PROPERTIES OF s-BLOCK ELEMENTS

Section - 1



Group - I

Introduction:

All the alkali metals have loosely held one s-electron in the outermost shell which they can readily lose to give monovalent (M^+) cation having stable noble gas configuration. Due to their tendency of loosing s-electron easily, they have low ionization energy and high metallic character. The size of atoms and ions of alkali metals increases down the group.

Physical Properties:

(i) Electropositive character

Alakali metals are highly electropositive in nature and electropositive character increases down the group.

(ii) Ionization Energy

Alkali metals have low ionisation energy and it decreases down the group. In fact K and Cs are used as cathodes in photoelectric cells.

(iii) Density

The density of alkali metals is quite low as compared to other metals. Li, Na and K are even lighter than water. As we go down the group, the mass and volume of alkali metals increases but mass increases by larger factor than the volume and the resulatant effect is that the density increases down the group with an exeption that potassium beigh lighter than Sodium. So, the trend is:

(iv) Melting Point and Boiling Point:

Melthing point and boiling point of alkali metals decreases down the group. The melting points range from lithium 181°C to caesium 28.5°C. These are extremely low values for metals, and contrast with the melting point of the transition metals, most of which are above 1000°C.

(v) Flame Test:

Group I elements give a varied range of colours in their flame test. Li emits crimson light, Na emits yellow, K emits lilac and Rb and Cs emit violer light.

Chemical Properties:

The alkali metals are highly reactive due to low ionization enthalpy and therfore they never occur in free state. The reactivity of these metals increases down the group.

(i) Reactivity towards air

Li react with air forming oxide Li_2O (and some Li_2O_2) and nitride Li_3N . Na react with air forming oxide (Na₂O) and peroxide (Na₂O₂). Peroxide is formed in large amount. K, Cs and Rb forms oxide (M₂O), peroxide (M₂O₂) and superoxide (MO₂). Superoxide is fromed in large amount. (Where M is K, Cs, Rb).

You can note here except Li all other alkali metals are forming oxide only, whereas Li form nitride also on buring in air. Li₃N is a ruby red salt which gives LiOH and $NH_3 \uparrow$ on dissolving in water while Li and nitrogen on simply heating. The increasing stability of peroxide or super-oxide, as size of the metal ion increases, is due to the stabilization of large anions by larger cation through higher lattice energies.

(ii) Reactivity towards water

Group 1 metals all react vigorously with water liberating hydrogen. The reaction becomes increasingly violent on descending the group.

$$M_{(s)} \longrightarrow M_{(sq)}^+ + le^-$$
; $H_2O + le^- \longrightarrow OH^- + \frac{1}{2} H_2$
 $M + H_2O \longrightarrow M^+ + OH^- + \frac{1}{2} H_2$ (M = Li, Na, K, Rb, Cs)

Reaction of sodium is os violent that it catches fire and is thus kept in kerosene in the laboratory.

Standard Reduction Potential

Standard Reduction potential of akali metals M is a value that represents the tendency to gain an electron

$$M_{(aq)}^+ + le^- \longrightarrow M_{(s)}$$

If standard Reduction potential is positive it means element desires to gain electrons and if it is negative it means element desires to loose electron.

Further, lower the standard reduction potential, higher will be the tendency to loose electron.

Standard reduction potential (E°) for an alkali metal represents the overall change:

$$M_{(s)} \longrightarrow M_{(g)}$$
 Sub lim ation enthalpy $M_{(g)} \longrightarrow M_{(g)}^+ + le^-$ Ionization enthalpy $M_{(g)}^+ + H_2O \longrightarrow M_{(aq)}^+$ hydration enthalpy

Lithium has the most negative standard reduction potential than any other element in the periodic table. Why?

$$\text{Li}_{(s)} \xrightarrow{\Delta_a H_{\text{Li}} = 159 \text{ KJ/mol}} \text{Li}_{(g)} \xrightarrow{\Delta_{\text{ion}} H_{\text{Li}} = 520.2 \text{ KJ/mol}}$$

$$\operatorname{Li}_{(g)}^{+} + \operatorname{le}^{-} \xrightarrow{\Delta_{\text{hydr}} H_{Li} = -520} \operatorname{Li}_{(aq)}^{+} + \operatorname{le}^{-}$$

