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Topic Covered s-block Elements

# s-BLOCK ELEMENT

# HYDROGEN

# **1. INTRODUCTION**

The most abundant element of universe (≈76%), the fifteenth most abundant in the earth, and the tenth most abundant in earth crust Hydrogen is the lightest, smallest and first element of periodic table with atomic number one.

In nature, hydrogen is found in the free as well as in the combined state.

In the atmosphere, the presence of hydrogen is found to very minute (only one part in a million by volume) owing to its high chemical reactivity. Low abundance in the atmosphere is also due to the earth's gravitational field which is too small to hold on to so light an element.

### Hydrogen

Symbol: H

Placed with alkali metals as well as Halogens

Electronic configuration - 1s1

# 2. POSITION OF HYDROGEN IN PERIODIC TABLE

Hydrogen is a unique element, it has only one electron in the 1s-orbital and no electrons in the other shell. It may donate one electron forming H<sup>+</sup> (like alkali metals) or may accept one electron forming H<sup>-</sup> (like halogens). It ranges in character from being a strong Lewis base ( $H^{-}$ ) to being a strong Lewis acid ( $H^{+}$ ). It is this nature which makes it difficult for us to assign hydrogen its proper place in the periodic table because of its resemblance with halogens as well as with alkali metals.

# 2.1 Resemblance with Alkali Metals

Hydrogen resembles alkali metals in the following respects:

- (a) Electronic Configuration Like alkali metals, hydrogen also has one valence electron.
- (b) Electropositive Character Like other alkali metals, Hydrogen readily forms the Hydronium ion, which is very stable.

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- (c) Reaction with Non-Metals Forms sulphides, oxides and halides same as alkali metals.
- (d) Reducing action Like alkali metals, hydrogen also acts as strong reducing agent.

E.g.,  $F_2 + H_2 \rightarrow 2HF$ 

### 2.2 Resemblance with Halogens

(a) **Electronic configuration:** Like halogens, hydrogen is short of one electron for stability in the outer orbit as explained below-

 $H + e^- \rightarrow H^ F + e^- \rightarrow F^-$ 

**(b)** Atomicity: All halogens exist as diatomic covalent molecules  $F_{2'}$  Cl<sub>2'</sub> etc. In a similar way hydrogen is a diatomic covalent molecule.

E.g.  $H_{2'}$   $Cl_{2'}$   $Br_{2}$ 

- (c) Physical state: Hydrogen is a gas like F<sub>2</sub> and Cl<sub>2</sub>.
- (d) Ionization potential: I.P of hydrogen is very high, same as in the case of halogens.
  - H 13.12 eV
  - F 16.8 eV
  - Cl 12.55 eV
- (e) **Reaction with non-metals:** Both, halogens and hydrogen combine with other non-metals by forming single bonds to give compounds like CCl<sub>4</sub>, CH<sub>4</sub>, and SiCl<sub>4</sub>.

# **3. SPECIAL FORMS OF HYDROGEN**

### 3.1 Nascent Hydrogen

(a) Nascent H is hydrogen at the moment of its generation, i.e., when it is just set free in a chemical reaction.

 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H_{(Nascent hydrogen)}$ 

(b) This hydrogen is more reactive and a more powerful reducing agent than ordinary H<sub>2</sub>. It reduces the following:

(i) Decolourizes yellow colour of FeCl<sub>3(aq)</sub>.

 $\begin{array}{c} \mathsf{H} + \mathsf{FeCl}_3 \longrightarrow \mathsf{FeCl}_2 + \mathsf{HCl} \\ \text{Yellow} & \text{Colourless} \end{array}$ 

(ii) Decolourizes violet colour of KMnO<sub>4</sub>.

$$2KMnO_4 + 3H_2SO_4 + 10H \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O_{Colourless}$$

(iii) Turns K, Cr, O, solution to green.

$$\begin{array}{c} K_2 Cr_2 O_7 + 4H_2 SO_4 + 6H \longrightarrow K_2 SO_4 + Cr_2 (SO_4)_3 + 7H_2 O_{Green} \end{array}$$

No such change in colour is produced when  $H_2$  is bubbled through the solution of FeCl<sub>3</sub>, KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

# 3.2 Adsorbed Hydrogen (Occluded Hydrogen)

 $H_2$  on bubbling at the surface of platinum black, is adsorbed there and becomes capable of bringing out many chemical changes such as reduction and hydrogenation. This type of hydrogen is named as adsorbed  $H_2$ . Similarly  $H_2$ , occluded or adsorbed on Palladium is a very strong reducing agent and combines with halogens even in the dark, precipitates Hg from HgCl<sub>2</sub>.

# 3.3 Atomic Hydrogen

In 1922, Langmuir showed that H<sub>2</sub> placed in contact with a tungsten wire, heated by an electric arc at low pressure dissociates into atoms with an absorption of 104.0 kcal of heat per mol.

 $H_2 \xrightarrow{\text{Electric Arc}} 2H, \Delta H = 104 \text{ kCal mol}^{-1} (t_{1/2} \text{ for atomic hydrogen is 0.3 seconds only})$ 

# 3.4 Ortho and Para Hydrogen

When the spins of both the protons (nucleus) in the hydrogen molecule are in the same direction then this form is known as ortho hydrogen. The molecule of hydrogen in which both the protons are spinning in opposite directions known as para hydrogen. These are nuclear isomers.

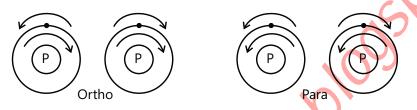


Figure 15.1: Spins for Ortho and Para Hydrogen

At normal temperature the ratio of ortho and para hydrogen is 3:1, but as the temperature is lowered, the proportion of para hydrogen increases (at 20°C).

### PLANCESS CONCEPTS

- Difference between Nascent and Atomic Hydrogen Scientifically, nascent refers to the substance at the point at which it forms. Such as Zinc reacts with sulphuric acid, individual hydrogen atom forms but very quickly reacts with other hydrogen atom forming H<sub>2</sub> molecule. This is the only common situation at which atomic hydrogen exists even very fleetingly.
- Since ortho is more stable than para form at room temperature. Para readily gets converted into ortho by following reaction:

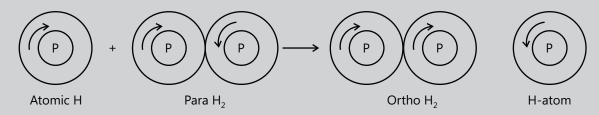


Figure 15.2: Conversion of para H<sub>2</sub> to ortho H<sub>2</sub>

• Adsorbed H<sub>2</sub> is more reactive than normal dihydrogen.

### Vaibhav Krishnan (JEE 2009, AIR 22)

# 4. DIHYDROGEN OR DIPROTIUM

# 4.1 Methods of Preparation of Dihydrogen

### 4.1.1 From Water

The cheapest and most widely available source of hydrogen is water.  $H_2$  can be obtained from water using any one of the processes given below:

(a) By action of water on metals

(b) By action of water on hydrides

(c) By action of water on methane

(d) By electrolysis of water

### 4.1.2 From Acids

Metals which lie above hydrogen in electro-chemical series i.e. metals with positive  $E^{\circ}_{OP}$  do not displace  $H_2$  from dilute mineral acid like HCl or  $H_2SO_4$ . Metals having negative  $E^{\circ}_{OP}$  (i.e. metals lying below hydrogen in ECS) displace  $H_2$  from acids, e.g., Zn, Mg, Fe etc. displace  $H_2$  from acids.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2^{\uparrow}$$

### 4.1.3 From Alkali

Certain metals like Zn, Sn, Al, Pb, Si etc. (amphoteric metals) react with boiling NaOH to liberate H<sub>2</sub>.

 $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$ Sodium zincate

 $2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3H_2 \uparrow$ 

# 4.2 Manufacture of H<sub>2</sub> on Commercial Scale

# 4.2.1 By Electrolysis of Water

The water containing a small amount of an acid or alkali (about 15-20%) is electrolysed in an electrolytic cell. The anode and cathode are separated by an asbestos diaphragm. The cathode is usually made up of iron and anode usually of nickel.

At anode: OH<sup>-</sup> ions are discharged and oxygen is evolved.

 $40H^{-} \longrightarrow 2H_2O + O_2 + 4e^{-}$ 

At cathode: H<sup>+</sup> ions are discharged and hydrogen is evolved.

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

## 4.2.2 Bosch Process

This process is most common, and in this process, first steam is passed over hot coke at 1000°C to obtain water gas or Synthesis gas or Syn gas.

$$C_{(s)} + H_2O_{(V)} \xrightarrow{Ni/1000^{\circ}C} \underbrace{CO + H_2}_{Syn.gas}$$

This process of obtaining 'Synthesis gas' from coal or coke is called "Coal gasification"

### 4.2.3 Lane's Process

This process involves the decomposition of steam by heated Fe (550 - 800°C). The reaction is known as **"gassing reaction".** 

 $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\uparrow;\Delta\text{H} = -160.7\text{kJ}$ 

### 4.2.4 From Hydrocarbons

- (a) Thermal Cracking:  $CH_4 \xrightarrow{Catalyst/\Delta} C + 2H_2^{\uparrow}$
- **(b)** By partial oxidation:  $CH_4 + H_2O \xrightarrow{Ni/1000^{\circ}C} \underbrace{CO + 3H_2}_{Sum cas}$

### 4.3 Physical Properties of Dihydrogen

- (a) Colourless, odourless, tasteless gas
- (b) Sparingly soluble in water due to non-polar nature
- (c) Density is 0.09 gm/lit
- (d) B.P is 20.4 K
- (e) Pd metal can adsorb  $H_2$  gas

## 4.4 Chemical Properties of Dihydrogen

- (a) Nature: H<sub>2</sub> is neutral and so it does not affect litmus.
- (b) **Combustion:** H<sub>2</sub> is highly combustible and in presence of air, it burns with pale blue flame. It does not support combustion.

 $2H_2 + O_2 \longrightarrow 2H_2O_{(l)} \qquad \Delta H = -285.9 \text{ kJmol}^+$ 

Reaction is highly exothermic and its calorific value is higher than other fuels.

(c) **Reducing action:** Dihydrogen reduces oxides of certain less electropositive metals (generally less electropositive than Zn and placed above H in ECS) like Fe, Pb, Cu etc. The product is metal, e.g.,

 $Fe_{2}O_{3} + 3H_{2(g)} \xrightarrow{\Delta} 2Fe + 3H_{2}O$   $CuO_{(s)} + H_{2(g)} \xrightarrow{\Delta} Cu + H_{2}O$ 

(d) Reaction with non-metals: With non-metals, hydrogen forms covalent hydrides, e.g.,  $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O_2$ 

 $3H_2 + N_2 \xrightarrow{750K/Fe,Mo} 2NH_3$  (Haber's process)

(e) **Reaction with Metals**: Under suitable conditions, H<sub>2</sub> reacts with metals to form hydrides which are chiefly ionic. Alkali metals and alkaline earth metals (except Be) react with H<sub>2</sub> directly.

 $2M + H_2 \rightarrow 2MH$  (M = Li, Na, K, Rb etc.)

 $M+H_2 \rightarrow MH_2$  (M = Mg, Ca, Ba etc.)s

### PLANCESS CONCEPTS

Hydrogen is a diatomic gas having H—H bond. H—H bond is strongest known single bond (Bond energy =  $435.9 \text{ kJ mol}^{-1}$ ) between two atoms of any element.

 $H_2$  is not very reactive at normal temperature and pressure. This lack of reactivity is due to thermodynamics, not kinetics as it is related to bond strength. Since the H—H bond energy is very high it reacts at high temperature only and in the presence of catalysts which further lower the activation energy.

### Nikhil Khandelwal (JEE 2009, AIR 94)

# 5. HEAVY HYDROGEN OR DEUTERIUM

### **5.1 Preparation of Deuterium**

 $D_2$  can be absorbed from  $H_2$  by distillation, diffusion and other chemical properties. One notable method is adsorption of  $H_2$  on charcoal leaving out  $D_2$ .

### **5.2 Physical Properties**

- (a) It is colourless, odourless, tasteless, water insoluble, diatomic gas
- (b) Its physical constants like b.pt., m.pt., triple point etc. are higher than H<sub>2</sub>.
- (c) Being heavier than  $H_{2'}$  it diffuses at less speed than  $H_2$

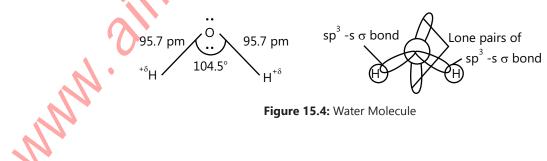
### **5.3 Chemical Properties**

 $D_2$  resembles with  $H_2$ , in its chemical properties, but reacts at a slower rate than  $H_2$ , because it's bond strength is greater than that of  $H_2$ . There is marked isotope effect as mol. wt. of  $D_2$  is twice to  $H_2$ . Also, its adsorption on the surface of metals is also slower than  $H_2$ .

# 6. WATER

## 6.1 Structure of Water **•**

Molecule of water is V-shaped and its structure is given below: In water, the central oxygen atom is sp<sup>3</sup> hybridised. Out of four sp<sup>3</sup> hybrid orbitals, two form  $\sigma$  bond with s-orbital of H-atom while rest two are occupied by lone pairs of electrons. Due to Ip-bp repulsion, the H—O—H bond angle is contracted to 104.5°. O—H bond length is 95.7pm. Due to its V-shaped structure, H<sub>2</sub>O is a polar molecule ( $\mu$  = 1.84 D).



# 6.2 Structure of Ice

In ice, each oxygen atom is bonded to 4 other oxygen atoms by hydrogen bonds as

shown in Fig. This gives ice, an open framework. When ice melts, some hydrogen bonds are broken. The 'bridges' and the open framework collapse, causing water molecules to fall into the empty spaces.

This close packing of molecules allows the liquid to occupy a smaller volume than the ice, and the density increases.

# 6.3 Physical Properties of Water

Pure water is a colourless, odourless and tasteless liquid. It gives a bluish tinge in thick layers. Water has an abnormally high freezing point, boiling point, heat of vaporization, heat of fusion. Water has a high specific heat, surface tension and thermal conductivity than most other liquids. These properties are responsible for water to play a vital role in life processes. These unique properties of water are due to the presence of hydrogen bonding.

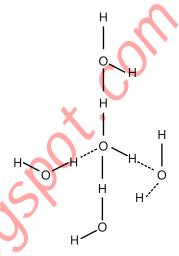


Figure 15.3: Structure of Ice

### **6.4 Chemical Properties of Water**

(a) Acid-Base Nature: Water acts as both an acid and a base, and is said to be amphoteric. Water acts as a base towards acids stronger than itself and as an acid in the presence of a base stronger than itself, as shown below:

$$H_{2}O_{(I)} + HCI_{(aq.)} \xrightarrow{} H_{3}O^{+}_{aq} + CI^{-}_{aq.}$$
Base Acid Acid Base
$$H_{2}O_{(I)} + NH_{3(aq.)} \xrightarrow{} NH_{4}^{+}_{(aq.)} + OH^{-}_{(aq.)}$$
Acid Base

(b) Oxidation and Reduction: Water acts both as an oxidizing as well as a reducing agent.

e.g.  $2Na + H_2O \longrightarrow 2NaOH + H_2$ 

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

(c) Hydrolytic Reaction: Compounds like calcium hydride, aluminium nitride, calcium phosphide, calcium carbide, silicon halide etc. undergo hydrolysis with water.

 $CaH_2+2H_2O \longrightarrow Ca(OH)_2 + 2H_2$ AIN + 3H\_2O \longrightarrow AI(OH)\_3 + NH\_3

(d) Hydrate Formation: Water reacts with certain metal salts to form hydrates. In hydrated salts water may remain in 5 types:

(i) Co-ordinated water, (ii) Hydrogen bonded water, (iii) Lattice water, (iv) Zeolitic water, (v) Clathrate water.

# 6.5 Soft and Hard Water

A sample of water which easily produces lather with soap is known as "Soft Water" while "hard water" doesn't produce lather with soap easily.

The soluble Ca<sup>+2</sup>, Mg<sup>+2</sup> or Fe<sup>+2</sup> ions react with soap to give Ca or Mg soap which being insoluble in water get precipitated.

 $MgCl_2 + 2C_{17}H_{35}COONa \longrightarrow (C_{17}H_{35}COO)_2Mg \downarrow + 2NaCl$ 

 $CaCl_{2} + 2C_{17}H_{35}COONa \longrightarrow 2NaCl + (C_{17}H_{35}COO)_{2}Ca \downarrow$ 

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#### Hardness of Water and Removal

(a) **Temporary hardness:** It is due to the dissolution of bicarbonates of Ca and Mg in water. It can be removed by boiling.

$$Ca(HCO_3)_2 \xrightarrow{Boiling} CaCO_3 + H_2O + CO_2$$

 $Mg(HCO_3)_2 \xrightarrow{Boiling} MgCO_3 + H_2O + CO_2$ 

It can also be done by adding lime

 $Ca(HCO_{3})_{2} + Ca(OH)_{2} \longrightarrow 2CaCO_{3} + 2H_{2}O$  $Mg(HCO_{3})_{2} + Ca(OH)_{2} \longrightarrow CaCO_{3} + MgCO_{3} + 2H_{2}O$ 

(b) **Permanent Hardness and its Removal:** Permanent hardness happen due to the dissolution of chloride and sulphates of Ca, Mg, Fe. It cannot be removed by boiling of water.

It can be removed by following

- (i) Adding washing soda:  $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl_3$
- (ii) Permutit Method: Permutit is an artificial zeolite. It is sodium alumino orthosilicates i.e. Na2Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>. The hardness causing ions are retained by the bed and Na<sup>+</sup> ions from bed, form soluble salt like NaHCO<sub>3</sub>. To recharge the bed after complete exhaustion, it is treated with NaCl solution which regenerates the zeolite bed. This process removes both types of temporary and permanent hardness.

$$Na_{2}Z + Ca(HCO_{3})_{2} \downarrow \longrightarrow CaZ \downarrow + 2NaHCO_{3}$$

$$CaZ \text{ (or MgZ)} + 2NaCI \xrightarrow{(\text{or MgHCO}_{3})} Na_{2}Z + CaCl_{2} \text{ (or MgCl}_{2})$$

(iii) **Calgon Process:** Calgon which is also known as Grahm's salt is the trade name of sodium hexametaphosphate (NaPO<sub>3</sub>)<sub>6</sub>. The Ca<sup>+2</sup> and Mg<sup>+2</sup> ions dissolved in hard water react with calgon to produce complex anions, which are very inactive and don't produce a ppt. with soap.

 $Na_{2}[Na_{4}(PO_{3})_{6}] + 2CaCl_{2} \longrightarrow Na_{2}[Ca_{2}(PO_{3})_{6}] + 4NaCl_{2}[Ca_{2}(PO_{3})_{6}] + 4NaCl_{2}[Na_{4}(PO_{3})_{6}] + 4NaCl_{2}[Na_{4}(PO_{3$ 

- (iv) By Ion Exchange Resin: Resins are giant organic molecules attached with acidic or basic groups. Cation exchange resin contain -COOH or  $-SO_3H$  groups. These remove cations like Na<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Fe<sup>+2</sup> etc by exchange with H<sup>+</sup>. Anion exchange resins contain  $-NH_2$  group they are represented by  $RNH_3^+$  OH<sup>-</sup>. These resins remove negative ions such as Cl<sup>-</sup>,  $SO_4^{-2}$ ,  $NO_3^{-2}$  etc.
- (c) Degree of Hardness: Degree of hardness is usually expressed in parts per million (ppm) and thus may be defined as the number of parts by weight of CaCO<sub>3</sub> (equivalent to calcium and magnesium salt) present in a million (10<sup>6</sup>) parts by weight of water.

1 ppm = 1 part of  $CaCO_3$  in 10<sup>6</sup> parts of water.

## 6.6 Heavy Water

Heavy water is extensively used as a moderator in nuclear reactors and in exchange reactions for the study of reaction mechanisms. It can be prepared by exhaustive electrolysis of water or as a by-product in some fertilizer industries.

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

$$CaC_{2} + 2D_{2}O \longrightarrow C_{2}D_{2} + Ca(OD)_{2}$$
  

$$SO_{3} + D_{2}O \longrightarrow D_{2}SO_{4}$$
  

$$AI_{4}C_{3} + 12D_{2}O \longrightarrow 3CD_{4} + 4AI(OD)_{3}$$

### PLANCESS CONCEPTS

The dissociation constant of  $D_2O$  is less than  $H_2O$  because O-D bond is stronger than O-H bond so it takes more energy to break O-D bond owing to more atomic mass of D than H which stabilises the bond by reducing the vibration of bonds.

 $H_2O \Longrightarrow H^+ + OH^-; \qquad K_w = 1.0 \times 10^{-14}$  $D_2O \Longrightarrow D^+ + OD^-; \qquad K_w = 1.95 \times 10^{-15}$ 

Use of Organic resins for softening the hard water is the best method because purification can be easily done so it is used commercially.

Saurabh Gupta (JEE 2010, AIR 443)

# 7. HYDROGEN PEROXIDE

## 7.1 Preparation of H<sub>2</sub>O<sub>2</sub>

(a) Lab method of preparation of  $H_2O_2 - H_2O_2$  obtained by passing a current of  $CO_2$  through a cold pasty solution of  $BaO_2$  in water.

 $BaO_2 + CO_2 + H_2O \longrightarrow H_2O_2 + BaCO_3$ 

- (b) Treating Na<sub>2</sub>O<sub>2</sub> with  $H_2SO_4^{-2}$ 
  - (i)  $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$
  - (ii) Also, by small amount of Na<sub>2</sub>O<sub>2</sub> added to ice cold water.
  - (iii)  $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$
- (c) Industrial process: By electrolysis of 50% H<sub>2</sub>SO<sub>4</sub> at 0°C using Pt electrode.

 $2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$ 

At cathode: (Cu) –  $2H^+ + 2e^ H_2$ 

At anode: (Pt) –  $2HSO_4^ \rightarrow$   $H_2S_2O_8^-$  +  $2e^-$ 

 $H_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2H_2SO_4$ 

(d) Electrolysis of ammonium hydrogen sulphate: In the electrolysis of ammonium hydrogen sulphate, ammonium per sulphate is formed. It is separated and distilled with dil.H<sub>2</sub>SO<sub>4</sub> to give 30 - 40% H<sub>2</sub>O<sub>2</sub> (aqueous solution)

 $NH_4HSO_4 \Leftrightarrow NH_4SO_4^- + H^+$ 

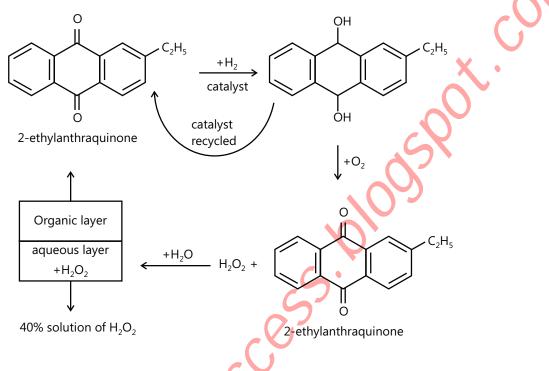
At cathode:  $2H^+ + 2e^- \longrightarrow H_2($  reduction)

At anode:  $2NH_4 SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$  (oxidation)

**Distillation:** (NH<sub>4</sub>)  $S_2O_8 + 2H_2O \xrightarrow{H_2SO_4} 2NH_4HSO_4 + H_2O_2$ 

(e) Auto - oxidation of 2-ethyl anthraquinone: This is the most modern method and needs H<sub>2</sub>, atmospheric oxygen and water as the major raw materials.

First and foremost, 2-ethyl anthraquinone is catalytically reduced to 2-ethyl anthraquinol in organic solvent by  $H_2$  and Pd (catalyst). Secondly, 2-ethyl anthraquinol is oxidised by air to 2-ethyl anthraquinone.  $H_2O_2$  obtained in the process is extracted with water to give 20%  $H_2O_2$  solution. 2-ethyl anthraquinone is thus reused. The process is repeated, thus it is a cyclic process.



# 7.2 Physical Properties of H<sub>2</sub>O<sub>2</sub>

(a) Pure H<sub>2</sub>O<sub>2</sub> is weakly acidic in nature and exists as an associated liquid due to hydrogen bonding.

- (b) Smell of  $H_2O_2$  resembles like nitric acid.
- (c) It causes blisters on skin.
- (d) Stored in plastic containers after addition of stabilizers.
- (e) A dilute solution of  $H_2O_2$  is concentrated by vacuum distillation or by distillation under pressure.

## 7.3 Chemical Properties

- (a) Decomposition  $2H_2O_2 \rightarrow 2H_2O+O_2$ ;  $\Delta H = -196kJ$
- **(b)** Oxidising and reducing nature : H<sub>2</sub>O<sub>2</sub> acts as a strong oxidising agent under acidic and alkaline conditions. Oxidation in the acidic medium is slow while rapid in an alkaline solution as H<sub>2</sub>O<sub>2</sub> itself is a weak acid.

$$H_{2}O_{2} + 2H + 2e \longrightarrow 2 H_{2}O$$

$$H_{2}O_{2} \longrightarrow H_{2}O + [O]$$

$$PbS + 4H_{2}O_{2} \longrightarrow PbSO_{4} + 4H_{2}O$$

$$2KI + H_{2}O_{2} \longrightarrow 2KOH + I_{2}$$

$$2KI + H_{2}SO_{4} + H_{2}O_{2} \longrightarrow K_{2}SO_{4} + 2H_{2}O_{2} + I_{2}$$

$$H_{2}O_{2} + H_{2}S \longrightarrow 2H_{2}O + S$$

$$2K_{4} \left[ Fe(CN)_{6} \right] + H_{2}O_{2} \longrightarrow 2K_{3} \left[ Fe(CN)_{6} \right] + 2KOH$$

$$\begin{split} & K_2 Cr_2 O_7 + H_2 SO_4 + 4H_2 O_2 \longrightarrow K_2 SO_4 + 2CrO_5 + 5H_2 O_{(Blue)} \\ & H_2 O + 2OH^- + 2e^- \longrightarrow 2H_2 O_2 + 2O_2 \\ & 2HCHO + H_2 O_2 \longrightarrow 2HCOOH + H_2 \end{split}$$

#### **Reducing nature**

 $\begin{aligned} & 2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \\ & K_2Cr_2O_7 + 4H_2SO_4 + 3H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \\ & O_3 + H_2O_2 \longrightarrow H_2O + 2O_2 \\ & Cl_2 + H_2O_2 \longrightarrow 2HCI + O_2 \\ & 2K_3\left[Fe(CN)_6\right] + 2KOH + H_2O_2 \longrightarrow 2K_4\left[Fe(CN)_6\right] + 2H_2O + O_2 \end{aligned}$ 

(c) Bleaching action:  $H_2O_2$  acts as a bleaching agent due to its oxidising nature e.g., bleached human hair (black to golden brown), ivory, silk, wool, feather etc.  $H_2O_2 \longrightarrow H_2O_2 + [O]$ 

#### (d) Addition properties

$$\begin{array}{c} \mathsf{CH}_2\\ || & \mathsf{H}_2\mathsf{O}_2 \longrightarrow \begin{array}{c} \mathsf{CH}_2\mathsf{O}\\ \mathsf{H}_2 \end{array} \xrightarrow{} \begin{array}{c} \mathsf{CH}_2\mathsf{O}\\ | & \mathsf{I} \end{array}$$

# 7.4 Uses of H<sub>2</sub>O<sub>2</sub>

Its wide scale use has led to the tremendous increase in the industrial production of  $H_2O_2$ . Some of the uses are listed below:

- (a) In daily life, it is used as a hair bleach and as a mild disinfectant. As an antiseptic, it is sold in the market as perhydrol.
- (b) It is used to manufacture chemicals like sodium perborate and per-carbonate, which are used in high quality detergents.
- (c) It is used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (d) It is employed in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (e) Nowadays, it is also used in Environmental (Green) Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage wastes, etc.

# 7.5 Tests for H<sub>2</sub>O<sub>2</sub>

(a) An acidified solution of titanium salt when treated with  $H_2O_2$  a yellow or orange colour is developed due to formation of pertitanic acid.

 $\text{Ti}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 + 2 \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{TiO}_4 + 2\text{H}_2\text{SO}_4$ 

- (b) It liberates iodine from KI solution which gives a blue colour with starch solution
- (c)  $H_{0_2}$  on shaking with acidified  $K_2 Cr_2 O_7$  with little ether, blue colour is produced.

# 7.6 Structure of H<sub>2</sub>O<sub>2</sub>

All four atoms in  $H_2O_2$  are non-planar. Structure of  $H_2O_2$  has an open book structure having two leaves at 90° the H-atoms are placed one on each core, the H–O making an angle of 101.5° with O–O bond.

Bond Angle: Dipole moment value of H<sub>2</sub>O<sub>2</sub> suggests that all the four atoms in H<sub>2</sub>O<sub>2</sub> do not lie in a plane, and the structure can be compared with a book open at angle 94°.

The H—O—O bond angle is 97°.

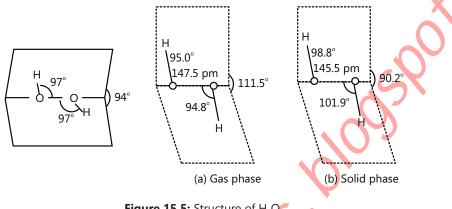


Figure 15.5: Structure of H<sub>2</sub>Q

# 7.7 Strength of H<sub>2</sub>O<sub>2</sub>

- (a) As percentage: The strength of H<sub>2</sub>O<sub>2</sub> is sometimes reported in percentage. Bottles containing H<sub>2</sub>O<sub>2</sub> are labelled as 40%, 60%... etc. This means that 100 ml solution of H<sub>2</sub>O<sub>2</sub> contains 40 g H<sub>2</sub>O<sub>2</sub>.
- (b) As number volume: The strength of hydrogen peroxide is often expressed in terms of the volume of oxygen evolved on heating. Bottles containing hydrogen peroxide are labelled as '10 Volume',

'20 Volume', '100 Volume' etc. This means that one volume of hydrogen peroxide solution gives so many volumes to oxygen (after complete decomposition) at N.T.P.

Thus 1 mL of '10 Volume' solution produces 10 mL of oxygen at N.T.P, 1,000 mL of a '10 Volume' solution produce 10,000 mL of oxygen at N.T.P, 1000 mL of a '20 Volume' solution produce 20,000 mL of oxygen at N.T.P. etc.

### PLANCESS CONCEPTS

- % strength =  $\frac{17}{56}$  × volume strength
- Volume strength =  $5.6 \times normality$
- Volume strength =  $11.2 \times \text{molarity}$

 $H_2O_2$  is a very unstable compound which can easily decompose in the presence of metallic impurities sometimes leading to explosions. To avoid this, stabilizers such as  $H_3PO_4$  or glycerol are use to maintain the equilibrium backward.

Neeraj Toshniwal (JEE 2009, AIR 21)

**Illustration 1:** (i) Convert 20 vol.  $H_2O_2$  into % strength.

(ii) Convert 6.8% strength H<sub>2</sub>O<sub>2</sub> into volume strength.

(JEE MAIN)

**Sol:** (i) 20 vol.  $H_2O_2$  means 1 mL of  $H_2O_2$  solution gives 20 mLO<sub>2</sub>

ospot.

 $2H_2O_2 \longrightarrow 2H_2O + O_2$ 2 mole 1 mole
= 68g 22400 mL at NTP

 $\therefore$  22400 mL O<sub>2</sub> is obtained by 68 g H<sub>2</sub>O<sub>2</sub>

 $\therefore$  20 mL O<sub>2</sub> is obtained by  $\frac{68 \times 20}{22400}$  = 0.0607 g H<sub>2</sub>O<sub>2</sub>

or 1 mL  $H_2O_2$  solution = 0.0607g  $H_2O_2$ 

:. 100 mL  $H_2O_2$  solution = 0.0607 × 100 g  $H_2O_2$  = 6.07%

(ii) 6.8% strength  $H_2O_2$  solution means 6.8 g  $H_2O_2$  is present in 100 mL  $H_2O_2$ 

 $\therefore$  68 g H<sub>2</sub>O<sub>2</sub> gives 22400 mL O<sub>2</sub> at NTP

:. 6.8g H<sub>2</sub>O<sub>2</sub> gives  $\frac{22400 \times 6.8}{68}$  = 2240 mL O<sub>2</sub>

:. Volume strength of  $H_2O_2$  gives =  $\frac{2240}{100}$  = 22.4 Volume

# 8. HYDRIDES

Binary compounds of hydrogen with other elements, are generally called hydrides, but strictly speaking, this term should be applied to compounds of hydrogen with elements, which are less electronegative than hydrogen. They may be of MH<sub>a</sub> or M<sub>m</sub>H<sub>a</sub> type.

## 8.1 Ionic Hydrides

- (a) They are hydrides of elements having low electronegativity (ranging between 0.9 to 1.2 usually). They are formed by alkali metals, alkaline earth metals (except Be and Mg) and some lanthanides.
- (b) In these hydrides, hydrogen accepts electrons from combining elements and exists as H<sup>-</sup>
- (c) These hydrides can be prepared by heating ( $\approx$  1000 1100 K) metals with hydrogen directly.

E.g. 2Na +  $H_2 \rightarrow 2NaH$ 

### Some Important Chemical Properties

- (a) Stability: Ionic hydrides have quite high heats of formation and consequently high stability. On moving down in the group, the stability decreases which may be attributed to a poor overlap between the relatively smaller 1s orbital of hydrogen and larger s-orbital of heavier metals.
  LiH > NaH > KH > RbH > CsH
- (b) Gets hydrolyzed by giving alkali and H2 gas.
- (c) At high temperatures, act as strong reducing agents.

# 8.2 Covalent Hydrides

- (a) These hydrides are formed mainly by p-block elements (except noble gases) and by some s-block elements like Be and Mg.
- (b) These hydrides usually consist of discrete covalent molecules held together by weak 'Vander Waals' forces and so these hydrides are usually volatile. The melting points and boiling points of covalent hydrides are low. Some of them are liquids or even solids in a few cases.
- (c) They do not conduct electricity and their general formula may be MHX (for s-block metals) or MH(8–n) (for s-block elements), here n is the number of valence electrons. This generalization is not valid for the boron family.

Covalent hydrides can be electron deficient also such as DIBORANE B<sub>2</sub>H<sub>6</sub> and other such bridge bond hydrides.

They can be electron precise as well as electron rich such as CH<sub>4</sub> and NH<sub>3</sub> respectively.

# 8.3 Metallic / Interstitial Hydrides

(a) These hydrides are formed by d- and f-block metals, with electronegativity ranging from 1.2 to 1.4.

(b) These hydrides are usually non-stoichiometric (e.g. TiH<sub>1.73</sub>, LaH<sub>2.8</sub> etc.) and these hydrides have properties similar to those of parent metals i.e. why they are called metallic hydrides.

In these hydrides, hydrogen occupies some interstitial sites in the metallic lattice i.e. why they are called interstitial hydrides. However it is not certain whether the interstitial hydrogen is present as H or H<sup>+</sup> with delocalised electrons.

# 8.4 Polymeric Hydrides and Complex Hydrides

- (a) Polymeric hydrides are formed by elements having electro- negativity in the range 1.4 to 2.0. e.g.,  $(BeH_2)_{n'}$   $(AIH_{3n'} (InH_3)_{n'} (SiH_4)_n$  etc.
- (b) In complex hydrides H<sup>-</sup> acts as a ligand and is attached to the central metal atom, e.g.LiAlH<sub>4</sub>, LiBH<sub>4</sub>, NaBH<sub>4</sub> etc.

