), (iv)

EXERCISE - 3**SUBJECTIVE**

- 1*.** Explain the following :
- (i) The reaction between marble and dilute H_2SO_4 is not used to prepare carbon dioxide.
 - (ii) Lime water becomes turbid on passing CO_2 through it, but becomes clear when more CO_2 is passed.
 - (iii) Alkaline earth metals have higher melting points than alkali metals.
 - (iv) Beryllium does not exhibit a covalency beyond 4.
- 2.** PbO_2 is soluble in NaOH and also in HCl . What does it reflect about the nature of PbO_2 ?
- 3.** What happens when :
- (i) Hot and concentrated caustic soda solution reacts with iodine.
 - (ii) White phosphorus is heated with caustic soda.
 - (iii) Excess of caustic soda reacts with zinc sulphate solution.
 - (iv) Excess of NaOH is added to AlCl_3 solution.
- 4.** Write balanced equation for reaction between
- (i) Na_2O_2 and water
 - (ii) KO_2 and water
 - (iii) Na_2O_2 and CO_2
- 5.** Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. Identify A, B, C and D.
- 6.** In water LiF is least soluble fluoride among fluorides of alkali metals, but its solubility increases as HF is added in aqueous solution, why?
- 7*.** What happens when $\text{CuSO}_4(\text{aq.})$ is treated with excess of $\text{Na}_2\text{S}_2\text{O}_3$ solution?
- 8*.** Arrange the following in order of increasing
- | | |
|--|--|
| (i) Thermal stability | $\text{BeSO}_4, \text{MgSO}_4, \text{CaSO}_4$ |
| (ii) Polarising power | $\text{Be}^{2+}, \text{Mg}^{2+}, \text{Ca}^{2+}$ |
| (iii) Solubility in H_2O | $\text{Be}(\text{OH})_2, \text{Mg}(\text{OH})_2, \text{Ca}(\text{OH})_2$ |
| (iv) Covalent nature | $\text{BeCl}_2, \text{MgCl}_2, \text{CaCl}_2$ |
| (v) Hydrolysis nature | $\text{BeCl}_2, \text{MgCl}_2, \text{CaCl}_2$ |
| (vi) Lattice energy | $\text{CaF}_2, \text{MgF}_2, \text{BaF}_2$ |
| (vii) Hydration energy | $\text{Be}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}$ |
| (viii) Solubility in water | $\text{MgF}_2, \text{BaF}_2, \text{BeF}_2$ |
| (ix) Basic nature | $\text{Be}, \text{Mg}, \text{Ca}, \text{Sr}$ |
- 9.** Hydrogen reacts with a metal (A) to give an ionic hydride (B). The metal (A) gives brick red colour with bunsen flame. The hydride formed is commonly known by its trade name. The compound (B) on treating with water gives back H_2 and (C). Identify (A), (B) and (C).
- 10*.** Write the product of heating of following nitrates.
- (A) LiNO_3 (B) KNO_3 (C) $\text{Pb}(\text{NO}_3)_2$ (D) AgNO_3
- 11.** Arrange in the correct order of the solubility of sulphates of alkaline earth metals.
- 12.** BeF_2 is soluble in water, whereas, the fluorides of other alkaline earth metals are insoluble. Explain why?
- 13.** Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble. Explain why?
- 14*.** A compound X on heating gives a colourless gas. The residue is dissolved in water to obtain Y. Excess CO_2 is bubbled through aqueous solution of Y, Z is formed. Z on gently heating gives back X. The compound X is:
- 15.** Write the composition of portland cement.

EXERCISE - 4
RECAP OF AIEEE/JEE (MAIN)

1. A metal M readily forms its sulphate MSO_4 which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is:- **[AIEEE-2002]**
 (A) Mg (B) Ba (C) Ca (D) Be
2. KO_2 is used in space and submarines because it **[AIEEE-2002]**
 (A) Absorbs CO_2 and increase O_2 concentration (B) Absorbs moisture
 (C) Absorbs CO_2 (D) Produces ozone
- 3*. In curing cement plasters, water is sprinkled from time to time. This helps in :- **[AIEEE-2003]**
 (A) Hydrating sand and gravel mixed with cement
 (B) Converting sand into silicate
 (C) Developing interlocking needle like crystals of hydrated silicates
 (D) Keeping it cool
- 4*. The solubilities of carbonates decreases down the magnesium group due to decrease in- **[AIEEE-2003]**
 (A) Inter-ionic attraction (B) Entropy of solution formation
 (C) Lattice energy of solids (D) Hydration energy of cations
5. The substance not likely to contain $CaCO_3$ is :- **[AIEEE-2003]**
 (A) Sea shells (B) Dolomite (C) A marble statue (D) Calcined gypsum
6. One mole of magnesium nitride on reaction with excess of water gives :- **[AIEEE-2004]**
 (A) Two mole of HNO_3 (B) Two mole of NH_3 (C) 1 mole of NH_3 (D) 1 mole of HNO_3
7. The ionic mobility of alkali metal ions in aqueous solution is maximum for :- **[AIEEE-2006]**
 (A) Rb^+ (B) Li^+ (C) Na^+ (D) K^+
- 8*. Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? **[AIEEE-2012]**
 (A) NH_4NO_3 (B) $NaNO_3$ (C) $KClO_3$ (D) $CaCO_3$
9. Fire extinguishers contain H_2SO_4 and which one of the following :- **[AIEEE-2012]**
 (A) $CaCO_3$ (B) $NaHCO_3$ and Na_2CO_3
 (C) Na_2CO_3 (D) $NaHCO_3$
10. Which one of the following will react most vigorously with water ? **[AIEEE-2012]**
 (A) Li (B) K (C) Rb (D) Na
- 11*. A metal M on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour, Y is :- **[AIEEE-2012]**
 (A) NH_3 (B) MgO (C) Mg_3N_2 (D) $Mg(NO_3)_2$
- 12*. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **[JEE MAINS - 2015]**
 (A) $CaSO_4$ (B) $BeSO_4$ (C) $BaSO_4$ (D) $SrSO_4$

- 13*.** Which of the following statements about water is **FALSE**? [JEE MAINS - 2016]
 (A) Water is oxidized to oxygen during photosynthesis.
 (B) Water can act both as an acid and as a base.
 (C) There is extensive intramolecular hydrogen bonding in the condensed phase.
 (D) Ice formed by heavy water sinks in normal water.
- 14*.** The main oxides formed on combustion of Li, Na and K in excess of air are respectively : [JEE MAINS - 2016]
 (A) Li_2O , Na_2O and KO_2 (B) LiO_2 , Na_2O_2 and K_2O
 (C) Li_2O_2 , Na_2O_2 and KO_2 (D) Li_2O , Na_2O_2 and KO_2
- 15.** Both lithium and magnesium display several similar properties due to the diagonal relationship ; however, the one which is incorrect is : [JEE MAINS - 2017]
 (A) Both form basic carbonates
 (B) Both form soluble bicarbonates
 (C) Both form nitrides
 (D) Nitrates of both Li and Mg yield NO_2 and O_2 on heating
- 16.** In KO_2 , the nature of oxygen species and the oxidation state of oxygen atom are, respectively [JEE MAINS - 2018]
 (A) Superoxide and $-1/2$ (B) Oxide and -2 (C) Peroxide and $-1/2$ (D) Superoxide and -1
- 17.** The alkaline earth metal nitrate that does not crystallise with water molecules, is : [JEE MAINS - 2019]
 (A) $\text{Sr}(\text{NO}_3)_2$ (B) $\text{Mg}(\text{NO}_3)_2$ (C) $\text{Ca}(\text{NO}_3)_2$ (D) $\text{Ba}(\text{NO}_3)_2$
- 18.** Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of : [JEE-MAIN-2019]
 (A) sodium ion–ammonia complex (B) sodamide
 (C) sodium–ammonia complex (D) ammoniated electrons
- 19.** The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are : [JEE-MAIN-2019]
 I. They activate many enzymes
 II. They participate in the oxidation of glucose to produce ATP
 III. Along with sodium ions, they are responsible for the transmission of nerve signals
 (A) I, II and III (B) I and III only (C) III only (D) I and II only
- 20.** The metal used for making X-ray tube window is : [JEE-MAIN-2019]
 (A) Mg (B) Na (C) Ca (D) Be
- 21.** Match the following items in column I with the corresponding items in column II. [JEE-MAIN-2019]
- | Column I | Column II |
|--|--|
| (i) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | (P) Portland cement ingredient |
| (ii) $\text{Mg}(\text{HCO}_3)_2$ | (Q) Castner-Kellner process |
| (iii) NaOH | (R) Solvay process |
| (iv) $\text{Ca}_3\text{Al}_2\text{O}_6$ | (S) Temporary hardness |
| (A) (i) \rightarrow (R); (ii) \rightarrow (Q); (iii) \rightarrow (S); (iv) \rightarrow (P) | (B) (i) \rightarrow (R); (ii) \rightarrow (S); (iii) \rightarrow (Q); (iv) \rightarrow (P) |
| (C) (i) \rightarrow (S); (ii) \rightarrow (P); (iii) \rightarrow (Q); (iv) \rightarrow (R) | (D) (i) \rightarrow (Q); (ii) \rightarrow (R); (iii) \rightarrow (P); (iv) \rightarrow (S) |

- 22.** The amphoteric hydroxide is : **[JEE-MAIN-2019]**
 (A) Ca(OH)_2 (B) Be(OH)_2 (C) Sr(OH)_2 (D) Mg(OH)_2
- 23.** A metal on combustion in excess air forms X, X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is : **[JEE-MAIN-2019]**
 (A) Rb (B) Na (C) Mg (D) Li
- 24.** The covalent alkaline earth metal halide ($\text{X} = \text{Cl, Br, I}$) is :
 (A) CaX_2 (B) SrX_2 (C) BeX_2 (D) MgX_2
- 25.** Magnesium powder burns in air to give: **[JEE-MAIN-2019]**
 (A) MgO only (B) MgO and $\text{Mg(NO}_3)_2$ (C) MgO and Mg_3N_2 (D) $\text{Mg(NO}_3)_2$ and Mg_3N_2
- 26.** The structures of beryllium chloride in the solid state and vapour, phase, respectively, are : **[JEE-MAIN-2019]**
 (A) chain and dimeric (B) chain and chain (C) dimeric and dimeric (D) dimeric and chain
- 27.** The alloy used in the construction of aircrafts is :- **[JEE-MAIN-2019]**
 (A) Mg – Sn (B) Mg – Mn (C) Mg – Al (D) Mg – Zn
- 28.** A hydrated solid X on heating initially gives a monohydrated compound Y. Y upon heating above 373K leads to an anhydrous white powder Z. X and Z, respectively, are: **[JEE-MAIN-2019]**
 (A) Washing soda and soda ash. (B) Washing soda and dead burnt plaster
 (C) Baking soda and dead burnt plaster. (D) Baking soda and soda ash

EXERCISE - 5**RECAP OF IIT-JEE/JEE (ADVANCED)**

1. **Statement-1** : Alkali metals dissolve in liquid ammonia to give blue solutions. [JEE-2007]
Statement-2 : Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.
2. The compound(s) formed upon combustion of sodium metal in excess air is(are) : [JEE-2009]
(A) Na_2O_2 (B) Na_2O (C) NaO_2 (D) $NaOH$
- 3*. The reagent(s) used for softening the temporary hardness of water is(are) [JEE-2010]
(A) $Ca_3(PO_4)_2$ (B) $Ca(OH)_2$ (C) Na_2CO_3 (D) $NaOCl$

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	C	B	B	B	A	B	D	D	D	A	A	C	B	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	B	A	C	C	C	D	D	A	C	B	B	A	C	B	A

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	AB	ACD	ABC	ABD	ABC	BCD	CD	AB	AB	ABC
Que.	11	12	13	14	15					
Ans.	ABC	AB	ABCD	AC	ABCD					

• Match the Column

16*. (A) → p,r ; (B) → p,q ; (C) → p ; (D) → s

17. (A) → r,s ; (B) → r,s ; (C) → p ; (D) → q

• Comprehension Based Questions

Comprehension 1 :

18*. (C)

19*. (D)

20*. (C)

Comprehension 2 :

21*. (C)

22*. (A)

23*. (D)

24*. (D)

25*. (A)