 $Total\ energy\ aborbed\ = \Delta aH_{Li} + \Delta_{ion}H_{Li}\ + \Delta_{hydn}H_{Li} = 159\ +\ 520.2\ -\ 520\ =\ 159.2\ \ KJ\ /\ mol.$

$$Na_{\left(s\right)} \xrightarrow{\quad \Delta_{a}H_{Na} = 107 \text{ KJ/mol} \quad} Na_{\left(g\right)} \xrightarrow{\quad \Delta_{ion}H_{Na} = 495.8 \text{ KJ/mol} \quad}$$

$$Na_{(g)}^+ + le^- \xrightarrow{\Delta_{hydr} H_{Na} = -406 \text{ K/mol}} Na_{(aq)}^+ + le^-$$

Total energy absorbed

$$= \Delta_a H_{Na} + \Delta_{ion} H_{Na} + \Delta_{hydr} HNa^+ = 107 + 495.8 - 406 = 196.8 \text{ KJ}? \text{mol}$$

Hnece total energy absored in $\text{Li}_{(s)} \longrightarrow \text{Li}^+_{(aq)} + \text{le}^-$ is less and also least as compared to any other element. Therefore it has most negative standard reduction potential.

 $\text{Li has most negative standard reduction ptoential (or highest tendency for } \text{Li}_{\left(s\right)}^{+} \longrightarrow \text{Li}_{\left(aq\right)}^{+} + \text{le}^{-}).$

It seems that reaction of Li with water should be most vigourous. But it is surprising that Li reacts less vigorously with water than other alkali metals. The explanation lies in the kinetics (that is the rate at which the reaction proceeds) rather than in the thermodynamics (that is total amount of energy absorbed). You will study more about kinetics in upcoming modules.

(iii) Reducing Character

Among alkali metals, Lithium has strongest reducing character and sodium has least reducing character and rest are almost the same.

[Lower the standard reduction potential (considering the sign also) higher is the reducing character]

(iv) Solution in liquid Ammonia

Liquid Ammonia is also a good polar solvent next the water. Ammonia gas (b.p. = - 33°C) is condensed to give liquid ammonia. Both water and ammonia undergo self - ionization :

$$2H_2O \Longrightarrow H_3O^+ + OH^-$$
 ; $2NH_3 \Longrightarrow NH_4^+ + NH_2^-$

When small amount of sodium is added in liquid ammonia (i.e.: Dilute Solutions of Na in liquid Ammonia), sodium metal looses an electron to give sodium cation, both of these ions are solvated by liquid ammonia to give a blue coloured solution which is highly conducting.

$$M + (x + y) NH_3 \longrightarrow \left[M(NH_3)_x\right]^+ + \left[e(NH_3)_y\right]^-$$

The blue colour of the solution is due to the 'ammoniated electron' which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The conducting nature is also mainly due to solvated electron.

The solution is paramagnetic in nature and on standing slowly liberates hydrogen resulting in the formation of amide.

$$e^- + NH_{3(\ell)} \longrightarrow NH_{2(ammoniated)}^- + \frac{1}{2}H_{2(g)}$$

Concentrated solution of Na in liquid ammonia is metallic bronze in colour and diamagnetic in nature due to formation of metal ion clusters.



Introduction:

All the alkaline earth metals have two s-electron in the outermost shell which if they lose, they will give divalent (M^{2+}) cation having stable noble gas configuration. The size of atoms and ions of alkaline earth metals increases down the group.

Physical Properties:

(i) Electropositive character

Alkaline earth metals are highly electropositive in nature and Electropositive character increase down the group.

(ii) Ionization Enthalpy

Second ionization enthalpy is very high than first ionization enthalpy. It is due to the fact that extracting an electron from a positive ion becomes difficult. Both first and second ionization energy decreases down the group.

(iii) Density

The density of alkaline earth metals is high as compared to alkali metals. And as we go down the group both the mass and volume of alkali metals increases but the resultant effect that is the density do not show a regular change. As we move down the group, it first decrease (upto Ca) and then increases. So, the trend is: Ba > Sr > Be > Mg > Ca

(iv) Melting point and Boiling Point

Melthing point and boiling point of alkaline earth metals is higher than the alkali metals. As we move down the group,

Melthing point and Boiling point don't show a regular change.

Chemical propeties:

(i) Reactivity towards air

Alakaline earth metals react with air forming an oxide and a nitride.

$$M_{(s)} \xrightarrow{air} MO + M_3N_2$$
 (where M = Be, Mg, Ca, Sr, Ba)

The case of above reaction depends on electropositive character and hence increases down the group. In the case of Mg, it burns with a dazzling white light which is used to provide light in flash photography using light bulks.