# 8.5 Hydrogen Economy - Use of Hydrogen as a Fuel

**Advantage:** (i)  $H_2$  is an environmentally clean fuel because it gives water on combustion. However, a small amount of nitrogen oxides may be formed due to high temperatures.

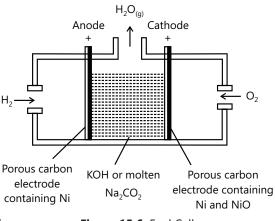
(ii)  $H_2$  has the highest calorific value and it is a better fuel than any other fuel.

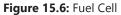
# 8.6 Fuel Cell

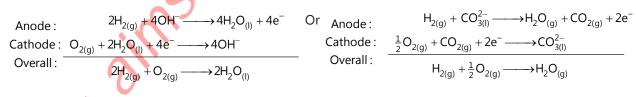
In a fuel cell,  $H_2$  and  $O_2$  combines with each other, where,  $H_2$  is oxidised at anode, while,  $O_2$  is reduced at cathode. The fuels ( $H_2$  and  $O_2$ ), do not react directly.

A fuel cell is represented in the fig.

The cell contains porous carbon electrodes impregnated with metal catalysts and an electrolyte consisting of hot aqueous KOH or molten Na<sub>2</sub>CO<sub>3</sub>. The fuel (gaseous H<sub>2</sub>) and the oxidising agent (gaseous O<sub>2</sub>) do not react directly, but instead flow into separate cell compartments where H<sub>2</sub> is oxidised at the anode and O<sub>2</sub> is reduced at the cathode. The overall cell reaction is simply the conversion of hydrogen and oxygen to water.



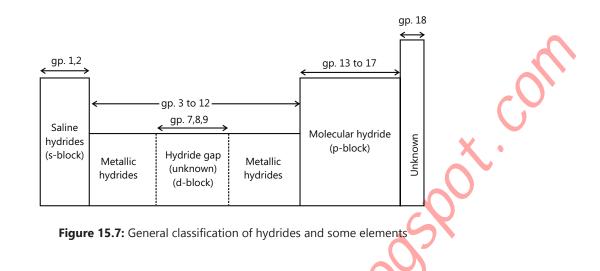




Fuel cells are very efficient and about 75% of bond energy is converted into electricity.

**Disadvantages:** No doubt,  $H_2$  is the best alternative to fossil fuels, but the use of hydrogen as a fuel is very dangerous and needs attention. The storage of the mixture of  $H_2$  and  $O_2$  is very risky. In 1986, the space shuttle Challenger, an explosion occurred in the fuel tank containing  $H_2$  and  $O_2$ .

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### **PLANCESS CONCEPTS**

- The above table shows a general classification of hydrides and some elements form intermediate hydrides while hydrides of some others are unknown or unstable.
- The hydrolysis of hydrides with H<sub>2</sub>O is highly exothermic and may be explosive as H<sub>2</sub> catches fire. This fire can't be extinguished by CO<sub>2</sub> as it gets reduced by a hot metal hydride. Here only sand must be used.

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Aman Gour (JEE 2012, AIR 230)
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**Illustration 2:** On reaction of equal masses of LiH and CaH, with water, which will give more H<sub>2</sub>? (JEE MAIN)

Sol: LiH +H<sub>2</sub>O →LiOH+ H<sub>2</sub>  
(1 mole=8g)  

$$\boxed{8g \text{ LiH gives } 2g \text{ H}_2}$$
  
 $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$   
(1 mole = 42 g)  
 $\frac{42}{2} = 21 \text{ gCaH}_2 \text{ gives } 2g \text{ H}_2$   
 $\boxed{8g \text{ CaH}_2 \text{ gives } \frac{2}{21} \times 8 = 0.762 \text{ g H}_2}$ 

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# s-block elements

# **1. INTRODUCTION**



The elements in which the last electron enters the outermost s-orbital, belong to the s-block of elements. As the s-orbital can accommodate only two electrons, two groups (1 & 2) belong to the s-block of the periodic table.

	1	11												IV	V	VI	VII	VIII/0
I	н			d-Block														
Ш	Li	Ве										V						
111	Na	Mg													$\mathbf{)}$			
IV	К	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
V	Rb	Sr	V	Zr	Nb	Мо	Тс	Ru	Th	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
VI	Cs	Ва	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	Ti	Pb	Bi	Ро	At	Rn
VII	Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Une	Uun			2	p	)-b	loc	:k	
s-l	s-block																	

Figure 15.8: Position of s-block elements in the periodic table

**Properties of s-block:** Table Group 1 of the periodic table consists of the elements: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). Collectively known as the alkali metals, because they form hydroxides on reaction with water, which are strongly alkaline in nature. The elements of Group 2 include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). These elements with the exception of beryllium are commonly known as the alkaline earth metals. These are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust. The general electronic configuration of s- block elements is [noble gas] ns<sup>1</sup> for alkali metals and [noble gas] ns<sup>2</sup> for alkaline earth metals.

# 2. TRENDS IN PHYSICAL AND CHEMICAL PROPERTIES

# 2.1 Electronic Configuration

All alkali metals have one valence electron, ns<sup>1</sup> outside the noble gas core. The single valence electron is at a long distance from the nucleus and is held weakly. Hence, the loosely held s electrons in the outermost valence shell of these elements make them the most electropositive metals. They readily lose electrons to give monovalent  $M^+$  ions. Hence, they are never found in the free state in nature. Alkaline earth metals have two electrons in the s-orbital of valence shell. The compounds of these elements are also predominantly ionic.

Element	Symbol	Electronic configuration
Lithium	Li	1s <sup>2</sup> 2s <sup>2</sup>
Sodium	Na	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>
Potassium	К	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup>
Rubidium	Rb	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 5s <sup>1</sup>

<b>Table 15.1 :</b> Electronic configuration of s-block elements
--

Element	Symbol	Electronic configuration	
Caesium	Cs	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup>	Å
		4p <sup>6</sup> 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup> 6s <sup>1</sup> or [Xe]6s <sup>1</sup>	
Francium	Fr	[Rn] 7s <sup>1</sup>	$\sim$
Beryllium	Ве	1s <sup>2</sup> 2s <sup>2</sup>	V
Magnesium	Mg	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	×.•
Calcium	Са	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup>	$\mathbf{O}$
Strontium	Sr	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 5s <sup>2</sup>	$\sim$
Barium	Ва	1s <sup>2</sup> 2s <sup>6</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup> 3d <sup>10</sup> 4s <sup>2</sup>	X
		4p <sup>6</sup> 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup> 6s <sup>2</sup> or [Xe] 6s <sup>2</sup>	
Radium	Ra	[Rn] 7s <sup>2</sup>	

## 2.2 Atomic and Ionic Radii

The alkali metal atoms have the largest size in a particular period of the periodic table. The atomic and ionic radii of alkali metals increase down the group i.e., they increase in size while going from Li to Cs. Due to the increased nuclear charge in these elements, the atomic and ionic radii of the alkaline earth metals are smaller than those of the corresponding alkali metals in the same periods. Within the group, the atomic and ionic radii increase with the increase in atomic number due to the increase in number of atomic shells.

# 2.3 Ionization Enthalpy

The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect of increasing size outweighs the increasing nuclear charge and the outermost electron is very well screened from the nuclear charge. The second ionization energy is extremely high because of the removal of the 2nd electron from a stable noble gas electron configuration of the monovalent metal cation. The alkaline earth metals have low ionization enthalpies due to the fairly large size of the atoms. Since the atomic size increases down the group, their ionization enthalpy decreases. Due to their small size as compared to the corresponding alkali metals, the first ionization enthalpy of the alkaline earth metals is higher than those of the corresponding Group 1 metals for the same period. The second ionization enthalpies of the alkaline earth metals are smaller than those of the corresponding alkali metals because for the alkali metals, the second electron is to be removed from an inert gas configuration.

**Physical Properties:** All alkali metals are silvery white, soft and light metals. This is due to having only one valence electron which participates in bonding. These elements have a low density which increases down the group from Li to Cs, because of their larger size. However, potassium is lighter than sodium because of its larger atomic volume. The melting and boiling points of the alkali metals are low, which indicate weak metallic bonding, due to the presence of only a single valence electron in them. The strength of the metallic bond decreases down the group, and the m.p. decreases accordingly. The m.p of lithium is nearly twice as high as that of sodium because of the stronger metallic bonding on account of its smaller size. However, the m.p. of all the others are close together. The alkali metals and their salts impart a characteristic colour to oxidizing flames. This is because the heat from the flame excites the outermost orbital electron to a higher energy level. When the excited electrons come back to the ground state, there is an emission of radiation in the visible region as given below:

Table 15.2 (a) : Characteristic flame color of group 1 elem	nents
---	-------

Metal	Li	Na	К	Rb	Cs
Colour	Crimson red	Yellow	Violet/Lilac	Red violet	Blue

When these elements are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. This property makes caesium and potassium useful as electrodes in photoelectric cells. The alkaline earth metals, in general, are silvery white, lustrous and relatively soft, but are however, harder than the alkali metals. Beryllium and magnesium appear to be somewhat greyish. The melting and boiling point of these metals are higher than alkali metals due to their smaller size and two valence electrons. Due to their low ionization enthalpies, they are strongly electropositive in nature. The electropositive character increases down the group from Be to Ba. Calcium, strontium and barium, all impart a characteristic colour to the flame.



Metal	Ве	Mg	Са	Sr	Ва
Colour	No Colour	No colour	Brick red	Crimson	Apple green

The electrons in beryllium and magnesium are too strongly bound to get excited by the flame. Hence, these elements do not impart any colour to the flame. Like alkali metals, the electrical and thermal conductivity of alkaline earth metals are high.

### **PLANCESS CONCEPTS**

Softness increases from Li to Cs due to weakening of interatomic attractions

### **Note: Trends of Melting and Boiling Points:**

In case of Alkali Metals – Li > Na > K > Rb > Cs > Fr

In Case of alkaline earth metals – Be > Mg > Ca > Sr > Ba

Note-Trends in case of heat of atomization:

In case of alkali metals – Li > Na > K > Rb > Cs > Fr

Not - In Case of density, following trend is observed:

### The reason for this type of trend is:

Explanation: On moving down, both atomic mass and atomic volume increase, but increase in atomic volume can't compensate for the increase in atomic mass. An exceptionable is the lower density of K as compared to Na, which is due to the abnormal increase in the size of K.

### Note: Trends of density in case of alkaline earth metals:

All are light metals, since the densities of alkaline earth metals decrease slightly from Be to Ca after which there is an increase.

### Saurabh Gupta (JEE 2010, AIR 443)

# 2.4 Hydration Enthalpy

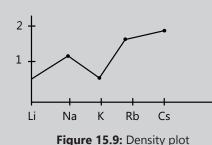
Hydration represents the dissolution of a substance in water by adsorbing a water molecule by weak valency forces. **Note:** The hydration is an exothermic process, i.e., energy is released during hydration

### PLANCESS CONCEPTS

Smaller the cation, greater is the degree of hydration energy

 $Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Rb^{\oplus} > Cs^{\oplus}$ 

Saurabh Gupta (JEE 2010, AIR 443)





The hydration enthalpies of alkali metal ions, decrease with the increase in ionic sizes. Li<sup>+</sup> has a maximum degree of hydration and for these reasons lithium salts are mostly hydrated e.g., LiCl.2H<sub>2</sub>O. Like alkali metal ions, hydration enthalpies of alkaline earth metal ions decrease with the increase in ionic size down the group.

The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus compounds of alkaline earth are more extensively hydrated than those of alkali metals, e.g., MgCl<sub>2</sub> are CaCl<sub>2</sub> exist as MgCl<sub>2</sub>.6H<sub>2</sub>O and CaCl<sub>2</sub>.6H<sub>2</sub>O while NaCl and KCl do not form such hydrates.

PLANCESS CONCEPTS	×.						
Relative conducting power $\infty \frac{1}{\text{Relative hydrated}}$	Neeraj Toshniwal (JEE 2009, AIR 21)						
Therefore, the Trend of Relative Conducting Power	in case of Alkali Metals Would be:						
$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$							
Note: The Trend in Case of Relative ionic radii is:	Note: The Trend in Case of Relative ionic radii is:						
$Cs^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$	G						
Reverses in Case of Relative Hydrated radii:							
$Cr^{\oplus} > Rb^{\oplus} > K^{\oplus} > Na^{\oplus} > Li^{\oplus}$							
2.5 Standard Oxidation Potential and Rec	lucing Properties in case of Alkali metals						
(a) Since alkali metals easily lose electrons, they have reducing nature.	high values of oxidation potential accounting for the good						
(b) Standard oxidation potentials are listed below:							
Li Na K	Rb Cs						
$E_{OP}^{0}$ +3.05 +2.71 +2.93	+2.99 +2.99						
(c) More the oxidation potential, more is the tendence nature in an aqueous medium.	cy, to get oxidized and thus more powerful is the reducing						
(d) Alkali metals liberate $H_2$ from $H_2O$ and HCl							
$2H_2O + 2M \rightarrow 2MOH + H_{2}2HCI + 2M \rightarrow 2N$	1Cl + H <sub>2</sub>						

**PLANCESS CONCEPTS** 

From the ionization energy trend, we expect Li to have the lowest oxidation potential. But that is not so. The greatest reducing nature of Li in an aqueous medium is accounted for, due to the maximum hydration energy of the Li<sup>®</sup> ion.

Aman Gour (JEE 2012, AIR 230)

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#### In case of Alkaline Earth Metals,

- (a) Standard oxidation potential Ra > Ba > Sr > Ca > Mg > Be
- (b) The reducing character increases from Be to Ba, due to the increasing order of the oxidation potential.

# **3. CHEMICAL PROPERTIES**

Alkali metals are highly reactive due to their larger size and low ionization enthalpy. The reactivity of these metals increases down the group. The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

### **Reasons for High Reactivity of Alkali Metals-**

Alkali metals exhibit very high chemical reactivity, and the reasons for their high reactivity are:

- (a) Low IE,
- (b) Low heat of atomization
- (c) High heats of hydration

### 3.1 Reactivity towards Air and Water

Alkali metals tarnish in dry air due to the formation of their oxides which in tum react with moisture to form hydroxides. They burn vigorously in oxygen, forming oxides.

Lithium forms a monoxide, sodium forms a peroxide, and the other metals form a superoxide. The superoxide  $O_2^-$  ion is stable only in the presence of larger cations such as K, Rb, Cs,

4Li + 
$$O_2 \rightarrow 2Li_2O$$
 (oxide): 2Na +  $O_2 \rightarrow Na_2O_2$  (peroxide)

$$M + O_2 \rightarrow MO_2$$
 (superoxide) (where  $M = K$ , Rb, Cs).

All five metals can be induced to form the normal oxides, peroxides or superoxides by dissolving the metal in liquid ammonia and bubbling in the appropriate amount of oxygen. Lithium shows exceptional behaviour in a reaction directly with nitrogen of air to form the nitride, Li<sub>N</sub>.Li<sub>3</sub>N is ionic

 $(3Li^+ \text{ and } N^{3-})$ , and is ruby red.

$$2\text{Li}_{3}\text{N} \xrightarrow{\Delta} 6\text{Li} + \text{N}_{2}$$
 :  $\text{Li}_{3}\text{N} + 3\text{H}_{2}\text{O} \rightarrow 3\text{LiOH} + \text{NH}_{3}$ 

The alkali metals react with water to form hydroxides and dihydrogen. The reaction becomes increasingly violent on descending the group. Although lithium the has most negative electrode potential (E<sup>o</sup>) value, its reaction with water is less vigorous than that of sodium which has the least negative electrode potential (E<sup>o</sup>) value among the alkali metals. This behaviour of lithium is attributed to its small size and very high hydration energy. Other metals of the group react explosively with water.

 $2M + 2H_2O \rightarrow 2MOH + H_2$  (M = alkali metal cation).

They also react with proton donors such as alcohol, gaseous ammonia and alkynes. This is because of their high reactivity towards air and water, the alkali metals are normally kept in kerosene oil. Beryllium and magnesium are inert to oxygen and water because of the formation of an oxide film on their surface. However, powdered beryllium burns brilliantly on ignition in air to give BeO and Be<sub>3</sub>N<sub>2</sub>.

Magnesium is more electropositive and burns with a dazzling brilliance in air to give MgO and Mg<sub>3</sub>N<sub>2</sub>.

Calcium, strontium and barium are readily attacked by air to form the oxide and nitride. They also react with water with increasing its reactivity.

# 3.2 Reactivity towards Dihydrogen

The alkali metals react with dihydrogen at about 673 K (lithium at 1073 K) to form hydrides. All the metal hydrides are ionic solids with high melting points.

All alkaline earth metals except beryllium combine with hydrogen upon heating to form their hydrides, MH<sub>2</sub>, which are also high melting solids. BeH<sub>2</sub> however, can be prepared by the reaction of BeCl<sub>2</sub> with LiAlH<sub>4</sub>.

 $2\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow 2\text{BeH}_2 + \text{LiCl} + \text{AlCl}_3$ 

### **3.3 Reactivity towards Halogens**

Reactivity towards halogens: The alkali metals readily react vigorously with halogens to form ionic halides, MX. However, lithium halides are somewhat covalent. This is because of the high polarization capability of the lithium ion. The Li<sup>+</sup> ion is very small in size and has a high tendency to distort electron clouds around the negative halide ion. Since anion with larger sizes can be easily distorted, among halides lithium iodide is the most covalent in nature. All the alkaline earth metals combine with halogens at elevated temperatures forming their halides.

 $M + X_2 \rightarrow MX_2 (X = F, CI, Br, I)$ 

## **3.4 Reducing Nature**

Alkali metals, are strong reducing agents, lithium being the most and sodium the least powerful with the small size of its ion, lithium has the highest hydration enthalpy which accounts for its high negative E<sup>o</sup> value and its high reducing power. Like alkali metals, the alkaline earth metals are strong reducing agents. This is indicated by the large negative value of their reduction potentials. Beryllium has a less negative value compared to other alkaline earth metals, due to a relatively large value of the atomization enthalpy of the metal. However, its reducing nature is due to a large hydration energy associated with the small size of Be<sup>2+</sup> ion.

## 3.5 Solution in Liquid Ammonia

The alkali metals dissolve in liquid ammonia giving deep blue solutions.

 $\mathsf{M} + (\mathsf{x} + \mathsf{y}) \mathsf{NH}_{\mathsf{3}} \rightarrow [\mathsf{M} (\mathsf{NH}_{\mathsf{3}})_{\mathsf{x}}]^{+} + [\mathsf{e} (\mathsf{NH}_{\mathsf{3}})_{\mathsf{3}}]^{-} \checkmark$ 

In dilute solutions, the main species are metal ions (M<sup>+</sup>) and electrons, which are solvated (i.e.ammoniated). The blue colour, corresponding to a broad absorption band near 1500 nm that falls into the visible range, is attributed to the solvated electron.

The blue solution of alkali metals in liquid ammonia, decompose very slowly with the liberation of hydrogen (i.e., reduction of the solvent).

 $M^{+}(aq) + e^{-}(aq) + NH_{3}(\ell) \rightarrow MNH_{2}(aq) + 1/2 H_{2}(g)$ 

(Where 'am' denotes solution in ammonia). Or,  $NH_3 + e^- \rightarrow NH_2^- + \frac{1}{2}H_2$ .

Decomposition is accelerated by the presence of many transition metal compounds, e.g., by stirring the solution with a rusty iron wire. The solution of metals in liquid ammonia act as powerful reducing agents (it even reduces the aromatic ring).

 $O_2 + e^- \rightarrow O_{2'} O_2 + 2e^- \rightarrow O_2^{2-}$  (change of oxidation states from 0 to -1).

[Ni (CN)  $_{4}$ ]<sup>2-</sup>  $\leftrightarrow$  2e<sup>-</sup>  $\rightarrow$  [Ni (CN)  $_{4}$ ]<sup>4-</sup> (change of oxidation states from +2 to 0).

 $\text{GeH}_4 + e^- \rightarrow \text{GeH}_2^- + \frac{1}{2} \text{H}_2 \text{S} + 2e^- \rightarrow \text{S}^{2-}$  (change of oxidation states from 0 to – 2).

 $[Fe(CO)_{5}] + 2e^{-} \rightarrow [Fe(CO)_{4}]^{2-} + CO (change of oxidation states from 0 to - 2).$ 

Like alkali metals, the alkaline earth metals, except beryllium, dissolve in liquid ammonia to give a deep blue-black solution forming ammoniated ions. The colour is due to the spectrum from solvated electrons.

 $M + (x + y) \operatorname{NH}_{3} \rightarrow [M (\operatorname{NH}_{3})_{x}]^{2+} + 2[e (\operatorname{NH}_{3})_{y}]^{-}$ 

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These solution decompose very slowly forming amides but the reaction is accelerated by many transition metals and their compounds.  $2NH_3 + 2e^- \rightarrow 2NH_2^- + H_2$ 

Evaporation of ammonia from the solution of alkali metals yields the metal, but with alkaline earth metals evaporation of ammonia gives hexammoniates of the metals,  $[M(NH_3)_6]^{2+}$ . These slowly decompose to give amides. M  $(NH_2)_3 \rightarrow M (NH_2)_3 + 4NH_2 + H$ 

**Illustration 1:** The correct order of size of the ions is:

**Sol:** Down the group, the size of ions increases because of the increase in the number of atomic shells.

The increase in the number of atomic shells over weighs the increase in effective nuclear charge.

Therefore (B) option is correct.

**Illustration 2:** Which of the following has the highest hydration enthalpy in an aqueous solution?

(A) Na<sup>+</sup> (B) Be<sup>2+</sup> (C) Ba<sup>2+</sup> (D) Cs<sup>+</sup>

**Sol:** The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions on earth metal ions decrease with increase in ionic size down the group.

 $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ . Therefore (B) option is correct.

**Illustration 3:** Which one the following metals is most commonly used in photoelectric cells?

(A) Li (B) Ca (C) Cs (D) Fr

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**Sol:** The ionization enthalpies of the alkali metals are considerably low and decrease down the group from Li to Cs. This is because the effect increasing size outweighs the increasing nuclear charge, and the outermost electrons are very well screened from the nuclear charge. When alkali metals are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. This property make caesium and potassium useful as electrodes in photoelectric cells. Therefore (c) option is correct.

**Illustration 4:** A blue coloured solution of sodium in liquid ammonia at –33°C behaves as strong reducing agent because of: (JEE ADVANCED)

(A) The formation of ammoniated sodium (B) The formation of ammoniated electron

(C) The formation of sodium amide

(D) The formation of sodium nitride

**Sol**: The solution of metals in liquid ammonia act as powerful reducing agents (it even reduces the aromatic ring) because of ammoniated electron,

Na + (x + y) NH<sub>3</sub>  $\rightarrow$  [Na (NH<sub>3</sub>)<sub>x</sub>]<sup>+</sup> + [e (NH<sub>3</sub>)<sub>y</sub>]<sup>-</sup>

E.g.,  $O_2 + e^- \rightarrow O_2^{2-}, O_2^{2-} + 2e^- \rightarrow O_2^{2-}$  (change of oxidation states from 0 to – I),

 $[Ni(CN)_4]^{2-}$  +  $2e^{-} \rightarrow [Ni(CN)_4]^{4-}$  change of oxidation states from + II to 0).

# 4. GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS AND ALKALINE EARTH METALS

Compounds of the alkali metals are generally ionic in nature. On combustion, in the excess of air, alkali metals form different type of oxides as given in the following table:

Alkali Metal	Oxide	Peroxide	Superoxide
Li	Li <sub>2</sub> O	(Li <sub>2</sub> O <sub>2</sub> )	
Na	(Na <sub>2</sub> O)	Na <sub>2</sub> O <sub>2</sub>	
К			KO2
Rb			RbO <sub>2</sub>
Cs			CsO <sub>2</sub>

Table 15.3: Principal Combustion Product (Minor Product)

The increasing stability of the peroxide or superoxide, as the size of the metal ion increases, is due to the stabilization of large anions by larger cations through lattice energy effects, these oxides are easily hydrolyzed by water to form hydroxides according to the following reactions:

$$\begin{split} \mathsf{M}_2\mathsf{O} + \mathsf{H}_2\mathsf{O} &\rightarrow 2\mathsf{M}^+ + 2\mathsf{O}\mathsf{H}^- \\ \mathsf{M}_2\mathsf{O}_2 + 2\mathsf{H}_2\mathsf{O} &\rightarrow 2\mathsf{M}^+ + 2\mathsf{O}\mathsf{H}^- + \mathsf{H}_2\mathsf{O}_2 \\ 2 \ \mathsf{M}\mathsf{O}_2 + 2\mathsf{H}_2\mathsf{O} &\rightarrow 2\mathsf{M}^+ + 2\mathsf{O}\mathsf{H}^- + \mathsf{H}_2\mathsf{O}_2 + \mathsf{O}_2 \end{split}$$

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour.  $LiO_2$  and  $NaO_2$  are yellow.  $KO_2$  and  $CsO_2$  are orange whereas  $RbO_2$  is brown in colour. The superoxides are also paramagnetic. The hydroxide are all white crystalline solids. The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with the evolution of much heat on the account of intense hydration. The melting and boiling points of alkali metal halides always follow the trend: fluoride > chloride > bromide > iodide. All alkali metal halides are generally soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy whereas the low solubility of Cs is due to the smaller hydration enthalpy of its two ions. Other halides of lithium are soluble in ethanol. Acetone and ethyl acetate; LiCl is soluble in pyridine also.

The alkali metals form salts with all the oxo-acids. The thermal stability of oxy-acid salts generally increases down the group with increasing metallic character, i.e. electropositive character. They are generally soluble in water and thermally stable. Their carbonates ( $M_2CO_3$ ) and in most cases the hydrogencarbonates ( $MHCO_3$ ) also are highly stable to heat. As the electropositive character increases down the group, the stability of the carbonate and hydrogencarbonates increases.

Group 1 metals are so strongly basic, that they (except lithium) also form solid bicarbonates. No other metals form solid bicarbonates. Lithium carbonate is not so stable to heat. Its hydrogencarbonates do not exist as solids. Although  $NH_4HCO_3$  also exists as a solid. The crystal structures of  $NaHCO_3$  and  $KHCO_3$  both show hydrogen bonding, but are different.

(a) In NaHCO<sub>3</sub>, the  $HCO_3^-$  ions are linked into an infinite chain and (b) in KHCO<sub>3</sub>,  $HCO_3^-$  forms a dimeric anion.

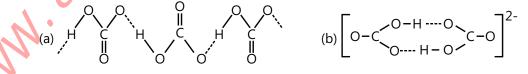


Figure 15.10: Hydrogen Bonding in NaHCO<sub>3</sub> and KHCO<sub>3</sub>

The solubility of the alkali metal salts except fluorides, carbonates and hydroxides decreases down the group from Li to Cs. This is because of the fact that down the group with the increasing size of the cation the lattice energy as well as hydration energy also decrease but the change in hydration energy is more as compared to that of lattice energy. The alkaline earth metals form compounds which are predominantly ionic but less ionic than the alkaline earth metals, which forms compounds of alkali metals. This is due to an increased nuclear charge and smaller size. The oxide and other compounds of beryllium and magnesium are more covalent than those formed by the heavier and large sized member (Ca, Sr. Ba). The alkaline earth metals bum in oxygen to form the monoxide, MO which, except for BeO has a rock-salt structure. The BeO is essentially covalent in nature. The enthalpies of formation of these oxides are quite high and consequently they are very stable to heat. BeO is amphoteric while oxides of other elements are ionic in nature. All these oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides. MO +  $H_2O \rightarrow M(OH)_2$ . The solubility, thermal stability and the basic character of these hydroxides increases with the increasing atomic number from Mg(OH)<sub>2</sub> to Ba (OH)<sub>2</sub>. The alkaline earth metal hydroxides are however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with acid and alkali both.

 $Be(OH)_2 + 2OH^- \rightarrow [Be(OH)_4]^{2-}$  (beryllate ion)

 $\mathsf{Be}(\mathsf{OH})_2 + 2\mathsf{HCI} + 2\mathsf{H}_2\mathsf{O} \rightarrow [\mathsf{Be}(\mathsf{H}_2\mathsf{O})_4]\mathsf{Cl}_2.$ 

The anhydrous halides of alkaline earth metals are polymeric .Except for beryllium halides, all other halides of alkaline earth metal are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents. Beryllium chloride vapours contains  $BeCl_2$  and  $(BeCl_2)_2$  but the solid is polymerized. Beryllium chloride in the solid state has a chain structure as shown below:

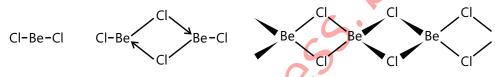


Figure 15.11: Beryllium chloride in solid state

In the vapour phase BeCl<sub>2</sub> tends to form a chloro-bridged dimer which dissociates into the linear monomer at a high temperature of the order of 1200 K. The tendency to form halide hydrates gradually decreases (for example, MgCl<sub>2</sub>.6H<sub>2</sub>O, CaCl<sub>2</sub>.6H<sub>2</sub>O, SrCl<sub>2</sub>.6H<sub>2</sub>O and BaCl<sub>2</sub>.2H<sub>2</sub>O) down the group. The dehydration of hydrated chlorides, bromides and iodides of Ca, Sr and Ba can be achieved on heating; however, the corresponding hydrated halides of Be and Mg on heating suffer hydrolysis. The fluorides are relatively less soluble than the chlorides owing to their high lattice energies. Carbonate of alkaline earth metals are insoluble in water and can be precipitated by the addition of a sodium or ammonium carbonate solution to a solution of a soluble salt of these metals. The solubility of carbonates in water decreases as the atomic number of the metal ion increases. All carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO<sub>2</sub>. The thermal stability increases with increasing cationic size. The sulphates of the alkaline earth metals are all white solids and are stable to heat. BeSO<sub>4</sub> and MgSO<sub>4</sub> are readily soluble in water, the solubility decreases from CaSO<sub>4</sub> to BaSO<sub>4</sub>. The greater hydration enthalpies of Be<sup>2+</sup> and Mg<sup>2+</sup> ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

The nitrates are made by the dissolution of the carbonate in dilute nitric acid, magnesium nitrate crystallizes with six molecules of water, whereas barium nitrate crystallizes as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size and decreasing hydration enthalpy. All of them decompose on heating to give an oxide like lithium nitrate.

2M  $(NO_3)_2 \rightarrow 2MO + 4 NO_2 + O_2$  (M = Be, Mg, Ca, Sr, Ba)

The solubility of the alkaline earth metal salts except hydroxides and fluorides decreases down the group from Be to Ba. This is because of the fact that down the group with the increasing size of the cation, the lattice energy as well as hydration energy also decreases, but the change in hydration energy is more as compare to that of lattice energy. Except  $BeF_2$  all other fluorides are water insoluble. The solubility of beryllium fluoride in water is due to higher solvation energy on account of the higher polarizing power of  $Be^{2+}$ . The thermal stability of oxy-acid salts of alkaline earth metals generally increases down the group with increasing metallic character, i.e. electropositive character.

### PLANCESS CONCEPTS

Low thermal stability of Li<sub>2</sub>CO<sub>3</sub> can be explained as follows:

The small Li<sup>+</sup> ion exerts a strong polarizing action and distorts the electron cloud of nearby oxygen atom of the large  $CO_3^{2-}$  ion. This results in the weakening of C–O bond and strengthening of Li–O bond, favouring the formation of Li<sub>2</sub>O and CO<sub>2</sub>. High lattice energy of Li<sub>2</sub>O than Li<sub>2</sub>CO<sub>3</sub> also favours the decomposition of Li<sub>2</sub>CO<sub>3</sub>

**Figure 15.10:** Li<sub>2</sub>CO<sub>3</sub> molecule

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Illustration 5: Select the correct set of statements.

(i) Solubility of alkali hydroxides is in order, CsOH > RbOH > KOH > NaOH > LiOH

(ii) Solubility of alkali carbonates is in order,  $Li_2CO_3 > Na_2CO_3 > K_2CO_3 > K_2CO_3 > Rb_2CO_3 > Cs_2O_3$ 

(iii) Hydrated radii is in order, Li < Na $^{+}$  < K $^{+}$  < Rb $^{+}$  < Cs $^{+}$ 

(iv) Stability of peroxides is in order,  $Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2$ 

The options are: (A) (i), (iv) (B) (i), (iii) (C) (ii), (iii), (iv)

Sol: Compare the lattice energy and the hydration energy of the cations.

(i) While going from lithium to cesium hydroxide, the decrease in lattice energy is more as compared to that of hydration energy. So, the solubility of hydroxides increases down the group (iv). This is because of fact that the bigger cation stabilizes the bigger anion through crystal lattice energy. Therefore (A) option is correct.

# 5. ANOMALOUS PROPERTIES OF LITHIUM

The anomalous behaviour of lithium is due to the: (i) exceptionally small size of its atom and ion, and (ii) high polarizing power (i.e., charge/radius ratio). As a result, there is an increased covalent character of lithium compounds, which is responsible for their solubility in an organic solvent. Further, lithium shows a diagonal relationship to magnesium.

### Points of difference between lithium and other alkali metals

- (a) Lithium is much harder. Its melting point and boiling point are higher than the other alkali metals.
- (b) Lithium is the least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li<sub>2</sub>O and the nitride, Li<sub>3</sub>N unlike other alkali metals.
- (c) The lithium ion itself, and also its compounds are more heavily hydrated than those of the rest of the group. LiCl is deliquescent and crystallizes as a hydrate, LiCl.2H<sub>2</sub>O whereas other alkali metal chlorides do not form hydrates.
- (d) Lithium hydrogencarbonates is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (e) Lithium unlike other alkali metal forms no ethynide on reaction with ethyne.
- (f) Lithium nitrate when heated gives lithium oxide, Li<sub>2</sub>O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

 $4LiNO_{3} \rightarrow 2Li_{2}O + 4NO_{2} + O_{2}$   $2NaNO_{3} \xleftarrow{500^{\circ}C} 2NaNO_{2} + O_{2}; \quad 4NaNO_{3} \xleftarrow{500^{\circ}C} 2Na_{2}O + 5O_{2} + 2N_{2}$ 

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 $2NaNO_2 + 2HCI \rightarrow 2NaCI + H_2O + NO_2 + NO;$   $2NO + O_2 \rightarrow 2NO_2$ 

 $2NaNO_3 + C \rightarrow 2NaNO_2 + CO_2$ ;  $KNO_3 + Zn \rightarrow KNO_2 + ZnO_3$ 

- (g) LiF and Li<sub>2</sub>O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.
- (h) Lithium hydroxide is less basic than the other hydroxides in the group and therefore, many of its salts are less stable, Li<sub>2</sub>CO<sub>3</sub>, LiNO<sub>3</sub> and LiOH all form the oxides on gentle heating; the analogues compounds of the rest of the group are stable. Another example of its less basic nature is that though lithium forms a bicarbonates in solution, it does not form a solid bicarbonate, whereas the other all form stable solid carbonates.
- (i) Lithium reacts directly with carbon to form anionic carbide. None of the other group 1 elements do this, but group 2 elements all react similarly with carbon.
- (j) Lithium has a great tendency to form complexes than have the heavier elements, and ammoniated salts such as [Li (NH<sub>3</sub>),]<sup>+</sup> exist as solids.