EXERCISE-3

- 1*. (i) Insoluble CaSO_4 is formed which deposits on the surface of marble and prevents further action of dilute H_2SO_4 , so the evolution of CO_2 ceases after sometime.
- (ii) Insoluble CaCO_3 is first precipitated which dissolves in excess of CO_2 due to the form of $\text{Ca}(\text{HCO}_3)_2$.
- $$\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O};$$
- (Insoluble)
- $$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{Ca}(\text{HCO}_3)_2$$
- (Soluble)
- (iii) Metallic bonding is much stronger in alkaline earth metals as two electrons are present in valence shell.
- (iv) The outermost energy shell in beryllium is the second. It cannot accommodate more than 8 electrons and hence a covalency limit 4 cannot be exceeded.
2. PbO_2 are amphoteric nature
- $$\text{PbO}_2 + 4\text{HCl} \longrightarrow \text{PbCl}_4 + 2\text{H}_2\text{O}$$
- $$\text{PbO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{PbO}_3 + \text{H}_2\text{O}$$
3. (i) $3\text{I}_2 + 6\text{NaOH} \longrightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O}$
- (ii) $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$
- (iii) $\text{ZnSO}_4 + 2\text{NaOH} \longrightarrow \text{Zn}(\text{OH})_2 + \text{Na}_2\text{SO}_4$
- $$\text{Zn}(\text{OH})_2 + 2\text{NaOH} \longrightarrow \text{Na}_2[\text{Zn}(\text{OH})_4]$$
- (iv) $\text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al}(\text{OH})_3 + 3\text{NaCl}$
- $$\text{Al}(\text{OH})_3 + \text{NaOH} \longrightarrow \text{Na}[\text{Al}(\text{OH})_4] \text{ or } \text{NaAlO}_2$$
4. (i) $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$
- (ii) $\text{KO}_2 + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2\text{O}_2 + \text{O}_2$
- (iii) $2\text{Na}_2\text{O}_2 + 2\text{CO}_2 \longrightarrow 2\text{Na}_2\text{CO}_3 + \text{O}_2$
5. A = Ca ; B = Ca_3N_2 ; C = $\text{Ca}(\text{OH})_2$; D = NH_3

6. In presence of HF, F^- is converted into bifluoride ion HF_2^- , allowing further dissolution of solid LiF.
- 7*. $CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$
 $2CuS_2O_3 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2S_4O_6$
 Cupric thiosulphate
 $3CuS_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$
 Sodium cuprothiosulphate.
- 8*. (i) $BeSO_4 < MgSO_4 < CaSO_4$ (ii) $Ca^{2+} < Mg^{2+} < Be^{2+}$
 (iii) $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2$ (iv) $CaCl_2 < MgCl_2 < BeCl_2$
 (v) $CaCl_2 < MgCl_2 < BeCl_2$ (vi) $BaF_2 < CaF_2 < MgF_2$
 (vii) $Ba^{2+} < Mg^{2+} < Be^{2+}$ (viii) $BaF_2 < MgF_2 < BeF_2$
 (ix) $Be < Mg < Ca < Sr$
9. (i) Ca gives brick red colour to flame
 (ii) $Ca + H_2 \longrightarrow CaH_2$ (hydrolith, trade name)
 (A) (B)
 (iii) $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$
 (B) (C)
- 10*. (A) $2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 \uparrow \text{ (brown)} + \frac{1}{2} O_2 \uparrow$ (B) $KNO_3 \xrightarrow{\Delta} KNO_2 + \frac{1}{2} O_2 \uparrow$
 (C) $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 \uparrow \text{ (brown)} + \frac{1}{2} O_2 \uparrow$ (D) $2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 \uparrow \text{ (brown)} + O_2 \uparrow$
11. $Be > Mg > Ca > Sr > Ba$
12. Greater hydration energy of Be^{2+} ion as compared to lattice energy
13. The hydration energy of sodium sulphate is more than its lattice energy
- 14*. $CaCO_3 \xrightarrow{X} CaO + CO_2$, $CaO + H_2O \xrightarrow{Y} Ca(OH)_2$,
 $Ca(OH)_2 + 2CO_2 \xrightarrow{Z} Ca(HCO_3)_2$, $Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$
15. The mixture of $MgCl_2$ and MgO is called sorrel cement. Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as **Sorrel's cement**. The composition is $MgCl_2 \cdot 5MgO \cdot xH_2O$.

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	A	C	D	D	B	A	D	C	C	C	B	C	D	A
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	A	D	D	A	D	B	B	A	C	C	A	C	A		

EXERCISE-5

1. (B) 2. (AB) 3*. (BCD)

p-BLOCK ELEMENT (Group - 13 & 14)

Index

GROUP 13 ELEMENTS:

THE BORON FAMILY :

1.0 OCCURANCE

- 1.1 Electronic Configuration
- 1.2 Atomic Radii
- 1.3 Ionization Enthalpy
- 1.4 Electronegativity
- 1.5 Physical Properties
- 1.6 Chemical Properties
- 1.7 Reactivity towards air
- 1.8 Reaction with Air at Water
- 1.9 Reactivity towards acids and alkalies
- 1.10 Reactivity towards halogens :
- 1.11 Important Trends and Anomalous Properties of Boron

2.0 PREPARATION OF BORON

3.0 SOME IMPORTANT COMPOUNDS OF BORON

- 3.1 Borax
- 3.2 Orthoboric acid
- 3.3 Diborane, B_2H_6

4.0 COMPOUNDS OF ALUMINIUM

- 4.1 Al_2O_3
- 4.2 $AlCl_3$
- 4.3 Alums

5.0 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

- 5.1 Boron
- 5.2 Aluminium

GROUP 14 ELEMENTS

1.0 OCCURRENCE OF ELEMENT

- 1.1 Electronic Configuration
- 1.2 Covalent Radius
- 1.3 Ionization Enthalpy

- 1.4 Melting and Boiling Points
- 1.5 Electronegativity
- 1.6 Physical Properties
- 1.7 Chemical Properties
- 1.8 Reactivity towards oxygen
- 1.9 Reactivity towards water
- 1.10 Reactivity towards halogen
- 1.11 Important Trends and Anomalous Behaviour of Carbon
- 1.12 Catenation Property

2.0 ALLOTROPES OF CARBON

- 2.1 Graphite
- 2.2 Fullerenes
- 2.3 Uses of Carbon

3.0 SOME IMPORTANT COMPOUNDS OF CARBON

- 3.1 Types of Carbide
- 3.2 Carbon Monoxide

4.0 SILICON (Si)

- 4.1 Occurrence
- 4.2 Physical Properties
- 4.3 Chemical Properties

5.0 COMPOUNDS OF SILICON

- 5.1 Silane
- 5.2 Silicones
- 5.3 Silica (SiO_2)
- 5.4 Silicates

6.0 TIN & ITS COMPOUND

7.0 COMPOUNDS OF LEAD

EXERCISE-1

EXERCISE-2

EXERCISE-3

EXERCISE-4

EXERCISE-5

p-BLOCK ELEMENT (GROUP 13 & 14)

GROUP 13 ELEMENTS: THE BORON FAMILY :

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character.

1.0 Occurance

Boron : Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3) , borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%).

ALUMINIUM

Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and cryolite, Na_3AlF_6 are the important minerals of aluminium.

1.1 ELECTRONIC CONFIGURATION

The outer electronic configuration of these elements is ns^2np^1 . A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 *d*-electrons, and thallium has noble gas plus 14 *f*-electrons plus 10 *d*-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

1.2 ATOMIC RADII

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

Atomic radii order



Ionic Radii order (+3 OS)



Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 *d*-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

1.3 Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

Ionization Enthalpies order



The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of *d*- and *f*-electrons, which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent during study their chemical properties.

1.4 Electronegativity

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

1.5 Physical Properties

- Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.
- Rest of the members are soft metals with low melting point and high electrical conductivity.
- It is worth while to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.
- Density of the elements increases down the group from boron to thallium.

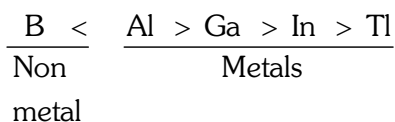
Melting and Boiling points order

M.P. $B > Al > Tl > In > Ga$

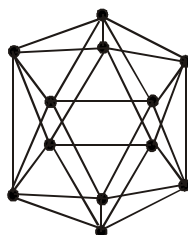
B.P. $B > Al > Ga > In > Tl$

Electropositive Character

Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [\therefore B is nonmetals and other elements are metals.]



Note : Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form : α - rhombohedral boron.

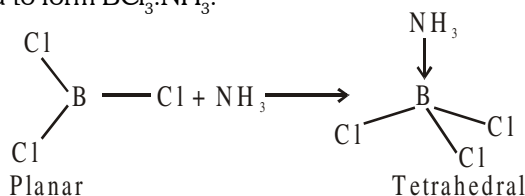


But Al, In & Tl all have close packed metal structure.

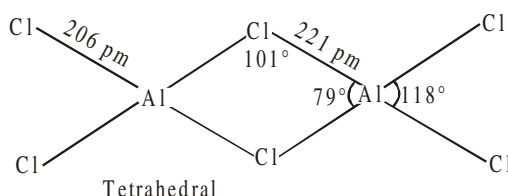
1.6 Chemical Properties

Oxidation state and trends in chemical reactivity

- Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. In fact, aluminium is a highly electropositive metal.
- However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electrons may be involved in bonding. In fact in Ga, In and Tl, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: $Al < Ga < In < Tl$. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character.
- The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.
- In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$.



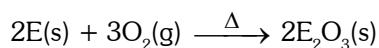
$AlCl_3$ achieves stability by forming a dimer



- (v) In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; the hybridisation state of element M is sp^3 . Aluminium chloride in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2

1.7 REACTIVITY TOWARDS AIR

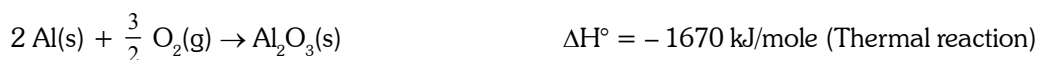
- (i) Boron is unreactive in crystalline form.
 (ii) Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
 (iii) Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

1.8 Reaction with Air at Water

Al should react air to form a very thin oxide film (10^{-4} to 10^{-6} mm thick) on the surface and protects the metal from further attack

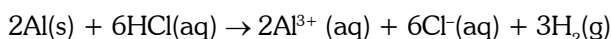


Ga and In are attacked neither by cold water nor hot water unless oxygen is present. Tl form an oxide on surface.

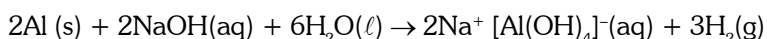
1.9 REACTIVITY TOWARDS ACIDS AND ALKALIES :

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

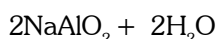


However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.



Sodium tetrahydroxoaluminate(III)

or



Ga, In, Tl dissolve in dilute acids liberating H_2 . Ga is amphoteric like Al and it dissolves in aq. NaOH liberating H_2 and forming gallates.

1.10 Reactivity towards halogens :

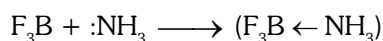
These elements react with halogens to form trihalides (except Tl I_3).



1.11 IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

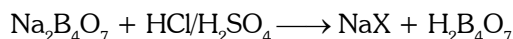
The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.