(ii) Reactivity towards water

$$OHC: \ M_{\left(s\right)} {\longrightarrow} \ M_{\left(aq\right)}^{2+} + 2e^{-} \\ RHC: 2H_{2}O_{\left(\ell\right)} + 2e^{-} {\longrightarrow} \ H_{2} + 2OH^{-}$$

Now, to check the case of reaction for different metals, we have to check the Oxidation Half Cell reaction and this reaction refers to the reducing ability (Standard Reduction Potential) of the metal.

And, Since for alkaline earth metals reducing character increases down the group, the case of reaction of alkaline earth metals with water increases down the group.

Experimentally, it is see that Be reacts only with steam and Magnesium can react with both hot water and steam and Ca. Sr, Ba ract even with cold water rapidly.

(iii) Solution in liquid ammonia

In liquid ammonia, group II metals form bright blue dilute solutions containing solvated electrons and metal hexaammoniates. The metal hexammoniates form ammides on heating which further form nitrides and NH_3 concentrated solution are bronze coloured.

(iv) Reducing character

Less is the standard reduction potential more will be reducing character and since the standard reduction potential decreases down the group, the reducing character of alkaline earth metals increases down the group.

In this section we will discuss some important concepts related to s-block elemets.

Lattice enthalpy

It is the energy required to separate one mole of a solid ionic compound completely in gaseous ions.

Lattice Enthalpy of breaking solid NaCl in gaseous Na⁺ and Cl⁻ is + 788 KJ/mol.

In a system of + ve and -ve ion the energy required to separate the two ions is inversely proportion to the distance between the centres of the two ions.

$$\Rightarrow \qquad LE \propto \ \frac{1}{r^+ + r^-}$$

(r^+ is the radius of +ve ion and r^- is the radius of -ve ion.)

For a given anion and different cations as we move down the group the size of cation increase and consequently the interionic distance between cation and anion increases. Hence, the lattice enthalpy would decrease dwon the group.

Also you may not that as the charge of ion increases the Lattice Enthalpy increases. Therefore, Lattice Enthalpy of group II metal salt is more as compared to corresponding group I metal salts.

Hydration Enthalpy

Hydration Enthalpy refets to the energy released when one mole of gaseous ion is dissolved (or hydrated) in water. Strictly speacking, value of Hydration Enthalpy is equal to the energy absorbed when one mole of gaseous ion is dissolved in water. For example, if energy is released on dissolving some ion in water, its hydration enthalpy will be negative quantity and its magnitude will be equal to the magnitude of energy released.

When an ion is dissolved in water it attracts water molecules. Thus, a number of water molecules surround it and a cluster is formed. The number of water molecules surrounded by a cation depend on the ability of the cation to polarise the water molecule. More the polarizing power of cation, the large the number of water molecules will surround it. Among alkalie metals cations, Li⁺ has highest polarising power, hence, a large number of water molecules will surround it. The numbere is so large that the hydrated Li⁺ becomes heavier than hydrated Na⁺. The hydrated Na⁺ being lighter moves easily in water as compared to hydrated Li⁺, hence Na⁺ is more conduction than the solution of Li⁺.

Also, note that more that polarising power of cation, more it will be hydrated and more energy will be released. And therefore, hydration enthalpy will be more negative. Thus down the group magnitude of hydration enthalpies of metal ions decreases.

Thermal Stability

Hereby we will discuss the thermal stability of group I and group II metal oxosalts. i.e. carbonates, nitrates, sulphates etc. For simplicity let us consider metal carbonates and discuss their thermal stability.

Example:

The effect of Heat on the metal carbonates:

All the carbonates undergo thermal decomposition to give the metal oxide and carbon dioxide gas. Thermal decomposition is the term given to splitting up a compound by heating it.

$$XCO_3(s) \longrightarrow XO(s) + CO_2(g)$$

As you go down the group, the carbonates have to be heated more strongly before they will decompose. i.e. Thermal stability of metal carbonates increase down the group. Let us try to understand the explanation of this fact.

Explanining the trend the terms of the polarising ability of the positive ion:

A small cation has a lot of charge packed into a small volume of space. It has a high *charge density* and will have a marked distorting effect on any negative ions which happen to be near it.

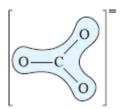
A bigger cation has the same charge spread over a larger volume of space. Its charge denisty will be lower, and it will cause less distortion to nearby negative ions.