**Illustration 6:** Which of the following alkali metal ions has the lowest mobility in aqueous solution?

(A) Li<sup>+</sup> (B) Na<sup>+</sup> (C) K<sup>+</sup> (D) Cs<sup>+</sup>

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**Sol:** Mobility depends upon the cationic size and the tendency of the cation to get hydrated. Because Li<sup>+</sup> has the smallest size, so it is highly hydrated and its effective size becomes larger therefore mobility decreases in aqueous medium.

Therefore (A) option is correct.

**Illustration 7:** Give the reaction of the thermal decomposition of the nitrate of sodium. Explain the occurrence of the reaction in term of energy factor. What is the pH expected of an aqueous solution of NaNO<sub>3</sub>. Why?

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**Sol:** The occurrence of the reaction depends upon the stability of the reactant and the products formed pH depends upon the hydrolysis extent.

 $NaNO_3(s) \rightarrow NaNO_2(s) + \frac{1}{2}O_2(g)$ 

Since the size of  $NO_2^-$  is less than that of  $NO_3^-$ , this results in the formation of a more stable ionic lattice when bonded to a sodium ion. The pH of solution would be about 7 since neither the cation nor the anion undergoes hydrolysis to any appreciable extent.

# 6. POINTS OF SIMILARITIES BETWEEN LITHIUM AND MAGNESIUM

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii: Li<sup>+</sup> = 76 pm, Mg<sup>2+</sup> = 72 pm. The main points of similarity are:

- (a) Both lithium and magnesium are harder and lighter than other elements in their respective groups.
- (b) Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating. Both form a nitride,  $Li_3 N$  and  $Mg_3N_2$ , by a direct combination with nitrogen.
- (c) The oxides. Li<sub>2</sub>O and MgO do not combine with excess oxygen to give any superoxide.
- (d) The carbonates of lithium and magnesium decompose easily on heating to form the oxides and CO<sub>2</sub>. Solid hydrogencarbonates are not formed by lithium and magnesium.
- (e) Both LiCl and  $MgCl_2$  are soluble in ethanol.
- (f) Both LiCl and MgCl<sub>2</sub> are deliquescent and crystallize from aqueous solution as hydrates, LiCl.2H<sub>2</sub>O and MgCl<sub>2</sub>. 6H<sub>2</sub>O.

**Illustration 8:** About alkali metal-liquid NH<sub>3</sub> solution which of following statement is not true?

(A) Blue colour is due to ammoniated electrons.

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(B) Blue colour changes to bronze on dilution due to formation of metal ion clusters.

(C) With an increase in concentration of alkali metals paramagnetic nature decreases due to electron-electron combination.

(D) On heating, the blue colour becomes colourless due to the formation of a metal amide and H<sub>2</sub> gas.

**Sol:** The change depicts the formation of some complex structures.

Blue colour changes to bronze with increase in concentration of alkali metal due to formation of metal ion clusters. Therefore (B) option is correct.

Illustration 9: (A) Give the three different crystal structures of NaO<sub>2</sub>?

(B) Sodium sulphide is readily oxidized by air to form sodium thiosulphate. Write the chemical reaction only.

(C) Group 1 sulphides hydrolyze appreciably in water, giving strongly alkaline solutions. Explain?

**Sol:** Sodium, the alkali metal has been discussed over here, which is a highly reactive metal and forms sodium thiosulphate in its sulphide form.

(A)  $NaO_2$  exists in following three different crystal structures at different temperatures.

(i) Marcasite structure at – 50°C,

(ii) Pyrite structure between -77°C and -50°C,

(iii) Calcium carbide structure at room temperature.

(B)  $2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$ 

(C) Na<sub>2</sub>S hydrolyses in water according to the following reaction.  $2Na_2S + H_2O \rightarrow NaSH + NaOH$ 

**Illustration 10:** The properties of Li are similar to those of Mg. This is because.

(A) Both have nearly the same size

(C) Both have similar electronic configurations. (D) Both

(D) Both are found together in nature

(B) The ratio of their charge to size is nearly the same.

**Sol:** We discuss about the diagonal relation of the alkali and the alkaline earth metals over here, wherein similarities are pointed out.

They are diagonally related because of same polarizing power, polarizing power = charge on cation / size of cation. Therefore. (B) Option is correct

Illustration 11: Magnesium burns in air to give:

(A) MgO (B) Mg<sub>3</sub>N<sub>2</sub> (C) MgCO<sub>3</sub> (D) MgO and Mg<sub>3</sub>N<sub>2</sub> both

Sol: Magnesium

Mg burns in air to form both MgO and Mg<sub>3</sub>N<sub>2</sub>

 $2Mg + O_2 \xrightarrow{A} 2MgO$ ;  $3Mg + N_2 \xrightarrow{A} Mg_3N_2$  Therefore, (D) option is correct.

(JEE ADVANCED)

(JEE ADVANCED)

# 7. ANOMALOUS BEHAVIOUR OF BERYLLIUM

Beryllium, the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members of the group. Further, it shows a diagonal relationship to aluminium.

- (a) Beryllium has an exceptionally small atomic and ionic size and thus does not compare well with other members of the group. Because of the high ionization enthalpy and small size it forms compound, which is largely covalent and gets easily hydrolyzed.
- (b) Beryllium does not exhibit a coordination number more than four as in its valence shell there are only four orbitals. The remaining members of the group can have a coordination number of six by making use of d-orbitals.
- (c) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements Figure 15.12: Complexes in the group, are amphoteric in nature.
- (d) Beryllium hydride is electron deficient and polymeric, with multi-center bonding like aluminium hydride.
- (e) The most unusual oxygen containing complexes of Be have the formula  $Be_4O$  (O<sub>2</sub>CR)<sub>6</sub> and are formed by refluxing Be (OH), with carboxylic acids. These white crystalline compounds are soluble in non-polar organic solvents, such as alkanes, but are insoluble in water and lower alcohols. In a solution, the compounds are unionized and monomeric.

of Be

The central oxygen atom is tetrahedral surrounded by the four Be atoms and each Be atom is tetrahedrally surrounded by four oxygen atoms. The six acetate groups are arranged along the six edges of the tetrahedral ion.

### Diagonal relationship between beryllium and aluminium

The ionic radius of  $Be^{2+}$  is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the  $Al^{3+}$  ion. Hence beryllium resembles aluminium in some ways. Some of the similarities are:

- (a) Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal, i.e. they are rendered passive by nitric acid.
- (b) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, [Be (OH), ]<sup>2-</sup>just as aluminium hydroxide gives the aluminate ion, [AI (OH) ]<sup>-</sup>
- (c) The chlorides of both beryllium and aluminium have Cl<sup>-</sup> bridged chloride structure in the vapour phase.
- (d) Both the chlorides are soluble in organic solvents and are strong Lewis acids. They are used as Friedel Craft catalysts.
- (e) Beryllium and aluminium ions have a strong tendency to form complexes,  $BeF_4^{2-}$  and  $AIF_6^{3-}$  respectively.

# 8. COMPOUNDS OF ALKALI METALS

# 8.1 Sodium Oxide (Na<sub>2</sub>O)

### **Preparation:**

(a) By reduction of nitrites and nitrates of sodium with metallic sodium:

$$2NaNO_3 + 10Na \rightarrow 6Na_2O + N_2;$$
  $2NaNO_2 + 6Na \rightarrow 4Na_2O + N_2$ 

- (b) By heating sodium in limited supply of air at 180°C: Na +  $O_2 \rightarrow Na_2O$
- (c) Pure sodium oxide is formed when the mixture of sodium azide and sodium nitrite is heated

 $3NaN_3 + NaNO_2 \rightarrow 2Na_2O + 5N_2$ 

#### **Properties:**

- (a) It is a white amorphous substance. It reacts with water violently forming sodium hydroxide and evolving a large amount of heat energy  $Na_2O + H_2O \rightarrow 2NaOH$
- (b) On heating at 400°C, it decomposes forming sodium peroxide and metallic sodium vapour.

$$2Na_2O \xrightarrow{400^{\circ}C} Na_2O_2 + 2Na_2O_2$$

(c) Reaction with liquid ammonia;  $Na_2O + NH_3 \rightarrow NaNH_2 + NaOH$ 

Use: It is used as a dehydrating and polymerizing agent in organic chemistry.

### 8.1 Sodium Peroxide (Na<sub>2</sub>O<sub>2</sub>)

#### **Preparation:**

- (a) It is formed by heating sodium in an excess of air, free from moisture and carbon dioxide or in excess of pure oxygen.  $2Na + O_2$  (excess)  $\xrightarrow{350^\circ C} Na_2O_2$
- (b) Industrial method: It is a two stage reaction in the presence of excess air.

$$2Na + \frac{1}{2}O_2 \rightarrow Na_2O; \qquad Na_2O + \frac{1}{2}O_2 \rightarrow Na_2O_2$$

#### **Properties:**

(a) It is a pale yellow (when impure) hygroscopic powder stable towards heat in dry air. On exposure to moist air, it becomes white as it reacts with moisture and carbon dioxide.

 $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$  $2NaOH + CO_2 \rightarrow Na_2O_2 + H_2O_2$ 

$$2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$$

- (b) Action of water:  $Na_2O_2 + 2H_2O \xrightarrow{cold} 2NaOH + H_2O_2$ ;  $2Na_2O_2 + 2H_2O \xrightarrow{warm} 4NaOH + O_2$
- (c) Action of acid:

 $Na_2O_2 + H_2SO_4 \_ cold \rightarrow Na_2SO_4 + H_2O_2$ 

 $2Na_2O_2 + H_2SO_4 \xrightarrow{\text{warm}} 2Na_2SO_4 + 2H_2O + O_2$ 

(d) Reaction with CO and CO<sub>2</sub>: Na<sub>2</sub>O<sub>2</sub>+CO  $\rightarrow$  Na<sub>2</sub>CO<sub>3</sub>; 2Na<sub>2</sub>O<sub>2</sub> + 2CO<sub>2</sub>  $\rightarrow$  2Na<sub>2</sub>CO<sub>3</sub> + O<sub>2</sub>

So, it is used to purify the air in a submarine and confined spaces as it removes both CO and  $CO_2$  and gives oxygen.

- (e) It is a powerful oxidant and many of its reactions are dangerously violent, particularly with the reducing agents, such as Al powder charcoal, sulphur and many organic liquids.
  - (i) Chromic compounds are oxidized to chromates  $2Cr(OH)_{3} + 3Na_{3}O_{2} \rightarrow 2Na_{3}CrO_{4} + 2NaOH + 2H_{2}O \text{ or } 2Cr (OH)_{3} + 3O_{2}^{2-} \rightarrow 2CrO_{4}^{2-} + 2OH^{-} + 2H_{2}O$

$$MnSO_4 + 2Na_2O_2 \rightarrow Na_2MnO_4 + Na_2SO_4 \text{ or } Mn (OH)_2 + 2O_2^{2-} \rightarrow MnO_4^{2-} + 2OH^{-1}$$

(iii) Sulphides are oxidized to corresponding sulphates

$$Na_2O_2 \rightarrow Na_2O + [O] \qquad ; \qquad Na_2S + 4[O] \rightarrow Na_2SO_4$$
  
(iv) 
$$Na_2O_2 \rightarrow Na_2O + [O] \qquad ; \qquad 2AI + 3[O] \rightarrow AI_2O_2$$

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- (v) Benzoyl peroxide (bleaching agent) is formed when  $C_6H_5COCI$  reacts with  $Na_2O_2$ .  $2C_6H_5COCI + Na_2O_2 \rightarrow (C_6H_5CO)_2O_2$  (benzoyl peroxide) + 2NaCl
- (vi) Reduces stronger oxidizing agent such as acidified KMnO<sub>4</sub>

$$2\mathsf{MnO}_{4}^{-} + 16\mathsf{H}^{+} + 5\mathsf{O}_{2}^{2-} \rightarrow 2\mathsf{Mn}^{2+} + 8\mathsf{H}_{2}\mathsf{O} + 5\mathsf{O}_{2}; \mathsf{Na}_{2}\mathsf{O}_{2} + \mathsf{O}_{2} \xrightarrow{450^{\circ}} 2\mathsf{NaO}_{2} \xrightarrow{200 \text{ stm}} 2\mathsf{NaO}_{2}$$

#### Use:

- (a) Used for the production of oxygen under the name ozone.
- (b) It is used as a bleaching agent for bleaching wood pulp, paper and fabrics such as cotton and linen.

### 8.3 Potassium Superoxide (KO<sub>2</sub>)

#### **Preparation:**

(a) It is prepared by burning potassium in the excess of oxygen free from moisture.

$$K + O_2 \rightarrow KO_2$$

#### **Properties:**

- (a) It is an orange coloured (chrome yellow) powder and reacts with water according to following reaction.  $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$
- (**b**) It reacts directly with CO and CO<sub>2</sub>.  $2KO_2 + CO \rightarrow K_2CO_3 + O_2$ ;  $2KO_2 + CO_2 \rightarrow K_2CO_3 + \frac{3}{2}O_2$

If more CO<sub>2</sub>, in presence of moisture is present; then  $4KO_2 + 4CO_2 + 2H_2O \rightarrow 4KHCO_3 + 3O_2$ 

- (c) On heating with sulphur, it forms potassium sulphate;  $2KO_2 + S \rightarrow K_2SO_4$
- **Use:** It is used as an oxidizing agent and air purifier in space capsules, submarine and Breathing mask as it produces O<sub>2</sub> and removes CO<sub>2</sub>.

## 8.4 Potassium Sesquioxide (K<sub>2</sub>O<sub>3</sub>)

It is obtained when oxygen is passed through liquid ammonia containing potassium.

4K (dissolved in liquid NH<sub>3</sub>)  $\xrightarrow{3O_2}$  2K<sub>2</sub>O<sub>3</sub>

## 8.5 Sodium Hydroxide or Caustic Soda (NaOH)

Preparation: It is most conveniently manufactured by one of the following processes,

- (a) Methods involving sodium carbonate as a starting material:
- (i) Gossage process (causticising process):  $Na_2CO_3 + Ca (OH)_2 \implies CaCO_3 + 2NaOH$

The most suitable concentration of sodium carbonate taken in this process is 15 - 20%. The caustic soda produced by this method is not pure and contains some calcium carbonate, sodium carbonate and calcium hydroxide as impurities.

(ii) Lowig's process:  $Na_2CO_3 + Fe_2O_3 \xrightarrow{\text{red heat}} 2NaFeO_2 + CO_2$ 

The sodium ferrite is cooled and thrown into hot water, the hydrolysis of sodium ferrite occurs forming NaOH. 2NaFeO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  2NaOH + Fe<sub>2</sub>O<sub>3</sub>

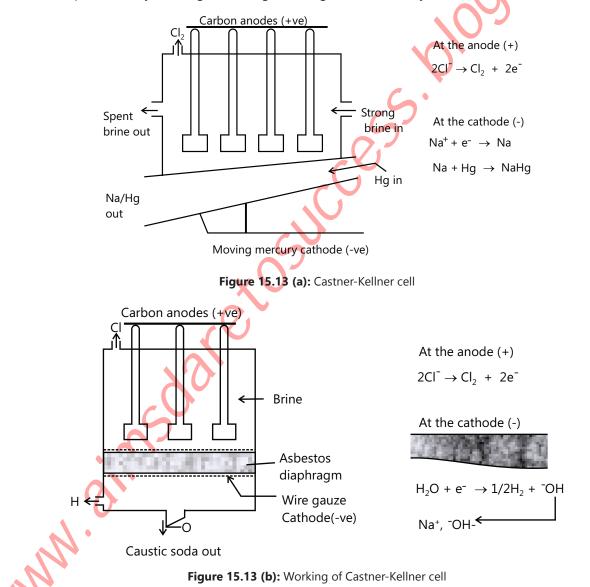
(iii) Methods involving sodium chloride as starting material: Electrolysis of sodium chloride solution occurs according to following principle.

NaCl  $\implies$  Na<sup>+</sup> + Cl<sup>-</sup>; H<sub>2</sub>O  $\implies$  H<sup>+</sup> + OH<sup>-</sup>

On passing electricity, Na<sup>+</sup> and H<sup>+</sup> ions move towards cathode and Cl<sup>-</sup> and OH<sup>-</sup> ions move towards the anode. The discharge potential of H<sup>+</sup> ions is less than Na<sup>+</sup> ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl<sup>-</sup> ions are easily discharged as their discharge potential is less than that of OH<sup>-</sup> ions. Cl<sub>2</sub> gas is, therefore, liberated at the anode. It is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis, otherwise the following reaction will take place. 2NaOH +  $Cl_2 \rightarrow NaCl + NaClO + H_2O$ 

To overcome this problem, the anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode.

(a) The mercury cathode cell (Castner-Kellner cell): In this cell mercury flows along the bottom of the cell and is a made cathode. The brine solution flows in the same direction and the anode consists of a number of graphite blocks. The brine is electrolyzed and since, hydrogen has a high overvoltage at the mercury cathode, sodium is preferentially discharged forming an amalgam with mercury.



The sodium amalgam flows out and is reacted with water to give NaOH

 $2NaHg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$ 

The mercury is re-circulated to the cell. Hydrogen and chlorine are the two important by-products.

- (b) **Diaphragm cell:** In this type of cell alkali and chlorine are kept separate by the use of a diaphragm and on contact with a negative wire gauze, electrolysis begins. Chlorine is liberated at the graphite anode and sodium hydroxide is formed at the outside edges of the cathode.
- (c) Using Nafion Membrane Cell: The natural brine (NaCl) is now electrolyzed in a membrane cell in which the anode and the cathode are separated by a NAFION membrane. Nafion is a copolymer of tetrafluoromethylene and pentafluorosulphonyl ethoxyether. The copolymer is supported by a Teflon mesh.

2NaCl (aq) + H<sub>2</sub>O ( $\ell$ )  $\xrightarrow{\text{Electrolysis}}$  2NaOH (aq) + H<sub>2</sub> (g) + Cl<sub>2</sub> (g)

Presently the method makes use of Nafion membrane in place of diaphragm.

### 8.5.1 Preparation of Pure Sodium Hydroxide

Commercial sodium hydroxide is purified with the help of an alcohol. Sodium hydroxide dissolves in alcohol, while impurities like NaCl,  $Na_2CO_3$ ,  $Na_2SO_4$  etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distils off while pure solid sodium hydroxide is left behind.

### **Properties:**

- (a) It is a white crystalline solid and has a soapy touch.
- (b) Its density is 2.13 g/mL and melting point is 318.4°C.
- (c) It is highly soluble in water and is bitter in taste, and is corrosive in nature.
- (d) Neutralization and hydrolysis reactions:

 $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O; NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$ These are non-redox type of reactions.

- (e) Reaction with acidic oxides:  $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O_2NaOH + 2NO_2 \rightarrow NaNO_2 + NaNO_3 + H_2O; 2NaOH + SO_3 \rightarrow Na,SO_4 + H_2O_2NaOH + SO_3 \rightarrow Na,SO_4 + H_2O_2 \rightarrow Na,SO_4 + H_2O_2NAOH + SO_3 \rightarrow Na,SO_4 + H_2O_2 \rightarrow Na,SO_4 + H_2O_2$
- (f) Reaction with amphoteric oxides:

PbO + 2NaOH  $\rightarrow$  Na<sub>2</sub>PbO<sub>2</sub> + H<sub>2</sub>O; ZnO + 2NaOH  $\rightarrow$  Na<sub>2</sub>ZnO<sub>2</sub> + H<sub>2</sub>O

 $SnO + 2NaOH \rightarrow Na_2SnO_2 + H_2O_2^* + 2NaOH \rightarrow Na_2SnO_3 + H_2O_2^*$ 

### (g) Reacts with non-metals:

- (i) Halogens
  - With cold & dilute NaOH: 2NaOH +  $Br_2 \rightarrow NaBr + NaOBr + H_2O$
  - With hot & concentrated NaOH:  $6NaOH + 3Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$ F<sub>2</sub> with cold & dilute NaOH gives OF<sub>2</sub> and with hot & concentrated NaOH gives O<sub>2</sub>
- (ii) With white phosphorus:  $3NaOH + P_4 \rightarrow 3NaH_2PO_2 + PH_3$
- (iii) With sulphur:  $6NaOH + 4S \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O_3$
- (iv) With boron:  $2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$
- (v) With silicon: 2NaOH + Si + H<sub>2</sub>O  $\rightarrow$  Na<sub>2</sub>SiO<sub>3</sub> + 2H<sub>2</sub>
- (h) Reaction with metals and salts:
  - (i) Reaction with amphoteric metals (e.g. Al, Pb, Sn, Zn etc.):
    - They liberate hydrogen gas.

 $4NaOH + 2H_2O + 2AI \rightarrow 2NaAIO_2 + 3H_2$ 

 $6NaOH + 2AI \rightarrow 2Na_3AIO_3 + 3H_2;$  Zn + NaOH  $\rightarrow Na_2ZnO_2 + H_2$ 

- (ii) Reaction with salts of amphoteric metals: Salts dissolves in sodium hydroxide (excess)  $SnCl_2 + 2NaOH \rightarrow Sn (OH)_2 \downarrow$  (white) + 2NaCl; Sn (OH)<sub>2</sub> + 2NaOH  $\rightarrow$  Na<sub>2</sub>SnO<sub>2</sub> + 2H<sub>2</sub>O
- (iii) Reaction with salts of Cr, Ni, Fe, Mn. Cu etc.

### Form insoluble hydroxides

 $CrCl_3 + 3NaOH \rightarrow Cr (OH)_3 \downarrow (green) + 3NaCl; CuCl_2 + 2NaOH \rightarrow Cu (OH)_2 \downarrow (blue) + 2NaCl_2 \downarrow (blue) + 2Na$ 

- (iv) Reaction with salts of Hg and Ag: HgCl<sub>2</sub> + 2NaOH $\rightarrow$  Hg (OH)  $_{2} \downarrow$  + 2NaCl; Hg (OH)  $_{2} \rightarrow$  HgO  $\downarrow$  (yellow or brown) + H<sub>2</sub>O 2AgNO<sub>3</sub> + 2NaOH  $\rightarrow$  2AgOH + 2NaNO<sub>3</sub>; 2AgOH  $\rightarrow$  Ag<sub>2</sub>O  $\downarrow$  (black) + H<sub>2</sub>O
- (v) Reaction with ammonium salts: It liberates ammonia from both ammonium salts and coordination complexes where ammonia acts as ligand.

 $(NH_4)_2SO_4 + NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O;$ 

6NaOH + 2[Co (NH<sub>3</sub>)<sub>6</sub>] Cl<sub>3</sub> 
$$\rightarrow$$
 12NH<sub>3</sub> + Co<sub>2</sub>O<sub>3</sub> + 6NaCl + 3H<sub>2</sub>O

- (vi) Reaction with carbon monoxide: NaOH + CO  $\xrightarrow{150-200^{\circ}C}$  HCOONa
- (vii) Reaction with H<sub>2</sub>S: NaOH + H<sub>2</sub>S  $\rightarrow$  NaSH + H<sub>2</sub>O; NaSH + NaOH  $\rightarrow$  Na<sub>2</sub>S + H<sub>2</sub>O.

It is used to remove mercaptans from petroleum products.

(viii) Reaction with alcohols: NaOH + EtOH  $\rightarrow$  NaOEt + H<sub>2</sub>O.

**Caustic property:** Sodium hydroxide is a powerful cautery and breaks down the proteins of skin to a pasty mass. On account of this property, it is commonly called caustic soda.

# 8.6 Potassium Hydroxide (KOH)

It is prepared by the electrolysis of KCl solution. KOH resembles NaOH in all its reactions. However KOH is much more soluble in alcohol. This accounts for the use of alcoholic KOH in organic chemistry.

KOH is called caustic potash, because of their corrosive properties (for example on glass or on skin) and its aqueous solution is known as potash lye.

 $2\text{KOH} + 4\text{NO} \rightarrow 2\text{KNO}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}; 4\text{KOH} + 6\text{NO} \rightarrow 4\text{KNO}_2 + \text{N}_2 + 2\text{H}_2\text{O}$ 

It is used for the absorption of gases like  $CO_2$ ,  $SO_2$ , etc. It is used for making soft soaps.

# 8.7 Sodium Carbonate or Washing Soda (Na<sub>2</sub>CO<sub>3</sub>)

### **Preparation:**

(a) By Solvay ammonia soda process: It involves followings steps.

(i) **Saturation of brine with ammonia and CO**<sub>2</sub> (In ammonia absorber):

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

$$CaCl_2 + (NH_4)_2CO_2 \rightarrow CaCO_3 \downarrow + 2NH_4Cl; MgCl_2 + (NH_4)_2CO_3 \rightarrow MgCO_3 \downarrow + 2NH_4Cl$$

Ammoniated brine is filtered to remove calcium and magnesium impurities as their insoluble carbonates.

(ii) Formation of insoluble NaHCO<sub>3</sub> (In carbonation tower):

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3; NH_4HCO_3 + NaCl \xrightarrow{30^{\circ}C} NaHCO_3 + NH_4Cl$$

Reaction is exothermic and hence there is a cooling arrangement.

NaHCO<sub>3</sub> is insoluble in cold brine solution because of the common ion effect. It is separated by filtration and the filtered is used for recovering  $NH_3 \& CO_2$ 

- (iii) Calcination to get sodium carbonate:  $2NaHCO_3 \xrightarrow{150^{\circ}C} Na_2CO_3 + CO_2 + H_2O$
- (iv) Recovery of ammonia and carbon dioxide (In recovery tower):

 $NH_4HCO_3 \xrightarrow{\Delta} NH_3 + CO_2 + H_2O; 2NH_4CI + Ca (OH)_2 \xrightarrow{\Delta} 2NH_3 + 2H_2O + CaCl_2$ 

CaCl<sub>2</sub> is obtained as by product.

(v) Preparation of CO<sub>2</sub> (In lime kiln):

CaCO<sub>3</sub>  $\xrightarrow{1375k}$  CaO + CO<sub>2</sub>; CaO + H<sub>2</sub>O  $\rightarrow$  Ca (OH)<sub>2</sub> (slaked lime)

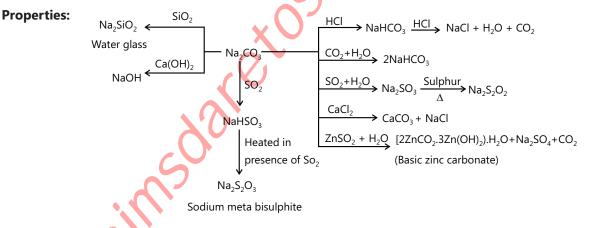
### (b) Le-Blanc process: It involves following steps

(i) NaCl +  $H_2SO_4$  (cone.)  $\xrightarrow{\Lambda}_{fumace}$  NaHSO<sub>4</sub> (salt cake) + HCl

(ii) NaHSO<sub>4</sub> + NaCl 
$$\xrightarrow{\Lambda}_{\text{fumace}}$$
 Na<sub>2</sub>SO<sub>4</sub> + HCl

(iii) 
$$Na_2SO_4 + CaCO_3 + 4C \xrightarrow{\Delta}_{fumace} \underbrace{Na_2CO_3 + CaS}_{Black ash} + 4CC$$

Black ash contains 45%  $Na_2CO_3$  is extracted with water when  $Na_2CO_3$  dissolves leaving behind insoluble as impurities called as alkali sludge or waste.



Flowchart 15.1: Chemical properties of sodium carbonate

- (a) It is white crystalline solid. It is known in several hydrated forms. The common form is decahydrate, Na<sub>2</sub>CO<sub>3</sub>10H<sub>2</sub>O. This form is called washing soda. The decahydrate form on standing in air effloresces and crumbles to powder. It is the monohydrate, Na<sub>2</sub>CO<sub>3</sub>.H<sub>2</sub>O.
- (b) It is soluble in water with the evolution of considerable amount of heat. The solution is alkaline in nature due to hydrolysis. Na<sub>2</sub>CO<sub>3</sub> + 2H<sub>2</sub>O  $\implies$  2NaOH + H<sub>2</sub>CO<sub>3</sub>

 $Na_2CO_3 + NO + NO_2 \rightarrow 2NaNO_2 + CO_2$ 

Bicarbonates precipitate normal carbonates while carbonates precipitate basic carbonates from some metal salt solutions.

$$\begin{split} \mathsf{MgCl}_2 + \mathsf{NaHCO}_3 &\to \mathsf{MgCO}_3 \downarrow + 2\mathsf{NaCI} + \mathsf{CO}_2 + \mathsf{H}_2\mathsf{O} \\ \mathsf{MgCl}_2 + 2\mathsf{Na}_2\mathsf{CO}_3 + \mathsf{H}_2\mathsf{O} &\to \mathsf{MgCO}_3 + \mathsf{Mg}(\mathsf{OH})_2 \downarrow + 4\mathsf{NaCI} + \mathsf{CO}_2 \\ \mathsf{NaNO}_3 + \mathsf{HCI} &\to \mathsf{KNO}_3 + \mathsf{NaCI} \end{split}$$

### 8.8 Potassium Carbonate, Potash or Pearl Ash (K,CO,)

### **Preparation:**

(a) By Le-Blanc process:

 $\begin{aligned} \mathsf{KCI} + \mathsf{H}_2\mathsf{SO}_4 &\to \mathsf{KHSO}_4 + \mathsf{HCI}; \ \mathsf{KHSO}_4 + \mathsf{KCI} \to \mathsf{K}_2\mathsf{SO}_4 + \mathsf{HCI} \\ \mathsf{K}_2\mathsf{SO}_4 + \mathsf{CaCO}_3 + 2\mathsf{C} \to \mathsf{K}_2\mathsf{CO}_3 + \mathsf{CaS} + 2\mathsf{CO}_2 \end{aligned}$ 

### (b) By Prechts process:

- (i)  $2\text{KCI} + 3(\text{MgCO}_3.3\text{H}_2\text{O}) + \text{CO}_2 \rightarrow 2(\text{MgCO}_3.\text{KHCO}_3.4\text{H}_2\text{O}) + \text{MgC}_2$
- (ii)  $2(MgCO_3 . KHCO_3 . 4H_2O) \xrightarrow{140^{\circ}C} 2MgCO_3 \downarrow + K_2CO_3 + 9H_2O + CO_2$  $2(MgCO_3 . KHCO_3 . 4H_2O) + MgO \xrightarrow{20^{\circ}C} 3(MgCO_3 . 3H_2O) \downarrow + K_2CO_3$

It is a white powder and deliquescent in nature. The mixture of  $K_2CO_3$  and  $Na_2CO_3$  is used as a fusion mixture in the laboratory. 2HNO<sub>3</sub> +  $K_2CO_3 \rightarrow 2KNO_3 + CO_2 + H_2O_3$ 

The potassium carbonate like sodium carbonate, cannot be prepared by Solvay process because of the intermediate, KHCO<sub>3</sub> formed which is soluble in an appreciable amount in water.

# 8.9 Sodium Bicarbonate or Baking Soda (NaHCO<sub>3</sub>)

It is obtained as the intermediate product in the Solvay ammonia soda process. Normal carbonate can be changed to bicarbonate by passing carbon dioxide through its saturated solution.  $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$  (sparingly soluble)

**Properties:** It is a white crystalline solid, sparingly soluble in water. The solution is alkaline in nature due to hydrolysis. The solution is weakly basic and gives a yellow colour with methyl orange but no colour with phenolphthalein. NaHCO<sub>3</sub> +  $H_2O \implies$  NaOH +  $H_2CO_3$ 

On heating, it loses carbon dioxide and water forming sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_3$$

**Use:** It is largely used for making baking powder. Baking powder contains NaHCO<sub>3</sub>, Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and starch. The Ca (H<sub>2</sub>PO<sub>4</sub>) is acidic and when water is added, it reacts with NaHCO<sub>3</sub>, giving CO<sub>2</sub>. The starch is a filler. Improved baking powder contains about 40% starch, 30% NaHCO<sub>3</sub>, 20% NaAl (SO<sub>4</sub>)<sub>2</sub> and 10% Ca (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>. The NaAl (SO<sub>4</sub>)<sub>2</sub> slows the reaction down so the CO<sub>2</sub> is given off more slowly.

Illustration 12: What happens when-

### (JEE ADVANCED)

-20°t.

or

(A) Anhydrous potassium nitrate is heated with excess of metallic potassium.

(B) Solution containing sodium carbonate and sodium sulphide is treated with sulphur dioxide.

**Sol:** Self-explanatory

(A)  $2KNO_3 + 10K \rightarrow 6K_2O + N_2$  (B)  $Na_2CO_3 + 2Na_2S + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$ 

## 8.10 Sodium Sulphate (Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O)

It is also known as Glauber's salt.

#### **Preparation:**

- (a) By heating NaCl with concentrated.  $H_2SO_4$ : 2NaCl +  $H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$
- (b) By Hargreaves process:  $4NaCl (dry lumps) + 2SO_2 (g) + 2H_2O (g) + O_2 (g) \rightarrow 2Na_2SO_4 + 4HCl$

#### **Properties:**

- (a) It is a white crystalline solid and effloresces readily in dry air to form anhydrous sodium sulphate.
- (b) It is reduced to sodium sulphide when heated with carbon. Na<sub>2</sub>SO<sub>4</sub> + 4C  $\rightarrow$  Na<sub>2</sub>S + 4CO  $\uparrow$
- (c) It forms sodium bisulphate when reacted with concentrated  $H_2SO_4$ . Na<sub>2</sub>SO<sub>4</sub> +  $H_2SO_4 \rightarrow 2NaHSO_4$
- (d) Reaction with metal salts.  $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 \downarrow + 2NaCl$ ; Pb (NO<sub>3</sub>) +  $Na_2SO_4 \rightarrow PbSO_4 \downarrow + 2NaNO_3$

## 8.11 Potassium Sulphate (K<sub>2</sub>SO<sub>4</sub>)

#### **Preparation:**

(a) It is prepared by the reaction of potassium chloride or hydroxide with concentrated.  $H_2SO_4$ .

$$2\text{KCI} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCI}; 2\text{KOH} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O};$$

**(b)**  $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2KCI \rightarrow 2K_3SO_4 + MgCl_2 + 6H_2O_4$ 

Properties: It is a white crystalline solid and soluble in water. It is used as a fertilizer for tobacco and wheat.

Illustration 13: Why is there a white deposit in the glass vessel containing NaOH solution noticed after some time? (JEE ADVANCED)

**Sol:**  $SiO_2$  present in glass reacts with NaOH to give insoluble silicate. 2NaOH +  $SiO_2 \rightarrow Na_2SiO_3 + H_2O$ 

Illustration 14:  $KO_2 + CO_2 + H_2O \xrightarrow{more CO_2} [X] + [Y]$ (JEE ADVANCED)Products [X] and [Y] are respectively: (A)  $K_2CO_3$ ,  $O_2$  (B)  $KHCO_3$ ,  $O_2$  (C) KOH,  $K_2CO_3$  (D)  $KHCO_3$ ,  $H_2O$ 

**Sol:**  $KO_2 + CO_2 + H_2O \xrightarrow{\text{more } CO_2} KHCO_3 + O_2$ 

## 9. COMPOUNDS OF ALKALINE EARTH METALS

## 9.1 Magnesium Oxide or Magnesia (MgO)

**Preparation:** It can be prepared by following reaction.

 $2Mg + O_2 \xrightarrow{\text{burning}} 2MgO; \qquad Mg (OH)_2 \xrightarrow{\text{heated}} MgO + H_2O$  $2Mg (NO_3)_2 \xrightarrow{\text{heated}} 2MgO + 4NO_2 + O_2; \qquad MgCO_3 \xrightarrow{\text{heated}} MgO + CO_2$ 

#### **Properties:**

- (a) It is slightly soluble in water and forms magnesium hydroxide. MgO +  $H_2O \rightarrow Mg$  (OH),
- (b) It is basic in nature. It reacts with acids to form corresponding salts. MgO + 2HCl  $\rightarrow$  MgCl<sub>2</sub> + H<sub>2</sub>O

(c) It is reduced by carbon at a very high temperature. MgO + C  $\rightarrow$  Mg + CO

Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as magnesia cement or Sorel's cement. The composition is MgCl<sub>2</sub>.5MgO. xH<sub>2</sub>O.