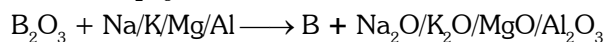
It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (e.g., $AlCl_3$) are dimerised through halogen bridging (e.g., Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

2.0 Preparation of Boron :

- (i) Preparation of B_2O_3 from Borax or Colemanite



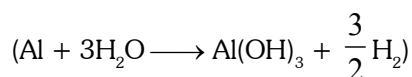
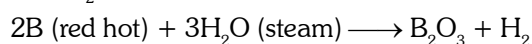
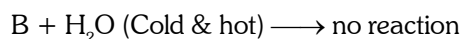
- (ii) Reduction of B_2O_3



□ Chemical Properties :

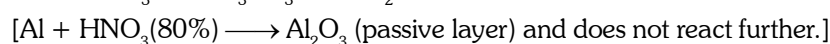
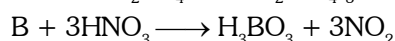
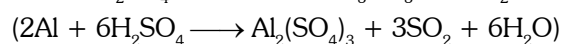
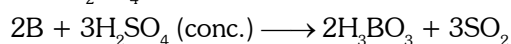
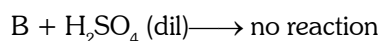
- (i) Burning in air :
- $$4B + 3O_2 \longrightarrow 2B_2O_3$$
- $$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

- (ii) Reaction with water

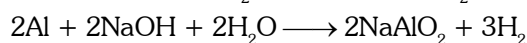


(red hot)

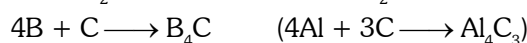
- (iii) $B + HCl \longrightarrow$ no reaction



- (iv) $2B + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaBO_2 + 3H_2$



- (v) $2B + N_2 \longrightarrow 2BN$ $(2Al + N_2 \longrightarrow 2AlN)$



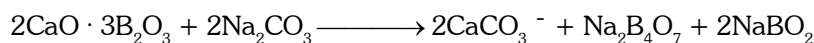
- (vi) $3Mg + 2B \longrightarrow Mg_3B_2$

3.0 SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

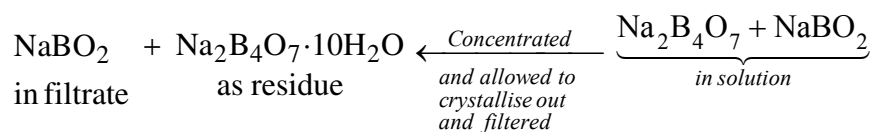
3.1 Borax

Preparation of Borax :

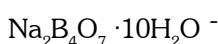
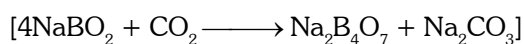


Colemanite

Filtered
- $CaCO_3$ (as residue)

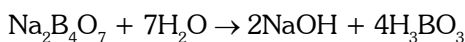


CO₂ passed and
crystallise out again



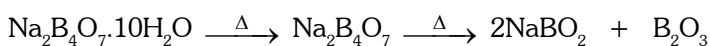
Properties :

- (i) It is a white crystalline solid of formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. In fact it contains the tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ and correct formula; therefore, is $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.
- (ii) Borax dissolves in water to give an alkaline solution.



Orthoboric acid

- (iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.



Sodium Boric
metaborate anhydride

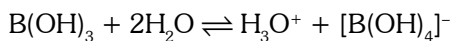
The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $\text{Co}(\text{BO}_2)_2$ bead is formed.

3.2 Orthoboric acid :**Preparation :**

- (i) It can be prepared by acidifying an aqueous solution of borax.
- $$\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} \rightarrow 2\text{NaCl} + 4\text{B}(\text{OH})_3$$
- (ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

Property :

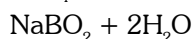
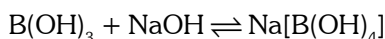
- (i) Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.
- (ii) It is sparingly soluble in water but highly soluble in hot water.
- (iii) H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH^- . It therefore is Lewis acid ($\text{B}(\text{OH})_3$)



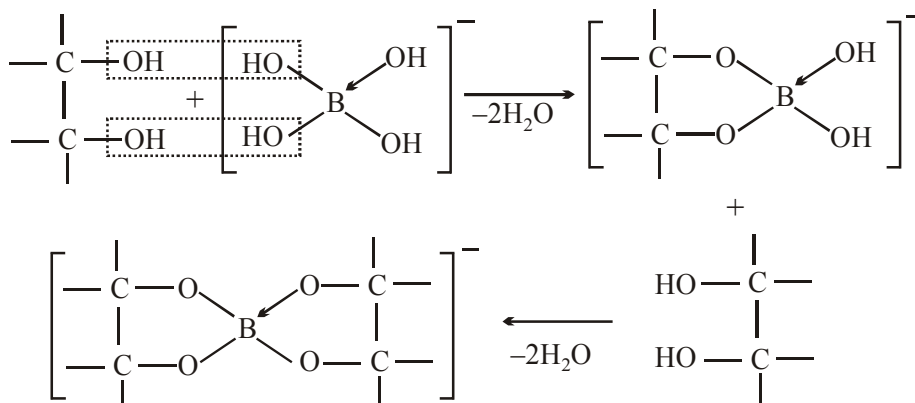
or



Since $\text{B}(\text{OH})_3$ only partially reacts with water to form H_3O^+ and $[\text{B}(\text{OH})_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $\text{B}(\text{OH})_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.

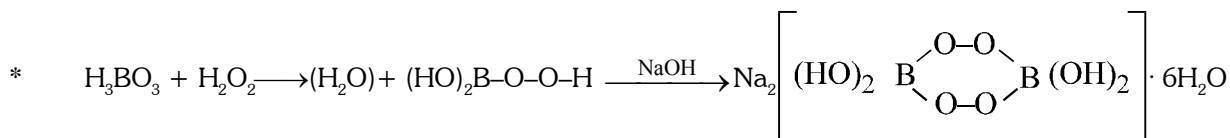
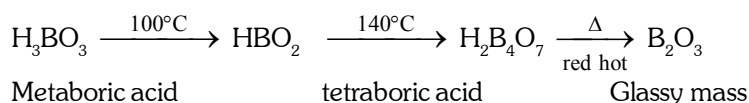


The added compound must be a diol to enhance the acidic properties in this way the cis-diol forms very stable complexes with $[\text{B}(\text{OH})_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3 .

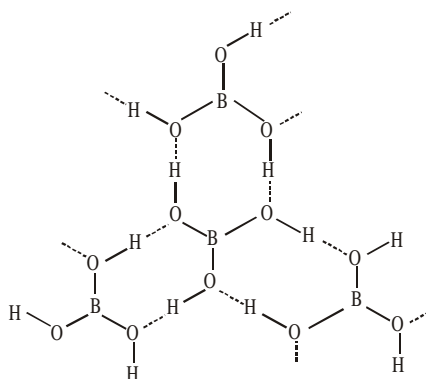
□ **Heating of boric acid :**



Sodium peroxy borate used in washing powder as brightner

STRUCTURE

It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in figure.



Structure of boric acid; the dotted lines represent hydrogen bonds

Uses of boric acid :

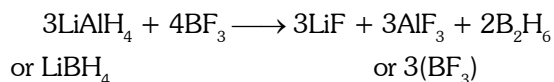
- (i) Boric acid is used in manufacturing of optical glasses
- (ii) With borax, it is used in the preparation of a buffer solution.

3.3 Diborane, B_2H_6

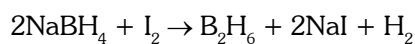
The simplest boron hydride known, is diborane.

Preparation :

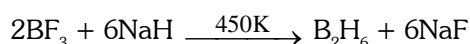
- (i) It is prepared by treating boron trifluoride with LiAlH_4 in diethyl ether.



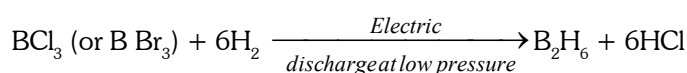
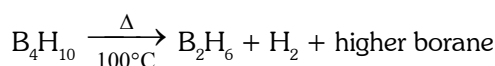
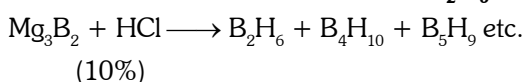
- (ii) **Laboratory** method : For the preparation of diborane involves the oxidation of sodium borohydride with iodine.



- (iii) **Industrial scale** : By the reaction of BF_3 with sodium hydride.

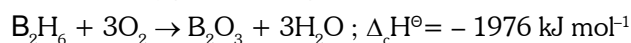


Other reaction of preparation of B_2H_6 :



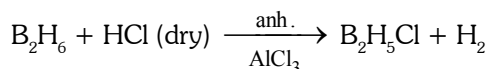
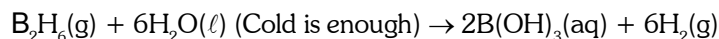
Properties :

- (i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.
 (ii) Diborane catches fire spontaneously upon exposure to air.
 (iii) It burns in oxygen releasing an enormous amount of energy.

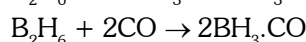
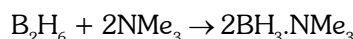


Most of the higher boranes are also spontaneously flammable in air.

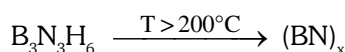
- (iv) Boranes are readily hydrolysed by water to give boric acid.



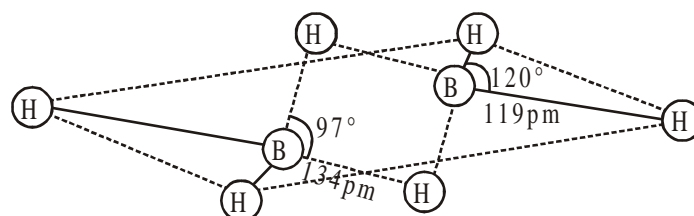
- (v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $\text{BH}_3 \cdot \text{L}$.



Reaction of ammonia with diborane gives initially $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which is formulated as $[\text{BH}_2(\text{NH}_3)_2]^+ [\text{BH}_4]^-$; further heating gives borazine, $\text{B}_3\text{N}_3\text{H}_6$ known as “inorganic benzene” in view of its ring structure with alternate BH and NH groups.

**Structure & bonding in diborane :**

The structure of diborane is shown in figure. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B–H bonds are regular two centre-two electron bonds while the two bridge (B–H–B) bonds are different and can be described in terms of three centre-two electron bonds shown in figure.



The structure of diborane, B_2H_6

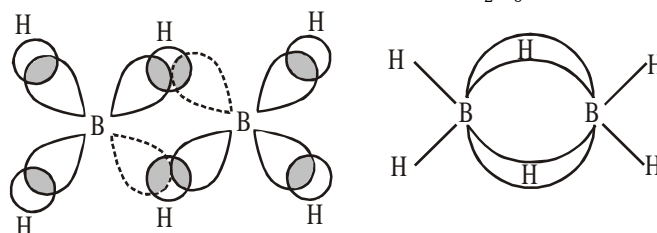
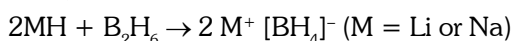


Figure: Bonding in diborane.

Each B atom uses sp^3 hybrid orbitals for bonding. Out of the four sp^3 hybrid orbital on each B atom, one is without an electron shown in broken lines. The terminal B–H bonds are normal 2-centre-2- electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

Note: Metal hydrido borates : Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[\text{BH}_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

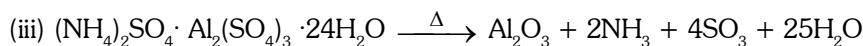
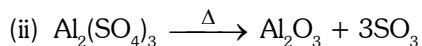
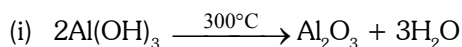


Both LiBH_4 and NaBH_4 are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

4.0 Compounds of Aluminium :

4.1 Al_2O_3

preparation :



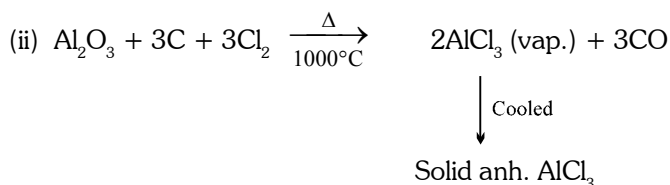
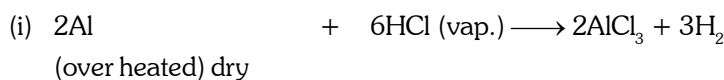
Uses: (i) In making refractory bricks

(ii) as an abrasive

(iii) To make high alumina cement

4.2 AlCl_3

preparation :

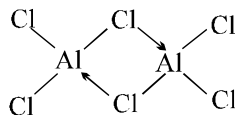


Properties :

(i) Its anhydrous form is deliquescent and fumes in air.

(ii) It sublimes at 180°C .

(iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alcohol, ether, benzene, where it is soluble in fair extent.



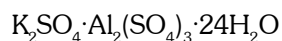
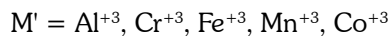
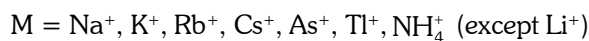
Uses: (i) Friedel-Craft reaction

(ii) Dyeing, drug & perfumes etc.