The structure of the carbonate ion:

If you worked out the structure of a carbonate ion, you would probably come up with:

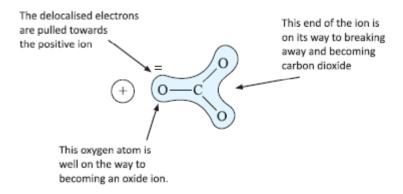
This show two single carbon-oxygen bonds and one double one, with two of the oxygens each carrying a negative charge. Unfortunately, in real carbonate ions all the bonds are identical, and the charges are spread out over the whole ion - although concentrated on the oxygen atoms. We say that the charges are delocalised.

The next diagram shows the delocalised electrons. The shading is intended to show that there is a greater chance of finding them around the oxygen atoms than near the carbon.



Polarisin the carbonate ion:

Now imagine what happens when this ion is placed next to a positive ion. The positive ion attracts the delocalised electrons in the carbonate ion towards itself. The carbonate ion becomes polarised.



If this is heated, the carbond dioxide breaks free to leave the metal oxide.

How much you need to heat the carbonate before that happens depends on how polarised the ion was. If it is highly polarised, you need less heat than if it is only slightly polarised.

The smaller the positive ion is, the higher the charge density, and the greater effect it will have on the carbonate ion. As the positive ions get bigger as you go down the Group, they have less effect on the carbonate ions near them. To compenstate for that, you have to heat the compound more in order to persuade the carbonal dioxide to break free and leave the metal oxide. In other words, as you go down the Group, the carbonates become more themally stable.

In case of Nitrates, Group II metal nitrates decompose to give metal oxide, nitrogen dioxide and oxygen gas while Group I metal nitrates except lithium) decompose to give metal nitrite and oxygen gas. Lithium nitrate behaves in a way similer to group II metals giving. LiO, NO₂ and O₂ on decopostion.

$$Ca(NO_3)_2 \xrightarrow{\Delta} CaO + NO_2 + O_2$$

$$Li(NO_3)_2 \xrightarrow{\Delta} Li_2O + NO_2 + O_2$$

$$NaNO_3 \xrightarrow{500^{\circ}C} NaNO_2 + O_2$$

$$NaNO_3 \xrightarrow{800^{\circ}C} Na_2O + N_2 + O_2$$

NaNO₃ on very strong heating gives Na₂O, N₂ and O₂. Metals sulphates decompose to give metal oxide, SO_2 and O_2 . Thermal stability of all these oxosalts increases down the group and the explanation lies in a way similar to as given for metal carbonates.

1. Oxides, Peroxide, Superoxides



Gruop - I

Alkali metals generally burn in air to form oxides, peroxides and superoxides (Lithium forms some nitride also). Lithium forms Li_2O (and some Li_2O_2) and Li_3N . Sodium form Na_2O_2 (and some Na_2O), and rest of the alkali metals form superoxides (major). The increasing stability of oxides, peroxides and superoxides, as the size of the metal ion increases, is due to the stabilisation of large anions by larger cations through lattice energy effects. The oxides and peroxides are colourless but the superoxides are orange or yellow. Oxides and peroxides ae diamagnetic while superoxides are paramagnetic. Alkali metal oxides, peroxides and superoxides dissove readily in water to give hydroxides along with a lot of heat. Peroxides and superoxides are good oxidants and generally used in bleaching.

1. Sodium Oxide [Na₂O]

Preparation:

- (i) Controlled oxidation of sodium in air gives Na₂O
- (ii) Industrially, Na₂O is prepared by heating sodium nitrate of nitrite with sodium.

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

(iii) In laboratory pure Na₂O is formed by heating mixture of sodium azide and sodium Nitrite.

$$3\text{NaN}_3 + \text{NaNO}_2 \xrightarrow{\Delta} 2\text{Na}_2\text{O} + 5\text{N}_2$$
(pure)

Porperties:

Na₂O is a white ionic solid and its aqueous solution is a strong base.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

2. Sodium Peroxide [Na₂O₂]

The trade name of sodium peroxide is oxone.

Preparation:

Burning Sodium in air mainly forms sodium peroxide.

Properties:

- (i) Na₂O₂ is colourless in pure form and stable at room temperature.
- (ii) Na_2O_2 is diamagnetic. All peroxides are regarded as salts of dibasic acid H_2O_2 .

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

(iii) Cold dilute acids always produce H₂O₂.

$$Na_2O_2 + HCl \xrightarrow{Cold} NaCl + H_2O_2$$

The reaction with CO₂ is used to purify air in submarinas but KO₂ is even better for this purpose.

(iv) It is strong oxidising agent. It oxidises Al to Al_2O_3 , Cr^{3+} to CrO_4^{2-} and SO_2 to SO_4^{2-} .

$$Na_2O_2 + Al \longrightarrow Al_2O_3 + Na_2O$$

 $Na_2O_2 + CO_2 \longrightarrow Na_2SO_4$

The reaction with CO₂ is used to purify air in submarines but KO₂ is even better for this purpose.