## 9.2 Magnesium Hydroxide [Mg(OH)<sub>2</sub>]

#### **Preparation:**

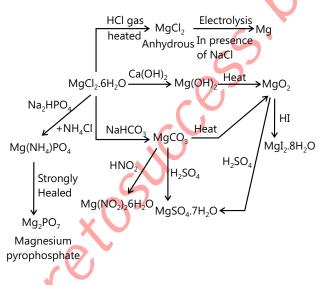
(i) MgO +  $H_2O \rightarrow Mg(OH)_2$ 

(ii) MgCl<sub>2</sub> + Ca (OH)  $_2 \rightarrow$  Mg (OH)  $_2$ +CaCl<sub>2</sub>,

(iii) MgCl<sub>2</sub> + 2NaOH  $\rightarrow$  Mg (OH)<sub>2</sub> + 2NaCl

**Properties:** It is a white powder. It is sparingly soluble in water. It is basic in nature and forms a salt with acids. It decomposes on heating. It readily dissolves in ammonium chloride solution and is, therefore, not precipitated in group III<sup>rd</sup> of qualitative analysis.

Mg (OH)  $_{2}$  + 2NH $_{4}$ Cl  $\implies$  MgCl $_{2}$  + 2NH $_{4}$ OH.



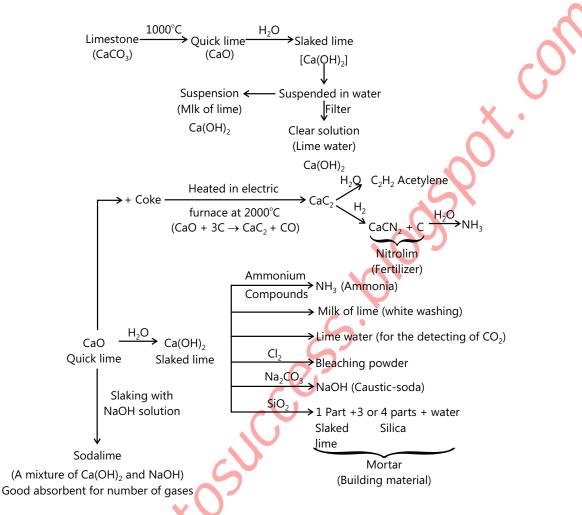
Flowchart 15.2: Chemical properties of Magnesium Hydroxide

Use: A suspension of Mg (OH), in water is used in medicine as an antacid under the name, milk of magnesia.

## 9.3 Magnesium Chloride (MgCl<sub>2</sub>.6H<sub>2</sub>O)

It occurs in nature as mineral carnallite, KCl, MgCl<sub>2</sub>. 6H<sub>2</sub>O.

Properties: It is a colourless crystalline solid, highly deliquescent and highly soluble in water.



#### 9.4 Quick Lime, Slaked Lime and Lime Water

Flowchart 15.3: Reactions of Quick lime, slaked lime and lime water

## 9.5 Magnesium Carbonate (MgCO<sub>3</sub>)

#### **Preparation:**

(a) It can be prepared by adding sodium bicarbonate to a hot solution of magnesium salt.

$$MgSO_4 + 2NaHCO_3 \rightarrow MgCO_3 + Na_2SO_4 + H_2O + CO_2$$

**(b)** 
$$2MgSO_4 + 2Na_2CO_3 + H_2O \rightarrow MgCO_3$$
. Mg (OH)  $_2 + 2Na_2SO_4 + CO_2$ 

When  $CO_2$  gas is passed through the suspension of the basic carbonate of magnesium, magnesium bicarbonate is formed which on heating forms MgCO<sub>3</sub>.

$$MgCO_3, Mg(OH)_2 + 3CO_2 + H_2O \rightarrow 2Mg(HCO_3)_2; Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2$$

#### **Properties:**

(a) It dissolves readily in water containing an excess of carbon dioxide.

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg (HCO_3)_2$$

(b) It dissolves in acids forming salts with evolution of  $CO_2$ .

 $MgCO_3 + 2HCI \rightarrow MgCl_2 + H_2O + CO_2$ 

On heating, it decomposes with the evolution of  $CO_2$ . MgCO<sub>3</sub>  $\rightarrow$  MgO + CO<sub>2</sub>

(c) It forms double carbonates with alkali metal carbonates.

 $MgCO_3 + Na_2CO_3 \rightarrow Na_2Mg (CO_3)_2$  (soluble)

## 9.6 Calcium Carbonate (CaCO<sub>3</sub>)

**Preparation:** It can be obtained by passing carbon dioxide through lime water or by adding sodium carbonate solution to  $CaCl_2 Ca (OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ ;  $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ 

The precipitate of CaCO<sub>3</sub> thus obtained is known as precipitated chalk.

**Properties:** It is a white powder insoluble in water. It dissolves in the presence of CO, due to the formation of calcium bicarbonate.  $CaCO_3 + H_2O + CO_2 \rightarrow Ca (HCO_3)_2$ 

#### Uses:

- (a) Precipitated chalk is used in tooth pastes and face powders, in medicine for indigestion, in adhesives and in cosmetics.
- (b) Chalk is used in paints and distempers.

## 9.7 Magnesium Sulphate (MgSO<sub>4</sub>)

It occurs in nature as minerals kiesserite (MgSO<sub>4</sub>.H<sub>2</sub>O), epsom salt (MgSO<sub>4</sub>.7H<sub>2</sub>O) and kainite (KCl.MgSO<sub>4</sub>.3H<sub>2</sub>O).

**Preparation:** It is prepared by reacting magnesite (MgCO<sub>2</sub>) or dolomite with dilute sulphuric acid.

 $MgCO_{3} + H_{2}SO_{4} \rightarrow MgSO_{4} + H_{2}O + CO_{2}$ MgCO\_{3}.CaCO\_{3} (dolomite) + 2H\_{2}SO\_{4} \rightarrow MgSO\_{4} + CaSO\_{4} + 2CO\_{2} + 2H\_{2}O

#### **Properties:**

(a) Heating effect: When heated to 150°C, it changes to monohydrate. On further heating, it becomes anhydrous at 200°C. On strong heating, it decomposes into MgO.

$$MgSO_{4}.7H_{2}O \xrightarrow{150^{\circ}C} MgSO_{4}.H_{2}O \xrightarrow{200^{\circ}} MgSO_{4} \xrightarrow{strong} MgO + SO_{2} + \frac{1}{2}O_{2}.$$

- (b) Magnesium sulphate when heated with lamp black at 800°C produces  $SO_2$  and  $CO_2$  gases.  $2MgSO_4 + C \rightarrow 2MgO + 2SO_2 + CO_2$
- (c) It forms double salts with alkali metal sulphates, e.g.,  $K_2SO_4$ . MgSO<sub>4</sub>.6H<sub>2</sub>O.

## 9.8 Calcium Sulphate (CaSO₄)

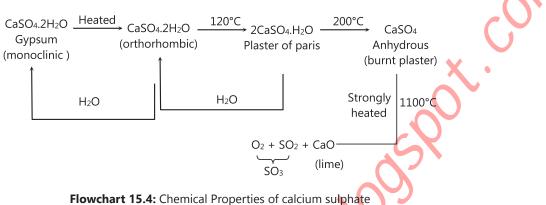
It is found in nature as an anhydride (CaSO<sub>4</sub>) and gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) It can be prepared by reacting any calcium salt with either sulphuric acid or a soluble sulphate. CaCl<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  CaSO<sub>4</sub> + 2HCl; CaCl<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  CaSO<sub>4</sub> + 2NaCl

## **Properties:**

- (a) (t is a white crystalline solid. It is sparingly soluble in water and solubility decreases as temperature increases.
- (b) It dissolves in dilute acids. It also dissolves in ammonium sulphate due to the formation of double sulphate,  $(NH_4)_2SO_4.CaSO_4.H_2O$

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(c) Gypsum when heated first changed from monoclinic form to orthorhombic form without loss of water. At 120°C, it loses three-fourth of its water of crystallization and forms hemihydrate, (2CaSO<sub>4</sub>.H<sub>2</sub>O) which is commonly known as the Plaster of Paris. At 200"C. it becomes anhydrous. The anhydrous form is known as burnt plaster or dead plaster.



- (d) Dead plaster has no setting property as it takes up water only very slowly.
- (e) A suspension of gypsum when saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertilizer  $2NH_3 + CaSO_4 + CO_2 + H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3$
- (f) When strongly heated with carbon, it forms calcium sulphide  $CaSO_4 + 4C \rightarrow CaS + 4CO$

Use: (a) For preparing blackboard chalk. (b) In anhydrous form as drying agent.

## 9.9 Plaster of Paris (2CaSO<sub>4</sub>.H<sub>2</sub>O) (Calcium sulphate hemihydrate)

Preparation: It is obtained when gypsum, calcium sulphate dihydrate (CaSO, 2H,O), is heated at 120°C (393K).

 $2[CaSO_4.2H_2O] \rightarrow 2CaSO_4.H_2O$  (calcium sulphate hemihydrate) +  $3H_2O$ 

Gypsum Plaster of Paris

#### **Properties:**

- (a) Plaster of Paris is a white powder.
- (b) It has the property of setting to a hard mass when a paste with water is allowed to stand aside for some time. Slight expansion occurs during the setting as water is absorbed to reform CaSO<sub>4</sub>. 2H<sub>2</sub>O (gypsum). The setting process is exothermic. The process of setting takes place in stages. In the first stage, there is a conversion of Plaster of Pairs into an orthorhombic form of gypsum (setting step) and in the second stage the orthorhombic form changes into a monoclinic form (hardening step).

$$2CaSO_{4}H_{2}O \xrightarrow{Setting} CaSO_{4} \cdot 2H_{2}O \xrightarrow{Hardening} CaSO_{4} \cdot 2H_{2}O$$
Plaster of Paris Orthorhombic Monoclinic

The setting of Plaster of Paris may be catalysed by sodium chloride while it is retarded by borax or alum. Addition of alum to Plaster of Paris makes the setting very hard. The mixture is known as Keene's cement.

**Illustration 15:** An element X exhibits only the +2 oxidation state in its compounds. The compounds are white and frequently crystallize as hydrates. Its hydroxide used as an antacid is the least soluble one in its family and can be precipitated from solutions containing  $X^{2+}$  by  $NH_3$  (g). Identity the element and give the balanced equations.

(JEE MAIN)

(a) For the effect of heat on its (hexahydrate) chloride.

(b) For the precipitation of the hydroxide using aq.  $NH_3$ .

**Sol:** The element is magnesium as its hydroxide known as milk of magnesia is used as an antacid.

 $\begin{array}{l} \mathsf{MgCl}_2 . \, \mathsf{6H}_2\mathsf{O}(\mathsf{s}) & \stackrel{\Delta}{\longrightarrow} \mathsf{MgO}(\mathsf{s}) + 2\mathsf{HCI}(\mathsf{g}) + 5\mathsf{H}_2\mathsf{O}(\mathsf{g}) \\ \\ \mathsf{Mg}^{2+}(\mathsf{aq}.) + 2\mathsf{NH}_3(\mathsf{aq}) + 2\mathsf{H}_2\mathsf{O}(\ell) \rightarrow \mathsf{Mg}(\mathsf{OH}_2)(\mathsf{s}) + 2\mathsf{NH}_4^+(\mathsf{aq}) \end{array}$ 

## PROBLEM SOLVING TACTICS

The correct order of stability of for the following supper oxides is:

(A)  $KO_2 > RbO_2 > CsO_2$  (B)  $RbO_2 > CsO_2 > KO_2$  (C)  $CsO_2 > RbO_2 > KO_2$ 

Solution: The approach should be as follows

(i) The stability of super oxides depend on the polarizing power of the cation. Lesser the polarizing power, greater is the stability of the superoxide ion.

(D)  $KO_2 > CsO_2 > RbO_2$ 

- (ii) The polarizing power of cations of the same charge decreases with the increase in the size.
- (iii) Therefore, the stability of super oxides increases with increase in the size of cations.
- (iv) The increasing order of size of ions is:  $K^+ < Rb^+ < Cs^+$ .
- (v) The correct order of stability is:  $CsO_2 > RbO_2 > KO_2$

Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?

(A)  $K_2O < Na_2O < Al_2O_3 < MgO$  (B)  $Al_2O_3 < MgO < Na_2O < K_2O$ (C)  $MgO < K_2O < Al_2O_3 < Na_2O$  (D)  $MgO < K_2O < Na_2O < Al_2O_3$ 

Explanation: (i) Basic nature of oxides increases with increase in the size of cation.

(ii) The increasing order of cations is:  $AI^{3+} < Mg^{2+} < Na^+ < K^+$ 

(iii) Therefore the increasing correct order of basic strength is:  $Al_2O_3 < MgO < Na_2O < K_2O$ 

Conclusion: Correct option is: 'B'.

# POINTS TO REMEMBER

Trends in Physical Properties of Alkaline Earth Metals:

Characteristic	Trend
Oxidation state	All elements show +2 oxidation state
Atomic / ionic radii	Be < Mg < Ca < Sr < Ba
	Size of the alkaline earth metals increases from top to bottom due to increase in the number of shells.
Ionization enthalpy	Be > Mg > Ca > Sr > Ba
	As the size increases it becomes easier to remove an electron from the outermost shell.

Electronegativity	Be > Mg > Ca > Sr > Ba	
	As the electropositive character increases from top to bottom due to decrease in ionization energy, electronegativity decreases from top to bottom.	
Metallic character	Be < Mg < Ca < Sr < Ba	
	Metallic character increases as we go down the group due to increase in electropositive character.	
Density	Generally density increases from top to bottom as the atomic mass increases.	
Melting point and boiling point	They show higher values of melting and boiling points as compared to alkali metals because of the smaller size and stronger metallic bonds. There is no regular trend down the group. It depends upon packing.	
Flame coloration	Except Be and Mg (due to small size and higher ionization enthalpy) all other alkaline earth metals impart characteristic colours to the Bunsen flame.	
	Ca Sr Ba Brick red Crimson Red Sea green	

## **Solved Examples**

## JEE Main/Boards

**Example 4:** Give chemical reaction of H<sub>2</sub> formation by Bosch and Lane process?

Sol: (i) Bosch process

$$C + H_2O \rightarrow CO + H_2$$

(ii) Lane process

$$3Fe + 4H_2O \xrightarrow{1000^{\circ}C} Fe_3O_4 + 4H$$

**Example 5:** What is the physical property of H<sub>2</sub>?

**Sol:** (i) Colourless, odourless, tasteless gas

(ii) Sparingly soluble in water due to non-polar nature

(iii) Density is 0.09 gm/t

(iv) B.P is 20.4 K

(v) Pd metal can adsorb  $H_2$  gas.

## **JEE Advanced/Boards**

## Hydrogen

**Example 1:** Which metals can adsorb largest volumes of hydrogen gas?

**Sol:** Acc. to amount of hydrogen occluded metal in decreasing order are - Colloidal Pd > Pt > Au > Ni

## Hydrogen

**Example 1:** When Ionic hydrides react with water it gives?

**Sol:** s-block elements form ionic hydrides which form basic hydroxide with water. Ex – NaOH

**Example 2:**  $H_2O_2$  reduces  $K_3[Fe(CN)_6]$  in which medium and give complete reaction ?

**Sol:** Potassium Ferricyanide is reduced by  $H_2O_2$  in basic medium

 $2 \text{ K}_{3}[\text{Fe}(\text{CN})_{6}] + 2 \text{ KOH} + \text{H}_{2}\text{O}_{2} \rightarrow 2 \text{K}_{4}[\text{Fe}(\text{CN})_{6}] + 2 \text{H}_{2}\text{O} + \text{O}_{2}$ (basic medium)

**Example 3:** In alkaline medium,  $H_2O_2$  reacts with Fe<sup>3+</sup> and Mn<sup>2+</sup> separately give reaction?

**Sol:**  $K_3Fe(CN)_6$  is reduced by  $H_2O_2$  in alkaline medium.  $2K_3Fe(CN)_6 + 2KOH + H_2O_2 \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$   $Mn(OH)_2$  is oxidised by  $H_2O_2$  in alkaline medium  $Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$  **Example 2**: Give one method of removal of Permanent hardness of water.

**Sol:** Permanent hardness of water can be removed by adding calgon  $(NaPO_3)_n$ .  $(NaPO_3)_n$  is used in calgon process, it forms soluble complex with Ca<sup>2+</sup> and Mg<sup>2+</sup> ions.

**Example 3:** What is the ratio of volumes of hydrogen evolved under similar conditions of pressure and temperature?

**Sol:** 2g of aluminium is treated separately with excess of dilute  $H_2SO_4$  and excess of NaOH.

 $2AI + 3H_2SO_4 \rightarrow AI_2(SO_4)_3 + 3H_2;$ 

 $2AI + 2NaOH + 2H_2O_2 \rightarrow 2NaAIO_2 + 3H_2$ 

Thus, ratio of volumes of hydrogen evolved is 1:1

**Example 4:** What is the degree of hardness of a sample of water containing 24 mg of  $MgSO_4$  (molecular mass 120) per kg of water?

**Sol:** 24 mg of MgSO<sub>4</sub> present in 103 g of water 106g water will contain 24000 mg of MgSO<sub>4</sub> = 24g of MgSO<sub>4</sub>

So, 24g of MgSO<sub>4</sub> =  $\frac{100}{120} \times 24 = 20$  g of CaCO<sub>3</sub> Hardness of water = 20 ppm

Example 5: Define ortho and para hydrogen

**Sol: Ortho and para hydrogen:** When the spins of both the protons (nucleus) in the hydrogen molecule are in the same direction then this form is known as ortho hydrogen. The molecule of hydrogen in which both the protons are spinning in opposite directions known as para hydrogen. These are nuclear isomers. At normal temperature the ratio of ortho and para hydrogen is 3: 1, but as the temperature is lowered, the proportion of para hydrogen increases (at 20°C).

## **JEE Main/Boards**

## Hydrogen

## **Exercise 1**

**Q.1** What is the importance of heavy water with regard to nuclear power generation?

**Q.2** Name two compounds which retard the decomposition of H<sub>2</sub>O<sub>2</sub> solution?

Q.3 What is water gas? How is it prepared?

Q.4 What is meant by autoprotolysis of water?

**Q.5** Explain why electrolysis of ordinary water occurs faster than heavy water?

**Q.6** How is dihydrogen obtained from: (i) Water, (ii) Dilute acids, (iii) Alkalis **Q.7** What are interstitial hydrides? Discuss their important uses?

**Q.8** Explain why water has high boiling and melting point as compared to H<sub>2</sub>?

**Q.9** What happens when H<sub>2</sub>O<sub>2</sub> is treated with

(i) Acidified potassium permanganate.

(ii) Lead sulphide.

- (iii) Alkaine potassium ferricyanide.
- (iv) Acidified ferrous sulphate.
- (v) Sulphurous acid.
- (vi) Sodium arsenite.

Q.10 What is the action of heavy water on

- (i) Sodium
- (ii) Sodium hydroxide
- (iii) Ammonium chloride
- (iv) Sulphur trioxide

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**Q.11** Find the volume of oxygen gas liberated at STP when 25 ml of '30 volumes'  $H_2O_2$  is completely decomposed.

**Q.12** Calculate the volume strength of 13.6% solution of  $H_2O_2$ 

**Q.13** Which solution is used for the removal of AsH<sub>3</sub> and PH<sub>3</sub> present in very small amounts in hydrogen sample?

#### Q.14 Complete the following reactions

(i) An alkaline solution of potassium ferricyanide is treated with hydrogen peroxide.

(ii) Chromium hydroxide is treated with hydrogen peroxide in the presence of NaOH.

**Q. 15** Why are the melting and boiling points of D<sub>2</sub>O are higher than those of ordinary water?

**Q.16** Why the presence of water is avoided in the preparation of  $H_2O_2$  from  $Na_2O_2$ ?

**Q.17** Why a mixture of hydrazine and  $H_2O_2$  is used as a rocket propellant?

**Q.18** Why hydrogen peroxide acts as an oxidizing agent as well as a reducing agent.

**Q.19** 20mL of  $H_2O_2$  after acidification with dilute  $H_2SO_4$  required 30 mL of N/12 KMnO<sub>4</sub> for complete oxidation. Calculate the percentage of  $H_2O_2$  in the solution. Equivalent mass of  $H_2O_2 = 17$ .

**Q.20** Why statues coated with white lead on long exposure to atmosphere turn black & the original colour can be restored on treatment with  $H_2O_2$ ?

**Q.21** When a substance A reacts with water, it produces a combustible gas B and a solution of substance C in water. D reacts with this solution C and produces the same gas B on warming. D can also produce gas B on reaction with dilute  $H_2SO_4$ . A imparts a deep golden yellow colour to smokeless flame. A, B, C and D respectively are?

**Q.22** What is false about  $H_2O_2$ ?

**Q.23** What happens, when  $H_2O_2$  is added to ice cold solution of acidified potassium dichromate in ether and the contents are shaken and allowed to stand?

**Q.24** 25 mL of  $H_2O_2$  is reacted with excess amount of I<sup>-</sup> to liberate I<sub>2</sub>. I<sub>2</sub> thus liberated reacts completely with 20 mL of 0.3 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Calculate volume strength of  $H_2O_2$ .

**Q.25** The electrolysis of water for manufacturing hydrogen gas is always carried out in presence of acid  $(H_2SO_4)$  or alkali (KOH), yet no  $SO_4^{2-}$  or K<sup>+</sup> ions are discharged. Explain.

**Q.26** Painting coated with white lead on long exposure to atmosphere turns black and the original colour can be restored on treatment with  $H_2O_2$ . Explain.

**Q.27** Why H<sub>2</sub>O<sub>2</sub> is stored in wax lined amber coloured bottles?

**Q.28** A small amount of phosphoric acid or glycerol or acetanilide is added in  $H_2O_2$  during its storage. Explain.

**Q.29** Find out the normality of the hydrogen peroxide bottle labelled as '10 V  $H_2O_2$ '

**Q.30** When electrolysis of 50%  $H_2SO_4$  is done compound (A) is obtained which acts as oxidising agent as well as reducing agent. (A) when reacted with Cr<sup>+3</sup> in basic medium gives (B) and which reacted with PbS gives (C). Find out (A),(B) and(C)

## Exercise 2

#### Single Correct Choice Type

**Q.1** Calgon (a water softener) is:

(A)  $Na_2[Na_4(PO_3)_6]$  (B)  $Na_4[Na(PO_3)]_6$ (C)  $Na_2[Na_4(PO_4)]_6$  (D)  $Na_4[Na_2(PO_4)_6]$ 

**Q.2** Which gas in cold, liquid form expands when it is further cooled:

(A) Liquid He	(B) Liquid NH <sub>3</sub>
(C) Liquid H	(D) Liquid O

**Q.3** Hydrogen has a tendency to gain one electron in order to acquire helium configuration. It thus resembles:

(A) Alkali metals	(B) Noble gases

(C) Halogens (D) Alkaline earth metals

- Q.4 When a molten metal hydride is electrolysed?
- (A)  $\mathsf{H}^{\scriptscriptstyle +}$  ions produced move towards the cathode
- (B)  $H^-$  ions produced move towards the anode
- (C)  $H_2$  is liberated at anode
- (D)  $H_2$  is liberated at cathode

Q.5 Which is true statement?

(A) The layer of ice on the surface of river in the winter acts as a thermal insulator between the water below and the air above

(B) The fish and other marine organism are enabled to survive long periods of freezing water due to the fact that ice is lighter than water

- (C) Both is correct
- (D) None is correct

Q.6 A sample of water contains sodium chloride. It is

(A) Hard water	(B) Soft water
(C) Moderately hard	(D) None of these

**Q.7** The bleaching properties of  $H_2O_2$  are due to its

- (A) Reducing properties (B) Oxidising properties
- (C) Unstable nature (D) Acidic nature

**Q.8** When 50% solution of  $H_2SO_4$  is electrolysed by passing a current of high density at low temperature the main products of electrolysis are

- (A) Oxygen and hydrogen
- (B) H<sub>2</sub> and peroxy disulphuric acid
- (C)  $H_2$  and  $SO_2$

(A) CaCl<sub>2</sub>

(D)  $O_2$  and peroxy disulphuric acid

**Q.9** Hardness producing salt, whose solubility in water decreases with rise of temperature is-

(B)  $CaSO_4$  (C)  $Ca(HCO_3)_2$  (D)  $MgSO_4$ 

**Q.10** Hydrolysis of one mole of peroxy disulphuric acid produces:

(A) Two moles of sulphuric acid

(B) Two moles of peroxymono sulphuric acid

(C) One mole of sulphuric acid and one mole of peroxy mono sulphuric acid

(D) One mole of sulphuric acid, one mole of peroxy monosulphuric acid and one mole of hydrogen peroxide.

Q.11 Which of the following is not a redox reaction

(A) KCl + 
$$K_2Cr_2O_7$$
 + con. $H_2SO_4 \longrightarrow CrO_2Cl_2 + K_2SO_4$   
+  $H_2O$   
(B)  $K_2Cr_2O_7$  +  $H_2O_2$  + con. $H_2SO_4 \longrightarrow K_2SO_4$  +  $CrO_5$   
+  $H_2O$   
(C)  $K_2Cr_2O_7$  +  $H_2O_2$  + dil.  $H_2SO_4 \longrightarrow K_2SO_4$  +  $Cr_2(SO_4)_3$   
+  $7H_2O$  +  $3O_2$   
(D)  $K_2Cr_2O_7$  +  $2KOH \longrightarrow 2K_2CrO_4$  +  $H_2O$ 

**Q.12** A sample of water containing some dissolved table sugar and common salt is passed through organic ion exchange resins. The resulting water will be -

(A) Tasteless (B) Sweet (C) Salty (D) None of these

Q.13 Which of the following reaction does not take place

(A)  $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$ (B)  $HgCl_2 + Fe \longrightarrow FeCl_2 + Hg$ (C)  $NaH + H_2O \longrightarrow NaOH + H_2$ (D)  $Na_2SO_3 + CO_2 \longrightarrow Na_2CO_3 + SO_2$ 

Q.14 If –O–H bond is weaker than –O–D bond,

(A) The biological growth of a plant which is fed by  $D_2O$  is fast

(B) The biological growth of a plant which is fed by  $\rm H_2O$  is fast

(C) The biological growth of a plant which fed both by  $H_2O$  or  $D_2O$  are same

(D) Water does not have any role in plant growth.

**Q.15** Water obtained by purification with organic ion Exchange resins is -

(A) Pure water

(B) Free from only Ca2+, Mg2+ ions

(C) Free from  $HCO_3^-$ ,  $SO_4^{2-}$  and  $CI^-$  ions only

(D) None of these

**Q.16** When two ice cubes are pressed over each other, they unite to form one cube. Which of the following forces is responsible to hold them together?

(A) Hydrogen bond formation

(B) Vander Waals' forces

(C) Covalent attraction

(D) Ionic interaction

**Q.17** Which of the following can effectively remove all types of hardness of water

(A) Soap	(B) Washing soda
	(=) ) ( )

(C) Slaked lime (D) None of these

#### Q.18 Fenton reagent is

(A) $FeSO_4 + H_2O_2$	(B) Zn + HCl
(C) Sn + HCl	(D) None of the above

Q.19 Which of the following is used as rocket fuel?

(A) Liquid O <sub>2</sub>	(B) Liquid N <sub>2</sub>
(C) Liquid NH <sub>3</sub>	(D) Liquid H <sub>2</sub>

**Q.20** Which of the following could act as propellant for rockets?

(A) Liquid oxygen + liquid argon

(B) Liquid nitrogen + liquid oxygen

(C) Liquid hydrogen + liquid oxygen

(D) Liquid hydrogen + liquid nitrogen

Q.21 Water is oxidised to oxygen by

- (A) Ozone (B) KMnO<sub>4</sub>
- (C)  $H_2O_2$  (D)  $F_2$

**Q.22** H<sub>2</sub>O<sub>2</sub> on reaction with PbS gives

- (A) PbO (B) PbSO<sub>4</sub>
- (C) PbO<sub>2</sub> (D) PbHSO<sub>4</sub>

Q.23 Hydrogen burns in air with a

(A) Light bluish flame (B) Yellow flame

(C) Green flame (D) None of these

Q.24 What is the product of the reaction of H<sub>2</sub>O with Cl<sub>2</sub>

(A)  $O_2$  + HOCI (C)  $H_2O$  + HCI (D) HCI +  $H_2$ 

**Q.25** When electric current is passed through an ionic hydride in molten state

(A) Hydrogen is liberated at anode

(B) Hydrogen is liberated at cathode

(C) Hydride ion migrates towards cathode

(D) Hydride ion remains in solution

**Q.26** Among CaH<sub>2</sub> NH<sub>3</sub>, NaH and  $B_2H_6$ , which are covalent hydrides ?

(A)  $NH_3$  and  $B_2H_6$  (B) NaH and  $CaH_2$ (C) NaH and  $NH_3$  (D)  $CaH_2$  and  $B_2H_2$ 

Q.27 Hydrogen is not obtained when zinc reacts with

- (A) Steam (B) Hot NaOH solution
- (C) Cone. H<sub>2</sub>SO<sub>4</sub>

(D) Dilute HCl

**Q.28** The hardness of water sample containing 0.002 mole of magnesium sulphate dissolved in a litre is expressed as

(A) 20 ppm (C) 2000 pM (D) 120 ppm

**Q.29** The bond angle and dipole moment of water respectively are -

(A) 109.5°, 1.84D	(B) 107.5°, 1.56D
(C) 104.5°, 1.84 D	(D) 102.5°, 1.56 D

**Q.30** Blackened oil painting can be restored into original form by the action of-

(A) Chlorine	(B) BaO <sub>2</sub>
(C) H <sub>2</sub> O <sub>2</sub>	(D) MnO <sub>2</sub>

Q.31 Ortho and para hydrogen have

(A) identical chemical properties but different physical properties

(B) identical physical and chemical properties

(C) identical physical properties but different chemical properties

(D) different physical and chemical properties

**Q.32** CO + H<sub>2</sub>  $\frac{300^{\circ}\text{C}/300 \text{ atm}}{\text{X(catalyst)}}$  CH<sub>3</sub>OH

The catalyst X is-

(A) Fe (B) Cr<sub>2</sub>O<sub>3</sub>/ZnO

(C)  $V_2O_5$  (D)  $AI_2O_3$ 

**Q.33** Which one of the following undergoes reduction with  $H_2O_2$  in an alkaline medium ?

(A) Mn <sup>2+</sup>	(B) HOCI
(C) PbS	(D) Fe <sup>2+</sup>

**Q.34** The reagent(s) used for softening the temporary hardness of water is/are

(A) Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(B) Ca(OH) <sub>2</sub>
(C) Na <sub>2</sub> CO <sub>3</sub>	(D) NaOCI

**Q.35** Polyphosphates are used as water softening agents because they:

- (A) Form soluble complexes with anionic species
- (B) Precipitate anionic species
- (C) Form soluble complexes with cationic species
- (D) Precipitate cationic species

Q.36 Pick out the correct statement-

(A) By decreasing the temperature pure parahydrogen can be obtained

(B) By increasing the temperature pure orthohydrogen can be obtained

(C) By decreasing the temperature pure orthohydrogen can be obtained

(D) By increasing the temperature pure parahydrogen can be obtained

**Q.37**  $H_2SO_5 + H_2O^{18} \rightarrow \text{product}$ 

(A)  $H_2SO_4 + HO - O - H$ 

(B) 
$$H_2SO_4 + H - O - O - H$$

(C) 
$$H - O - S - O - H$$

(D) 
$$H - O - S - O - H + H_2O_2$$

**Q.38** Which of the following statement is incorrect

(A) Germination of seeds in heavy water stops or slowdown

(B) The growth of plant slows down in heavy water

(C) Small fish die in heavy water

(D) In heavy water, NaCl solubility is more than normal (A) Fe water

		Chemistry   15.47	
ning the temporary	Previous Years		
	<b>Q.1</b> Polyphosphates a because they	re used as water softening agents	
	(A) Form soluble com	plexes with anionic species	
er softening agents	(B) Precipitate anionic species		
	(C) Forms soluble complexes with cationic species		
onic species	(D) Precipitate cationic species		
ionic species	<b>Q.2</b> One mole of calcium phosphide on reaction with excess water gives (1999)		
	(A) One mole of phos	phine	
	(B) Two moles of phos	sphoric acid	
pure parahydrogen	(C) Two moles of phos	sphine	
ure orthohydrogen	(D) One mole of phos	phorus pentoxide	
	Q.3 Hydrogen will not	t reduce (1985)	
ure orthohydrogen	(A) Heated cupric oxide		
pure parahydrogen	(B) Heated ferric oxide		
pure purunyurogen	(C) Heated stannic oxide		
	(D) Heated aluminium	oxide	
S	<b>Q.4</b> HCl is added to for give $H_2O_2$	bllowing oxides. Which one would (1998)	
χŲ	(A) MnO <sub>2</sub>	(B) PbO <sub>2</sub>	
	(C) BaO <sub>2</sub>	(D) None of these	
	<b>Q.5</b> Which of the f dihydrogen gas	ollowing pair will not produce ( <b>1994)</b>	
	(A) Cu + HCl(dil.)	(B) Fe + $H_2SO_4$	
	(C) Mg + steam	(D) Na +alcohol	
	<b>Q.6</b> The amount of H solution is	H <sub>2</sub> O <sub>2</sub> present in 1L of 1.5 N H <sub>2</sub> O <sub>2</sub> ( <b>1991)</b>	
ent is incorrect	(A) 2.5 g	(B) 25.5 g	
vy water stops or	(C) 3.0 g	(D) 8.0 g	
in heavy water	<b>Q.7</b> Hydrogen is evolv on	red by the action of cold dil. HNO <sub>3</sub> ( <b>1998)</b>	

A) Fe (B) Mn (C) Cu (D) Al

Read the following questions and answer as per the direction given below:

(A) Assertion is true; reason is true; reason is the correct explanation of assertion.

(B) Assertion is true; reason is true; reason is not the correct explanation of assertion.