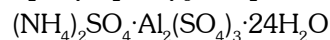
4.3 Alums : $\text{M}_2\text{SO}_4 \cdot \text{M}'_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Properties: Swelling characteristics

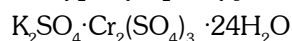
where



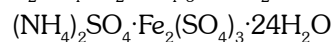
Potash alum



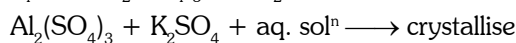
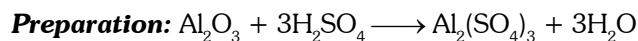
Ammonium alum



Chrome alum



Ferric alum



Uses: (i) Act as coagulant

(ii) Purification of water

(iii) Tanning of leather

(iv) Mordant in dyeing

(v) Antiseptic

5.0 USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

5.1 Boron :

- (i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.
- (ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- (iii) The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.
- (iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass.
- (v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.
- (vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

5.2 Aluminium :

- (i) Aluminium is a bright silvery-white metal, with high tensile strength.
- (ii) It has a high electrical and thermal conductivity.
- (iii) On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.
- (iv) Aluminium is used extensively in industry and every day life.
- (v) It forms alloys with Cu, Mn, Mg, Si and Zn.
- (vi) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.
- (vii) The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

BEGINNER'S BOX-1

1. Which of the following property does not support anomalous behaviour of boron ?
 (A) Small size (B) High electronegativity
 (C) High ionization energy (D) Formation of trihalides
2. Which species does not exist -
 (A) $[\text{BF}_6]^{-3}$ (B) $[\text{AlF}_6]^{-3}$ (C) $[\text{GaF}_6]^{-3}$ (D) $[\text{InF}_6]^{-3}$
3. Melting point is highest for -
 (A) B (B) Al (C) Ga (D) In
4. Which of the following oxides is acidic ?
 (A) B_2O_3 (B) Al_2O_3 (C) Ga_2O_3 (D) In_2O_3
5. BCl_3 does not exist as dimer but BH_3 exist as dimer (B_2H_6) because -
 (A) Chlorine is more electronegative than hydrogen
 (B) There is $\text{p}\pi\text{-p}\pi$ back bonding in BCl_3 but BH_3 does not contain such multiple bonding
 (C) Large sized chlorine atoms do not fit in between the small boron atoms whereas small sized hydrogen atoms get fitted in between boron atoms
 (D) None of the above
6. Boron does not form B^{3+} ions whereas Al forms Al^{3+} ions. This is because :
 (A) The size of B atom is smaller than that of Al
 (B) The sum of $\text{IE}_1 + \text{IE}_2 + \text{IE}_3$ of B is much higher than that of Al
 (C) The sum of $\text{IE}_1 + \text{IE}_2 + \text{IE}_3$ of Al is much higher than that of B
 (D) Both (A) and (B)

7. Borax on heating with cobalt oxide forms a blue bead of -
 (A) $\text{Co}(\text{BO}_2)_2$ (B) CoBO_2 (C) $\text{Co}_3(\text{BO}_3)_2$ (D) $\text{Na}_3\text{Co}(\text{BO}_3)_2$
8. $\text{BCl}_3 + \text{H}_2\text{O} \rightarrow \text{X}$
 The products formed in the above reaction are -
 (A) $\text{B}_2\text{O}_3 + \text{HOCl}$ (B) $\text{H}_3\text{BO}_3 + \text{HCl}$ (C) $\text{B}_2\text{H}_6 + \text{HCl}$ (D) No reaction
9. Which of the following statements regarding boric acid is false -
 (A) It acts as a tribasic acid (B) It has a planar structure
 (C) It acts as a monobasic acid (D) It is soluble in hot water
10. Boric acid is polymeric due to -
 (A) Its acidic nature (B) The presence of hydrogen bonds
 (C) Its monobasic nature (D) Its geometry
11. (a) $\text{Al} \xrightarrow{\text{N}_2} \text{A}$ (b) $\text{Al} \xrightarrow{\text{C}} \text{B}$
 Product A and B on hydrolysis yields respectively.
 (A) Ammonia and acetylene (B) Ammonia and methane
 (C) Nitric oxide and acetylene (D) None of these
12. Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is actually :-
 (A) $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (B) $\text{Na}_2[\text{B}_2\text{O}_4(\text{OH})_6] \cdot 7\text{H}_2\text{O}$
 (C) $\text{Na}_2[\text{B}_4\text{O}_3(\text{OH})_8] \cdot 6\text{H}_2\text{O}$ (D) $\text{Na}_2[\text{B}_4\text{O}_2(\text{OH})_{10}] \cdot 5\text{H}_2\text{O}$
13. By which of the following reactions is borazine prepared ?
 (A) $\text{B}_2\text{H}_6 + \text{NH}_3 \text{ (excess)} \xrightarrow{\text{Low temperature}}$ (B) $\text{B}_2\text{H}_6 + \text{NH}_3 \text{ (excess)} \xrightarrow{\text{High temperature}}$
 (C) $\text{B}_2\text{H}_6 + \text{NH}_3 \xrightarrow[\text{high temperature}]{\text{(ratio } 2\text{NH}_3 : 1\text{B}_2\text{H}_6)}$ (D) None of these
14. Boron has an extremely high melting point because of :
 (A) The strong vander Waals forces between its atoms
 (B) The strong binding forces in the covalent polymer
 (C) Its ionic crystal structure
 (D) Allotropy
15. When an inorganic compound (X) having 3c-2e as well as 2c-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z) :
 (A) (X) is B_2H_6 (B) (Z) is known as inorganic graphite
 (C) (Y) is $\text{B}_3\text{N}_3\text{H}_6$ (D) All of these

GROUP 14 ELEMENTS :

The carbon family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

1.0 Occurrence of element

- (i) **Carbon** : Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C . In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with half-life 5770 years and used for radiocarbon dating.
- (ii) **Silicon** : Silicon is the second (27.7 % by mass) most abundant element on the earth's crust and is present in nature in the form of silica and silicates. Silicon is a very important component of ceramics, glass and cement.
- (iii) **Germanium** : Germanium exists only in traces.
- (iv) **Tin** : Tin occurs mainly as cassiterite, SnO_2
- (v) **Lead** : Lead as galena, PbS .

Note : Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

1.1 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^2 . The inner core of the electronic configuration of elements in this group also differs.

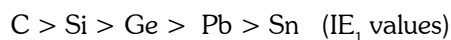
1.2 Covalent Radius

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.

Covalent radii : $\text{C} < \text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$

1.3 Ionization Enthalpy

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in $\Delta_i H$ from Si to Ge, Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.



1.4 Melting and Boiling Points

M.P. : $\text{C} > \text{Si} > \text{Ge} > \text{Pb} > \text{Sn}$

B.P. : $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$

1.5 Electronegativity

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

1.6 Physical Properties

All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

1.7 Chemical Properties

Oxidation states and trends in chemical reactivity

- (i) The group 14 elements have four electrons in outermost shell.
- (ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature.
- (iii) In heavier members the tendency to show +2 oxidation state increases in the sequence $\text{Ge} < \text{Sn} < \text{Pb}$. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.
- (iv) Carbon and silicon mostly show +4 oxidation state.

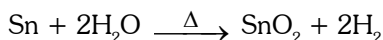
- (v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.
- (vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).
- (vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.
- (viii) In tetravalent state the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being *electron precise* molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of *d* orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, SiF_6^{2-} , $[\text{GeCl}_6]^{2-}$, $[\text{Sn}(\text{OH})_6]^{2-}$ exist where the hybridisation of the central atom is sp^3d^2 .

1.8 Reactivity towards oxygen

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e., monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states. The dioxides — CO_2 , SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

1.9 Reactivity towards water

Carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and dihydrogen gas.

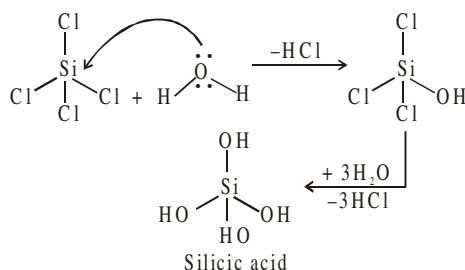


Lead is unaffected by water, probably because of a protective oxide film formation.

1.10 Reactivity towards halogen

- (i) These elements can form halides of formula MX_2 and MX_4 (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). Except carbon, all other members react directly with halogen under suitable condition to make halides.
- (ii) Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4 , which are ionic in nature.
- (iii) PbI_4 does not exist because Pb—I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom.
- (iv) Heavier members Ge to Pb are able to make halides of formula MX_2 .
- (v) Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2 , whereas PbX_2 is more than PbX_4 .
- (vi) Except CCl_4 , other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecule in *d* orbital.

Hydrolysis can be understood by taking the example of SiCl_4 . It undergoes hydrolysis by initially accepting lone pair of electrons from water molecule in *d* orbitals of Si , finally leading to the formation of $\text{Si}(\text{OH})_4$ as shown below :



1.11 IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy unavailability of d orbitals.

In carbon, only s and p orbitals are available for bonding and, therefore, it can accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals.

Carbon also has unique ability to form $p_{\pi} - p_{\pi}$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few examples of multiple bonding are: $C=C$, $C\equiv C$, $C=O$, $C=S$ and $C\equiv N$. Heavier elements do not form $p_{\pi} - p_{\pi}$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

1.12 Catenation Property

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called **catenation**. This is because $C-C$ bonds are very strong. Down the group the size increases and electronegativity decreases, and, thereby, tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is $C \gg Si > Ge \approx Sn$. Lead does not show catenation.

Bond	Bond enthalpy / kJ mol^{-1}
$C-C$	348
$Si-Si$	297
$Ge-Ge$	260
$Sn-Sn$	240

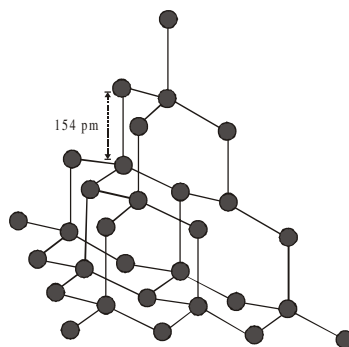
Due to property of catenation and $p_{\pi} - p_{\pi}$ bond formation, carbon is able to show allotropic forms.

2.0 ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985, third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E. Smalley and R.F. Curl. For this discovery they were awarded the Nobel Prize in 1996.

□ Diamond

- It has a crystalline lattice.
- In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.
- The $C-C$ bond length is 154 pm.
- The structure extends in space and produces a rigid three-dimensional network of carbon atoms. In this



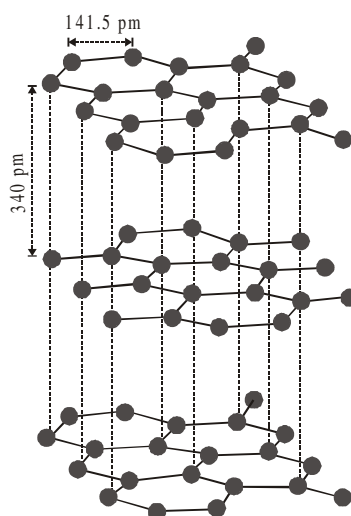
The structure of diamond

structure figure directional covalent bonds are present throughout the lattice. It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

Use : It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

2.1 Graphite

- (i) Graphite has layered structure figure.
- (ii) Layers are held by van der Waals forces and distance between two layers is 340 pm.
- (iii) Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.
- (iv) Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet.



The structure of graphite

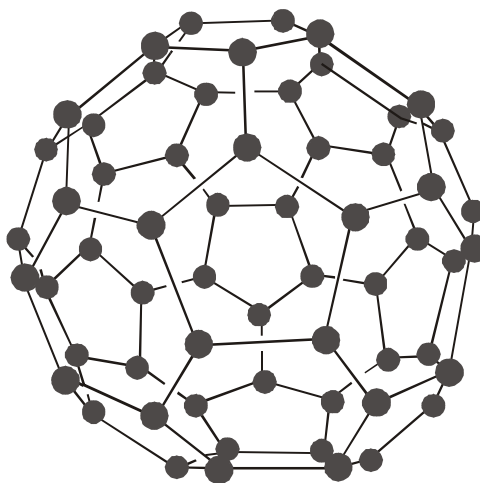
- (v) Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

2.2 Fullerenes

- (i) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called

Buckminsterfullerene.

- (ii) It contains twenty six- membered rings and twelve five membered rings.
- (iii) A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- (iv) All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule.
- (v) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C—C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.



The structure of C_{60} , Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).

Note: It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^\circ$ of graphite is taken as zero. $\Delta_f H^\circ$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol⁻¹, respectively.