Uses:

It is a powerful oxidant and used for bleaching wood pulp, paper and fabrics.

3. Potassium Superoxide [KO₂]

Preparation:

It is prepared by burning potassium in excess of oxygen.

$$K + O_2 \text{ (excess)} \longrightarrow KO_2$$

Porperties:

- (i) It is paramagnetic and orange coloured solid.
- (ii) Potassium superoxide is stronger oxidizing agent and gives both H₂O₂ and O₂ with either water or acids.

$$2\mathrm{KO}_2 + 2\mathrm{H}_2\mathrm{O} \longrightarrow 2\mathrm{KOH} + \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \quad ; \quad 2\mathrm{KO}_2 + 2\mathrm{HCl} \longrightarrow 2\mathrm{KCl} + \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$$

(iii) It readily reacts with CO and CO₂ producing Oxygen.

$$2KO_2 + CO \longrightarrow K_2CO_3 + O_2$$
; $2KO_2 + CO_2 \longrightarrow K_2CO_3 + 3/2O_2$

User:

Being oxidant, KO_2 produces oxygen and simulataneoulsy it absorbs CO_2 and becuase of its above life supporting properties it is used in space capsules, submarines and breathing masks.

Gruop - II

Alkaline earth metals burn in air to give normal metal nitrides. Generally, there are two methods of forming oxides, one is buring in air and other decomposing their oxosalts.

Metal oxides and hydroxides of group II are more stable than of group I, that is why oxosalts (carbonates, sulphates, nitrates,....) of group II are less stable to heat and decompose to give corresponding oxides.

Note: The stability of metal oxides decreases down the group. That is why, down the group metal oxides become more reactive. Down the group, alkaline earth metal oxide's basic character increases. BeO is amphoteric in nature.

1. Magnesium Oxide

Preparation

(i) Magnesium burns in air with a dazzaling flame and forms magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

(ii) Decomposing the oxosalt MgCO₃ also gives magnesium oxide.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

Properties:

- (i) It is light infusible (fusibility refers to conversion in liquid form) white powder. It fuses at 2800°C.
- (ii) It is reduced by carbon at very high temperature.

$$MgO + C \xrightarrow{2000^{\circ}C} Mg + CO$$

Uses:

(i) Buring of magnesium ribbon is used to initiate the thermite reaction. The thermite reaction goes as:

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$$

(ii) MgO being very less reactive and having high m.p., is used as a refractory material. Good conductivity of MgO towards heat and bad conductivity towards electricity also adds to its usefulness as refractory material.

2. Calcium Oxide [CaO] (Quick lime)

Prepartion:

It is prepared by decompostion of CaCO₃ in lime kilns (900°C).

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Properties

- (i) Calcium oxide is a white amorphous solid, having high melting point of about 2870K.
- (ii) Being a basic oxide, it combines with acidic oxides at high temperaure.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
; $6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$

(iii)
$$CaO + 3C \xrightarrow{300^{\circ}C} CaC_2 + CO \uparrow$$

Uses:

- (i) It is used in metallurgy to remove phosphates and silicates as slag.
- (ii) By mixing with SiO₂ and alumina or clay it is used to make cement.
- (iii) It is used for softening of water.

2. Hydroxides

🖵 Gruop - I

Hydroxides of alkali metals are strong base. Their basic character increases down the group. They dissolve readily in water giving much heat due to intense hydration. If we go down the group solubility of alkali metal hydroxides increases.

1. Sodium hydroxide [NaOH] (Caustic Soda)

Preparation:

(i) Heating 10% Na₂CO₃ Sol. with mild of lime (Lime - Caustic Soda process):

$$Na_2CO_3 + Ca(OH)_2 \Longrightarrow 2NaOH + CaCO_3$$

(ii) Electrolysis of brine:

Commercially, NaOH and Cl₂ are manufactured simultaneously by the electrolysis of brine (NaCl solution).

Reactions occuring at anode and cathode are:

$$NaCl \Longrightarrow Na^+ + Cl^-$$

At Anode:
$$2Cl^{-} \longrightarrow Cl_2 + 2e^{-}$$

At Cathode:
$$Na^+ le^- \longrightarrow Na$$

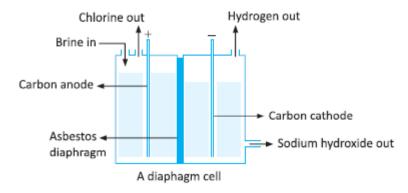
$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Another reaction may occur at the anode to a small extent.