- (C) Assertion is true; reason is false.
- (D) Assertion is false; reason is true

**Q.8** Assertion: Decomposition of  $H_2O_2$  is a disproportionate reaction. (1999)

**Reason:**  $H_2O_2$  molecule simultaneously undergoes oxidation and reduction.

**Q.9 Assertion:**  $H_2O_2$  has higher boiling point than water. (1997)

**Reason:**  $H_2O_2$  has stronger dipole-dipole interactions than water.

**Q.10** In which of the following pairs of molecules / ions, both the species are not likely to exist? (2013)

(A) 
$$H_2^+, He_2^{2-}$$
 (B)  $H_2^-, He_2^{2-}$  (C)  $H_2^{2+}, He_2$  (D)  $H_2^-, He_2^{2-}$ 

**Q.11** In which of the following reactions  $H_2O_2$  acts as a reducing agent? (2014)

(a)  $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (b)  $H_2O_22e^- \rightarrow O_2 + 2H^+$ (c)  $H_2O_2 + 2e^- \rightarrow 2OH^-$ (d)  $H_2O_2 + 2OH^- - 2e^- \rightarrow O_2 + 2H_2O$ (A) (a), (c), (B) (b), (d) (C) (a), (b) (D) (c), (d)

**Q.12** From the following statements regarding  $H_2O_2$  choose the **incorrect** statement : (2015)

(A) It can act only as an oxidizing agent

(B) It decomposes on exposure to light

(C) It has to be stored in plastic or wax lined glass bottles in dark

(D) It has to be kept away from dust

## **JEE Advanced/Boards**

## **Exercise 1**

**Q.1** What is understood by "Water gas shift reaction"? Discuss its use for the preparation of hydrogen.

**Q.2** A solution of ferric chloride acidified with HCl is unaffected when hydrogen is bubbled through it, but gas gets reduced when zinc is added to acidified solution. Why?

Q.3 What is r value?

**Q.4** Neutron diffraction data can usually give quite precise location of H-bonding but X-ray diffraction does not, why?

**Q.5** Explain the H-bond formed between NH<sub>3</sub> and H<sub>2</sub>O.

**Q.6** Presence of water is avoided in the preparation of  $H_2O_2$  from  $Na_2O_2$ .

**Q.7** Write down disproportionation reaction in H<sub>2</sub>O<sub>2</sub>

**Q.8** Calculate the hardness of water sample which contains 0.001 mole of  $MgSO_4$  dissolved per litre of water.

**Q.9** What mass of CaO will be required to remove the hardness of 1000 litres of water containing 1.62 g of calcium bicarbonate per litre?

**Q.10** 100 mL of tap water containing  $Ca(HCO_3)$  was titrated with N/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, calculate the temporary hardness as parts of CaCO<sub>3</sub> per 10<sup>6</sup> parts of water.

**Q.11** When 1.823 g of the hydrogen  $CaCrO_4.XH_2O$  was heated to 200°C, 1.479 of anhydrous  $CaCrO_4$  was formed. What is the formula of hydrate?

#### Q.12 What happens when

(i) Chromium hydroxide is treated with hydrogen peroxide in the presence of sodium hydroxide. Write the chemical equation.

(ii) Concentrated caustic potash solution is spilled on granulated zinc. Write the chemical equation.

(iii) Hydrolith is treated with water. Write the chemical equation.

(iv) Heavy water reacts with aluminium carbide. Write the chemical equation.

**Q.13** An aqueous solution of an unknown compound (X) gives the following reactions:

(i) It gives brown ppt. with alkaline  $KMnO_4$  solution.

(ii) It forms HCl and evolves  $O_2$  when reacts with  $Cl_2$  gas.

(iii) It liberates  $I_2$  form an acidified KI solution.

(iv) It gives orange yellow colour with acidified titanic sulphate solution.

Identify (X) and give the chemical equations for the reactions (i), (ii), (iii).

**Q.14** (i) Convert 20 vol.  $H_2O_2$  into % strength.

(ii) Convert 6.8 % strength  $H_2O_2$  into volume strength.

**Q.15** What is the volume strength of 1 molar solution of  $H_2O_2$ ?

**Q.16** Half litre each of three samples of  $H_2O_2$  labelled 10 vol., 15 vol., 20 vol., are mixed and then diluted with equal volume of water. Calculate relative strength of resultant  $H_2O_2$  solution.

**Q.17** What mass (in mg) of available per litre is present in a solution of  $H_2O_2$ . 10 mL of which when treated requires 25 mL of N/20 KMnO<sub>4</sub> for complete oxidation of it.

**Q.18** 25 mL of hydrogen peroxide solution were added to excess of acidified potassium iodide solution. The iodine so liberated required 20 mL of 0.1 N sodium thiosulphate solution. Calculate strength in terms of normality, percentage and volume. **Q.19** Excess of KI and dil.  $H_2SO_4$  were mixed in 50 mL  $H_2O_2$ . The I<sub>2</sub> liberated requires 20 mL of 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Find out the strength of H<sub>2</sub>O<sub>2</sub> in g/litre.

**Q.20** 20 mL of  $H_2O_2$  after acidification with dilute  $H_2SO_4$  required 30 mL of N/12 KMnO<sub>4</sub> for complete oxidation. Calculate the percentage of  $H_2O_2$  in g/litre. Equivalent mass of  $H_2O_2 = 17$ .

#### Q.21 What happens when?

(i) An alkaline solution of potassium ferricyanide reacts with  $H_2O_2$ .

(ii) Hydrogen peroxide is added to acidified potassium permaganate

(iii) Hydrogen peroxide is added to ferrous ammonium sulphate solution

## Exercise 2

#### Single Correct Choice Type

**Q.1** Nascent hydrogen consists of:

(A) Hydrogen atoms with excess energy

(B)Hydrogen molecules with excess energy

(C) Hydrogen ions in excited state

(D) Solvated protons

**Q.2** 30 volume hydrogen peroxide means:

(A) 30%  $H_2O_2$  solution

(B) 30 cm<sup>3</sup> of the solution contains 1 g of  $H_2O_2$ 

(C) 1 cm<sup>3</sup> of the solution liberates 30cm<sup>3</sup> of O<sub>2</sub> at STP

(D) 30 cm<sup>3</sup> of the solution contains 1 mole of  $H_2O_2$ 

**Q.3** The molarity of a 100 mL solution containing 5.1 g hydrogen peroxide is:

(A) 0.15M (B) 1.5 M (C) 3.0M (D) 50.0M

**Q.4** Moist hydrogen cannot be dried over concentrated  $H_2SO_4$  because:

(A) It can catch fire

(B) It is reduced by  $H_2SO_4$ 

- (C) It is oxidised by  $H_2SO_4$
- (D) It decomposes  $H_2SO_4$

# 

Q.5 An aqueous solution	of hydrogen peroxide is:
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(A) Alkaline (B) Neutral

(C) Strongly acidic (D) Weakly acidic

**Q.6** The structure of  $H_2O_2$ 

(A) In gas phase as well as in solid phase is same with the same dihedral angle

(B) In gas phase, is with dihedral angle of 111.5°

(C) Both (A) and (B)

(D) In solid phase, is with the dihedral angle of 180°

**Q.7** Which is not reduced by H<sub>2</sub> in hot solution:

(A)  $Fe_2O_3$  (B) CuO (C)  $K_2O$  (D)  $Ag_2O$ 

**Q.8** Hydrogen is evolved by the action of cold dilute  $HNO_3$  on:

(A) Fe (B) Mg or Mn (C) Cu (D) Al

**Q.9**  $H_2O_2$  when added to a solution containing KMnO<sub>4</sub> and  $H_2SO_4$  acts:

(A) As an oxidising agent

(B) As a reducing agent

(C) Both as an oxidising as well as a reducing agent

(D)  $KMnO_4$  will not react with  $H_2O_2$  in acidic in medium.

Q.10 Hydrogen can be produced by heating

- (A) Cu with  $H_2SO_4$  (B) Sodium formate
- (C) Sodium oxalate (D) None of these

**Q.11** Which of the following chemical reaction is not feasible?

(A) 
$$PbO_2 + dil. H_2SO_4 \longrightarrow PbSO_4 + H_2O + O_2$$
  
(B)  $H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O_2$   
(C)  $H_2O_2 + N_2H_4 \longrightarrow N_2 + H_2O$   
(D) Ti  $(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow H_2TiO_3 + H_2SO_4$ 

**Q.12** The reaction involved during the removal of temporary hardness of water is:

 $\begin{array}{ll} (A) \ 2CaCl_2 + (NaPO_3)_6 & \longrightarrow & Na_2(Ca_2(PO_3)_6) + 4NaCl \\ (B) \ CaCl_2 + Na_2CO_3 & \longrightarrow & CaCO_3 \downarrow & + 2NaCl \\ (C) \ MgSO_4 + Na_2Al_2Si_2O_8.xH_2O & \longrightarrow & MgAl_2Si_2O_7.xH_2O \\ & + \ Na_2SO_4 \end{array}$ 

(D) Ca(HCO<sub>3</sub>)<sub>2</sub> 
$$\longrightarrow$$
 CaCO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub>  $\uparrow$ 

**Q.13** Plumbosolvency is a health hazard in the transportation of

- (A) Hard water only
- (B) Soft water only
- (C) Both (A) and (B)
- (D) Water containing plum juice

**Q.14** In the laboratory,  $H_2O_2$  is prepared by the action of

(A) Cold dilute  $H_2SO_4$  on hydrated BaO<sub>2</sub>

- (B) Dil. HCl on MnO<sub>2</sub>
- (C) Cold  $H_2SO_4$  on MnO<sub>2</sub>
- (D) Aqueous alkali on Na<sub>2</sub>O<sub>2</sub>

**Q.15** When 50% solution of  $H_2SO_4$  is electrolysed by passing a current of high density at low temperature the main products of electrolysis are

(A) Oxygen and hydrogen

(B) H<sub>2</sub> and peroxy disulphuric acid

(C) H, and SO,

(D) O and peroxy disulphuric acid

#### Multiple Correct Choice Type

**Q.16** Which of the following will give hydrogen peroxide on hydrolysis

(A)  $H_2S_2O_8$  (B)  $H_2SO_5$  (C)  $H_3PO_5$  (D)  $HCIO_4$ 

**Q.17** When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with

(A) H<sup>+</sup> ion (B) Ca<sup>++</sup> ions

(C)  $SO_4^-$  ions (D) Mg<sup>++</sup>ions

**Q.18** Hydrogen can be obtained from water, by the action of water on-

(A) Calcium carbide (B) Calcium hydride

(C) Calcium oxide (D) Calcium

Q.19 What is true about ice

(A) Its density is more than water

(B) It is a good conductor of heat

- (C) It is a thermal insulator
- (D) Its density is less than water

Q.20 Hydrogen is obtained when zinc reacts with

on
on

(C) Conc, sulphuric acid (D) Dilute HCl

#### **Assertion Reasoning Type**

(A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.

(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true

**Q.21 Statement-I:** ZrH<sub>2</sub> is a non-stoichiometric hydride.

**Statement-II:** The composition of  $ZrH_2$  is exact same as its chemical formula.

**Q.22 Statement-I:** D<sub>2</sub> molecules are more stable than H<sub>2</sub>.

**Statement-II:** The bond dissociation energy of  $D_2$  is more than of  $H_2$ .

**Q.23 Statement-I:** Acetanilide acts as a negative catalyst for the decomposition of H<sub>2</sub>O<sub>2</sub>.

**Statement-II:** In the presence of acetanilide, the stability of H<sub>2</sub>O<sub>2</sub> increases

**Q.24 Statement-I:** Polarity of  $H_2O_2$ , is more than  $H_2O$  but  $H_2O$  is a better solvent.

**Statement-II:** In chemical reactions, H<sub>2</sub>O<sub>2</sub> is decomposed but H<sub>2</sub>O does not.

**Q.25 Statement-I:** When blood is added to a solution of H<sub>2</sub>O<sub>2</sub>, the solution bubbles furiously

**Statement-II:** Catalase (an enzyme) present in blood decomposes  $H_2O_2$  and produces bubbles of  $O_2$ .

**Q.26 Statement-I:** Pure zinc reacts slowly with sulphuric acid to produce hydrogen.

**Statement-II:** Hydrogen produced initially forms an extremely thin layer on zinc surface which prevents its dissolution in sulphuric acid.



#### **Comprehension Type**

**Paragraph 1:** Hydrogen peroxide is a powerful oxidizing agent. It is an electron acceptor in acidic and alkaline mediums.

$$H_2O_2+2H^++2e^- \longrightarrow 2H_2O$$

(in acidic medium)

 $H_2O_2 + 2e^- \longrightarrow 2OH^-$  (in alkaline medium)

It can also act as a reducing agent towards powerful oxidizing agents.

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$

In alkaline medium, however, its reducing nature is more effective.

$$H_2O_2+2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$$

**Q.27** In which of the following reaction,  $H_2O_2$  acts as a reducing agent.

(A)  $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$ (B)  $Na_2Sb_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$ (C)  $2KI + H_2O_2 \longrightarrow 2KOH + I_2$ (D)  $KNO_2 + H_2O_2 \longrightarrow KNO_3 + H_2O$ 

**Q.28** What is the product of the reaction of  $H_2O_2$  with  $Cl_2$ ?

(A) O <sub>2</sub> + HOCI	(B) HCl + O <sub>2</sub>
(C) H <sub>2</sub> O + HCl	(D) HCl + H <sub>2</sub>

**Paragraph 2:** Be and Mg, some amongst the p-block elements and most of the d-block elements give metallic or interstitial hydrides on reacting with hydrogen. The density of each compound is less than that of the metal itself and the properties are not much different from that of the metal. They give out hydrogen easily and are strong reducing agents. This suggests that hydrogen is present in the atomic state. These compounds are non-stoichiometric. The f-block elements (i.e., lanthanide and actinides) also form non-stoichiometric hydrides. These hydrides have lower densities than their respective metals. The metals of group 7, 8 and 9 do not form hydrides. This region of the periodic table is called 'hydride gap'.

**Q.29** Which type of hydride is formed by the clement having atomic number, Z = 43?

(A) Metallic hydride (B) Saline hydride

(C) Covalent hydride (D) No hydride

**Q.30** Which of the following has highest electrical conductance?

(A)  $BeH_2$  (B)  $MgH_2$  (C)  $CaH_2$  (D)  $ZrH_2$ 

Q.31 Interstitial hydride can not be used as,

(A) Storage of H<sub>2</sub>

- (B) Catalysts for hydrogenation reaction
- (C) Rocket propellant
- (D) Electric conductor

**Paragraph 3:** Hydrogen peroxide can be prepared in the laboratory by the action of dilute acids on metallic peroxide. In one method, sodium peroxide is added in small amount at a time to a dilute solution of sulphuric acid in cold. Sodium peroxide can be replaced by barium peroxide. In this case, a paste of BaO<sub>2</sub>.8H<sub>2</sub>O is prepared and added gradually to an ice-cold dilute sulphuric acid. Barium sulphate precipitates out leaving behind a dilute solution of hydrogen peroxide. Phosphoric acid can also be used in place of sulphuric acid.

**Q.32** The oxide that gives hydrogen peroxide on treatment with a dilute acid is:

(A)  $PbO_2$  (B)  $SrO_2$  (C)  $MnO_2$  (D) $TiO_2$ 

**Q.33** The correct increasing order of the acidity of CO<sub>2</sub>  $H_2O$  and  $H_2O_2$  is

(A)  $CO_2 < H_2O_2 < H_2O$  (B)  $H_2O < H_2O_2 < CO_2$ (C)  $H_2O < H_2O_2 > CO_2$  (D)  $H_2O_2 > CO_2 > H_2O$ 

**Q.34** Which of the following is used for the preparation of H<sub>2</sub>O<sub>2</sub>?

(A) Anhydrous  $BaO_2$  (B) Anhydrous  $Na_2O_2$ (C) TiO<sub>2</sub> (D) PbO<sub>2</sub>

**Paragraph 4:** Hydrogen peroxide has an ability to function as an oxidant as well as reductant in both acid and alkaline solutions. Hydrogen peroxide provides an atom of oxygen (Nascent oxygen) readily for oxidation and takes up an atom of oxygen to give water and oxygen gas. The strength of commercially available  $H_2O_2$  sample is described as volume strength. 30 volumes of  $H_2O_2$  means 30 cm1  $O_2$  is obtained at STP by decomposing 1 cm<sup>3</sup> of  $H_2O_2$  solution. Dark paraffin bottles are used for storage of  $H_2O_2$  as it is decomposed in light and catalysts

**Q.35** The normality of 30 volume  $H_2O_2$  solution is (A) 5.3 N (B) 11.2 N (C) 2 N (D)1 N **Q.36**  $xK_2Cr_2O_7 + y H_2SO_4 + z H_2O_2 \longrightarrow K_2SO_4$   $Cr_2(SO_4)_3 + w H_2 O + jO_2, x, y, z are$ (A) 4,1,3 (B) 2,4,8 (C) 1,8,2 (D)1,4,3

**Q.37**  $H_2O_2 + Na_3AsO_3 \longrightarrow X + Y.X$  and Y respectively are (A)  $Na_3AsO_4 + H_2O$  (B)  $As_2O_3 + H_2O$ 

(c)  $As(OH)_3 + H_2$  (D)  $As(OH)_5 + H_2$ 

**Q.38** For the decomposition of  $H_2O_2$  in  $H_2O$  and  $O_2$ ,  $\Delta G$  is (A) +ve (B)-ve (C) Zero (D) Either +ve or zero

**Paragraph 5:** Ordinary water is an oxide of common isotope of hydrogen called Protium while heavy water is oxide of heavier isotope of hydrogen called Deuterium. It is represented as  $D_2O$  and as molecular weight of  $D_2O$  is more than  $H_2O$ , there are slightly stronger Vander der Waals forces between  $D_2O$  molecules. Like ordinary water heavy water is a colorless, odorless and tasteless mobile liquid.

Q.39 Heavy water is used in atomic reactor as

- (A) Coolant
- (B) Moderator
- (C) Both moderator and coolant
- (D) Neither coolant nor moderator.

Q.40 Heavy water freezes at

(A) 0° C (B) 3.8° C (C) 38°C (D) -0.38°C

Q.41 The pH of D, O and H, O at 298 K is

(A) 7.0,7.0	(B) 7.35,7.0
(C) 7.0,6.85	(D) 6.85, 7.35

Q.42 Which of the following is not true?

(A) Ordinary water is electrolysed more rapidly than  $D_2 O$ 

(B) Reaction between  $\rm H_{2}$  and  $\rm Cl_{2}$  is much faster than  $\rm D_{2}$  and  $\rm Cl_{2}$ 

(C)  $D_2O$  freezes at lower temperature than  $H_2O$ 

(D) Bond dissociation energy for  $D_2$  is greater than  $H_2$ .

#### Match the Columns

#### **Q**.43

Column I	Column II
(For the production of $H_2O_2$ )	
(A) BaO <sub>2</sub> .8H <sub>2</sub> O	(p) Reduction and oxidation
(B) Na <sub>2</sub> O <sub>2</sub>	(q) reacts with NaOH
(C) H <sub>2</sub> SO <sub>4</sub>	(r) electrolysis then hydrolysis
(D) Ethyl derivative of anthraquinone	(s) Reacts with $H_2SO_4$

#### **Q**.44

Column –I	Column – II	
(Compound)	(Properties)	
(A) Perhydrol	(p) Dilute solution of $H_2O_2$	
(B) Water gas	(q) Manufacture of H <sub>2</sub>	
(C) Bosch's process	(r) CO+ H <sub>2</sub>	
(D) $CH_4 + H_2O$ (s) Antiseptic and germicide		

#### Q.45

Column –I	Column - II	
(Compound)	(Properties)	
(A) LiAlH <sub>4</sub>	(p) Binary hydride	
(B) NaBH <sub>4</sub>	(q) Reducing agent	
(C) CaH <sub>2</sub>	(r) Complex hydride	
(D) LiH	(s) Alanate	

**Q.46** Match the List I with List II and select the correct answer using the codes given below in the lists:

List I	List II
(A) Heavy water	(p) Bicarbonates of Mg and Ca in water
(B) Temporary hard water	(q) No foreign ions in water
(C) Soft water	(r) D <sub>2</sub> O
(D) Permanent hard water	(s) Sulphates and chlorides of Mg and Ca in water

## **Previous Years' Questions**

Q.1 A sample of water	contains	sodium	chloride.	It is	
				986)	

- (A) Hard water(B) Soft water(C) Moderately hard(D) None of these
- **Q.2** Pick out the correct statement
- Q.2 Pick out the correct statement (2008) (A) By decreasing the temperature pure para-hydrogen can be obtained

(B) By increasing the temperature pure ortho-hydrogen can be obtained

(C) By decreasing the temperature pure ortho-hydrogen can be obtained

(D) By increasing the temperature pure para-hydrogen can be obtained

Q.3 Hydrogen can be p	(1992)	
(a) Cu with $H_2SO_4$	(B) Sodium formate	
(C) Sodium oxalate (D) None of these		
<b>Q.4</b> Plumbosolvancy transportation of	is a health hazard	in the <b>(1994)</b>
(A) Hard water only	(B) Soft water only	
(C) Both (a) and (B)	(D) Water containing plu	ım juice

**Q.5** The critical temperature of water is higher than that of  $O_2$  because the  $H_2O$  molecule has (1997)

(A) Fewer electrons than  $O_2$  (B) Two covalent bonds

(C) V-shape (D) Dipole moment

Q.6 When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with (1990)

(A) H <sup>+</sup> ions	(B) Ca <sup>2+</sup> ions	
(C) $SO_4^{2-}$ ions	(D) Mg <sup>2+</sup> ions	(E) OH <sup>-</sup> ions

Q.7 The reagent (s) used for softening the temporary hardness of water is (are) (2010)

(A) Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(B) Ca(OH) <sub>2</sub>	(C) Na <sub>2</sub> CO <sub>3</sub>	(D) NaOCl
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**Q.8**  $H_2O_2 \rightarrow 2H^++O_2+2e^-$ ;  $E^\circ = -0.68$  V. This equation represents which of the following behaviour of  $H_2O_2$  (1995)

(A) Reducing	(B) Oxidising		
(C) Acidic	(D) Catalytic		

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(1999)

**Q.9** The structure of  $H_2O_2$  is

(A) Open book like (B) Linear

(C) Closed book (D) Pyramidal

**Q.10** On shaking H<sub>2</sub>O<sub>2</sub> with acidified potassium dichromate and ether, ethereal layer becomes **(1998)** (A) Green (B) Red (C) Blue (D) Black

- **Q.11** Hydrogen peroxide in its reaction with  $KIO_4$  and  $NH_2OH$  respectively, is acting as a (2014)
- (A) Reducing agent, oxidising agent
- (B) Reducing agent, reducing agent
- (C) Oxidising agent, oxidising agent
- (D) Oxidising agent, reducing agent

## **JEE Main/Boards**

## s-block Elements

## **Exercise 1**

**Q.1** Why Alkali and alkaline earth metals, cannot be obtained by chemical reduction methods?

**Q.2** Why sodium cannot be prepared by the electrolysis of aqueous solution of sodium chloride using platinum cathode?

**Q.3** Which of the two, sodium or potassium has higher melting point?

**Q.4** Complete the following equations for the reaction between,

(B) Ca(OH), + Cl,

(A) Ca +  $H_2O$ 

(C) BeO + 2NaOH (D)  $BaO_2 + H_2SO$ 

**Q.5** Differentiate between (a) quick lime (b) lime water (c) Slaked lime

**Q.6** Arrange the following in the order or increasing covalent character; MCI, MBr MF & MI, where M is alkali metal.

**Q.7** Ionization enthalpies of alkali metals decrease as the atomic number increases.

## Q.8 State as to why:

(i) Lithium on being heated in air mainly forms monoxide and not peroxide.

(ii) An aqueous solution carbonate is alkaline in nature.

(iii) Sodium is prepared by electrolytic reduction method and not by chemical reduction method.

Q.9 How would you explain Lil is more soluble than KI?

Q.10 Identity the following

Na<sub>2</sub>CO<sub>3</sub> Na<sub>2</sub>CO SO<sub>2</sub> →B Elemental S  $\xrightarrow{I_2} D$ C

Also mention the oxidation state of S in all the compounds.

Q.11 Why is sodium metal kept under kerosene oil?

**Q.12** What is the formula of gypsum? What happens when it is heated?

**Q.13** What is dead burnt plaster? What is formula of plaster of paris?

**Q.14** Why super oxide of alkali metals are para magnetic while normal oxides are diamagnetic?

**Q.15** It is necessary to add gypsum in the final stages of preparation of cement Explain why?

**Q.16** Why are potassium and caesium, rather than lithium used in photoelectric cells?

Q.17 Explain the following:

(i) Alkali metals are not in free form in nature

(ii) Alkali metals are good reducing agents.

#### Q.18 Explain the following:

(i) The softness of group IA metals increases down the group with increasing atomic number.

(ii) Lithium salts have a greater degree of covalent character than other halides of the group.

#### Q.19 Explain the following:

(A) Alkali metals are obtained by the electrolysis of the molten salts and not by the electrolysis of their aqueous solutions.

(B) Calcium chloride is added to NaCl in the electrolytic manufacture of sodium.

(C) On exposure to air, sodium hydroxide becomes liquid and after sometimes it changes to white powder.

(D) Sodium Carbonate is made by Solvay process but the same process is not extended to the manufacture of potassium carbonate,

(E) An aqueous solution of iodine becomes colorless on adding excess of sodium hydroxide

Q.20 Complete and balance the following equations

- $(A) \text{ KO}_2 + \text{H}_2\text{O} \rightarrow \dots + \text{O}_2$
- (B)  $PbO_2$  + NaOH  $\longrightarrow$  Heat  $\rightarrow$  Hard Hard (conc.)
- (C) KI +  $H_2SO_4 + H_2O_2 \rightarrow I_2 + \dots + H_2O_3$
- (D) NaOH +  $I_2 \rightarrow \dots + NalO_3 + H_2O$

Q.21 Answer the following:

(i) What is meant by black ash?

(ii) What is the action of NaOH on ammonium salts?

(iii) What is washing soda?

#### Q.22 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 AICl<sub>3</sub> solution

(v) Anhydrous potassium nitrate is heated with excess of metallic potassium

(vi) Sodium is strongly heated in oxygen and the product is treated with  $\rm H_2SO_4$ 

**Q.23** Write the balanced equations of the reactions of Caustic soda on the following

(i) Zinc, (ii) Silver nitrate, (iii) Phosphorus

**Q.24** Give one test each to make distinction between the folio wing pairs:

(i) NH<sub>4</sub>Cl and KCl (ii) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>

(iii) NaCl and KCl

Q.25 Arrange the following as indicated:

(A) LiOH, NaOH, KOH (Increasing solubility in water)

(B) LiHCO<sub>3</sub>, NaHCO<sub>3</sub>, KHCO<sub>3</sub> (Increasing solubility in water)

(C) Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> (Increasing solubility in water)

(D) Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup> (Increasing size of hydrated ion)

Q.26 What happen when the following are heated?

(A) Hydrated magnesium chloride,

(B) Gypsum,

(C) Bicarbonates of alkaline earth metals,

(D) Epsom salt, (v) Barium nitrate.

**Q.27** How would you explain?

(i) BeO is insoluble but  $BeSO_4$  is soluble water.

(ii) BaO is soluble but  $BaSO_4$  is insoluble water.

**Q.28** Explain the following:

(i) Alkali metals salts impart color to the flame.

(ii) Sodium is kept under kerosene

(iii) Potassium and caesium are used photoelectric cells.

#### **Q.29** Explain the following:

(i) Li<sup>+</sup> ion is far smaller than the other alkali metal ions but it moves through a solution less rapidly than the others.

(ii) Lithium fluoride has the lowest solubility of the group IA metal halides.

(iii) Salts of lithium having small anions are more stable than the salts having larger anions.

#### Q.30 Answer the following:

(A) What is the intermediate product in Solvay's process?

(B) Which chloride of an alkali metal is soluble in alcohol?

(C) Which substance is added to sodium chloride as to reduce its fusion temperature during manufacture of sodium?

(D) What product is formed when carbon monoxide is passed through sodium hydroxide under high pressure?

## Exercise 2

#### Single Correct Choice Type

Q.1 NaNO<sub>3</sub> on heating gives

(A)  $O_2$  (B)  $O_2$  and  $NO_2$  (C)  $NO_2$  (D)  $N_2O$  and  $O_2$ 

**Q.2** Sodium metal is prepared commercially by electrolysis of fused NaCl by

(A) Down's process	(B) Nelson cell
(C) Solvay process	(D) Castner and Kellner's cell

Q.3 When hydrated magnesium chloride is heated

(A) MgO is formed

(B) Mg (OH), is formed

(C) Mg (OH) Cl is formed

(D) Anhydrous MgCl<sub>2</sub> is formed

Q.4 Magnesium bums in air to give

(A) MgO (B)  $Mg_3N_2$  (C) MgCO<sub>3</sub> (D) Both (A) and (B)

Q.5 Which of the following is a Magnesite ore?

(A) CaCO<sub>3</sub> . MgCO<sub>3</sub> (B) MgSO<sub>4</sub> . 7H<sub>2</sub>O (C) KCl. MgCl<sub>2</sub> . 6H<sub>2</sub>O (D) MgCO<sub>3</sub>

**Q.6** On mixing with an adequate quantity of water, Plaster of Paris sets into a hard solid having the composition

(A) CaSO<sub>4</sub>.2H<sub>2</sub>O (B) CaSO<sub>4</sub>.H<sub>2</sub>O (C) CaSO<sub>4</sub>.Ca (OH) (D) (CaSO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O

**Q.7** Which of the following are arranged in correct increasing order of solubility?

(A)  $CaCO_3 < KHCO_3 < NaHCO_3$ (B)  $NaHCO_3 < KHCO_3 < CaCO_3$ (C)  $KHCO_3 < NaHCO_3 < CaCO_3$ (D)  $CaCO_3 < NaHCO_3 < KHCO_3$  Q.8 Nitrolim is

(A)  $CaCN_2 + C$ (C)  $CaC_2 + C$  (B) Ca  $(CN)_2 + C$ (D) All of these

e

**Q.9** 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 while the lattice energy of  $BaSO_4$  is more than its hydration energy

(B) The lattice energy has no role to play in solubility

(C) The lattice energy of  $Na_2SO_4$  is more than its hydration energy

(D) None of these

**Q.10** The following are some of the methods commonly employed for the extraction of metals from their ores. Which of the following methods is generally employed for the extraction of sodium?

(A) Reduction of an oxide with coke

(B) Electrolysis of an aqueous solution of a chloride

(C) Electrolysis of a molten chloride

(D) Reduction of a chloride with more reactive Metal

Q.11 Anhydrone is the name given to

(A) Mg (OH)  $_{2}$ .  $6H_{2}O$  (B) MgSO<sub>4</sub>.7H<sub>2</sub>O (C) Mg (OH). 7H<sub>2</sub>O (D) Mg (ClO<sub>4</sub>)<sub>2</sub>

**Q.12** The smallest alkali metal cation is

(A) Li<sup>+</sup> (B) Na<sup>+</sup> (C) K<sup>+</sup> (D) Fr<sup>+</sup>

**Q.13** Considering greater polarization in LiCl compared to that in NaCl, which of the following statements you would expect to be wrong?

(A) LiCl has lower melting point that NaCl

(B) LiCl dissolves more in organic solvents

(C) LiCl will ionize in water more than NaCl

(D) Fused LiCl would be less conducting than fused NaCl

**Q.14** Amongst the alkali metals, lithium is the strongest reducing agent in the aqueous solution. This is because within the group, it has the highest

(A) Ionization energy (B) Electrode potential

(C) Hydration energy (D) Electronegativity

**Q.15** A solid is a compound of group 1 element and it gives a bright red color in the flame test.

The solid is

(A) NaCl (B) KCl (C) LiBr (D) CsCl

**Q.16** Alkali metals readily dissolve in liquid ammonia to give blue colored solutions. The blue color is believed to be due to

(A) Ammoniated cations

(B) Ammoniated anions

(C) Ammoniated electrons

(D) Ammoniated cations and ammoniated electrons

**Q.17** Which of the following compounds possesses the largest lattice energy?

(A) LiF (B) NaCl (C) KH (D) Csl

**Q.18** On heating sodium metal in a current of dry ammonia, the compound formed is

(A) Sodium nitride (B) Sodium hydride

(C) Sodium amide (D) Sodium azide

**Q.19** The pair of compounds which cannot exist together in solution is

- (A) NaHCO<sub>3</sub> and NaOH (B) NaHCO<sub>3</sub> and H<sub>2</sub>O
- (C) NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> (D) Na<sub>2</sub>CO<sub>3</sub> and NaOH

**Q.20** Among alkali metal salts, the lithium salts are the poorest conductors of electricity in aqueous solution because of

(A) Easy diffusion of Li⁺ ions

(B) Lower ability of Li<sup>+</sup> ions to polarize water molecules

(C) Lowest charge to radius ratio

(D) Higher degree of hydration of Li<sup>+</sup> ions

**Q.21** The order of decreasing polarity in the compounds CaO, CsF, KCI, and MgO is

(A) CaO, CsF, KCl, MgO (B) MgO, KCl, CaO, CsF

(C) KCl, CaO, CsF, MgO (D) CsF, KCl, CaO, MgO

**Q.22** One of the following statements is incorrect.

(A) Elements of group 2 are good conductors of electricity and heat

(B) Compounds of group 2 elements are diamagnetic in nature

(C) The salts of group 2 elements are highly hydrated than those of elements of group 1

(D) Elements of group 2 are more electropositive than group 1 elements.

**Q.23** Alkaline earth metals form dipositive ions instead of unipositive ions because

(A) Dipositive ions carry more charge

(B) Their second ionization energies are not different from first ionization energy

(C) Unipositive ions do not have stable configuration

(D) Compounds containing dipositive ions have more lattice energy

**Q.24** Which element possesses maximum electropositive character?

(A) Mg (B) Be (C) P

P (D) Al

**Q.25**  $BeF_2$  is highly soluble in water whereas the fluorides of other alkaline earth metals are almost insoluble because

(A) BeF<sub>2</sub> is ionic in nature

(B) BeF<sub>2</sub> is covalent in nature

(C) Hydration energy of  $BeF_2$  is much higher than its lattice energy

(D) Lattice energy of  $BeF_2$  is much higher than that of its hydration energy.

**Q.26** Both Be and Al become passive on treatment with cone.  $HNO_3$  due to

(A) Non-reacting nature of the metals

(B) Non-oxidizing nature of the acid

(C) The formation of an inert layer of the oxide on the surface of the metals

(D) All are correct

Q.27 The value of x is maximum for

(A) MgSO<sub>4</sub>. xH<sub>2</sub>O
(B) CaSO<sub>4</sub>. xH<sub>2</sub>O
(C) BaSO<sub>4</sub>. xH<sub>2</sub>O
(D) All have the same value of x

**Q.28** The name 'Blue John' is given to which of the following compounds

(A)  $CaH_2$  (B)  $CaF_2$  (C)  $Ca_3 (PO_4)_2$  (D) CaO

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**Q.29** Amongst LiCl, RbCl, BeCl<sub>2</sub> and MgCl<sub>2</sub> the compounds with greatest and the least ionic character, respectively, are

(A) LiCl and RbCl	(B) RbCl and BeCl <sub>2</sub>
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(C) RbCl and MgCl<sub>2</sub> (D) MgCl<sub>2</sub> and BeCl<sub>2</sub>

Q.30 Among the following: NaOH, Ca (OH) ,

KOH and Zn (OH)<sub>2</sub>, the weakest base is

(A) NaOH	(B) Ca (OH) <sub>2</sub>
(C) KOH	(D) Zn (OH) <sub>2</sub>

**Q.31** The decreasing order of the second ionization potential of K, Ca and Ba

(A) K > Ca > Ba	(B) Ca > Ba > K
(C) Ba>K>Ca	(D) K>Ba>Ca

## **Previous Years' Questions**

**Q.1** Aqueous solution of  $Na_2S_2O_3$  on reaction with  $Cl_2$  gives: (2008)

(A)  $Na_2S_4O_6$  (B)  $NaHSO_4$  (C) NaCl (D) NaOH

**Q.2** Which of the following chemicals, in addition to water, are used in the manufacture of  $Na_2CO_3$  by Solvay process: (1999)

(A) NaCl, CO and  $NH_3$  (B) NaCl, CO<sub>2</sub> and  $NH_3$ 

(C) NaCl,  $NH_4Cl$  and  $CO_2$  (D) NaHCO<sub>3</sub>, CO and  $NH_3$ 

Q.3 When KI is added to acidified solution of sodium nitrite: (2008)

(A) NO gas is liberated & I, is set free

(B) N<sub>2</sub> gas is liberated & HI is produced

(C)  $N_2O$  gas is liberated &  $l_2$  is set free

(D)  $N_2$  gas is liberated & HOI is produced

Q.4 The metallic lustre exhibited by sodium is explained by: (1987)

(A) Diffusion of sodium ions

(B) Oscillation of loose electrons

(C) Excitation of free protons

(D) Existence of body centered cubic lattice

Q.5 Which of the following pair can't exist in solution: (1999)

(A) NaHCO<sub>3</sub> and NaOH (B) Na<sub>2</sub>CO<sub>3</sub> and NaOH (C) Na<sub>2</sub>CO<sub>3</sub> and NaCI (D) NaHCO<sub>3</sub> (D) NAH

**Q.6** Sodium thiosulphate is prepared by:

(A) Reducing  $Na_2SO_4$  solution with  $H_2S$ 

(B) Boiling  $Na_2SO_3$  solution with S in alkaline medium

(1996)

(C) Neutralizing  $H_2S_2O_3$  solution with NaOH

(D) Boiling Na<sub>2</sub>SO<sub>3</sub> solution with S in acidic medium

Read the following questions and answer as per the direction given below:

(A) Assertion is true; reason is true; reason is the correct explanation of assertion.