Note: Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes. Carbon black is obtained by burning hydrocarbons in a limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

2.3 Uses of Carbon

- Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.
- Crucibles made from graphite are inert to dilute acids and alkalis.
- Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminants and in airconditioning system to control odour.
- Carbon black is used as black pigment in black ink and as filler in automobile tyres.
- Coke is used as a fuel and largely as a reducing agent in metallurgy.
- Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

3.0 SOME IMPORTANT COMPOUNDS OF CARBON

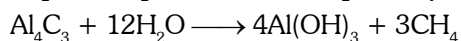
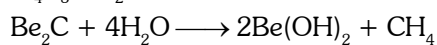
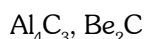
3.1 Types of Carbide

- Ionic and salt like:

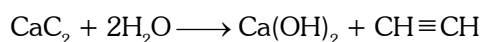
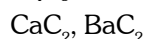
Classification on basis of
no. of carbon atoms
present in hydrocarbon
found on their hydrolysis

- | | |
|---|----------------|
| { | (a) C_1 unit |
| | (b) C_2 unit |
| | (c) C_3 unit |

C_1 unit:



C_2 unit:



C_3 unit:



(ii) Covalent carbide : SiC & B₄C

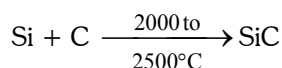
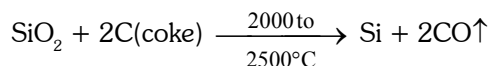
(iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metallic lustre and electrical conductivity. (∵ no chemical bond is present, no change in property)

SiC (Carborundum)

❑ **Preparation**



Note :

- (i) SiC has diamond like or wurtzite structure
- (ii) SiC is often dark purple, black or dark green due to traces of Fe and other impurities but pure sample are pale yellow to colourless.

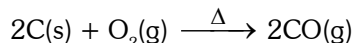
Properties

- (i) It is very hard and is used in cutting tools and abrasive powder (polishing material)
- (ii) It is very much inert
- (iii) It is not being affected by any acid except H₃PO₄

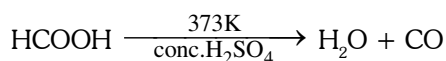
3.2 Carbon Monoxide

Preparation :

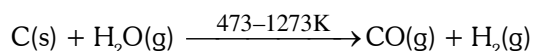
- (i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.



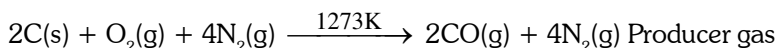
- (ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated H₂SO₄ at 373 K



- (iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H₂ thus produced is known as **water gas** or **synthesis gas**.

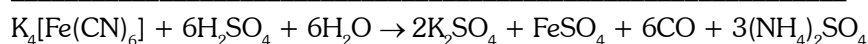
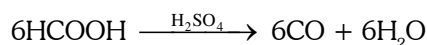
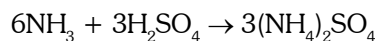
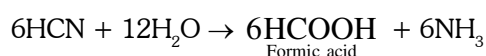
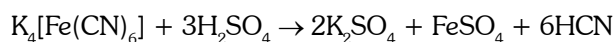


When air is used instead of steam, a mixture of CO and N₂ is produced, which is called **producer gas**.



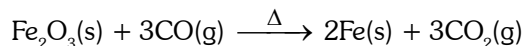
Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

- (iv) **By heating potassium ferrocyanide with conc. H₂SO₄** : When potassium ferrocyanide in powdered state is heated with concentrated H₂SO₄, CO is evolved. Dilute H₂SO₄ should never be used because it shall evolve highly poisonous gas HCN.

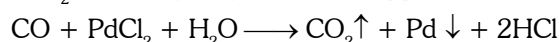


Properties :

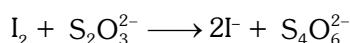
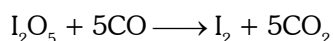
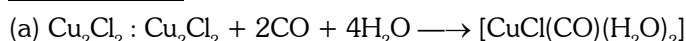
- (i) Carbon monoxide is a colourless, odourless and almost water insoluble gas.
- (ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.

**DETECTION**

- (a) burns with blue flame
- (b) CO is passed through PdCl_2 solution giving rise to black ppt.



Black metallic
deposition

ESTIMATION**ABSORBERS**

❑ **Bonding in CO mole**

In CO molecule, there are one sigma and two π bonds between carbon and oxygen. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

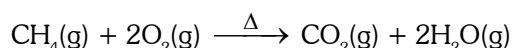
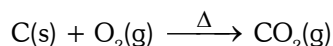
❑ **Poisonous nature of CO**

The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

❑ **Carbon Dioxide**

Preparation :

- (i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.



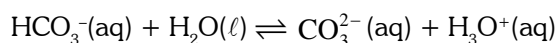
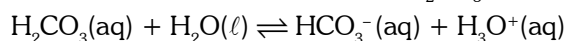
- (ii) **Laboratory** by the action of dilute HCl on calcium carbonate.



- (iii) Commercial scale by heating limestone.

Properties :

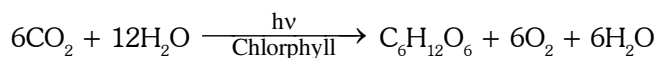
- (i) It is a colourless and odourless gas.
- (ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.
- (iii) With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:



$\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Use of CO₂

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO₂ into carbohydrates such as glucose. The overall chemical change can be expressed as:

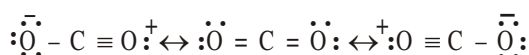


By this process plants make food for themselves as well as for animals and human beings.

Harmful effect of CO₂

Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO₂ content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

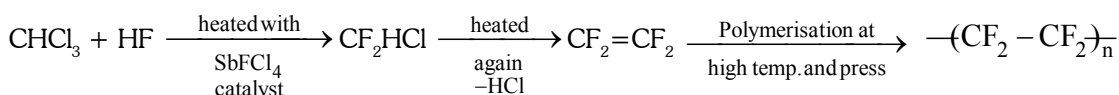
- Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO₂ to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.
- Gaseous CO₂ is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher.
- A substantial amount of CO₂ is used to manufacture urea. In CO₂ molecule carbon atom undergoes *sp* hybridisation. Two *sp* hybridised orbitals of carbon atom overlap with two *p* orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in *p_π-p_π* bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonating structures of carbon dioxide

Note : Carbongene has 95% O₂ and 5% CO₂ and is used as an antidote for poisoning of CO.

□ **Teflon** —(CF₂ — CF₂)_n



□ **Purpose**

Temperature with standing capacity upto 300°C (1st organic compound withstand this kind of high temperature)

4.0 SILICON (Si)

4.1 Occurrence

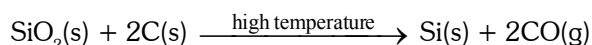
Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

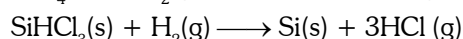
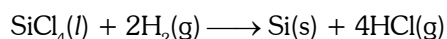
- Feldspar — K₂O. Al₂O₃. 6SiO₂
- Kaolinite — Al₂O₃. 2SiO₂. 2H₂O
- Asbestos — CaO. 3MgO. 4SiO₂

Preparation

- From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO₂) with high purity coke in an electric furnace.



- From silicon tetrachloride (SiCl₄) or silicon chloroform (SiHCl₃) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.



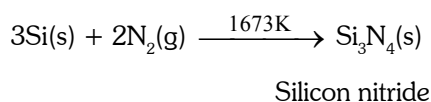
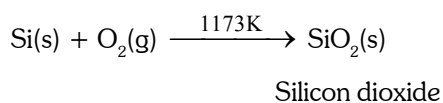
4.2 Physical Properties :

- (i) Elemental silicon is very hard having diamond like structure.
- (ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.
- (iii) Silicon exists in three isotopes, i.e. $^{28}_{14}\text{Si}$, $^{29}_{14}\text{Si}$ and $^{30}_{14}\text{Si}$ but $^{28}_{14}\text{Si}$ is the most common isotope.

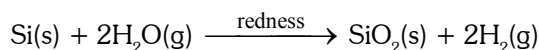
4.3 Chemical Properties :

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

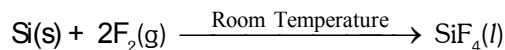
- (i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.



- (ii) **Action of steam :** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

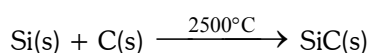


- (iii) **Reaction with halogens:** It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).



However, with other halogens, it combines at high temperatures forming tetrahalides.

- (iv) **Reaction with carbon :** Silicon combines with carbon at 2500 °C forming silicon carbide (SiC) known as carborundum.



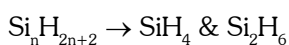
Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

Uses :

- (i) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.
- (ii) High purity silicon is used as semiconductors in electronic devices such as transistors.
- (iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

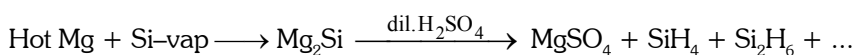
5.0 Compounds of Silicon :

5.1 Silane :



Only these two are found

Higher molecules are not formed. \therefore Si can't show catenation property

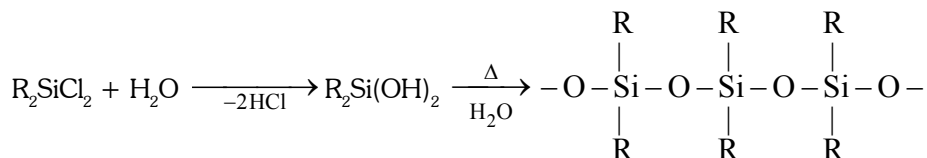


5.2 Silicones

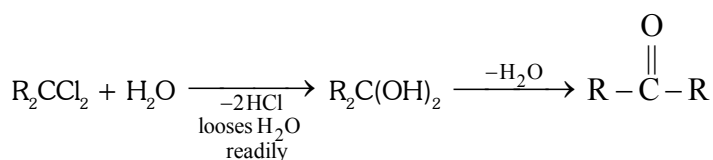
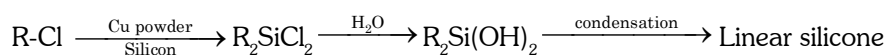
It is an organosilicon polymer

TYPES OF SILICONES :

(i) Linear silicones



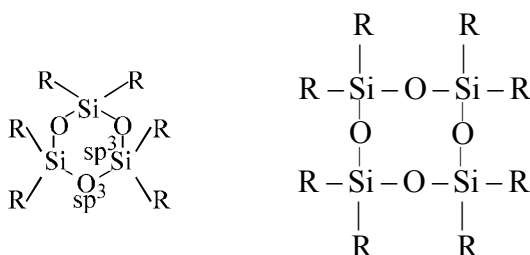
Linear silicone



(ii) Cyclic silicones

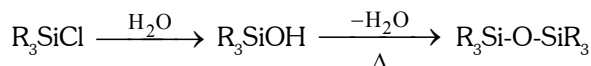
Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring.

Alcohol analogue of silicon is known as silanol



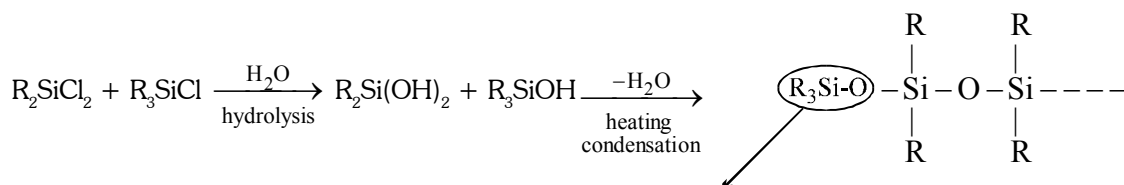
cyclic silicone not planar

(iii) Dimer silicones



Silanol

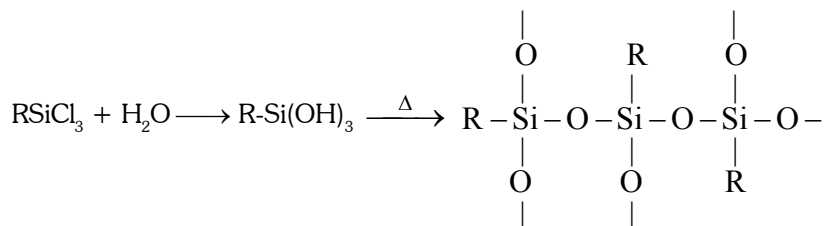
Note



This end of the chain can't be extended hence

R_3SiCl is called as chain stopping unit

* Using R_3SiCl in a certain proportion we can control the chain length of the polymer

(iv) Crossed linked silicones**cross linked silicone****3 dimensional network**

It provides the crosslinking among the chain making the polymer more hard and hence controlling the proportion of RSiCl_3 we can control the hardness of polymer.