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

Electrolysis is carried in either of two types of cell today, diaphragm and mercury cathode cells. NaOH made in this way always contanins some amount of NaCl.

(a) Diaphragm cell / Nelson: A porous diaphragm of asbestos is used to keep the H₂ and Cl₂ gases separated otherwise they react in an explosive chain reaction in dylight. Diaphragm also seperates the carbon anod and cathod.



(b) Mercury Cathod Cell / Castner - Kellner Cell : The anode is made up of carbon and the cathode of mercury. The reaction occurring at Hg cathode are thus :

Cathod:
$$Na^+ + e^- \longrightarrow Na$$

$$Na + Hg \longrightarrow Na - Hg_{(amalg am)}$$

The amalgam is pumped in a different comartment called *denuder* where water trickles over.

$$Na - Hg + H_2O \longrightarrow NaOH + \frac{1}{2}H_2 + Hg$$
 (recycled back to electrolysis tank)

Properties:

- (i) It is a white crystalline solid, deliquiscent (absorbs moisture from air), soluble in water, good conductor and gives silky touch like soap.
- (ii) It reacts with acid and acidic oxides to form salts

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
 $2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$
 $2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

(iii) It reacts with amphoteric metals such as Sn, Al, Zn and amphoteric metal oxides.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$
 (Sodium Zincate)
 $Al + NaOH + H_2O \longrightarrow NaAlO_2 + \frac{3}{2}H_2$ (Sodium Aluminate)
 $Sn + 2NaOH \longrightarrow Na_2SnO_2 + H_2$ (Sodium Stannate)
 $SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$
 $SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$
 $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

(iv) It reacts with ammonium salts to give ammonia, which serves as a test for ammonia.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3 \uparrow + H_2O$$

The above reaction is double displacement reaction only. NH_4OH must be formed as second product. But NH_4OH is never formed as a product. It decomposes to give $NH_3 + H_2O$.

(v) Disproportion of some non-metals in NaOH: (Learn these reactions)

$$X_2 + NaOH \longrightarrow NaX + NaOX + H_2O$$
 [X = Cl, Br, I]

$$X_2 + \underbrace{\text{NaOH}}_{\text{(hot and Conc.)}} \longrightarrow \text{NaX} + \text{NaOX}_3 + \text{H}_2\text{O}$$

$$P_4 + NaOH \longrightarrow NaH_2PO_2 + PH_3$$
 (phosphine)

[This reaction is used in the preparation of phosphine gas.]

$$S + NaOH \longrightarrow Na_2S + Na_2S_2O_3 + H_2O$$

(All above reactions can be balanced as Redox Reactions)

(vi) Reactio with salts of transition metals:

$$FeCl_3 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaCl$$

When hydroxides are unstable, the oxides are precipitated.

$$\operatorname{HgCl}_2 + 2\operatorname{NaOH} \longrightarrow \underbrace{\operatorname{HgO}(\downarrow) + \operatorname{H}_2O}_{\operatorname{Hg(OH)}_2} + 2\operatorname{NaCl}$$

$$2AgNO_3 + 2NaOH \longrightarrow \underbrace{Ag_2O(\downarrow) + H_2O}_{AgOH} + 2NaNO_3$$

2. Potassium Hydroxide [KOH] (Caustic Potash)

Preparation:

It can be prepared by electrolysis of KCl solution similar to electrolysis NaCl solution (brine)

At Cathode:
$$2K^+ + 2H_2O + 2e^- \longrightarrow 2KOH + H_2 \uparrow$$

At anode:
$$2Cl^- + 2e^- \longrightarrow Cl_2 \uparrow$$

Properties:

- (i) The properties are similar to those of NaOH but being expensive is less used.
- (ii) KOH is more soluble in alcohol than NaOH and produces $OC_2H_5^-$ ions.

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$$C_2H_5OH + OH \longrightarrow OC_2H_5^- + H_2O$$

This accounts for use of elcoholic KOH in OrganicChemistry which you will study in modules of organic.

Uses:

- (i) It is used in organic chemistry
- (ii) KOH is used as an absorbent for CO₂, for which is perferred over NaOH, since after absorption of CO₂, the KHCO₃ formed is solube whereas NaHCO₃ being sparingly soluble separates out, and chokes the absorption bulbs.



Gruop - 2

Alkaline earth metal oxides react with water to form sparingly soluble metal hydroxides.