(B) Assertion is true; reason is true; reason is not the correct explanation of assertion.

(C) Assertion is true; reason is false.

(D) Assertion is false; reason is true.

**Q.7 Assertion:** Radium is most abundant s-block element. *(1997)* 

**Reason:** s-block elements are non-radioactive in nature.

Q.8 Assertion: LiCl is predominantly a covalent compound. (1998)

**Reason:** Electronegativity difference between Li and Cl is too small.

Q.9 Assertion: The first ionization energy of Be is greater than that of B. (2001)

Reason: 2p-orbital is lower in energy than 2s orbital.

**Q.10 Assertion:** The alkali metals can form ionic hydrides which contains the hydride ion. (1994)

**Reason:** The alkali metals have low electronegativity, their hydrides conduct electricity when fused and liberate hydrogen at the anode.

Q.11 Assertion: Be does not impart any characteristic color to the Bunsen flame. (1990)

**Reason:** Due to its very high ionization energy, beryllium requires a large amount of energy for excitation of the electrons.

**Q.12** The coagulating power of electrolytes having ions  $Na^+$ ,  $Al^{3+}$  and  $Ba^{2+}$  for arsenic sulphide sol increases in the order: (2013)

**Q.13** Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? (2015)

(D) SrSO

(A) CaSO<sub>4</sub> (B) BeSO<sub>4</sub> (C) BaSO<sub>4</sub>

(A) 
$$AI^{3+} < Ba^{2+} < Na^{+}$$
 (B)  $Na^{+} < Ba^{2+} < AI^{3+}$   
(C)  $Ba^{2+} < Na^{+} < AI^{3+}$  (D)  $AI^{3+} < Na^{+} < Ba^{2+}$ 

## **JEE Advanced/Boards**

## **Exercise 1**

**Q.1** For the alkali metals, which of the following increases with increasing atomic number?

- (A) First ionization energy
- (B) Electronegativity
- (C) Hydration energy of the univalent ion
- (D) Atomic radius

**Q.2** 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 sulphate salts of alkali metals except lithium sulphate forms alum.

(C) All sulphate salts of alkali metals except lithium sulphate do not decompose at high temperature

(D) All of these

**Q.3** Which metal bicarbonates does not exist in solid state?

(i) LiHCO<sub>3</sub> (ii) Ca(HCO<sub>3</sub>)<sub>2</sub> (iii) Zn(HCO<sub>3</sub>)<sub>2</sub> (iv) AgHCO<sub>3</sub>

(A) i, ii, iii, iv (B) i, ii, iii (C) i, ii, iv (D) ii, iii, iv

**Q.4** When a standard solution of NaOH is left in air for a few hours:

- (A) A precipitate will form
- (B) Strength of solution will decrease
- (C) The strength of solution will increase

(D) The concentration of Na<sup>+</sup> ion in solution will remains same

- **Q.5** CaCl<sub>2</sub> is preferred over NaCl for clearing ice on roads particularly in very cold countries. This is because:
- (A) CaCl<sub>2</sub> is less soluble in H<sub>2</sub>O than NaCl
- (B) CaCl<sub>2</sub> is hygroscopic but NaCl is not

(C) Eutectic mixture of CaCl<sub>2</sub>/H<sub>2</sub>O freezes at  $-55^{\circ}$ C while that of NaCl/H<sub>2</sub>O freezes at  $-18^{\circ}$ C

(D) NaCl makes the road slippery but CaCl<sub>2</sub> does not

**Q.6** Calcium imide on hydrolysis gives gas (B) which on oxidation by bleaching powder gives gas (C) Gas (C) on reaction with magnesium give compound (D) which on hydrolysis gives again gas (B). Identify (B), (C) and (D).

Q.7 Which of the following statement is false?

(A) The milk of magnesia used as antacid is chemically MgO + MgCl<sub>2</sub>

(B) Stability of alkali metal peroxides increases with increase in atomic number

(C) Hydration energy of AgF is higher than its lattice energy

(D) Anhydrous  $\rm MgCl_{2}$  cannot be prepared by direct heating of  $\rm MgCl_{2}.6H_{2}O$ 

Q.8 Nitrogen dioxide cannot be obtained from:

(A) Cu  $(NO_3)_2$  (B) Hg  $(NO_3)_2$  (C) NaNO<sub>3</sub> (D) AgNO<sub>3</sub>

**Q.9** On treatment with cold water, an element (A) reacts readily liberating a colorless, odorless gas (B) and a solution (C). Lithium is reacted with (B) yielding a solid product (D) which effervesce with water to give a strongly basic solution (E). When  $CO_2$  gas is bubbled through solution (C), a white ppt. (F) is formed but this redissolved forming solution (G) when more  $CO_2$  is passed. Precipitate (F) effervesced when

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moistened with conc. HCl and give deep red coloration to a Bunsen burner flame, (F) on heating with excess of carbon at 2000°C give Answer the following questions on the basis of above passage. Metal (A) may be:

(A) Be (B) Ca (C) Sr (D) Ba

Q.10 solution (G) contains a salt which:

(i) Causes permanent hardness of water

(ii) Cannot be obtained in solid state

(iii) Causes temporary hardness of water

(iv) Can be obtained in solid state

Select the correct statements:

(A) (i) and (ii)	(B) (i) and (iv)
(C) (ii) and (iii)	(D) (ii) and (iv)

**Q.11** Solid (H) on hydrolysis gives a gas, which on passing through ammonical AgNO<sub>3</sub> solution, yields:

(A) White ppt.	(B) Red ppt.
(C) No ppt.	(D) Brown ppt.

**Q.12** Lithium only forms monoxide when heated in oxygen. Sodium forms monoxide and peroxide in excess of oxygen. Other alkali metals form superoxide with; oxygen, i.e.  $MO_2$ . The abnormal behavior of lithium is due to small size. The larger size of higher alkali metals also decides the role in formation of superoxides. All the three anions abstract proton from water. The three anions are related to each other as follows:

$$O^{2-} \xrightarrow{\frac{1}{2}O_2} O_2^{2-} \xrightarrow{O_2} 2O_2^{-}$$

Oxide ion peroxide ion superoxide ion

Consider the following reaction:

 $M + O_2 \rightarrow MO_2$ 

(M = alkali metal) (Stable superoxide)

(A) M cannot be Li and Na

(B) M cannot be Cs and Rb

(C) M cannot be Li and Rb

(D) None of these

Q.13 Which anion is stable towards water?

(B)  $O_2^{2-}$ (C)  $O_2^-$ (D) None of these (A) O

**Q.14** Which compound will liberate oxygen when reacts with water?

(A)  $Na_2O_2$  (B)  $KO_2$  (C)  $Na_2O$  (D)  $Cs_2O_2$ 

**Q.15** Choose the correct statement(s):

(A) BeCO<sub>3</sub> is kept in the atmosphere of  $CO_2$  since, it is least thermally stable

(B) Be dissolves in an alkali solution forming  $[Be(OH)_{a}]^{2-}$ 

(C)  $BeF_2$  forms complex ion with NaF in which Be goes with cation

(D)  $BeF_2$  forms complex ion with NaF in which B goes with anion

# Exercise 2

#### Single Correct Choice Type

**Q.1** When an aqueous solution of sodium chloride is electrolyzed using platinum electrodes, the ions discharged at the electrodes are:

(A) Sodium and hydrogen

(B) Sodium and chloride

(G) Hydrogen and chloride

(D) Hydroxyl and chloride

**Q.2** In the Caster-Kellner cell used for the manufacture of NaOH, the cathode in the central compartment is made up of

(A) Carbon (B) Iron (C) Mercury (D) Nickel

**Q.3** In the manufacture of NaOH by electrolysis of an aqueous solution of sodium chloride, the cathode and anode are separated by using a diaphragm or slate partitions because

(A) It increases the yield of  $Cl_2$ 

(B) It prevents the reaction taking place between NaOH and  $\text{Cl}_2$ 

(C) It prevents the mixing of NaOH and NaCl

(D) It prevents the reaction taking place between Na and  $\mathrm{Cl}_{\scriptscriptstyle 2}$ 

**Q.4** A compound X on heating gives a colorless gas. The residue is dissolved in water to obtain Y. Excess  $CO_2$  is passed through aqueous solution of Y when Z is formed. Z on gentle heating gives back X. The compound X is:

(A)  $NaHCO_3$  (C) Ca  $(HCO_3)_2$  (B)  $Na_2CO_3$  (D)  $CaCO_3$ 

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**Q.5** Potassium metal is commercially prepared by the reduction of molten KCl with metallic sodium at 850°C (1123 K). This method is based upon the following principle

(A) Sodium is more reactive than potassium at this temperature

(B) Potassium being more volatile distils off thus shifting the reaction forward

(C) Sodium prefers to bind to chloride ions in preference to potassium ions

(D) Potassium and sodium form an alloy at this temperature.

**Q.6** If Na<sup>+</sup> ion is larger than  $Mg^{2+}$  ion and S<sup>2</sup> ion is larger than  $Cl^-$  ion, which of the following will be least soluble in water?

(A) Sodium chloride (B) Sodium sulphide

(C)Magnesium chloride (D) Magnesium sulphide

**Q.7** Magnesium burns in CO<sub>2</sub> to form:

(A) MgO and CO	(B) MgCO <sub>3</sub>
(C) MgO and C	(D) MgO <sub>2</sub>

Q.8 Which one of the following is most soluble in water?

(A) Mg (OH)  $_2$  (B) Sr (OH)  $_2$  (C) Ca (OH)  $_2$  (D) Be (OH)  $_2$ 

**Q.9** The right order of the solubility of sulphates of alkaline earth metals in water is:

- (A) Be > Ca > Mg > Ba > Sr
- (B) Mg > Be > Ba > Ca > Sr
- (C) Be > Mg > Ca > Sr > Ba
- (D) Mg > Ca > Ba > Be > Sr

**Q.10** A metal salt solution forms a yellow precipitate with potassium chromate in acetic acid, a white precipitate with dilute sulphuric acid but gave no precipitate with sodium chloride or iodide. The white precipitate obtained when sodium carbonate is added to the metal salt solution will consist of

(A) Lead carbonate (B) Basic lead carbonate

(C) Barium carbonate (D) Strontium carbonate

**Q.11** Which of the following statement is false?

(A) Strontium decomposes water readily than beryllium

(B) Barium carbonate melts at a higher temperature than calcium carbonate

(C) Barium hydroxides is more soluble in water than magnesium hydroxide

(D) Beryllium hydroxide is more basic than barium hydroxide

**Q.12** A salt on treatment with dil. HCI gives a pungent smelling gas a yellow precipitate. The salt gives green flame test and a yellow precipitate with potassium chromate. The salt is:

(C) PbS<sub>0</sub>

(A)  $NiSO_4$  (B)  $BaS_2O_3$ 

(D) CuSO<sub>4</sub>

#### Multiple Correct Choice Type

**Q.13** In hydrolysis, the alkali metal oxides, peroxides and superoxides act as:

(A) Bronsted acid (B) Bronsted base

(C) Lewis acid (D) Lewis base

Q.14 Identify the incorrect statement (s):

(A) Magnesium is lighter than calcium

(B) The atomic radius of Mg is greater than that of Ca

(C) Mg alloys are used in the construction of air crafts

(D) Mg is used as a reducing agent

**Q.15** Which of the following statements about the elements, Mg, Ca, Sr and Ba and their compounds is true?

(A) Solubility of the hydroxides in water increases with increasing atomic number

(B) Thermal stability of the carbonates increases with increasing atomic number

(C) All given elements react with water or steam to give hydrogen

(D) Metal chlorides are all liquids at room temperature

**Q.16** Which statement is correct regarding the diagonal relationship between the Al and Be?

(A) BeO and  $Al_2O_3$  are amphoteric in nature

(B) Both carbide on hydrolysis produce same gas

- (C) Both can form complex
- (D) Both have nearly close m.p.

#### **Comprehension Type**

Paragraph 1: The thermal stability of the salts of the s-block elements is dependent upon three main factors. Firstly, the greater the charge of the ions involved, the stronger the interionic attraction and the more stable the salt. Also, the smaller the ions become in terms of their ionic radii the closer they approach each other in the crystal lattice of their salts and the more stable the salt. Thirdly, if the ions in the lattice are of comparable size, the crystal lattice is arranged in a more uniform fashion and thus possesses greater thermal stability. There is one other factor that affects thermal stability. The larger the anions in the crystal, for example  $CO_3^{2-}$ , unless the cation is of comparable size, the anions decompose on heating to give smaller anions such as O<sup>2-</sup>. This point is especially important when considering the thermal stability of the carbonates, nitrates and hydroxides of the s-block elements.

**Q.17** Comparing calcium oxide and magnesium oxide, which of the two would be more stable?

(A) Magnesium oxide would be more stable because the Magnesium cation is smaller

(B) Magnesium oxide would be more stable because Magnesium has a lower atomic mass than Calcium

(C) Calcium oxide would be more stable because the calcium anion is smaller than the Magnesium cation

(D) Calcium oxide would be more stable because calcium has a greater atomic mass than magnesium

**Q.18** The nitrates of the Group-I elements mainly decompose not to the oxide but to the nitrite  $(NO_2^-)$  although O<sup>2-</sup> is smaller than  $NO_2^-$  Why?

(A) Because only doubly charged anion like  $CO_3^{2-}$  decompose to the oxide

(B) Because the double charge on the oxygen would make the salt less stable than a singly charge nitrite anion

(C) Because the nitrite anion contains two oxygen atoms while the oxide anion contains only one

(D) Because the nitrite anion is probably about the same size as the Group I cations.

**Q.19** Given that  $CO_3^{2-}$  anion is approximately the same size as the early Group I cations, what would occur if Na<sub>2</sub>CO<sub>3</sub> were heated

(A) If would decompose to yield  $Na_2O$ 

(B) If would decompose to yield  $Na_2O + CO_2$ 

(C) If would decompose to yield NaOH

(D) No decomposition would occur

**Q.20**  $\text{Li}_2\text{O}$  is often considered to be covalent in nature because of the unusually high electronegativity of lithium. Which of the following would be a possible Lewis dot structure for the compound?

(A) 
$$\text{Li} - \text{Li} - \overset{\bullet}{O}$$
 (B)  $\text{Li} - \overset{\bullet}{O} - \text{Li}$  (C)  $\text{Li} = \overset{\bullet}{O} = \text{Li}$  (D)  $\text{Li} - \overset{\bullet}{O} = \text{Li}$ 

**Paragraph 2:** Most of the s-block metals form saline or ionic hydrides. These are non-volatile, non-conducting crystalline solids. However BeH<sub>2</sub> and MgH<sub>2</sub> have covalent polymeric structure. These ionic hydrides have rock salt like structure.

Electrolysis of solution of saline hydride produces  $H_2$  at anode. Saline hydrides react explosively with  $H_2O$ . The fire so produced cannot be extinguished with  $CO_2$  as it get reduced by hot metal hydrated. Only sand is useful as it is a solid.

**Q.21** When NaBH<sub>4</sub> is dissolved in water

(A) It decomposes with the evolution of  $H_2$ 

(B)  $Na^+$  and  $BH_4^-$  are formed which are stable

(C)  $BH_4^-$  ions formed initially decompose to produce  $OH^-$  ions, which prevent further decomposition

(D) NaH and  $B_2H_6$  are produced.

**Q.22** LiAlH<sub>4</sub> is obtained by reacting an excess of... with an ethereal solution of AlCl<sub>3</sub>

(A) LiCl (B) LiH (C) Li (D) LiOH

Q.23 Alkali metal hydrides react with water to give

- (A) Acidic solution (B) Basic solution
- (C) Neutral solution (D) Hydride ion

**Q.24** Amongst the alkali metal hydrides, the most stable one is

(A) LiH (B) NaH (C) KH (D) RbH

Q.25 Ionic hydrides are usually

- (A) Good electrically conductors when solid
- (B) Easily reduced
- (C) Good reducing agents
- (D) Liquid at room temperature.

#### **Assertion Reasoning Type**

Each of the questions given below consists of two statements, an Assertion and Reason. Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and R is the correct explanation of Assertion.

(B) If both assertion and reason are true but reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If both assertion and reason are false.

**Q.26 Assertion:** The radius of Na+ in aqueous solution is more than that of  $Li^+$  ion.

**Reason:** Na<sup>+</sup> is with high hydration energy compared to Li<sup>+</sup> ion in aqueous solution. LiNO<sub>3</sub>

**Q.27 Assertion:** and  $KNO_3$  both on decomposition give respective oxide and  $NO_2$  gas. Group-I.

**Reason:** Nitrates are highly stable, they do not undergo decomposition. Temperature.

**Q.28 Assertion:** Required for the decomposition of MgCO<sub>3</sub> is less than that of CaCO<sub>3</sub>.

**Reason:** Thermal stability of group II carbonates increases down the. Group.

Q.29 Assertion: .Li<sub>3</sub>N is known but K<sub>3</sub>N is not known.

**Reason:** Smaller sizes of lithium ion is able to form stable p bond with nitride ion.

**Q.30 Assertion:** Lithium can't be stored under kerosene whereas sodium can be stored,

Reason: Density of lithium is lower than that of sodium.

## **Previous Years** Questions

Q.1 The following compounds have been arranged in order of their increasing thermal stabilities. Identify the correct order. (1996)

(I) K<sub>2</sub>CO<sub>3</sub> (II) MgCO<sub>3</sub> (III) CaCO<sub>3</sub> (IV) BeCO<sub>3</sub> (A) I < II < III < IV (B) IV < II < III < I (C) IV < II < I < III (D) II < IV < III < I **Q.2** A dilute aqueous solution of  $Na_2SO_4$  is electrolyzed using platinum electrodes. The products at the anode and cathode are respectively (1996)

(A) 
$$O_{2'} H_2$$
 (B)  $S_2 O_8^{2-}$ , Na  
(C)  $O_{2'}$  Na (D)  $S_2 O_8^{2-}$ ,  $H_2$ 

**Q.3** A sodium salt of an unknown anion when treated with  $MgCl_2$  gives white precipitate only on boiling. The anion is: (2004)

(C) CO

(A)  $SO_4^{2-}$  (B)  $HCO_3^{-}$ 

(A) Na<sub>2</sub>O<sub>2</sub>

(D) NO<sub>3</sub>

**Q.4** The compound(s) formed upon combustion of sodium metal in excess air is (are): (2007)

Q.5 The reagent(s) used for softening the temporary hardness of water is (are): (2010)

(A)  $Ca_{3} (PO_{4})_{2}$  (B)  $Ca (OH)_{2}$ (C)  $Na_{2}CO_{3}$  (D) NaOCI

Q.6 MgCl<sub>2</sub>.6H<sub>2</sub>O on heating gives anhydrous MgCl<sub>2</sub> (1982)

Q.7 Sodium when burnt in excess of oxygen gives sodium oxide. (1987)

**Q.8** A white solid is either  $Na_2O$  or  $Na_2O_2$ . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid.

(i) Identify the substance and explain with balanced equation.

(ii) Explain what would happen to the red litmus if the white solid were the other compound. (1999)

**Q.9** Give reasons for the following in one or two sentences only: "BeCl<sub>2</sub> can be easily hydrolyzed." **(1992)** 

**Q.10** Identify (X) in the following synthetic scheme and write their structures.

 $BaCO_3 + H_2SO_4 \rightarrow X \text{ (gas) (C* denotes C^{14})}$  (2001)

# **PlancEssential** Questions

## **JEE Main/Boards**

Hydrogen

**Exercise 1** 

Q.6 Q.19 Q.21

**Exercise 2** 

Q.8 Q.15 Q.25 Q.29

**Previous Years' Questions** 

Q.5

## **JEE Main/Boards**

## s-Block Elements

## **Exercise 1**

Q.3 Q.8 Q.13 Q.23 Q.16 Q.19(iv) Q.26 (iv,v) Q.30

## **Exercise 2**

Q.6 Q.17

# Q.9

Q.25

## **Previous Years' Questions**

Q.6

## **JEE Advanced/Boards**

Q.19

0.43

**Exercise 1** 

Q.10 Q.17

Q.12

**Exercise 2** 

Q.6

**Previous Years' Questions** 

Q.6 Q.10

# JEE Advanced/Boards

**Exercise 1** 

Q.4 Q.12 Q.9 Q.15

## **Exercise 2**

Q.2 Q.4 Q.10 Q.22 Q.23

## **Previous Years' Questions**

Q.2 Q.3 Q.9

## **Answer Key**

## JEE Main/Boards

Hydrogen

**Exercise 1** 

**Q.11** 750 ml of O<sub>2</sub>, at NTP

**Q.12** 44.8.

**Q.13** AgNO<sub>3</sub> solution is used for the removal of AsH<sub>3</sub> and PH<sub>3</sub> present in very small amounts in hydrogen sample.

Q.14 (A) Potassium ferricyanide is reduced

 $2K_3Fe(CN)_6 + 2KOH + H_2O_2 ??2K_4Fe(CN)_6 + 2H_2O + O_2$ (B) Cr(OH)<sub>3</sub> is converted into yellow colored Na<sub>2</sub>CeO<sub>4</sub>

 $2Cr(OH)_3 + 4 NaOH + 3H_2O_2 \rightarrow$ 

 $2Na_2CrO_4 + 8H_2O$ 

**Q.15**  $D_2O$  has more molecular mass and greater degree of association than  $H_2O$  and thus shows higher m.pt. and b.pt.

**Q.16** Water reacts with  $Na_2O_2$  to produce NaOH which increases the decomposition of  $H_2O_2$ .

**Q.17** The reaction is highly exothermic. It brings large increase in volume also.

 $N_2H_4 + 2H_2O \rightarrow N_2(g) + 4H_2O(g)$ 

Q.18 This is due to the following reactions.

Oxidizing agent:

 $H_{2}O_{2} + 2H^{+} + 2e^{-} \rightarrow 2H_{2}O$  (acidic medium)

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$
 (alkaline medium)

Reducing agent:

 $H_2O_2 \rightarrow 2H^+ + O_2^- + 2e^-$ 

Q.19 0.2125

**Q.20** White lead is used as a pigment. The statues coated with white lead get blackened due to the action of H<sub>2</sub>S present in atmosphere in traces.

Pb(OH)<sub>2</sub>.2PbCO<sub>3</sub> + 3H<sub>2</sub>S → 3 PbS + 2CO<sub>2</sub> + 4H<sub>2</sub>O When White lead blackened statues are treated with 11,O,. the Pbs is oxidised to PbSO<sub>4</sub> which is colourless (white)

 $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O_{(white)}$ 

**Q.21** Na, H<sub>2</sub>, NaOH, Zn

Q.22 Two OH bonds lie in the same plane

**Q.23** A blue colour is obtained in ether due to formation of CrO<sub>5</sub>

Q.24 1.344

**Q.25** As potential discharge of  $K^+$  is higher than  $H^+$  ion and potential discharge of  $SO_4^{2-}$  is higher than  $OH^-$  ion.

**Q26** Pb from painting reacts with atmospheric  $H_2S$  to give black coloured PbS which on reaction with  $H_2O_2$  converts into PbSO<sub>4</sub>.

**Q.27** Traces of alkali present in glass bottles accelerates the decomposition of  $H_2O_{2'}$  hence glass is coated with wax.

**Q.28** During the storage of  $H_2O_{2'}$  addition of small amount of phosphoric acid or glycerol or acetanilide inhibits the decomposition of  $H_2O_2$ .

**Q.29** 1.7 N

**Q.30** (A)  $H_2O_2$  (B)  $CrO_4^{2-}$  (C)  $PbSO_4$ 

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Exercise 2									
Single Correct	Choice Type							<u>م</u>	
<b>Q.1</b> A	<b>Q.2</b> C	<b>Q.3</b> C	<b>Q.4</b> C		<b>Q.5</b> C	Q.6	В	<b>Q.7</b> B	•
<b>Q.8</b> B	<b>Q.9</b> B	<b>Q.10</b> C	<b>Q.11</b> D		<b>Q.12</b> B	Q.1	<b>B</b> D	Q.14 B	
<b>Q.15</b> D	<b>Q.16</b> A	<b>Q.17</b> A	<b>Q.18</b> A		<b>Q.19</b> D	Q.2	<b>0</b> C	<b>Q.21</b> D	
<b>Q.22</b> B	<b>Q.23</b> A	<b>Q.24</b> B	<b>Q.25</b> A		<b>Q.26</b> A	Q.2	<b>7</b> C	<b>Q.28</b> B	
<b>Q.29</b> C	<b>Q.30</b> C	<b>Q.31</b> B	<b>Q.32</b> B		<b>Q.33</b> A	Q.34	4 B	<b>Q.35</b> C	
<b>Q.36</b> B	<b>Q.37</b> C	<b>Q.38</b> D				Ċ	2.		
Previous Ye	ars' Questio	ns				$\sqrt{0}$	5		
<b>Q.1</b> C	<b>Q.2</b> C	<b>Q.3</b> D	<b>Q.4</b> C		<b>Q.5</b> A	Q.6	В	<b>Q.7</b> B	
<b>Q.8</b> A	<b>Q.9</b> C	<b>Q.10</b> C	<b>Q.11</b> B		Q.12 A	Y			
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JEE Adva	anced/Boa	ards			7				
Exercise 1				ۍ ک					
<b>Q.1</b> B	<b>Q.2</b> C	<b>Q.3</b> D	<b>Q.4</b> B	Ű	<b>Q.5</b> D	Q.6	В	<b>Q.7.</b> D	
<b>Q.8</b> A	<b>Q.9</b> A	<b>Q.10</b> A	<b>Q.11</b> D		<b>Q.12</b> C	<b>Q.1</b>	<b>3</b> D	<b>Q.14</b> B	
<b>Q.15</b> A	<b>Q.16</b> B	<b>Q.17</b> A	<b>Q.18</b> A		<b>Q.19</b> C	Q.2	<b>0</b> B	<b>Q.21</b> C	
<b>Q.22</b> C	<b>Q.23</b> A	Q.24 B	<b>Q.25</b> A		<b>Q.26</b> B	Q.2	<b>7</b> C	<b>Q.28</b> B	
<b>Q.29</b> C	<b>Q.30</b> D								
Exercise 2									
Single Correct	Choice Type								
<b>Q.1</b> A	Q.2 C	<b>Q.3</b> B		<b>Q.4</b> C		<b>Q.5</b> D		<b>Q.6</b> B	
<b>Q.7</b> C	Q.8 B	<b>Q.9</b> B		<b>Q.10</b> B	}	<b>Q.11</b> D		<b>Q.12</b> D	
<b>Q.13</b> B	<b>Q.14</b> A	<b>Q.15</b> B							
Multiple Correct Choice Type									
<b>Q.16</b> A, B, C	<b>Q.17</b> B, D	<b>Q.18</b> B, I	)	<b>Q.19</b> (	C, D	<b>Q.20</b> A,	B, D		
Assertion Rea	soning Type								
Q.21 C	<b>Q.22</b> A	<b>Q.23</b> A		<b>Q.24</b> A	A	<b>Q.25</b> A		<b>Q.26</b> A	

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Comprehension Type									
<b>Q.27</b> A	<b>Q.28</b> B	<b>Q.29</b> D		<b>Q.30</b> D	<b>Q.31</b> C	<b>Q.32</b> B			
<b>Q.33</b> B	<b>Q.34</b> B	<b>Q.35</b> A		<b>Q.36</b> D	<b>Q.37</b> A	<b>Q.38</b> B			
<b>Q.39</b> C	<b>Q.40</b> B	<b>Q.41</b> B		<b>Q.42</b> C		G			
Match the Col	umns					X·			
<b>Q.43</b> $A \rightarrow s; B$	$\rightarrow$ s; C $\rightarrow$ r; D $\rightarrow$	р		<b>Q.44</b> A $\rightarrow$ p, s; B $\rightarrow$ q, r; C $\rightarrow$ q, r; D $\rightarrow$ q, r					
<b>Q.45</b> $A \rightarrow q$ , r, s	s; B $\rightarrow$ q, r; C $\rightarrow$	p, q; D $\rightarrow$ p, q		<b>Q.44</b> A $\rightarrow$ p, s; B $\rightarrow$ q, r; C $\rightarrow$ q, r; D $\rightarrow$ q, r <b>Q.46</b> A $\rightarrow$ r; B $\rightarrow$ p; C $\rightarrow$ q; D $\rightarrow$ s					
Previous Ye	ars' Questio	ons							
<b>Q.1</b> B	<b>Q.2</b> A	<b>Q.3</b> B		<b>Q.4</b> B	<b>Q.5</b> C, D	<b>Q.6</b> B, D			
<b>Q.7</b> B, C	<b>Q.8</b> A	<b>Q.9</b> A		<b>Q.10</b> C	<b>Q.11</b> A				
				C					
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JEE Mair	n/Boards								
s-Block Elei	ments			$\mathbf{C}$					
Exercise 2			5						
Single Correct	Choice Type	~	$\mathbf{O}^{\prime}$						
<b>Q.1</b> A	<b>Q.2</b> A	Q.3 C	<b>Q.4</b> D	<b>Q.5</b> D	<b>Q.6</b> A	<b>Q.7</b> D			
<b>Q.8</b> A	<b>Q.9</b> A	Q.10 C	<b>Q.11</b> D	<b>Q.12</b> A	<b>Q.13</b> C	<b>Q.14</b> C			
<b>Q.15</b> C	<b>Q.16</b> C	<b>Q.17</b> A	<b>Q.18</b> C	<b>Q.19</b> A	<b>Q.20</b> D	<b>Q.21</b> D			
<b>Q.22</b> D	<b>Q.23</b> D	<b>Q.24</b> A	<b>Q.25</b> C	<b>Q.26</b> C	<b>Q.27</b> A	<b>Q.28</b> B			
<b>Q.29</b> B	<b>Q.30</b> D	<b>Q.31</b> A							
Previous Ye	ars' Questio	ons							
<b>Q.1</b> B	Q.2 B	<b>Q.3</b> A	<b>Q.4</b> B	<b>Q.5</b> A	<b>Q.6</b> B	<b>Q.7</b> D			
<b>Q.8</b> C	Q.9 C	<b>Q.10</b> A	<b>Q.11</b> A	<b>Q.12</b> B	<b>Q.13</b> B				
JEE Adv	JEE Advanced/Boards								
Exercise 1									
Q.1 D	<b>Q.2</b> A	<b>Q.3</b> B	<b>Q.4</b> C	<b>Q.5</b> A	<b>Q.6</b> A	<b>Q.7</b> C			
<b>Q.8</b> B	<b>Q.9</b> C	<b>Q.10</b> A	<b>Q.11</b> A			<b>Q.14</b> B			
<b>Q.15</b> A									

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## **Exercise 2**

Single Correc	t Choice Type					$\sim$
<b>Q.1</b> C	<b>Q.2</b> B	<b>Q.3</b> B	<b>Q.4</b> D	<b>Q.5</b> C	<b>Q.6</b> C	<b>Q.7</b> D
<b>Q.8</b> B	<b>Q.9</b> C	<b>Q.10</b> C	<b>Q.11</b> D	<b>Q.12</b> B		$\mathbf{G}$
Multiple Cor	rect Choice Type	9				x .
<b>Q.13</b> A, B	<b>Q.14</b> C, D	<b>Q.15</b> A, B, C	<b>Q.16</b> A, B, D		C	
Comprehens	ion Type					9
<b>Q.17</b> A	<b>Q.18</b> D	<b>Q.19</b> A	<b>Q.20</b> B	<b>Q.21</b> C	<b>Q.22</b> B	<b>Q.23</b> B
<b>Q.24</b> A	<b>Q.25</b> C					
Assertion Rea	asoning Type				$\sim$	
<b>Q.26</b> D	<b>Q.27</b> D	<b>Q.28</b> A	<b>Q.29</b> A	Q.30 A		
Previous Y	ears' Questic	ons				
<b>Q.1</b> B	<b>Q.2</b> A	<b>Q.3</b> B	<b>Q.4</b> A,B	<b>Q.5</b> B, C, D		
				?		

**Solutions** 

## **JEE Main/Boards**

## **Exercise 1**

## Hydrogen

**Sol 1:** Heavy water ( $D_2O$ ) is used as moderator as well as coolant in nuclear power generation  $D_2O$  is a stable molecule as compared to  $H_2O$  because molar mass of  $D_2O$  is greater so its bond have less vibration and they are more stable so thermal neutrons which are produced in nuclear fission, can be stopped or absorbed by  $D_2O$ .

**Sol 2:** Compound in which  $H_2O_2$  is stable is used as inhibitor in decomposition of  $H_2O_2$  is stable, is used as inhibitor in decomposition of  $H_2O_2$  solution.

CH<sub>2</sub> – OH Eg. Glycerol , Acetoanilide. CH<sub>2</sub> – OH

**Sol 3:** Water gas: CO + H<sub>2</sub>

This gas is made by passing steam over a red hot carbon fuel such as coke:

 $H_2O + C \rightarrow H_2 + CO; \Delta n = +ve$ 

**Sol 4:**  $H_2O$  is a polar molecule so it can also dissociate into  $H^+$  and  $OH^-$  and this equilibrium have its constant.

 $H_2O$   $H^+ + OH^- Kw = 10^{-14}$ 

This reaction is autoprotolysis of water and  ${\bf k}_{\rm w}$  is autoprotolysis constant.

So, 1 out of  $10^{14}$  molecules of  $\rm H_2O$  dissociate in  $\rm H^+$  and  $\rm OH^{-1}$ 

Sol 5: H,O molar mass is less than H,O

 $\therefore$  – O – H bond have more vibration than – O – D bond

So, -O - H bond is water than -O - D so it is easy to dissociate H<sub>2</sub>O, D<sub>2</sub>O is strong.

: Electrolysis of weaker occur faster than heavy water.