Uses

- (1) It can be used as electrical insulator (due to inertness of Si-O-Si bonds)
- (2) It is used as water repellant (\because surface is covered) eg. car polish, shoe polish, masonry works in buildings
- (3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.
- (4) As a lubricant in the gear boxes and light weight machinery

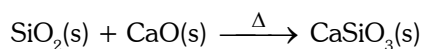
5.3 SILICA (SiO_2)**Occurrence :**

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar : $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, Kaolinite : $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ etc.

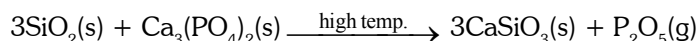
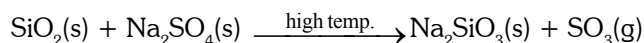
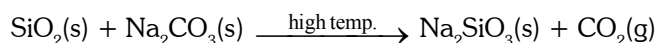
Properties :

- (i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.
- (ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$\text{SiO}_2(\text{s}) + 4\text{HF}(\text{l}) \longrightarrow \text{SiF}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$$
- (iii) It also combines with metallic oxides at high temperature giving silicates e.g.



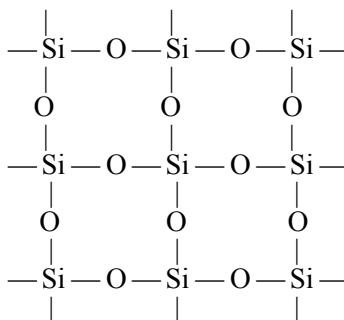
- (iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.



The first two examples quoted here are important in glass making.

□ Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is sp^3 -hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



Uses :

- Sand is used in large quantities to make mortar and cement.
- Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.
- Powdered quartz is used for making silica bricks.
- Silica gel ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

Quartz

Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

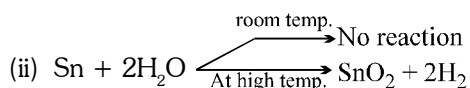
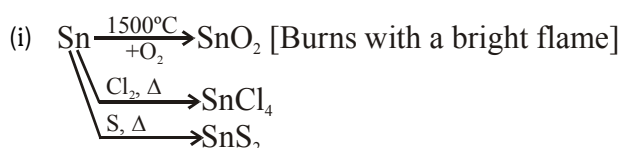
5.4 Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. Two important man-made silicates are glass and cement.

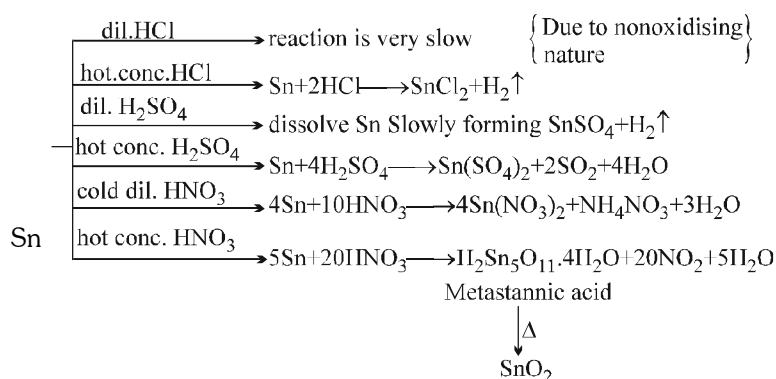
Zeolites

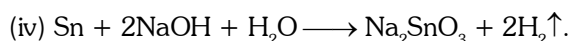
If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na^+ , K^+ or Ca^{2+} balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of “hard” water.

6.0 TIN & ITS COMPOUND



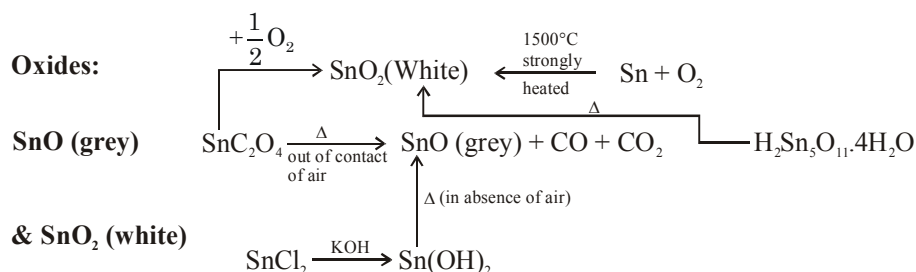
(iii) Reaction with acid.



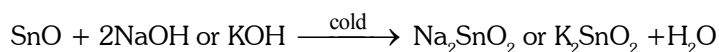
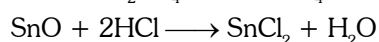
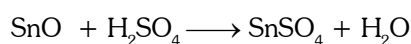


or

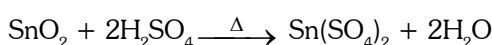
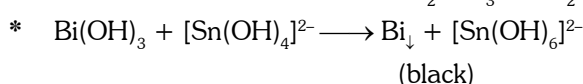
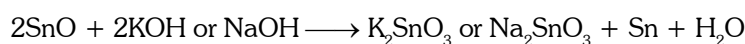
KOH [In absence of air K_2SnO_2 forms and in contact with air it readily converts into K_2SnO_3]



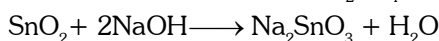
Both are amphoteric in nature :



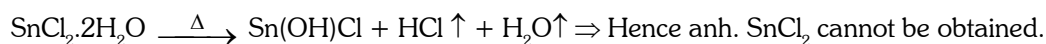
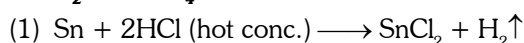
But conc. hot alkali behaves differently.



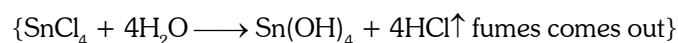
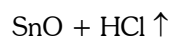
(Soluble only in hot conc. H_2SO_4)



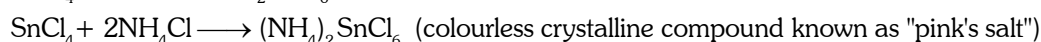
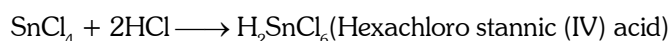
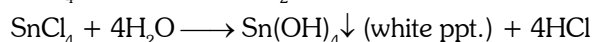
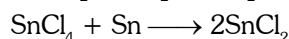
SnCl_2 & SnCl_4 :



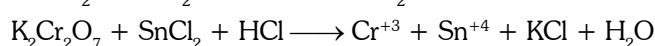
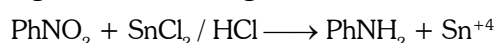
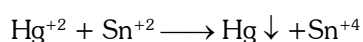
↓



(2) A piece of Sn is always added to preserve a solution of SnCl_2 . Explain.

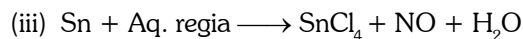
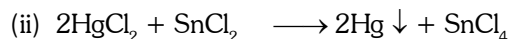
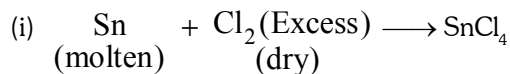


(4) Reducing Properties of SnCl_2 :



(5) Readily combines with $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$ This reaction is used to estimate tin.

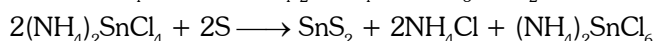
Formation of $SnCl_4$:



* $SnCl_4 \cdot 5H_2O$ is known as butter of tin \Rightarrow used as mordant.

$(NH_4)_2 SnCl_6$ is known as 'pink's salt' \Rightarrow used in calico printing.

Mosaic gold : SnS_2 yellow crystalline substance :



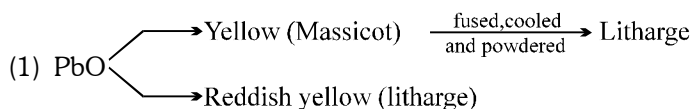
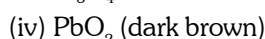
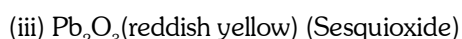
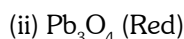
Note : Mosaic gold used for filling purpose (in joining gold pieces)

* **Distinction of Sn^{+2} / Sn^{+4} :**

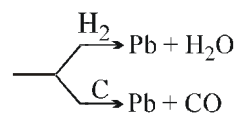
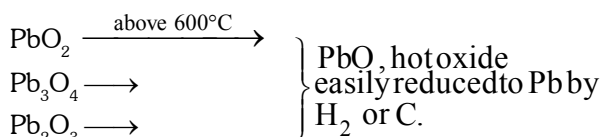


7.0 COMPOUNDS OF LEAD

Oxides of lead :



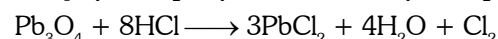
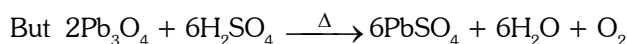
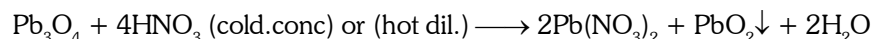
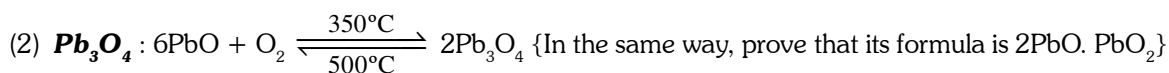
Laboratory Prepⁿ. :



Preparation of Pb_2O_3 :

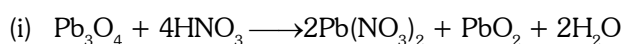


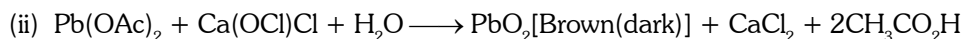
This reaction suggests that Pb_2O_3 contains PbO_2 .



(3) **PbO_2** : Insoluble in water :

HNO_3 , But reacts with HCl and H_2SO_4 (hot conc.) but does not react with HNO_3 and soluble in hot $NaOH$ / KOH .





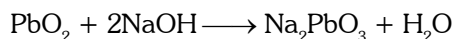
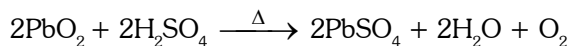
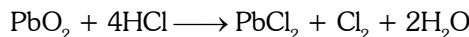
↓

Excess bleaching powder

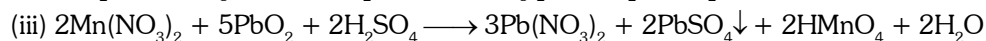
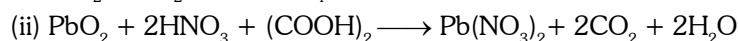
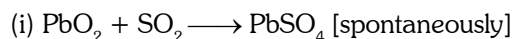
is being removed by stirring with

HNO_3

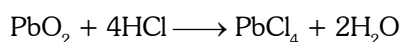
Reaction :



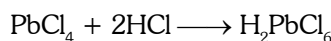
PbO₂ : Powerful oxidising agent :



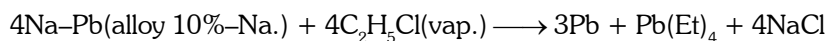
PbCl₄ : Exists as $\text{H}_2[\text{PbCl}_6]$



{ice cold conc. saturated with Cl_2 }



TetraEthyl lead :



It is antiknocking agent.