Alkaline earth metal hydrooxides are less basic and more stable than alkali metal hydroxides. The solubility, thermal stability and basic character of the hydroxides increases down the group. Beryllium hydroxide is amphoteric in nature as it reacts with both acids and bases.

$$\begin{array}{c} Be(OH)_2 + 2NaOH \longrightarrow Na_2 \Big[Be(OH)_4\Big] \\ Sodium \ beryllate \\ \\ Be(OH)_2 + 2HCl + \ 2H_2O \longrightarrow \Big[Be(OH)_4\Big]Cl_2 \end{array}$$

Rest of the alkaline earth metal hydroxide are basic in nature.

1. Magnesium Hydroxide [Mg(OH)₂]

Preparation:

Mg(OH)₂ is pepared by dissolving magnesium oxide in water.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

Properties:

- (i) It is a white powder extermely insoluble in water.
- (ii) It is weakly basic and suspension Mg(OH)₂ in water [milk of Magnesia] is used as an antacid.

2. Calcium Hydroxide [CaOH)₂]

Preparation:

Calcium hydroxide is prepared by adding water to quick lime (CaO).

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Properties

- (i) It is white powder, sparingly soluble in water.
- (ii) The aqueous sturated solution of Ca(OH)₂. is known as *lime water* and the suspension of *slaked lime* (solid Ca(OH)₂) in water is known as *milk of lime*.
- (iii) Bleaching powder is formed when chloring gas is passed through lime water.

$$3Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2$$
. $Ca(OH)_2$. $CaCl_2$. $2H_2O$

Uses:

- (i) It is used in white wash.
- (ii) It is used in the solvay's process.
- (iii) It is used to remove temperaray hardness of water:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$

(iv) When carbon dioxide is bubbled through lime water it turns milky and when excess carbon dioxide is passed, the precipitate (CaCO₃) dissolves forming Ca(HCO₃)₂.

$$\begin{array}{ccc} \text{Ca(OH)}_{2(\text{aq})} & \xrightarrow{\text{CO}_2} & \text{CaCO}_3(\downarrow) & \xrightarrow{\text{CO}_2} & \text{Ca(HCO}_3)_{2(\text{aq})} \\ & & \text{white precipitate} & \xrightarrow{\text{Excess}} & \text{ca(HCO}_3)_{2(\text{aq})} \end{array}$$

Similaraly, Ba(OH)₂ (Baryta water) responds, when CO₂ is bubbled through it.

$$Ba(OH)_2 \xrightarrow{CO_2} BaCO_3(\downarrow) \xrightarrow{CO_2} Ba(HCO_3)_{2(aq)}$$
milky so ln. Excess milkiness disappears

In this reaction $Ba(OH)_2$ is even more sensitive of CO_2 but $Ba(OH)_2$ being more expensive, $Ca(OH)_2$, is preffered to detect CO_2 in laboratory.

Note: The caustic alkalis (NaOH and KOH) are the strongest bases known in aqueous solution. *Soda lime* is a mixture of NaOH and Ca(OH)₂ and is made from quick lime (CaO) and aqueous NaOH. Soda lime is much easier to handle than NaOH.

3. Halides



💄 Gruop - I

Alakali metal halides like NaCl and KCl are generally found in sea water. Among Sodium halides, stability, melthing point and boiling point decreases down the group. Solubility for alkali metal halides doesnot show a regular trend.

1. NaCl

Preparation:

It occurs in sea water as deposits in mines as rock salt. It is extracted from sea water simply by solar evaporation. The crystals of NaCl are washed to remove more soluble MgCl₂.

Properties:

- (i) It is colourless crystalline (in pure form). it is NOT hydroscopic but pressence of MgCl₂ makes it deliquescent due to the high polarizing power of MgCl₂ (that attracts H₂O molecules)
- (ii) It is used to produce industrially important compounds like Na₂CO₃ and Cl₂.
 - (a) Na₂CO₃ is produced by Solvay's Process. (discussed later)
 - **(b)** Cl₂ is produced by:
 - (i) Electrolysis (NaOH is also a product) of brine.
 - (ii) Leblanc Process : NaCl + conc. $H_2SO_4 \longrightarrow NaHSO_4 + HCl$ $NaHSO_4 + NaCl \xrightarrow{heat} Na_2SO_4 + HCl$ $HCl + MnO_2 \longrightarrow Cl_2 + Mn^{2+}$

Uses:

- (i) Eating salt in food.
- (ii) It is used to lower the melting point of ice. Kulfi seller uses NaCl to sustain Kulfi for long time in summer.

KCl is also extracted from sea water. Its properties are almost similar to NaCl. It has an important use in producing fertilizers.