**Sol 6:** (i) Water 
$$\xrightarrow{\text{Electrolysis}}$$
 H<sub>2</sub> + O<sub>2</sub>

(ii) dilute acids  $\xrightarrow{\text{metals}}$  MCl<sub>2</sub> + H<sub>2</sub>

(iii) alkalis 
$$\xrightarrow{\text{amphoteric}}_{\text{metals}}$$
 Zn(OH)<sub>2</sub> + H<sub>2</sub>

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**Sol 7:** Interstitial hydrides are formed by Be, Mg (s-block) and transition metals. These are interstitial compound as the hydrogen atoms occupy interstitial places in the metallic lattices these are non-stoichiometric compounds and give out hydrogen easily and are used as strong reducing agents. This suggests that hydrogen is in atomic state having oxidation number zero.

**Sol 8:** Boiling point, melting point such physical properties depend upon intermolecular weak forces of attraction. H<sub>2</sub>O have hydrogen bonding with each other and it has comparatively high molar mass which result in more strong Vander waals forces than H<sub>2</sub>

 $\therefore$  H<sub>2</sub>S boiling point / melting point is less than H<sub>2</sub>O.

#### Sol 9: (a)

 $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$ Reduction (b) PbS +  $H_2O_2 \longrightarrow PbSO_4 + 4H_2O_4$ Oxidation (c)  $FeSO_4 + H_2SO_4 + 5H_2O_2 \longrightarrow FeSO_4 + H_2O$ Oxidation (d)  $2K_4 [Fe^{+2}(CN)_6] + H_2O_2 \longrightarrow 2K_3[Fe^{+3}(CN)_6 + 2KOH$ Oxidation (e)  $H_2SO_3 + H_2O_2 \longrightarrow H_2SO_4 + H_2O_4$ Oxidation (f) Na<sub>3</sub> As<sup>+3</sup>O<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>  $\longrightarrow$  Na<sub>3</sub>ASO<sub>3</sub> + H<sub>2</sub>C Reduction **Sol 10:** (i) Na +  $D_2O \longrightarrow NaOD + D_2$ (ii) NaOH + D<sub>2</sub>O  $\longrightarrow$  NaOD + H<sub>2</sub>O (iii)  $NH_{4}CI + D_{2}O \rightarrow ND_{4}CI + H_{2}O$ (iv)  $SO_3 + D_2O \longrightarrow D_2SO_4$ Sol 11:  $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ 30 volume means 1 ml of  $H_{2}O_{2}$  gives 30 ml of  $H_{2}O_{2}$  $\therefore$  25 ml will give 750 ml of H<sub>2</sub>O<sub>2</sub>

**Sol 12:** In 100 gm solution, 13. 6 gm H<sub>2</sub>O<sub>2</sub>

Molarity = 
$$\frac{13.6/34}{100}$$
 × 1000  
∴ Volume strength = Molarity × 11.2 = 44.8

**Sol 13:** AgNO<sub>3</sub> solution is used for removal of AsH<sub>3</sub> and PH<sub>3</sub> present in very small amounts in hydrogen sample.

**Sol 14:** (a)  $2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow$  $2K_4[Fe(CN)_6] + 2H_2O + O_2$ Reduction  $Fe^{3+} \longrightarrow Fe^{2+}$ (b)  $Cr(OH)_3 + H_2O_2 + OH \longrightarrow Cr(OH) + O_2 + H_2O$ Reduction

**Sol 15:**  $D_2O$  has more molecular mass and greater degree of association than  $H_2O$  and thus shows higher m.pt. and b.pt.

Sol 16: 
$$Na_2O_2 + H_2SO_4 \longrightarrow H_2O_2 + Na_2SO_4$$

But if water is added then,  $Na_2O_2$  will form NaOH which will retard the production of  $H_2O_2$ 

Sol 17: 
$$N_2H_4 + 2H_2O \longrightarrow N_2 + 4H_2O_{(g)}$$

The reaction is highly exothermic. It brings large increase in volume also.

**Sol 18:**  $H_2O_2$  act as oxidising as well as reducing agent because oxidation no. of oxygen in  $H_2O_2$  is -1 which is an intermediate state so it can go to -2 by reduction and also to O forming  $O_2$ 

Sol 19: 
$$N_1V_1 = N_2V_2$$
  
20 ×  $N_1 = 30 \times \frac{1}{12}$ ;  
 $N_1 = \frac{1}{8} \Rightarrow 0.2125\%$  of  $H_2O_2$  in solution.

**Sol 20:** Statues coated with white lead get blackened due to the action of  $H_2S$  present in atmospheric in traces.

 $Pb(OH)_2$ .  $2PbCO_3 + 3H_2S \longrightarrow 3PbS + 2CO_2 + 4H_2O$  white lead.

When blackened statues are treated with  $H_2O_2$  the PbS is oxidised to PbSO<sub>4</sub> which is colourless (white)

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O_4$$
 (white)

#### Sol 21:

$$A + H_2O \longrightarrow B \uparrow + C_{(ag)}$$

$$\Delta \downarrow D \xrightarrow{dil.} B \uparrow$$

$$B \uparrow$$

Deep golden yellow flame: Na

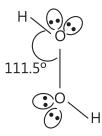
A: - Na

B: - H<sub>2</sub> inflammable gas

C: - NaOH

D: - Zn Amphoteric metal

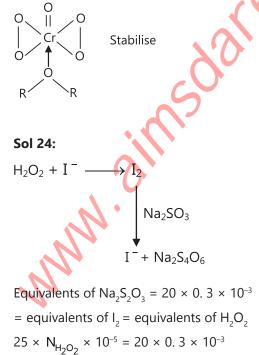
**Sol 22:**  $H_2O_2$  is a non-planar molecule with open book structure



#### Sol 23:

 $H_2O_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + 2CrO_5 + 5H_2O_6$ (Blue)

 $CrO_5$  is stable at low temperature and only in ether solution



 $N_{H_2O_2} = 0.24 \text{ N}$ 

 $\therefore$  Volume strength = 1.344

**Sol 25:** Discharge of any metal or non-metal depends on its discharge of potential. So, as potential of discharge of K<sup>+</sup> is higher than H<sup>+</sup> ion and potential discharge of  $SO_4^{2-}$  is higher than OH<sup>-</sup> ion.

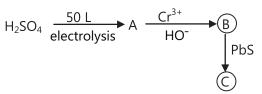
**Sol 26:** Pb from painting reacts with atmospheric  $H_2S$  to give black coloured PbS which on reaction with  $H_2O_2$  converts into PbSO<sub>4</sub>.

**Sol 27:**  $H_2O_2$  is a very unstable compound and readily decomposes in  $H_2O$  and  $O_2$  in presence of any catalyst or sunlight. Traces of alkali present in glass bottles accelerates the decomposition of  $H_2O_2$  hence glass is coated with wax.

**Sol 28:** During the storage of  $H_2O_2$ , addition of small amount of phosphoric acid or glycerol or acetanilide inhibits the decomposition of  $H_2O_2$ .

Normality = 
$$\frac{\text{volume strength}}{5.6} = \frac{10}{5.6} = 1.7$$

Sol 30:



(A) H<sub>2</sub>O<sub>2</sub> Oxidising as well as reducing agent

(B)  $CrO_{4}^{2}$ 

(C) PbSO<sub>4</sub>

## **Exercise 2**

#### Single Correct Choice Type

**Sol 1: (A)** Calgon: Na<sub>2</sub> [Na<sub>4</sub> (PO<sub>3</sub>)<sub>6</sub>]

It is a water softer because it removes Ca and Mg ions from hard water by forming a soluble complex.

 $2Ca^{2+} + Na_2[Na_4(PO_3)_6 \longrightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2[Na_4(PO_3)_6]$ 

hard water Calgon Soluble complex

**Sol 2: (C)** In liquid  $H_{2^{t}}$  the intermolecular weak attractive forces are dominate then repulsive forces.

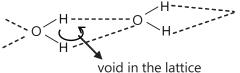
 $\therefore$  Liquid H<sub>2</sub> expands while cooling.

Sol 3: (C) Hydrogen electronic configuration is 1s<sup>1</sup>

 $\therefore$  By gaining 1 electron it can acquire helium  $1s^2$  configuration. Hydrogen has a tendency which resembles it to halogen because halogens are also only 1 electron has to stable noble gas configuration.

**Sol 4: (C)**  $H^-$  is oxidised at anode to  $H_2$ 

**Sol 5: (C)** Ice is lighter than water because ice has less density than water for this hydrogen bonding is responsible.



void in the lattice

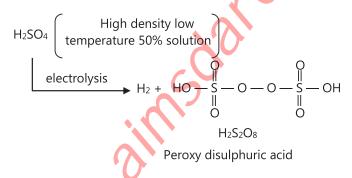
Sol 6: (B) NaCl is soluble salt

:. It is soft water

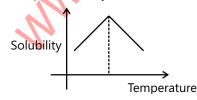
**Sol 7: (B)**  $H_2O_2$  show oxidising as well as reducing properties

 $\therefore$  H<sub>2</sub>O<sub>2</sub> bleaching properties is due to its oxidising nature.

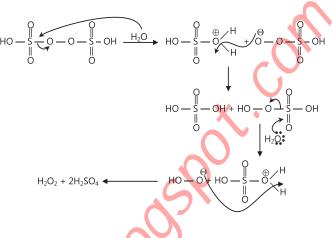
#### Sol 8: (B)



**Sol 9: (B)** CaSO<sub>4</sub> is a hardness producing salt and its solubility changes with rise in temperature. Its solubility increases till and then decreases when increases temperature beyond that



Sol 10: (C)



Sol 11: (D)  $K_2^{+6}Cr_2O_7 + 2KOH \longrightarrow 2K_2^{+6}CrO_4 + H_2O$ 

No change in oxidation state and no loss/gain of electron.

: Not a redox reaction

**Sol 12:** (B) Water + sugar + salt  $\xrightarrow{\text{Organic}}_{\text{resins}}$  organic

resins are generally used to soften the water.

When water is passed through it since Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> can be more attracted. So, resins attract them more and release H<sup>+</sup> in the water.

: NaCl can be removed from water and water turns sweet.

**Sol 13: (D)** (A)  $CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$ 

This reaction takes place in galvanic cell.

(B) E° of this reaction is positive

∴ Reaction is possible.

(C) Hydrides react violently with water providing dihydrogen gas.

(D) Na<sub>2</sub>CO<sub>3</sub> is better base than Na<sub>2</sub>SO<sub>3</sub>

 $\therefore$  Weak base and acid cannot produce strong base and acid.

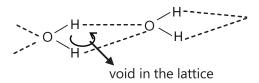
**Sol 14: (B)** Since bonding vibration of -O - H bond is more than -O - D. Energy required to break the bond is less in -O - H than -O - D

 $\therefore - O - H$  bond is weaker than - O - D

 $\therefore$  Biological growth of plant which is fed by H<sub>2</sub>O is fast because it requires less energy to break H<sub>2</sub>O.

Sol 15: (D) Conceptual fact.

**Sol 16: (A)** Water molecules in ice are held tight by hydrogen bond attraction



So the  $H_2O$  molecules on the border have free O and H-atoms to bond the lattice.

: When we press two ice-cube we do sufficient

amount of work to complete the hydrogen bond formation.

... These get unit forming ore ice cube.

**Sol 17: (A)** Washing soda only remove chlorides of Ca, Mg.

E.g.  $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2 NaCl$ 

Same as washing soda, related lime cannot remove all the slats from washing soda but soap can precipitate all type of ions by ion-exchange method.

MgCl<sub>2</sub> + 2C<sub>17</sub>H<sub>35</sub>COONa  $\longrightarrow$  (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub> Mg  $\downarrow$  + 2NaCl

**Sol 18: (A)** Fenton's Reagent: H<sub>2</sub>O<sub>2</sub> + FeSO<sub>4</sub>

Use to reduce organic compounds.

**Sol 19: (D)** Liquid  $H_2$  is the best pure fuel because it is not a reactive gas because its bond energy high. But it is inflammable and bonds in air forming water

 $2H_2 + O_2 \longrightarrow 2H_2O$ 

**Sol 20: (C)** In presence of oxidiser liquid oxygen, liquid hydrogen yields highest specific impulses.

## Sol 21: (D) $H_2O \xrightarrow{[0]} O_2$

This reaction is very difficult to do because its E<sup>o</sup> is highly negative.

 $\therefore$  Only  $F_2$  which is the strongest reducing agent can give oxygen from water.

**Sol 22:** (B)  $H_2O_2$  is an oxidising agent so it will oxidise sulphur

 $H_2O_2 + PbS \longrightarrow H_2O + PbSO_4$ 

It will not oxidise  $Pb^{2+} \longrightarrow Pb^{4+}$  because  $Pb^{4+}$  is not stable and can get easily oxidised due to inert-pair effect.

**Sol 23: (A)** Fact  $2H_2 + O_2 \longrightarrow 2H_2O$ 

**Sol 24: (B)** While reacting with  $Cl_2 H_2O_2$  will show its reducing mature.

 $H_2O_2 + CI_2 \longrightarrow 2HCI + O_2$ 

**Sol 25: (A)** Ionic Hydrides  $M^+H^-$  in which at anode during electrolysis,  $H^+$  gets oxidised and will produce  $H_2$  gas

$$H^- \longrightarrow \frac{1}{2}H_2 + e^-$$
 (Anode Reaction)

$$M^+ + e^- \longrightarrow M(Cathode Reaction)$$

**Sol 26: (A)** CaH<sub>2</sub>, NaH are group (I), (II) metal hydrides.

 $\therefore$  They are ionic in nature.

So  $NH_3$  and  $B_2H_6$  are covalent hydrides because N, B are non-metals.

Sol 27: (C) (A) 
$$Zn + H_2O \longrightarrow Zn(OH)_2 + H_2$$

(B) 
$$Zn + NaOH \longrightarrow Zn (OH)_2 + H_2 \uparrow$$
  
 $\downarrow XS NaOH$   
 $Na_2 [Zn(OH)_4]$ 

(C) 
$$Zn + conc H_2SO_4 \longrightarrow ZnSO_4 + H_2O + SO_2$$
  
(D)  $Zn + dil. HCl \longrightarrow ZnCl_2 + H_2$ 

**Sol 28: (B)** Moles of MgSO<sub>4</sub> = 0.002

:. No. of atoms of Mg<sup>2+</sup> = 0. 002 × 6 × 10<sup>23</sup> =  $12 \times 10^{20}$ 

No. of H<sub>2</sub>O particles =  $\frac{10^3}{18} \times 6 \times 10^{23} = \frac{10^{26}}{3}$  $\therefore$  No. of Mg<sup>2+</sup> per million H<sub>2</sub>O = 200 ppm

Sol 29: (C)



Dipole moment after calculation = 1.84 D

**Sol 30: (C)** Blackened oil painting can be restored into original form by the action of  $H_2O_2$  because its a strong oxidising (Bleaching) agent.

**Sol 31: (A)** Ortho and para hydrogen have similar chemical properties but differ in physical properties like BP, MP.

**Sol 32: (B)** CO + H<sub>2</sub>  $\xrightarrow{300^{\circ}C/300 \text{ atm}}{X(catalyst)}$  CH<sub>3</sub>OH

 $X \rightarrow Cr_2O_3$  / ZnO Reaction used in production of methanol

Sol 33: (A)  $H_2O_2 + HOCI^{+1} \longrightarrow O_2 + CI_2 + H_2O$ 

 $Mn^{2+}$  is oxidised to  $Mn^{4+}$  under alkaline medium.

**Sol 34: (B)** Washing soda is used to remove permanent hardness but  $Ca(OH)_2$  can be used to remove temporary hardness.

 $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$ 

**Sol 35: (C)** Polysulphates of Ca<sup>2+</sup>, Mg<sup>2+</sup> etc. are soluble in water. Polysulphates are used as water softening agent because they form soluble complexes with cationic species.

**Sol 36: (B)** Ortho form increases with increase in temperature.

(Sodium hexametaphosphates, sodium tripolyphosphate or STPP) form soluble complexes with Ca<sup>+2</sup>, Mg<sup>+2</sup> present in hard water.

**Sol 2: (C)**  $Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$ 

Cal. phosphide Phosphine

(1 mole)

(2 moles)

**Sol 3: (D)**  $H_2$  will not reduce heated  $Al_2O_3$ 

**Sol 4: (C)**  $BaO_2 + 2HCI \rightarrow BaCl_2 + H_2O_2$ .

**Sol 5: (A)** Cu and dil. HCl will not produce H<sub>2</sub>

Sol 6: (B) Strength = Normality × Eq. mass =  $1.5 \times 17$  (eq. mass of  $H_2O_2$ ) =  $25.5 \text{ gL}^{-1}$ 

**Sol 7: (B)** Mn+2HNO<sub>3</sub>(dil.) $\rightarrow$ Mn(NO<sub>3</sub>)<sub>2</sub>+H<sub>2</sub>

**Sol 8: (A)** Both Assertion and Reason are true and Reason is the correct explanation of Assertion.

**Correct Reason:**  $H_2O_2$  is a strong reducing agent.

**Sol 9: (C)** Assertion is correct but Reason is not the correct explanation of Assertion.

**Sol 10: (C)**  $H_2^{2+}$  and  $H_2$  does not exist.

**Sol 11: (B)**  $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^ H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$ 

**Sol 12: (A)** It can acts as an oxidising as well as reducing agent.

## **JEE Advanced/Boards**

## **Exercise 1**

**Sol 1:** The process of converting CO into by passing the gases obtained by steam and hydrocarbons or coke over iron oxide as catalyst at 673 K resulting in the generation of more is called water gas shift reaction.

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$
$$CO + H_2O \xrightarrow{673K} CO_2 + H_2$$

**Sol 2:** Reaction of Zn and HCl gives nascent hydrogen which is more powerful reducing agent than ordinary hydrogen and thus ferric chloride solution is reduced.

**Sol 3:**  $r_H = -\log P_{H_2}$ ,  $P_{H_2} = pressure of H_2$  in atmosphere

**Sol 4:** Scattreing thermal neutrons (0.1 ev or 9.6 kJ/mol) is roughly similar for all nuclei regardless of atomic number where scattering of X-rays depends upon electron density and is lowest for hydrogen.

Sol 5:

$$\begin{array}{cccc} H & H & H & H \\ I & I & I \\ H-N \parallel \parallel H-O \text{ and not } H-N-H \parallel \parallel \parallel O-H \\ H \end{array}$$

**Sol 6:** Water used during the reaction reacts with  $Na_2O_2$  to form NaOH which tends to decompose  $H_2O_2$ .

$$Na_2O_2 + 2H_2O \longrightarrow H_2O_2 + 2NaOH$$
$$2H_2O_2 \xrightarrow{NaOH} 2H_2O + O_2$$

**Sol 7:**  $2H_2O_2 \longrightarrow 2H_2O + O_2$ 

**Sol 8:** Moles of  $MgSO_4 = 0.001$ 

 $\therefore$  Mole of CaCO<sub>3</sub> = 0.001

(:: Mg and Ca both are bivalent)

:. Wt. of 
$$CaCO_3 = 0.001 \times 100 = 0.1 \text{ g}$$

 $\therefore$  10<sup>3</sup> mL water contains 0.1 g CaCO<sub>3</sub>

$$\therefore 10^3$$
 mL water contains  $\frac{0.1 \times 10^6}{10^3} = 100$  ppm

**Sol 9:** CaO + Ca
$$(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$$

For one litre water

Meq. of CaO = Meq. of Ca(HCO<sub>3</sub>)<sub>2</sub>

$$\frac{w \times 1000}{56/2} = \frac{1.62 \times 1000}{162/2}$$

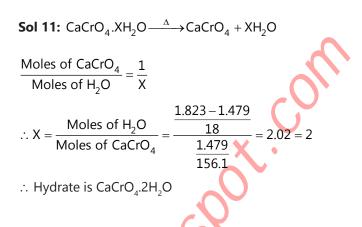
$$\therefore w_{CaO} = 0.56 g$$

Thus CaO required for  $10^3$  litre H<sub>2</sub>O = 0.56 ×  $10^3$  = 560 g

**Sol 10:** Meq. of  $CaCO_3 = Meq.$  of  $Ca(HCO_3)_2 = Meq.$  of HCl

$$\frac{w}{100/2} \times 1000 = \frac{1}{50} \times 30$$
  

$$w_{CaCO_3} = \frac{3 \times 100}{5 \times 2000} = 0.03 \text{ g}$$
  
∴ 100 mL of HO contains = 0.03 g  
∴ 10<sup>6</sup> mL H<sub>2</sub>O contains  $\frac{0.03 \times 10^6}{100} = 300 \text{ ppm}$ 



**Sol 12:** (i) Chromium hydroxide is converted into soluble yellow sodium chromate.

$$\begin{bmatrix} H_2O_2 \longrightarrow H_2O + \begin{bmatrix} O \end{bmatrix} \end{bmatrix} \times 3$$

$$2Cr(OH)_3 + 4NaOH + 3\begin{bmatrix} O \end{bmatrix} \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

(ii) Zinc dissolves in caustic potash solution evolving hydrogen.

$$\text{Zn} + 2\text{KOH} \longrightarrow \text{K}_2\text{ZnO}_2 + \text{H}_2 \uparrow$$
Pot. zincate

(iii) Hydrolysis of CaH<sub>2</sub> occurs with evolution of  $H_2$ 

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

(iv) Deuterometahne is evolved.

$$AI_4C_3 + \frac{12D_2O}{Heavy water} \rightarrow 4AI(OD)_3 + \frac{3CD_4}{Deuteromethane}$$

**Sol 13:** It is clear from point (iv) that (X) is  $H_2O_2$ .

$$\mathsf{Ti}(\mathsf{SO}_{4})_{2} + 2\mathsf{H}_{2}\mathsf{O} + \mathsf{H}_{2}\mathsf{O}_{2} \longrightarrow \underset{(X)}{\overset{\mathsf{Pertitanic acid}}{\overset{\mathsf{Pertitanic acid}}{\overset{Pertitanic acid}}{\overset{Pertitanic acid}}{\overset{Pertitanic acid}}{\overset{Per$$

(i) 
$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$$

$$\begin{array}{c} H_2O_2 + O \longrightarrow H_2O + O_2 & Or \\ (X) \\ 2KMnO_4 + 2KOH + H_2O_2 \longrightarrow 2K_2MnO_4 + 2H_2O + O_2 \\ (X) \end{array}$$

$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + O_2 + 4KOH$$
(Brown ppt.)

(ii) 
$$\begin{array}{c} H_2O_2 + CI_2 \longrightarrow 2HCI + O_2 \\ (x) \end{array}$$

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(iii)  $\underset{(X)}{\text{H}_2\text{O}_2} + 2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{I}_2 \uparrow$ Hence (X) is  $\text{H}_2\text{O}_2$ .

**Sol 14:** (i) 20 vol.  $H_2O_2$  means 1 mL of  $H_2O_2$  solution gives 20 mL  $O_2$ .

 $2H_2O_2 \longrightarrow 2H_2O + O_2$ 2 mole 1 mole = 68 g 22400 mL at NTP

- $\therefore$  22400 mL of O<sub>2</sub> is obtained by 68 g H<sub>2</sub>O<sub>2</sub>
- $\therefore$  20 mL of O<sub>2</sub> is obtained by

 $\frac{68 \times 20}{22400} = 0.0607 \, \text{g of } \text{H}_2\text{O}_2$ 

Or 1 mL of  $H_2O_2$  solution = 0.0607 g

:. 100 mL of  $H_2O_2$  solution = 0.0607 × 100 = 6.07%

(ii) 6.8% strength  $\rm H_2O_2$  solution means 6.8 g  $\rm H_2O_2$  is present in 100 mL  $\rm H_2O_2$ 

:. 6.8 g H<sub>2</sub>O<sub>2</sub> gives  $\frac{22400 \times 6.8}{68} = 2240 \text{ mL O}_2$ 

:. Volume strength of  $H_2O_2$  gives =  $\frac{2240}{100}$  = 22.4 Volume

**Sol 15:** 1 molar  $H_2O_2$  solution means 1 mole (or 34 g  $H_2O_2$ ) is present in 10<sup>3</sup> mL solution.

$$\therefore$$
 68 g H<sub>2</sub>O<sub>2</sub> gives 22400 mL O<sub>2</sub>

:. 34 g H<sub>2</sub>O<sub>2</sub> gives  $\frac{22400 \times 34}{78} = 11200 \text{ mL O}_2$ 

 $\therefore \text{ Volume strength} = \frac{11200}{10^3} = 11.2$ 

**Sol 16:** Volume strength of  $H_2O_2 = 5.6 \times N$ 

15 vol.  $H_2O_2 = \frac{15}{5.6} NH_2O_2$ 

: 10 vol.  $H_2O_2 = \frac{10}{5.6} NH_2O_2$ 

20 vol.  $H_2O_2 = \frac{20}{5.6} NH_2O_2$ 

Let 500 mL of each is mixed then total volume of mixture = 1500 mL; Also this is diluted to double its volume i.e., 3000 m

 $N \times 3000 = \frac{10 \times 500}{5.6} + \frac{15 \times 500}{5.6} + \frac{20 \times 500}{5.6}$ Or  $N_{H_2O_2}$  mixture =  $\frac{500 \times 45}{5.6 \times 3000}$  = 1.339  $\therefore$  Vol. strength of H<sub>2</sub>O<sub>2</sub> = 1.339 × 5.6 = 7.5 Sol 17: The given reaction is:  $2KMnO_{4} + 5H_{2}O_{2} + 4H_{2}SO_{4}$  $\longrightarrow$  2KHSO<sub>4</sub> + 2MnSO<sub>4</sub> + 8H<sub>2</sub>O + 5O<sub>4</sub> Meq. of  $O_2 = Meq.$  of  $H_2O_2 = Meq.$  of  $KMnO_4$  $N \times 10 = 25 \times \frac{1}{20}$  $\therefore N_{H_2O} = \frac{25}{200} = 0.125$  $:. N_{O_2} = 0.125$ Or  $w_{0_2} = 0.125 \times 16 = 2 \text{ g / litre}$ **Sol 18:**  $O_2^- + 2e \longrightarrow 2O^{2-}$  $2I^- \longrightarrow I_2 + 2e$  $2(S^{2+})_2 \longrightarrow (S^{5/2+})_4 + 2e;$  $I_2 + 2e \longrightarrow 2I^-$ Meq. of  $H_2O_2$  = Meq. of  $I_2$  = Meq. of  $Na_2S_2O_3$  = 20 × 0.1  $\frac{W \times 1000}{34/2} = 2$  $\therefore w_{H_2O_2} = 0.034 \text{ g per } 25 \text{ mL}$  $\therefore N_{H_2O_2} = \frac{0.034 \times 1000}{34 / 2 \times 25} = 0.08$ Also, Volume strength =  $5.6 \times 0.08 = 0.448$ % strength =  $\frac{17}{56} \times 5.6 \times 0.08 = 0.136\%$ **Sol 19:** Meq. of KI = Meq. of H<sub>2</sub>O<sub>2</sub> in 50 mL = Meq of  $Na_2S_2O_3$  $\frac{w \times 1000}{34/2} = 20 \times 0.1$ 

 $\therefore W_{H_2O_2}$  in 50 mL

$$= \frac{20 \times 0.1 \times 34}{2000} = 0.034$$
  
$$\therefore w_{H_2O_2} \text{ in } 1000 \text{ mL} = \frac{0.034 \times 1000}{50} = 0.68 \text{ g}$$

**Sol 20:** For 20 mL H<sub>2</sub>O<sub>2</sub>;

Meq. of  $O_2$  = Meq of  $H_2O_2$  = Meq. of  $KMnO_4$ 

$$\frac{w \times 1000}{34/2} = \frac{1}{2} \times 30$$
  

$$\therefore w_{H_2O_2} = 0.255 \text{ g}/20 \text{ mL}$$
  

$$\therefore N_{H_2O_2} = \frac{0.255}{34/2} \times \frac{1000}{20} = 0.75$$

Strength =  $0.75 \times 17 = 12.75 \text{ g}$  / litre

**Sol 21:** (i) Potassium ferricyanide is reduced to potassium ferrocyanide.

$$\frac{2K_{3}\left[Fe(CN)_{6}\right]+2KOH\longrightarrow 2K_{4}\left[Fe(CN)_{6}\right]+H_{2}O+\left[O\right]}{H_{2}O_{2}+\left[O\right]\longrightarrow H_{2}O+O_{2}}$$

$$\frac{2K_{3}\left[Fe(CN)_{6}\right]+2KOH+H_{2}O_{2}\longrightarrow 2K_{4}\left[Fe(CN)_{6}\right]+2H_{2}O+O_{2}}{2K_{3}\left[Fe(CN)_{6}\right]+2H_{2}O+O_{2}}$$

(ii) Potassium permanganate is decolourised due to reduction.

$$\frac{2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]}{\left[H_2O_2 + [O] \longrightarrow H_2O + O_2\right] \times 5}$$

$$\frac{2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 2MnSO_4}{2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 2MnSO_4}$$

(iii) Ferrous ammonium sulphate is oxidised to ferric salt.

$$H_{2}O_{2} \longrightarrow H_{2}O + [O]$$

$$\frac{2FeSO_{4} + H_{2}SO_{4} + [O] \longrightarrow Fe_{2}(SO_{4})_{3} + H_{2}O}{2FeSO_{4} + H_{2}SO_{4} + H_{2}O_{2}} \longrightarrow Fe_{2}(SO_{4})_{3} + 2H_{2}O$$

Exercise 2

Single Correct Choice Type

Sol 1: (A)  $H_2 \longrightarrow 2H + energy$ 

So, we can say nascent hydrogen consists of Hydrogen atoms with excess energy.

**Sol 2: (C)** Volume strength of  $H_2O_2$  is determined by its  $O_2$  giving ability.

So volume  $H_2O_2$  means 1 cm<sup>3</sup> of the solution liberate 10 cm<sup>3</sup> of O<sub>2</sub> at STP.

Sol 3: (B) Molarity = 
$$\frac{\text{no. of moles}}{\text{volume}} \times 1000$$
  
=  $\frac{5.1}{\frac{34}{100}} \times 1000 = 1.5 \text{ M}$   
Sol 4: (C) H<sub>2</sub> + Conc. H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  H<sub>2</sub>O + SO<sub>2</sub>  
Oxidation  
Reduction

**Sol 5: (D)** Nature of  $H_2O_2$  is weakly acidic because  $H_2O_2 \longrightarrow H - O - O^{\Theta} + H^+$  this equilibrium exist and its equilibrium constant K > 1

**Sol 6: (B)** Structure of  $H_2O_2$  is open book line structure in gas phase

**Sol 7: (C)**  $H_2 + K_2O \longrightarrow 2K + H_2O$ ;  $E^o < O$  $\therefore$  Reduction of  $K^+$  is not possible by  $H_2$  gas

So 8: (B) Mg/Mn +  $HNO_3 \longrightarrow MgO + H_2O + H_2$ (dil)

**Sol 9: (B)**  $H_2O_2$  act as a reducing agent with acidified  $KMnO_4$ , because it is a better reducing agent than  $KMnO_4$ 

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

**Sol 10: (B)** (A) Cu +  $H_2SO_4 \longrightarrow No$  reaction if dilute (B)  $HCOO^- Na^+ \longrightarrow H_2 + Na_2CO_3 + H_2O$ (C)  $Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO_2 + CO + H_2O$ 

**Sol 11: (D)**  $H_2O_2$  do not show this property.

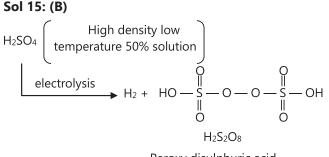
**Sol 12: (D)** (A) Temporary hardness of water can be removed by calgon but it only reacts with sulphate/ bicarbonates of  $Ca^{2+}/Mg^{2+}$  etc.

(D) Boiling of water can decompose calcium bicarbonate into calcium carbonate and  $CO_2$  molecules. So, this is a method to remove temporary hardness of water.

**Sol 13: (B)**  $Pb^{2+}$  is soluble in  $H_2O$  only. So, it will poison only soft water but not hard water. In hard water, it will precipitate as insoluble salt.

**Sol 14: (A)** In laboratory,  $H_2O_2$  is prepared by passing a current of  $CO_2$  through a cold pasty solution of  $BaO_2$  in water

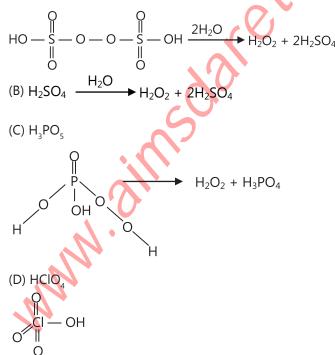
$$BaO_2 + CO_2 + H_2O \longrightarrow H_2O_2 + BaCO_3$$



Peroxy disulphuric acid

#### **Multiple Correct Choice Type**

Sol 16: (A, B, C)



**Sol 17: (B, D)** Na<sup>+</sup> is exchanged with Ca<sup>2+</sup> and Mg<sup>2+</sup> because Ca<sup>2+</sup> and Mg<sup>2+</sup> have higher charge density so anions of silicate will attract them by releasing Na<sup>+</sup>

**Sol 18: (B, D)** Group (I), (II) match violently reacts with water giving hydroxides and hydrogen gas.

 $CaH + H_2O \longrightarrow Ca(OH)_2 + H_2$  $Ca + H_2O \longrightarrow Ca(OH)_2 + H_2$ 

**Sol 19: (C, D)** Ice forms cage like structure due to hydrogen bonding. Its density is less than water.

Sol 20: (A, B, D) 
$$Zn + dil, HCl \longrightarrow ZnCl_2 + H_2 Zn + Hot NaOH \longrightarrow Zn(OH)_2 + H_2$$
  
(Solution)  
ZN + Conc. Sulphuric  $\longrightarrow ZnSO_4 + H_2O + SO_2$   
(Acid)

 $Zn + Cold water \longrightarrow Zn(OH)_2 + H_2$ 

#### **Assertion Reasoning Type**

**Sol 21:** (C) Since  $ZrH_2$  is a non-stoichiometric hydride, the composition of  $ZrH_2$  will be different than its chemical formula.

**Sol 22: (A)** Molecular weight of  $D_2$  is more than  $H_2$  So, there will be less bond vibration in  $D_2$  because deuterium atom is heavier than  $H_2$ 

 $\therefore$  D<sub>2</sub> is more stable than H<sub>2</sub>

**Sol 23: (A)** Acetanilide form stable complex with  $H_2O_2$  because of which stability of  $H_2O_2$  increases and in its decomposition reaction, it acts as an inhibitor / negative catalyst.

**Sol 24: (A)** Statement-II is correct explanation of 1 gets decomposed in reactions.

**Sol 25: (A)**  $H_2O_2$  is a very unstable compounds by any onzymic / catalytic activity it decomposes producing  $O_2$  gas.

 $\therefore$  When  $H_2O_2$  is injected in blood it decomposes producing  $O_2$  bubbles seriously.

Sol 26: (A) Statement-II is the correct reason for statement-I

#### **Comprehension Type**

Sol 27: (A)

(A) 
$$\begin{array}{c} \stackrel{+4}{\text{PbO}_2 + \text{H}_2 \text{O}_2^{-1}} \longrightarrow \stackrel{+2}{\text{PbO}} + \text{H}_2 \text{O} + \text{O}_2 \\ & & \\$$

(B) 
$$Na_{2}SO_{3} + H_{2}O_{2} \longrightarrow Na_{2}SO_{4} + H_{2}O$$
  
Oxidation

(C) 
$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$
  
Oxidation

(D) 
$$(D) \xrightarrow{+3}{\text{KNO}_2 + \text{H}_2\text{O}_2} \xrightarrow{+5}{\text{KNO}_3 + \text{H}_2\text{O}_3} + \text{H}_2\text{O}_3$$

Sol 28: (B) 
$$H_2O_2^{-1} + Cl_2 \longrightarrow H_2O^{+2} + HCl$$
  
Reduction

Sol 29: (D) Z = 43 Technetium. It do not form hydride.