BEGINNER'S BOX-2

1. Which element-element bond has the highest bond dissociation energy ?
 (A) C-C (B) Si-Si (C) Ge-Ge (D) Sn-Sn
2. Silicones have the general formula
 (A) SiO_4^{4-} (B) $\text{Si}_2\text{O}_7^{6-}$ (C) $(\text{R}_2\text{SiO})_n$ (D) $(\text{SiO}_3)_n^{2-}$
3. Solid carbon dioxide is used as :
 (A) Poison (B) Fire extinguisher (C) Refrigerant (D) Artificial respirant
4. Which of the following statements is correct :
 (A) Aluminium carbide as well as beryllium carbide produce methane gas on treatment with water
 (B) On reacting with water, calcium carbide (CaC_2) produces acetylene while magnesium carbide (Mg_2C_3) gives propyne
 (C) Both of these
 (D) None of these
5. Which does not exist :
 (A) $[\text{CCl}_6]^{2-}$ (B) $[\text{SiF}_6]^{2-}$ (C) $[\text{GeF}_6]^{2-}$ (D) $[\text{SnCl}_6]^{2-}$
6. Ge (II) compounds are powerful reducing agents whereas Pb(IV) compounds are strong oxidants. It can be due to
 (A) Pb is more electropositive than Ge
 (B) Ionization potential of lead is less than that of Ge
 (C) Ionic radii of Pb^{2+} and Pb^{4+} are larger than those of Ge^{2+} and Ge^{4+}
 (D) More pronounced inert pair effect in lead than in Ge

7. Carbon differs from the rest of the family members because of -
 (A) Number of unpaired electrons in valence shell
 (B) Low ionization
 (C) Non-availability of vacant orbitals in valence shell
 (D) Non-availability of d-orbitals in valence shell
8. In silicon dioxide :
 (A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (C) Silicon atom is bonded to two oxygen atoms
 (D) There are double bonds between silicon and oxygen atoms
9. SiCl_4 is easily hydrolysed by water whereas CCl_4 is stable towards hydrolysis in water because:
 (A) CCl_4 exists as a molecule whereas SiCl_4 is ionic
 (B) The C-Cl bond is stronger than the Si-Cl bond
 (C) Silicon has vacant 3d orbital available for further co-ordination with water whereas carbon has no d orbital for bonding
 (D) Silicon is more electropositive than carbon
10. Carbon shows strong catenation while silicon shows little or no catenation because :
 (A) Silicon is a metalloid and carbon is a nonmetal
 (B) Silicon forms ionic compounds whereas carbon forms covalent compounds
 (C) The Si-Si bond is stronger than the C-C bond
 (D) The C-C bond is stronger than the Si-Si bond
11. The thermal stability order for gp. 14 tetra halides is:
 (A) $\text{CX}_4 > \text{SiX}_4 > \text{GeX}_4 > \text{SnX}_4$
 (B) $\text{SnX}_4 > \text{GeX}_4 > \text{SiX}_4 > \text{CX}_4$
 (C) $\text{SiX}_4 > \text{CX}_4 > \text{GeX}_4 > \text{SnX}_4$
 (D) None of these
12. Which of the following is more stable :
 (A) Pb^{4+} (B) Sn^{4+} (C) Ge^{4+} (D) Si^{4+}
13. Least stable hydride is:
 (A) Methane (B) Plumbane (C) Silane (D) Stibine
14. When CO is heated with NaOH under pressure, we get :
 (A) Sodium benzoate (B) Sodium acetate (C) Sodium formate (D) Sodium oxalate
15. The species present in solution when CO_2 is dissolved in water are
 (A) $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$
 (B) $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
 (C) $\text{CO}_3^{2-}, \text{HCO}_3^-$
 (D) $\text{CO}_2, \text{H}_2\text{CO}_3$

ANSWERS

BEGINNER'S BOX-1

1. (D) 2. (A) 3. (A) 4. (A) 5. (C) 6. (D) 7. (A) 8. (D)
 9. (A) 10. (B) 11. (B) 12. (A) 13. (C) 14. (B) 15. (D)

BEGINNER'S BOX-2

1. (A) 2. (C) 3. (C) 4. (C) 5. (A) 6. (D) 7. (D) 8. (A)
 9. (C) 10. (D) 11. (A) 12. (D) 13. (B) 14. (C) 15. (A)

EXERCISE - 1**MCQ (SINGLE CHOICE CORRECT)**

- An inorganic compound (A) made of two most occurring elements into the earth crust, having a polymeric tetrahedral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be
 (A) $\text{SiO}_2, \text{CO}_2$ (B) SiO_2, CO (C) SiC, CO (D) SiO_2, N_2
- $\text{H}_3\text{BO}_3 \xrightarrow{\text{T}_1} \text{X} \xrightarrow{\text{T}_2} \text{Y} \xrightarrow{\text{redhot}} \text{B}_2\text{O}_3$
 if $\text{T}_1 < \text{T}_2$ then X and Y respectively are
 (A) X = Metaboric acid and Y = Tetraboric acid
 (B) X = Tetraboric acid and Y = Metaboric acid (C) X = Borax and Y = Metaboric acid
 (D) X = Tetraboric acid and Y = Borax
- $\text{B(OH)}_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na[B(OH)}_4] + \text{H}_2\text{O}$
 How can this reaction is made to proceed in forward direction?
 (A) addition of cis 1,2 diol (B) addition of borax
 (C) addition of trans 1,2 diol (D) addition of Na_2HPO_4
- An aqueous solution of borax is
 (A) Neutral (B) Amphoteric (C) Basic (D) Acidic
- Boric acid is polymeric due to
 (A) Its acidic nature (B) The presence of hydrogen bonds
 (C) Its monobasic nature (D) Its geometry
- The type of hybridisation of boron in diborane is
 (A) sp (B) sp^2 (C) sp^3 (D) dsp^2
- Thermodynamically the most stable form of carbon is
 (A) Diamond (B) Graphite (C) Fullerenes (D) Coal
- Elements of group 14
 (A) Exhibit oxidation state of +4 only (B) Exhibit oxidation state of +2 and +4 only
 (C) Form M^{2-} and M^{4+} ions (D) Form M^{2+} and M^{4+} ions
- $\text{RCl} \xrightarrow[\text{Si}]{\text{Cu-powder}} \text{R}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{R}_2\text{Si(OH)}_2 \xrightarrow{\text{condensation}} \text{A}$
 Compound (A) is
 (A) a linear silicone (B) a chlorosilane (C) a linear silane (D) a network silane
- Which of the following halides is least stable and has doubtful existence ?
 (A) CCl_4 (B) GeI_4 (C) SnI_4 (D) PbI_4

11. Column-I

- (P) Dry ice
 (Q) Carbongene
 (R) Carborundum
 (S) Teflon

Code :

	P	Q	R	S
(A)	4	1	3	2

Column-II

- (1) Used as antidote for CO-poisoning
 (2) Used as nonstick coating
 (3) Used as refrigerant
 (4) Used as abrasive

	P	Q	R	S
(B)	4	2	1	3

EXERCISE – 2
MCQ (ONE OR MORE CHOICE CORRECT)

- Which of the following statements is/are correct regarding B_2H_6 ?
 (A) banana bonds are longer but stronger than normal B–H bonds
 (B) B_2H_6 is also known as 3c–2e compound
 (C) the hybrid state of B in B_2H_6 is sp^3 while that of sp^2 in BH_3
 (D) it cannot be prepared by reacting BF_3 with $LiBH_4$ in the presence of dry ether
- When an inorganic compound (X) having 3c–2e as well as 2c–2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a slippery substance (Z). Then
 (A) (X) is B_2H_6 (B) (Z) is known as inorganic graphite
 (C) (Z) having structure similar to graphite (D) (Z) having structure similar to (X)
- Boric acid
 (A) exists in polymeric form due to inter-molecular hydrogen bonding.
 (B) is used in manufacturing of optical glasses.
 (C) is a tri-basic acid
 (D) with borax, it is used in the preparation of a buffer solution.
- The correct statement(s) related to allotropes of carbon is/are
 (A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon (sp^2)
 (B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of C(sp^3)
 (C) fullerene (C_{60}) is recently discovered non-crystalline allotrope of carbon having a football-like structure.
 (D) Vander Waal's force of attraction acts between the layers of graphite 6.14 Å away from each other
- $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$, then
 (A) X is a white coloured compound (B) X is insoluble in excess of NH_4OH
 (C) X is soluble in NaOH (D) X cannot be used as an antacid
- Select correct statement(s):
 (A) Borax is used as a buffer
 (B) 1 M borax solution reacts with equal volumes of 2 M HCl solution
 (C) Titration of borax can be made using methyl orange as the indicator
 (D) Coloured bead obtained in borax-bead test contains metaborate
- Which of the following is / are correct for group 14 elements?
 (A) The stability of dihalides are in the order $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$
 (B) The ability to form $p\pi-p\pi$ multiple bonds among themselves increases down the group
 (C) The tendency for catenation decreases down the group
 (D) They all form oxides with the formula MO_2 .
- Zeolite is used in which of the following cases :
 (A) Conversion of alcohols into gasoline (B) Cracking of hydrocarbon
 (C) Isomerisation of hydrocarbons (D) Softening of hard water
- Which of the following oxides are mixed oxide ?
 (A) PbO_2 (B) SnO_2 (C) Pb_2O_3 (D) Pb_3O_4

10. Which of the following oxide(s) gives brown ppt on reaction with conc. HNO_3 :
 (A) PbO (B) SnO (C) Pb_2O_3 (D) Pb_3O_4
11. $\text{Ca}_2\text{B}_6\text{O}_{11} + \text{Na}_2\text{CO}_3 \xrightarrow{\Delta} [\text{X}] + \text{CaCO}_3 + \text{NaBO}_2$ (Unbalanced equation)
 Correct statement for [X]
 (A) Structure of anion of crystalline (X) has one boron atom sp^3 hybridised and other three boron atoms sp^2 hybridised
 (B) (X) with NaOH(aq.) gives a compound which on reaction with H_2O_2 in alkaline medium yields a compound used as brightner in soaps
 (C) Hydrolysis of (X) with HCl or H_2SO_4 yields a compound which on reaction with HF gives fluoroboric acid
 (D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead
12. (A) + $2\text{C} \xrightarrow[2500^\circ\text{C}]{2000^\circ\text{C}}$ (B) + $2\text{CO} \uparrow$
 (B) + Carbon $\xrightarrow[2500^\circ\text{C}]{2000^\circ\text{C}}$ (C)
 If A is an example of 3-d silicate then select the correct statements about (C)
 (A) Central atom of C is sp^3 hybridised
 (B) (C) is non planar and all atoms are sp^3 hybridised
 (C) (C) has diamond like structure, and it is coloured when impurity is present but pale yellow to colourless solid at room temperature
 (D) (C) is silicon carbide (SiC) and it is not being affected by any acid except H_3PO_4

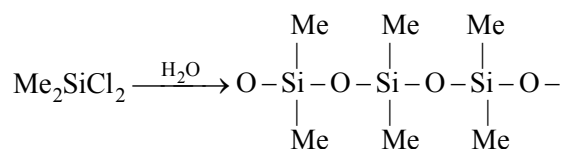
Paragraph for Question No. 13 & 14

Read the following write-ups and answer the questions at the end of it.

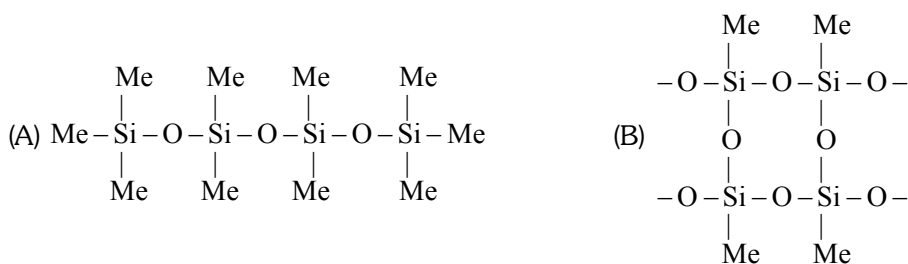
Silicons are synthetic polymers containing repeated R_2SiO units. Since, the empirical formula is that of a ketone (R_2CO), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

R_2SiCl_2 [R=methyl (Me) or phenyl (ϕ)]



13. If we mix Me_3SiCl with Me_2SiCl_2 , we get silicones of the type:



(C) both of the above

(D) none of the above

14. If we start with MeSiCl_3 as the starting material, silicones formed is:

- (A) $\begin{array}{ccccccc} & \text{Me} & & \text{Me} & & \text{Me} & & \text{Me} \\ & | & & | & & | & & | \\ \text{Me} & -\text{Si} & -\text{O} & -\text{Si} & -\text{O} & -\text{Si} & -\text{O} & -\text{Si} & -\text{Me} \\ & | & & | & & | & & | \\ & \text{Me} & & \text{Me} & & \text{Me} & & \text{Me} \end{array}$
- (B) $\begin{array}{c} \text{Me} \quad \text{Me} \\ | \quad | \\ -\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ -\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}- \\ | \quad | \\ \text{Me} \quad \text{Me} \end{array}$
- (C) Both of the above
- (D) None of the above

EXERCISE - 3**SUBJECTIVE**

1. Compounds X on reduction with LiAlH_4 gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y.
2. Starting from SiCl_4 , prepare the following in steps not exceeding the number given in parenthesis (reactions only)
 - (i) Silicon (1)
 - (ii) Linear silicon containing methyl group only (4)
 - (iii) Na_2SiO_3 (3)

EXERCISE - 4
RECAP OF AIEEE/JEE (MAIN)

- Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite: **[AIEEE-2003]**
 (A) Has molecules of variable molecular masses like polymers
 (B) Has carbon atoms arranged in large plated of rings of strongly bonded carbon atoms with weak interplate bonds
 (C) Is a non crystalline substance
 (D) Is an allotropic form of diamond
- Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- **[AIEEE-2004]**
 (A) $\text{Al}^{3+} + 3\text{Cl}^-$ (B) $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{Cl}^-$ (C) $[\text{Al}(\text{OH})_6]^{3-} + 3\text{HCl}$ (D) $\text{Al}_2\text{O}_3 + 6\text{HCl}$
- The soldiers of Napoleon army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder. This transformation is related to:- **[AIEEE-2004]**
 (A) An interaction with water vapour contained in humid air
 (B) A change in crystalline structure of tin
 (C) A change in the partial pressure of O_2 in air
 (D) An interaction with N_2 of air at low temperature
- Heating an aqueous solution of aluminium chloride to dryness will give :- **[AIEEE-2005]**
 (A) AlCl_3 (B) Al_2Cl_6 (C) Al_2O_3 (D) $\text{Al}(\text{OH})\text{Cl}_2$
- Which one of the following is the correct statement **[AIEEE-2005]**
 (A) Boric acid is a protonic acid
 (B) Beryllium exhibits coordination number of six
 (C) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
 (D) $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ is known as "inorganic benzene"
- In silicon dioxide : **[AIEEE-2005]**
 (A) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (B) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
 (C) Silicon atom is bonded to two oxygen atoms
 (D) There are double bonds between silicon and oxygen atoms
- The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: **[AIEEE-2007]**
 (A) $\text{GeX}_2 \ll \text{SiX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$ (B) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{PbX}_2 \ll \text{SnX}_2$
 (C) $\text{SiX}_2 \ll \text{GeX}_2 \ll \text{SnX}_2 \ll \text{PbX}_2$ (D) $\text{PbX}_2 \ll \text{SnX}_2 \ll \text{GeX}_2 \ll \text{SiX}_2$
- Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is **[AIEEE-2008]**
 (A) R_4Si (B) RSiCl_3 (C) R_2SiCl_2 (D) R_3SiCl

9. Boron cannot form which one of the following anions ? [AIEEE-2011]
 (A) $\text{B}(\text{OH})_4^-$ (B) BO_2^- (C) BF_6^{3-} (D) BH_4^-
10. In view of the signs of $\Delta_r G^\circ$ for the following reactions
 $\text{PbO}_2 + \text{Pb} \rightarrow 2 \text{PbO}$, $\Delta_r G^\circ < 0$
 $\text{SnO}_2 + \text{Sn} \rightarrow 2 \text{SnO}$, $\Delta_r G^\circ > 0$,
 Which oxidation states are more characteristic for lead and tin ? [AIEEE-2011]
 (A) For lead + 4, for tin + 2 (B) For lead + 2, for tin + 2
 (C) For lead + 4, for tin + 4 (D) For lead + 2, for tin + 4
11. The formation of molecular complex $\text{BF}_3 - \text{NH}_3$ results in a change in hybridisation of boron :- [JEE MAIN-2012]
 (A) from sp^3 to sp^3d (B) from sp^2 to dsp^2
 (C) from sp^3 to sp^2 (D) from sp^2 to sp^3
12. The catenation tendency of C, Si and Ge is in the order $\text{Ge} < \text{Si} < \text{C}$. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively : [JEE MAIN-2013]
 (A) 348, 260, 297 (B) 348, 297, 260 (C) 297, 348, 260 (D) 260, 297, 348
13. The gas evolved on heating CaF_2 and SiO_2 with concentrated H_2SO_4 , on hydrolysis gives a white gelatinous precipitate. The precipitate is: [JEE MAIN-2014]
 (A) silica gel (B) silicic acid
 (C) hydrofluosilicic acid (D) calciumfluorosilicate
14. In the following sets of reactants which two sets best exhibit the amphoteric character of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$? [JEE MAIN-2014]
Set-1 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{OH}^- (\text{aq})$
Set-2 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O} (\ell)$
Set-3 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{H}^+ (\text{aq})$
Set-4 : $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{NH}_3 (\text{aq})$
 (A) 1 and 2 (B) 2 and 4 (C) 1 and 3 (D) 3 and 4
15. The one that is extensively used as a piezoelectric material is : [JEE-MAIN-2019]
 (A) Quartz (B) Amorphous silica (C) Mica (D) Tridymite
16. Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to : [JEE-MAIN-2019]
 (A) lanthanoid contraction (B) lattice effect
 (C) diagonal relationship (D) inert pair effect
17. Correct statements among a to d regarding silicones are : [JEE-MAIN-2019]
 (a) They are polymers with hydrophobic character
 (b) They are biocompatible.
 (c) In general, they have high thermal stability and low dielectric strength.
 (d) Usually, they are resistant to oxidation and used as greases.
 (A) (a), (b) and (c) only (B) (a), and (b) only

- (C) (a), (b), (c) and (d) (D) (a), (b) and (d) only
- 18.** The electronegativity of aluminium is similar to : [JEE-MAIN-2019]
 (A) Boron (B) Carbon (C) Lithium (D) Beryllium
- 19.** The element that does NOT show catenation is [JEE-MAIN-2019]
 (A) Sn (B) Ge (C) Si (D) Pb
- 20.** The chloride that CANNOT get hydrolysed is : [JEE-MAIN-2019]
 (A) SiCl_4 (B) SnCl_4 (C) PbCl_4 (D) CCl_4
- 21.** Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively: [JEE-MAIN-2019]
 (A) HBO_2 and H_3BO_3 (B) H_3BO_3 and B_2O_3 (C) B_2O_3 and H_3BO_3 (D) B_2O_3 and $[\text{BH}_4]^-$
- 22.** C_{60} , an allotrope of carbon contains : [JEE-MAIN-2019]
 (A) 20 hexagons and 12 pentagons. (B) 12 hexagons and 20 pentagons.
 (C) 18 hexagons and 14 pentagons. (D) 16 hexagons and 16 pentagons
- 23.** The amorphous form of silica is : [JEE-MAIN-2019]
 (A) quartz (B) kieselguhr (C) cristobalite (D) tridymite
- 24.** The correct statements among I to III regarding group 13 element oxides are, [JEE-MAIN-2019]
 (I) Boron trioxide is acidic.
 (II) Oxides of aluminium and gallium are amphoteric.
 (III) Oxides of indium and thallium are basic.
 (A) (I), (II) and (III) (B) (II) and (III) only (C) (I) and (III) only (D) (I) and (II) only
- 25.** The correct order of catenation is : [JEE-MAIN-2019]
 (A) $\text{C} > \text{Si} > \text{Ge} \approx \text{Sn}$ (B) $\text{C} > \text{Sn} > \text{Si} \approx \text{Ge}$ (C) $\text{Ge} > \text{Sn} > \text{Si} > \text{C}$ (D) $\text{Si} > \text{Sn} > \text{C} > \text{Ge}$
- 26.** The correct statements among (a) to (d) are: [JEE-MAIN-2019]
 (a) saline hydrides produce H_2 gas when reacted with H_2O .
 (b) reaction of LiAlH_4 with BF_3 leads to B_2H_6 .
 (c) PH_3 and CH_4 are electron - rich and electron-precise hydrides, respectively.
 (d) HF and CH_4 are called as molecular hydrides.
 (A) (c) and (d) only (B) (a), (b) and (c) only (C) (a), (b), (c) and (d) (D) (a), (c) and (d) only
- 27.** The basic structural unit of feldspar, zeolites, mica, and asbestos is : [JEE-MAIN-2019]
 (A) $(\text{SiO}_3)^{2-}$ (B) SiO_2 (C) $(\text{SiO}_4)^{4-}$ (D) $\begin{array}{c} \text{R} \\ | \\ \text{-(Si-O)}_n\text{-} \\ | \\ \text{R} \end{array}$ ($\text{R}=\text{Me}$)
- 28.** The C–C bond length is maximum in [JEE-MAIN-2019]
 (A) graphite (B) C_{70} (C) diamond (D) C_{60}

EXERCISE - 5**RECAP OF IIT-JEE/JEE (ADVANCED)**

- 1.** H_3BO_3 is – **[IIT-2002, 3]**

(A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid
 (C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid
- 2.** $(\text{Me})_2\text{SiCl}_2$ on hydrolysis will produce – **[IIT-2003]**

(A) $(\text{Me})_2\text{Si}(\text{OH})_2$ (B) $(\text{Me})_2\text{Si}=\text{O}$
 (C) $[\text{—O—}(\text{Me})_2\text{Si—O—}]_n$ (D) $\text{Me}_2\text{SiCl}(\text{OH})$
- 3.** $\text{B}(\text{OH})_3 + \text{NaOH} \rightleftharpoons \text{NaBO}_2 + \text{Na}[\text{B}(\text{OH})_4] + \text{H}_2\text{O}$ how can this reaction is made to proceed in forward direction ? **[IIT-2006]**

(A) Addition of cis 1, 2 diol (B) Addition of borax
 (C) Addition of trans 1, 2 diol (D) Addition of Na_2HPO_4
- 4.** **Statement-I** : Boron always forms covalent bond **[IIT-2007]**
Because :
Statement-II : The small size of B^{3+} favours formation of covalent bond.
 (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I
 (B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-II
 (C) Statement-I is True, Statement-II is False
 (D) Statement-I is False, Statement-II is True
- 5.** **Statement-I** : In water, orthoboric acid behaves as a weak monobasic acid. **[IIT-2007]**
Statement-II : In water, orthoboric acid acts as a proton donor.
 (A) Statement-I is True, Statement-II is True, Statement-II is a correct explanation for Statement-I
 (B) Statement-I is True, Statement-II is True, Statement-II is not a correct explanation for Statement-II
 (C) Statement-I is True, Statement-II is False
 (D) Statement-I is False, Statement-II is True
- 6.** With respect to graphite and diamond, which of the statement(s) given below is (are) correct? **[JEE-2012]**

(A) Graphite is harder than diamond.
 (B) Graphite has higher electrical conductivity than diamond.
 (C) Graphite has higher thermal conductivity than diamond.
 (D) Graphite has higher C–C bond order than diamond.
- 7.** The **CORRECT** statements(s) for orthoboric acid is / are – **[IIT-2014]**

(A) It behaves as a weak acid in water due to self ionization
 (B) Acidity of its aqueous solution increases upon addition of ethylene glycol
 (C) It has a three dimensional structure due to hydrogen bonding.
 (D) It is a weak electrolyte in water
- 8.** Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are **[IIT-2015]**

(A) CH_3SiCl_3 and $\text{Si}(\text{CH}_3)_4$ (B) $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$
 (C) $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 (D) SiCl_4 and $(\text{CH}_3)_3\text{SiCl}$

- 9.** The increasing order of atomic radii of the following group 13 elements is : **[IIT-2016]**
(A) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$ (B) $\text{Ga} < \text{Al} < \text{In} < \text{Tl}$
(C) $\text{Al} < \text{In} < \text{Ga} < \text{Tl}$ (D) $\text{Al} < \text{Ga} < \text{Tl} < \text{In}$
- 10.** The crystalline form of borax has **[IIT-2016]**
(A) Tetranuclear $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ unit
(B) All boron atoms in the same plane
(C) Equal number of sp^2 and sp^3 hybridized boron atoms
(D) One terminal hydroxide per boron atom
- 11.** Among the following, the correct statement(s) is are **[IIT-2017]**
(A) $\text{Al}(\text{CH}_3)_3$ has the three-centre two-electron bonds in its dimeric structure
(B) AlCl_3 has the three-centre two-electron bonds in its dimeric structure
(C) BH_3 has the three-centre two-electron bonds in its dimeric structure
(D) The Lewis acidity of BCl_3 is greater than that of AlCl_3

ANSWERS

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11
Ans.	B	A	A	C	B	C	B	D	A	D	C

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ans.	ABC	ABC	ABD	AB	ABC	ABCD	ACD	ABCD	CD	CD	BCD	ABCD	A	B

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	B	B	B	C	C	A	C	B	C	D	D	B	B	C	A
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	D	C	D	D	D	C	A	B	A	A	C	C	C		

EXERCISE-5

Que.	1	2	3	4	5	6	7	8	9	10	11
Ans.	A	C	A	A	C	BD	BD	B	B	ACD	ACD

[illegible]

[illegible]

This image shows a full page of blank white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page, providing a template for writing or drawing. There are no margins, text, or other markings on the page.