**Sol 30: (D)** ZrH<sub>2</sub> is most metallic hydride

: It has highest electrical conductance.

**Sol 31: (C)** Interstitial hydride do not give hydrogen ion to get oxidised.

... It cannot be used as rocket propellant.

Sol 32: (B) (A)  $PbO_2 \longrightarrow Pb^{4+} + 2O^{2-}$ (B)  $SrO_2 \longrightarrow Sr^{2+} + O^- \longrightarrow O^- \longrightarrow HO \longrightarrow OH$ (C)  $MnO_2 \longrightarrow Mn^{4+} + 2O^{2+}$ (D)  $TiO_2 \longrightarrow Ti^{4+} + 2O^{2-}$ 

**Sol 33: (B)**  $H_2O_2$  is more acidic than  $H_2O$  because the anion is more stable.

 $\therefore H_2 O < H_2 O_2 < CO_2$ 

Because carbonic acid is stronger acid than  $H_2O_2$ 

**Sol 34: (B)** Anhydrous Na<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>O  $\longrightarrow$  H<sub>2</sub>O<sub>2</sub> + NaOH  $\therefore \frac{\text{volume strength}}{5.6} = \text{Normality}$ Sol 35: (A) 30 Volume H<sub>2</sub>O<sub>2</sub>  $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ Normality =  $\frac{\text{VS}}{5.6} = \frac{30}{5.6} = 5.35$ 

**Sol 36:** (**D**)  $xK_2Cr_2O_7 + yH_2SO_4 + 2H_2O_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + COH_2O + iO_2$ 

By balancing it with exchange of electrons,

Sol37: (A) +3 H<sub>2</sub>O<sub>2</sub> + NaAsO<sub>3</sub>  $\longrightarrow$  Na<sub>3</sub>AsO<sub>4</sub> + H<sub>2</sub>O

Will show its oxidising nature

**Sol 38: (B)** 
$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

This reaction is feasible.

 $\therefore \Delta G$ = -ve at room temperature

**Sol 39: (C)** Heavy water  $D_2O$  is more heavier than  $H_2O$  because of which vibration of bond is less and it is more stable so it can be used as moderator as well as coolant to absorb the high kinetic energy value neutrons, which get evolved in nuclear fission.

Sol 40: (B) Fact.

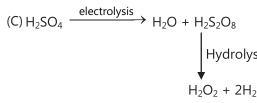
**Sol 41: (B)**  $D_2O$  is more acidic than  $H_2O$  so its neutral point will shift towards right and will be (> 7)

**Sol 42: (C)** D<sub>2</sub>O freezes at higher temperature than H<sub>2</sub>O.

#### Match the Columns

 $\textbf{Sol 43:} A \rightarrow s; \ B \rightarrow s; \ C \rightarrow r; \ D \rightarrow p$ 

(A)  $BaO_2 \cdot 8H_2O \xrightarrow{H_2SO_4} BaSO_4 + H_2O_2$ (B)  $Na_2O_2 \xrightarrow{H_2SO_4} H_2O_2 + 2NaOH$ 



(D) – S

**Sol 44:**  $A \rightarrow p$ , s;  $B \rightarrow q$ , r;  $C \rightarrow q$ , r;  $D \rightarrow q$ , r

(A) Perhydrol is a dilute solution of  $H_2O_2$  and is used as an antiseptic and germicide.

(B) Water gas CO +  $H_2$ , gives  $H_2$ 

(C) Bosch's process is used for the manufacture of  $H_2$ 

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

(D) 
$$CH_4 + H_2O \longrightarrow CO + H_2$$

It is used to manufacture H<sub>2</sub> gas.

It is called water gas (CO +  $H_2$ )

**Sol 45:** A  $\rightarrow$  q, r, s; B  $\rightarrow$  q, r; C  $\rightarrow$  p, q; D  $\rightarrow$  p, q (A) LiAIH,

Complex hydride

$$Na^{+} \begin{pmatrix} H \\ H \end{pmatrix} B \begin{pmatrix} H \\ H \end{pmatrix}$$

Complex hydride

(C) CaH<sub>2</sub>  $\longrightarrow$  Ca<sup>2+</sup> + 2H<sup>-</sup> Reducing agent

(D) LiH  $\longrightarrow$  Li<sup>+</sup> +

Reducing agent

**Sol 46:**  $A \rightarrow r$ ,  $B \rightarrow p$ ,  $C \rightarrow q$ ,  $D \rightarrow s$ 

(A) Heavy water: D<sub>2</sub>O

(B) Temporary hard water: Mg(HCO<sub>3</sub>)<sub>2</sub>; Ca(HCO<sub>3</sub>)<sub>2</sub>

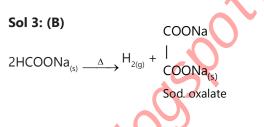
(C) Soft water: only H<sub>2</sub>O

(D) Permanent hard water: Sulphate and chloride of  $Mg^{2\star}\,/\,Ca^{2\star}$ 

## **Previous Years' Questions**

Sol 1: (B) NaCl does not make water hard.

**Sol 2: (A)** Pure para form can be obtained at low temperature (20K) but pure orthoform is very difficult to obtain.



**Sol 4: (B)** Presence of  $CO_3^2$  and  $SO_4^{2-}$  ions in water reduces the tendency of dissolution of Pb in water as  $Pb(OH)_2$ 

**Sol 5: (C, D)** Critical temperature of water is higher than  $O_2$  because  $H_2O$  molecule has dipole moment, which is due to its V-shape.

**Sol 6: (B, D)** Both Ca<sup>2+</sup> and Mg<sup>2+</sup> ions present in hard water are exchanged by Na<sup>+</sup> ions present in zeolite.

**Sol 7: (B, C)** (b)  $HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-}$  and  $CaCO_3$  will get precipitated.

(C) 
$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3$$

(White)

precipitate

**Sol 8: (A)** As  $H_2O_2$  is loosing electrons, it acts as a reducing agent.

**Sol 9: (A)** The structure of  $H_2O_2$  is open book like.

**Sol 10: (C)** This is due to the formation of  $CrO_5$ .

$$\mathrm{K_2Cr_2O_7} + \mathrm{H_2SO_4} + \mathrm{H_2O_2} \rightarrow \mathrm{K_2SO_4} + 2\mathrm{CrO_5} + 5\mathrm{H_2O_5}$$

Sol 11: (A)

$$KIO_4 + H_2O_2 \xrightarrow{\text{R.A.}} KIO_3 + H_2O + O_2$$
$$NH_2OH + H_2O_2 \xrightarrow{\text{O.A.}} H_2O + N_2O_3$$

## **JEE Main/Boards**

## **Exercise 1**

#### s-Block Elements

**Sol 1:** For metal to be obtained by chemical reduction, we need another element which is more electropositive (or have affinity towards oxygen) for reduction. All alkali & alkaline earth metals are the most electropositive elements of the periodic table. So, they cannot be obtained by chemical reduction methods.

**Sol 2:** During the electrolysis of NaCl solution, water molecules are reduced at cathode to form  $OH^-$  ions &  $H_2$  gas. The obtained  $OH^-$  ions react with Na<sup>+</sup> ions to form NaOH. So, we cannot produce Na through electrolysis of NaCl solution.

**Sol 3:** Sodium has a higher melting point because of strong metallic bonds compound to potassium. It is because of low distance between nucleus & delocalised electrons in Na compare to K.

**Sol 4:** (i) Ca +  $2H_2O \rightarrow Ca(OH)_2 + H_2 \uparrow$ 

(ii)  $2Ca(OH)_2 + 2CI_2 \rightarrow Ca(OCI)_2 + CaCI_2 + 2H_2O$ 

(iii)  $Be(OH)_2 + 2NaOH \rightarrow Na_2 Be(OH)_4$  (or  $Na_2BeO_2$ )

(iv)  $BaO_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2$ white ppt

**Sol 5:** Quick lime  $\rightarrow$  CaO powder (grains)

Slaked lime  $\rightarrow$  Water added to quick lime i.e. Ca(OH)<sub>2</sub>. Its dry, light-coloured power.

Lime water  $\rightarrow$  It's a saturated solution of Ca(OH) $_{\rm 2}$  in water.

**Sol 6:** The more the difference of electonegativities, the more is the ionic character.

:. Covalent character of

MI > MBr > MCl > MF

**Sol 7:** Ionisation enthalpy is the energy required to remove the outermost electron from an atom. If we go down the group, the distance between nucleus and the outer electrons increase. So, I.E. will decrease.

**Sol 8:** (i) Li<sup>+</sup> forms an oxide due to its small size. It can polarise the peroxide ion. And lattice energy of Li<sub>2</sub>O is high.

(ii)  $Na_2CO_3$  is formed from NaOH &  $H_2CO_3$ , NaOH is a very strong base &  $H_2CO_3$  is a weak acid.  $\therefore$  resulting solution is alkaline in nature.

(iii) Na can't be prepared by chemical reduction, because of it's high electropositivity. We need an element with more electropositivity to reduce it chemically.

**Sol 9:** Lil is more soluble than KI because of very high hydration energy of Li<sup>+</sup> ion. Due to its small size, Li<sup>+</sup> has a high hydration energy. So, Lil is more soluble.

**Sol 10:** 
$$Na_2CO_3 \xrightarrow{SO_2} NaHSO_3 \xrightarrow{Na_2CO_3} Na_2SO_3$$
  
$$\xrightarrow{Elemental S} Na_2S_2O_3 \xrightarrow{I_2} Na_2S_4O_6$$

**Sol 11:** Sodium metal is highly reactive in the presence of oxidising chemicals whereas kerosene is chemically inactive. So, Na is stored in kerosene.

Sol 12: Gypsum 
$$\rightarrow$$
 CaSO<sub>4</sub> . 2H<sub>2</sub>O  
 $\downarrow \Delta$   
CaSO<sub>4</sub> .  $\frac{1}{2}$ H<sub>2</sub>O  
Plaster of Paris

**Sol 13:** Dead burnt plaster is obtained on strong heating of POP

$$CaSO_4 \cdot \frac{1}{2}H_2O \longrightarrow CaSO_4$$

Plaster of Paris Dead burnt plaster

**Sol 14:** Super oxide  $\rightarrow MO_2$ 

i.e. M<sup>+</sup>, O<sub>2</sub><sup>-</sup>

 $O_2^-$  contain 17 electrons i.e. odd no. of electrons, So, atleast 1 e<sup>-</sup> will be unpaired, so its paramagnetic. Normal oxide ions are  $O^{2-}$ . It's complete filled octet with no unpaired e<sup>-</sup>. So, it's diamagnetic.

**Sol 15:** The main reason behind adding gypsum to cement is to control the rate of hardening of cement.

The cement will set immediately after mixing of water leaving no time for concrete placing.

**Sol 16:** Cs, K act as cathode in photoelectric cells. Cathodes must easily give e<sup>-</sup>, Cs, K have low ionisation potentials but Li has relatively high IP, So, it is not preferred.

**Sol 17:** (i) Alkali metals are not in free form in nature because of their high reactivity. They either react with oxidising agents or these metals reduce other compounds.

(ii) Alkali metals are good reducing agents because they are the most electropositive elements. They have very low IP. So, they can lose an e<sup>-</sup> very easily.

**Sol 18:** (i) As we go down a group, the strength of metallic bonds decrease due to increase in size between nucleus and delocalised electrons. So, their melting points decrease down the group, So, the softness increases down the group.

(ii) Lithium salts have greater covalent character because  $Li^+$  is a small ion. So, it has high polarising power. So, covalent character increases.

**Sol 19:** (i) In the electrolysis of alkali salt solutions, the obtained  $M^+$  ions react with  $OH^-$  ion at cathode to produce hydroxides.

(ii)  $CaCl_2$  helps in reducing the melting point of the mixture and it acts as a flux.

(iii) NaOH  $\xrightarrow{CO_2} Na_2CO_3 \xrightarrow{H_2O(g)} Na_2CO_3$  in moist form. After becoming crystals, it slowly loses water of crystallisation and becomes powder.

(iv) In Solvay's process, we get NaHCO<sub>3</sub> ppt as an intermediate, we obtain Na<sub>2</sub>CO<sub>3</sub> from that precipitate. But, in case of potassium KHCO<sub>3</sub>, it is soluble. So, getting  $K_2CO_3$  is an expensive & difficult process.

(v) On adding excess of NaOH, all of the iodine becomes 1- & loses its colour.

**Sol 20:** (i)  $2KO_2 + 2H_2O \rightarrow 2KOH + O_2 + H_2O_2$ (ii)  $PbO_2 + 2NaOH \xrightarrow{A} Na_2PbO_3 + H_2O$ 

(iii) 
$$2KI + H_2SO_4 + H_2O_2 \rightarrow I_2 + K_2SO_4 + 2H_2O_4$$

(iv)  $6NaOH + 3I_2 \rightarrow 5Na + NaIO_3 + 3H_2O$ 

**Sol 21:** (i) Black Ash :- It is the impure form of  $Na_2CO_3$ . Its produced in Leblanc process

(ii) Action of NaOH of ammonium salts gives a sodium salt with liberation of NH<sub>3</sub> (Ammonia)

(iii) Washing soda :- Na<sub>2</sub>CO<sub>3</sub> . 10H<sub>2</sub>O

Sol 22: (i)  $6NaOH + 3I_2 \rightarrow 5NaI + NaIO_3 + 3H_2O$ (ii)  $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$ (iii)  $2nSO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$ (iv)  $AICI_3 + 3NaOH \rightarrow 3NaCI + AI(OH)_3$   $\downarrow NaOH_{NaAIO_2 + 2H_2O}$ (v) 10 K + 2KNO<sub>3</sub>  $\rightarrow 6K_2O + N_2$ (vi)  $2Na + O_2 \xrightarrow{\Delta} Na_2O_2$   $\downarrow H_2SO_4$   $H_2O_2 + Na_2SO_4$ Sol 23: (i)  $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$ (ii)  $2AgNO_3 + 2NaOH \rightarrow 2NaNO_3 + Ag_2O + H_2O$ 

2AgOH

(iii)  $3NaOH + P_4 + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$ Disproportionation (Phosphine)

**Sol 24:** (i) NH<sub>4</sub>Cl & KCl Reaction with NaOH NH<sub>4</sub>Cl liberates NH<sub>3</sub> No effect of KCl (ii) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> Na<sub>2</sub>SO<sub>3</sub> on action with a strong acid produce SO<sub>2</sub> gas

(iii) NaCl, KCl

Flame test

Gives different colours for different metals. Most of the chemical tests will fail to differentiate between them.

**Sol 25:** (i) KOH > NaOH > LiOH

because of Ionic character) (ii)  $LiHCO_3 < NaHCO_3 < KHCO_3$ (iii)  $Li_2(CO_3) < Na_2CO_3 < K_2CO_3$ (iv)  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$  It is because of high positive charge density in smaller ions. So, it gets hydrated for more layers.

**Sol 26:** (i) MgCl<sub>2</sub>2H<sub>2</sub>O 
$$\xrightarrow{\Delta}$$
 MgCl<sub>2</sub>H<sub>2</sub>O  $\xrightarrow{\Delta}$ 

Mg(OH)Cl

L

High lattice energy

(ii) 
$$CaSO_4 \cdot 2H_2O \xrightarrow{\Delta} CaSO_4 \cdot \frac{1}{2}H_2O$$
  
<sub>Gypsum</sub>  
 $\xrightarrow{\Delta} CaSO_4$   
 $\xrightarrow{\Delta} T70^\circC$   
 $CaSO_4$   
 $\downarrow \Delta$   
 $CaO + SO_2 + \frac{1}{2}O_2$ 

Even  $CaSO_4$  can be the final product.

(iii) 
$$M(HCO_3)_2 \xrightarrow{\Delta} MCO_3 + H_2O + CO_2$$

(iv) 
$$MgSO_4.7H_2O \xrightarrow{\Delta} MgSO_4.H_2O$$
  
Epsom salt

 $\xrightarrow{\Delta} MgSO_4$   $\int \Delta$   $MgO + SO_2\uparrow + \frac{1}{2}O_2$ 

Even here, MgSO<sub>4</sub> can be the last product.

(v)  $Ba(NO_3)_2 \xrightarrow{\Lambda} BaO + NO_2 + O_2$ 

**Sol 27:** (i) BeO is insoluble due to its high covalent nature. Be<sup>2+</sup> has high polarising power and  $O^{2-}$  has high polarisability.

(ii) The covalent character of  $BaSO_4$  is greater than that of BaO. It's because both of  $Be^{2+}$  and  $SO_4^{2-}$  are similar in size.

**Sol 28:** (i) The energy of the flame causes an excitation of the outer most electron which on return on its original position gives out energy released increases in accordance with the formula E = hv. The frequency of light is minimum in lithium which corresponds to red light.

(ii) Sodium is highly electropositive and hence is very reactive. It readily combines with oxygen, moisture and  $CO_2$  of the atmosphere. Hence it is always kept in kerosene as to prevent the action of atmosphere.

(iii) Because of low ionization potentials, potassium and caesium are used in photoelectric cells. The low energy photons (light) can eject electrons from their metal surface.

**Sol 29:** (i) The dense charge of Li<sup>+</sup> attracts several layers of water molecules around it, i.e., Li<sup>+</sup> has maximum degree of hydration. Thus, the size of the hydrated metal ions which affects its movement in solution.

(ii) The small size of both the  $Li^+$  and  $F^-$  ions leads to a very large lattice energy and thus, the crystal is very hard to break apart.

(iii) The salts of Li<sup>+</sup> with small anions have high lattice energy and thus very stable while with large anion, the lattice energy decreases and the salts become less stable.

**Sol 30:** (i) Sodium Bicarbonate; (ii) Lithium Chloride; (iii) Calcium Chloride; (iv) Sodium Formate

## Exercise 2

#### Single Correct Choice Type

Sol 1: (A)  $2NaNO_3 \longrightarrow 2NaNO_2 + O_2^{\uparrow}$ 

**Sol 2: (A)** In Downs process, we take fused NaCl for electrolysis so, we get Na in that Down's process.

**Sol 3: (C)**  $MgCl_2 \cdot 2H_2O \xrightarrow{\Lambda} MgCl_2 \cdot H_2O \xrightarrow{\Lambda} Mg(OH)Cl$ 

**Sol 4: (D)** 
$$2Mg + O_2 \rightarrow MgO$$
 ......(i)  
 $3Mg + N_2 \rightarrow Mg_3N_2$  ......(ii)

**Sol 5: (D)** Magnesite ore  $\rightarrow$  MgCO<sub>3</sub> (It can have impurities of iron carbonate)

**Sol 6: (A)** 
$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{Water} CaSO_4 \cdot 2H_2O \xrightarrow{Gypsum}$$

**Sol 7: (D)** For 1A metals,  $M(HCO_3)$  solubilities increase down the group. They are greater that  $NCO_3$  where N is a alkali earth metal. (because of more covalent character and lattice energy)

 $\therefore$  CaCO<sub>3</sub> < NaHCO<sub>3</sub> < KHCO<sub>3</sub>

**Sol 8: (A)** Nitrolium  $\rightarrow$  CaCN<sub>2</sub> + C obtained by

 $\begin{array}{ccc} CaC_2 + & N_2 & \longrightarrow CaCN_2 + C\\ Calcium & Nitrogen \\ carbide \end{array}$ 

**Sol 9: (A)** Sodium sulphate is soluble because, it's hydration energy > lattice energy it is reverse for Barium sulphate.

**Sol 10: (C)** For alkali metals, electrolysis of molten salt is the most suitable method because of their high reactivities (in other methods, they give different compounds).

**Sol 11: (D)** Anhydrone :- Mg(ClO<sub>4</sub>)<sub>2</sub>

Sol 12: (A) The smallest alkali metal cation is Li<sup>+</sup>.

**Sol 13: (C)** Due to more covalent character, LiCl is less soluble then NaCl in water.

**Sol 14: (C)** Li<sup>+</sup> have very high hydration energy due to high charge density. So, Li can act as reducing agent in solution state.

**Sol 15: (C)** Na  $\rightarrow$  Intense yellow

 $K \rightarrow Lilac$ 

 $\text{Li} \rightarrow \text{Crimson (bright red)}$ 

 $Cs \rightarrow Blue violet$ 

**Sol 16: (C)** The blue colour is due to the presence of dissolved  $e^-$  in NH<sub>3</sub> solution. The  $e^-$  are from metal ions.

**Sol 17: (A)** LiF  $\rightarrow$  because of small size of ions.

Sol 18: (C) 2Na + 2NH<sub>3</sub>  $\xrightarrow{dry}$  2NaNH<sub>2</sub>+H<sub>2</sub> Sodum amide

**Sol 19: (A)** NaHCO<sub>3</sub> and NaOH can't exist together in a solution as NaOH is a base and NaHCO<sub>3</sub> has an acidic hydrogen we will get Na<sub>2</sub>CO<sub>3</sub>

**Sol 20: (D)** Due to high hydration of Li<sup>+</sup>, it's size increases drastically, decreasing it's mobility. So, it's a poor conductor.

Sol 21: (D) Polarity  $\infty$  electronegativity difference

CsF > KCl > CaO > MgO

**Sol 22: (D)** It is clearly wrong as group elements have only 1 unpaired e<sup>-</sup> in its outer shell. So, group IA elements are more electropositive than group IIA.

**Sol 23: (D)** In their unipositive state, they have 1 unpaired  $e^-$ . It's not stable. Thus, loses another  $e^-$  very easily.  $M^{2+}$  configuration is stable as it has filled orbitals. They have more lattice energy.

**Sol 24: (A)** As Mg, P, Al are in a period & electropositivity decrease, if we go right in a period.

So EP<sub>mg</sub> > EP<sub>AT</sub> > EP<sub>P</sub> & down a group, EP increases

So  $EP_{Mg} > EP_{Be}$ . Mg has maximum EP in the given elements.

**Sol 25: (C)** For an ionic compound to be soluble in water, it's hydration energy must be greater than lattice energy. For alkaline earth metals, Be<sup>2+</sup> has very low size. So, it's hydration energy is very high. So, its soluble.

**Sol 26:** (C) As  $HNO_3$  is a strong oxidising agent, it oxidizes the surface of Be, Al. As BeO &  $Al_2O_3$  have high lattice energies, the oxides acts as a protective layer and prevents the inner part of metal from undergoing reaction.

**Sol 27: (A)** (a) Epsom salt  $\rightarrow$  MgSO<sub>4</sub>. 7H<sub>2</sub>O

(b) Gypsum  $\rightarrow$  CaSO<sub>4</sub> . 2H<sub>2</sub>O

(c)  $BaSO_4$  .  $H_2O$ 

**Sol 28: (B)** Blue john is a fluorite mixture (CaF<sub>2</sub>).

Sol 29: (B) Ionic character & Electronegativity difference

 $\therefore$  Greatest  $\rightarrow$  RbCl

 $\text{Least} \rightarrow \text{BeCl}_2$ 

**Sol 30: (D)**  $Zn(OH)_2$  because Zn is from d-block. It's amphoteric and not as electropositive as s-block elements.

**Sol 31: (A)** 2<sup>nd</sup> IP of IA metals will be very high as they will have inert gas configuration

 $2^{nd}$  IP of IIA metals will be low as they will have s' configuration

 $\therefore$  K > Ca > Ba

## **Previous Years' Questions**

**Sol 1: (B)**  $Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$ 

Sol 2: (B)

 $NaCI + H_2O + CO_2 + NH_3 \longrightarrow NaHCO_3 + NH_4CI$ 

 $2NaHCO_{3} \longrightarrow Na_{2}CO_{3} + H_{2}O + CO_{2}$ 

**Sol 3: (A)**  $2I^- + 4H^+ + 2NO_2^- \rightarrow 2NO + I_2 + 2H_2O$ 

**Sol 4: (B)**  $2Na + 2H_2O \rightarrow 2NaOH + H_2$ 

Sol 5: (A)  $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$  $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$  $Na_2CO_3 + 2HCI \rightarrow 2NaCI + H_2O + CO_2$ 

 $\begin{array}{c} \text{NaCl} \xrightarrow{\text{Electrolysis}} \text{Na}^{+} + \text{Cl}^{-} \\ \text{(Molten)} & \downarrow^{+}e^{-} & \downarrow^{-}e^{-} \\ \text{Na} & \text{Cl} \end{array}$ 

**Sol 6: (B)**  $Na_2SO_3 + S \xrightarrow{NaOH} Na_2S_2O_3$ Sod. thiosulphate

**Sol 7: (D)** Both assertion and reason are false. Radium is the rarest of all s-block elements comprising only 10<sup>-10</sup> percent of igneous rocks. Francium (s-block member) is radioactive; its long lived isotope <sup>223</sup>Fr has a half life of only 21 minutes.

Sol 8: (C) Assertion is true but reason is false.

Due to high polarizing power of Li<sup>+</sup>, LiCl is a covalent compound.

**Sol 9: (C)** Assertion is true but reason is false.

Be has fully filled 2s<sup>2</sup>-orbital which gives a relatively more stable electronic configuration.

**Sol 10: (A)** Both assertion and reason are true and reason is the correct explanation of assertion.

**Sol 11: (A)** Both assertion and reason are true and reason is the correct explanation of assertion.

Sol 12: (B) Factual.

**Sol 13: (B)** BaSO<sub>4</sub> is least soluble.

BeSO<sub>4</sub> is most soluble.

## JEE Advanced/Boards

**Exercise** 1

**Sol 1: (D)** For alkali metals, the no. of shells go on increasing as we go down the group.

**Sol 2: (A)** Li is one of the elements coming as an exceptional case where in the bonding shows a covalent nature rather than ionic.

Sol 3: (B) Bigger atomic sizes.

**Sol 4: (C)** Readily absorbs moisture & carbon dioxide from air; reacts with  $CO_2$  to form sodium carbonate.

**Sol 5: (A)** It's crystal lattice is quite rigid, has a very high enthalpy change of solution.

#### Sol 6: (A)

 $\begin{aligned} & \mathsf{Ca}(\mathsf{NH}_2)_2 \underline{\mathsf{H}_2\mathsf{O}}\mathsf{Ca}(\mathsf{OH})_2 + \mathsf{NH}_3 \\ & \overset{(B)}{\mathsf{B}} \\ & \mathsf{NH}_3 + \mathsf{Ca}\mathsf{Cl}(\mathsf{OCI}) \to \mathsf{Ca}\mathsf{Cl}_2 + \mathsf{H}_2\mathsf{O} + \mathsf{N}_2 \\ & \overset{(B)}{\mathsf{D}} \\ & \mathsf{N}_2 + \mathsf{Mg} \to \mathsf{Mg}_3 \mathsf{N}_2 \\ & \overset{(D)}{\mathsf{D}} \\ & \mathsf{Mg}_3\mathsf{N}_2 + \mathsf{H}_2\mathsf{O} \to \mathsf{Mg}(\mathsf{OH})_2 + \mathsf{NH}_3 \end{aligned}$ 

**Sol 7: (C)** Fluorine being the halogen, its smallest atomic size & higher electronegativity accounts for the high lattice energy.

Sol 8: (B) Stability factor.

Solution for Q.9: (C), Q.10: (A) and Q.11: (A)

$$Sr + H_2O \rightarrow Sr(OH)_2 + H_2 \xrightarrow[(B)]{Li} LiH_2 + H_2O \rightarrow Li(OH)_{(E)}$$
$$Sr(OH)_2 + CO_2 \rightarrow Sr(CO_3)_2 \xrightarrow[(CO_2]{CO_2} Sr(HCO_3)_2_{(CI)}$$

Sol 12: (D) Self explanatory.

Sol 13: (B) The only existing one.

Sol 14: (B)  $KO_2 + H_2O \rightarrow KOH + O_2$ 

Sol 15: (A) Lattice energy.

## Exercise 2

## Single Correct Choice Type

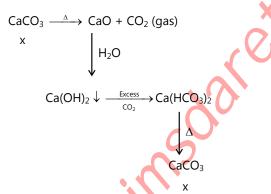
Sol 1: (C) At one electrode  $2CI^- \rightarrow CI_2 + 2e^-$ At another  $Na^+ + H_2O \rightarrow NaOH + H^+$  $\therefore CI^- \& H^-$ 

Sol 2: (B) Iron (see the setup of Castner - Kelner cell)

**Sol 3: (B)** Electrolysis of aq. NaOH gives  $Cl_{2'}$ , NaOH,  $H_2$  If NaOH and  $Cl_2$  get in contact, they react again to give NaCl.

**Sol 4: (D)** Generally on passing excess of CO<sub>2</sub>, we get bicarbonates and bicarbonates give carbonates.

So, x must be carbonate and heating  $Na_2CO_3$  doesn't give  $CO_2$  easily



**Sol 5: (C)** As potassium has less BP & MP, it's more volatile and distils off at that temperature, moving the reaction in the forward direction.

**Sol 6: (C)** If the lattice energy is high, then solubility decreases.

... MgS is least soluble in water.

Sol 7: (D) Mg is more electropositive than C

 $\therefore$  2Mg + CO<sub>2</sub>  $\rightarrow$  2MgO + C.

**Sol 8: (B)** Solubility of hydroxides increases down the group in IIA metals.

 $\therefore$  Sr(OH)<sub>2</sub> is most soluble

**Sol 9: (C)** For sulphates & carbonates, hydration energy factor wins over lattice energy because of large anion size

 $\therefore$  Be > Mg > Ca > Sr > Ba

Sol 10: (C)  $BaCO_3 \xrightarrow{H_2SO_4} BaSO_3$ 

and barium chromate is yellow.

**Sol 11: (D)** Strontium decompose water readily than Be because of high electropositivity.

White ppt

MP of BaCO<sub>3</sub> > CaCO<sub>3</sub> Ba(OH), is more basic than  $Be(OH)_2$ 

**Sol 12: (B)** Pungent smelting gas is of the barium salt, which is yellow in colour  $Ba \rightarrow green$  on flame test

 $\therefore$  Salt is BaS<sub>2</sub>O<sub>3</sub>

## **Multiple Correct Choice Type**

Sol 13: (A, B) Refer features of Bronsted acid /base.

Sol 14: (C, D) Aluminium alloys one used in aircraft.

Sol 15: (A, B, C) Properties of group-II elements.

Sol 16: (A, B, D) Diagonal Relationships.

## Comprehension Type

**Sol 17: (A)** Lattice of MgO > CaO

because size of  $Mg^{2+} < Ca^{2+}$ 

So, MgO is more stable.

**Sol 18: (D)** In cation and anion are of similar size then the resultant salt will be quite stable.

Sol 19: (A)  $Na_2CO_3 \xrightarrow{\Delta} Na_2O + CO_2(g)$ Sol 20: (B)  $Li_2O$  $Li - \ddot{O} - Li$ 

## 

**Sol 21: (C)**  $BH_4^-$  is a covalent hydride

 $BH_4^- \longrightarrow OH^-$  lons.

**Sol 22: (B)** We need  $H^-$  ions to react with  $AlCl_3$  to get  $AlH_3$ . LiH is suitable.

**Sol 23: (B)** We get H<sub>2</sub> and metal. So, it will be highly basic.

**Sol 24: (A)** LiH  $\rightarrow$  because of high lattice energy

**Sol 25: (C)** In ionic hydrides, H<sup>-</sup> acts as a strong reducing agent.

#### **Assertion Reasoning Type**

**Sol 26:** (D) Assertion is wrong as  $Li^+$  is highly hydrated compared to  $Na^+$ . So, size of hydrated  $Li^+$  > hydrated  $Na^+$ . Even reaction is false as hydration energy of  $Li^+$  >  $Na^+$ .

**Sol 27: (D)** MnO<sub>3</sub>  $\xrightarrow{\Delta}$  MnO<sub>2</sub> +  $\frac{1}{2}$ O<sub>2</sub>  $\uparrow$  in case of alkali metals.

So, both A and R are false.

**Sol 28: (A)** CaCO<sub>3</sub>  $\rightarrow$  nearly 840°C

 $MgCO_3 \rightarrow nearly 660^{\circ}C$ 

though the lattice energy of  $MgCO_3$  is more than  $CaCO_3$ , the temperature depends also on the lattice energy of obtained products i.e. MgO, CaO and difference in lattice energies of MgO & CaO is pretty high.

**Sol 29: (A)**  $K_3N$  is not possible because of high polarising power of  $N^{-3}$ 

Li<sub>3</sub>N is covalent with stable p bonds

So, R is correct explanation of A

**Sol 30: (A)** Li cannot be stored in kerosene because of its low density (i.e. more volatility) So, it floats in kerosene and has a probability of getting in contact in air. This may lead to an explosive reaction.

## **Previous Years' Questions**

**Sol 1: (B)** Thermal stability of salts with common anion depends on polarizing power of cation. Greater the polarizing power, lower will be the thermal stability. Hence,  $BeCO_3$  (IV) <  $MgCO_3$  (II) <  $CaCO_3$  (III) <  $K_2CO_3$  (I)

**Sol 2: (A)** Electrolysis of aqueous  $Na_2SO_4$  gives  $H_2$  (g) at cathode and  $O_2$ (g)at anode.

**Sol 3: (B)** Mg(HCO<sub>3</sub>)<sub>2</sub> on boiling decomposes to give white precipitate of MgCO<sub>3</sub> as

 $Mg(HCO_3)_{2(aq)} \xrightarrow{Heat} MgCO_3 \downarrow + H_2O + CO_2 \uparrow$ 

**Sol 4: (A, B)** When sodium metal is burnt in excess of air, mainly sodium peroxide  $(Na_2O_2)$  with little sodium oxide  $(Na_2O)$  are formed.

**Sol 5:** (**B**, **C**, **D**)  $Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O_3$ 

(Clark's method)

 $NaOCI + H_2 \rightarrow NaOH + HOCI$ 

 $HO^- + HCO_3^- \rightarrow CO_3^2 + H_2O$ 

 $Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaHCO_3$ 

**Sol 6:** Heating MgCl<sub>2</sub> .6H<sub>2</sub>O brings about partial dehydration as

$$MgCl_2.6H_2O \xrightarrow{\Lambda} Mg(OHCI) + HCI + 5H_2O$$

**Sol 7:** Sodium when burnt in excess of oxygen, gives sodium peroxide as major product

$$Na + O_2 \xrightarrow{\Delta} Na_2O_2 + Na_2O_{minor}$$

**Sol 8:** The substance is  $Na_2O_2$ . When  $Na_2O_2$  is dissolved in water, it forms NaOH and  $H_2O_2$ . In this case, NaOH is a strong base while  $H_2O_2$  is a weak acid.

(i)  $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$ 

 $H_2O_2$  decolourises red litmus paper due to its bleaching action which is due to its oxidizing character.

$$H_2O_2 \rightarrow H_2O + [O]$$
  
bleaches colour  
of red litmus

(ii) If the compound is  $Na_2O$ , it will hydrolyse to form NaOH.

 $Na_{2}O + H_{2}O \rightarrow 2NaOH$ 

NaOH solution formed above will change colour of red litmus paper into blue.

**Sol 9:** Be in  $BeCl_2$  is electron deficient, short of two lone pair of electrons from stable octet.  $H_2O$  has lone pair of electrons, reacts with  $BeCl_2$ 

**Sol 10:** 
$$BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + H_2O + CO_2 C = C^{14}$$

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