Gruop - II

Alkaline earth metal halides are generally made by heating matals with halogen or by action of halogen acid on metal or metal carbonates. Beryllium halides are covalent while rest of the alkaline earth metals form ionic halides.

BeCl, has a chain structure as shown in the figure.

Here Cl bonded to one Be uses a lone pair of e-s to form a coordinate bond to another Be atom.

Dehydration of hydrated chlorides, bromides and iodies of Ca, Sr, Ba can be achieved on heating but the hydrated halides of Be and Mg suffer hydrolysis on heating. In aqueous solution BeCl₂, Be exists as

$$\left[\operatorname{Be}(H_2O)_4\right]^{2+}$$
 or $\left[\operatorname{Be}(H_2O)_4\right]\operatorname{Cl}_2$.

$$\left\lceil \operatorname{Be}(H_2O)_4 \right\rceil \operatorname{Cl}_2 \xrightarrow{\operatorname{heat}} \operatorname{Be}(OH)_2 + 2\operatorname{HCl}$$

1. Magnesium Chloride [MgCl₂ . 6H₂O]

Preparation

(i) It is prepared by passing dry HCl over Magnesium.

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2 \uparrow$$

(ii) Dow's process:

The extraction of Magnesium from sea water depends on the fact that $Mg(OH)_2$ is very much less soluble than $Ca(OH)_2$.

$$\begin{split} &\operatorname{Ca(OH)_2} + \operatorname{MgCl_2} \longrightarrow \operatorname{Mg\ (OH)_2} \downarrow + \operatorname{CaCl_2} \\ &\operatorname{Mg\ (OH)_3} \xrightarrow{\operatorname{acidified}} \operatorname{MgCl_{2(aq)}} (\equiv \operatorname{MgCl_2} . \ 6\operatorname{H_2O}) \\ &\operatorname{MgCl_2} . \ 6\operatorname{H_2O} \xrightarrow{\operatorname{dry\ HCl}} \operatorname{MgCl_2} + \operatorname{6H_2O} \end{split}$$

Note: If $MgCl_2$. $6H_2O$ is heated, then the products are MgO and HCl. So water of crystallisation are removed by passing $dry \, HCl/Cl_2 \, or \, SOCl_2$.

Properties

- (i) It is colourless solid, highly soluble in water.
- (i) When heated, it decomposes

$$\begin{array}{c} \text{MgCl}_2 \text{ .} \text{ 6H}_2\text{O} & \xrightarrow{\Delta} \text{Mg(OH) Cl} + \text{HCl} + \text{5H}_2\text{O} \\ \\ \text{Mg(OH) Cl} & \xrightarrow{\Delta} \text{MgO} + \text{HCl} \end{array}$$

Uses:

It is used in electrolytic method for extracting Magnesium.

2. Calcium Chlorid [CaCl₂ . 6H₂O]

Preparation

It is formed as Solvay's Process' by-product.

Properties

- (i) It reduces the freezing pt. of water.
- (ii) Anhydrous salt is an excellent drying agent. It forms addition compounds with NH₃ and CH₃OH (CaCl₂ . 8NH₂ and CaCl₂ . 4CH₂OH) and hence cannot be used to dry them.

Uses:

It is sprinkled on roads in hilly areas to remove snow.

4. Carbonates:



Alakli metal carbonates are basic salts. The stability of alkali metal carbonates towards heat increases down the gourp. Thye quite stable and melt before they eventually decompose into oxides (at above 1000°C).

1. Sodium Carbonate (Na₂CO₂):

Washing soda is Na_2CO_3 . $10H_2O$

Soda ash in Na₂CO₃

Preparation:

Solvays's Process (Ammonia-Soda Process)

The process is much more complicated than the overall equation and since the reactions involved are reversible only 75% of the NaCl is converted.

The purified brine (NaCl) solution is first saturated with ammonia and then carbonated with ${\rm CO_2}$ forming ${\rm NaHCO_3}$

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \qquad ; \qquad NH_3 + H^+ \longrightarrow NH_4^+ \\ NH_4^+ + HCO_3^- + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

The NaHCO₃ formed is insoluble in the brine solution becasue of the common ion effect and so can be filtered off. This is then heated to form anhydrous Na_2CO_3 .

$$2\text{NaHCO}_3 \xrightarrow{150^{\circ}\text{C}} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

 $\mathrm{NH_4Cl}$ produced above reacts with lime water forming a very good dehydrating agent ($\mathrm{CaCl_2}$) and evolving $\mathrm{NH_3}$ gas.

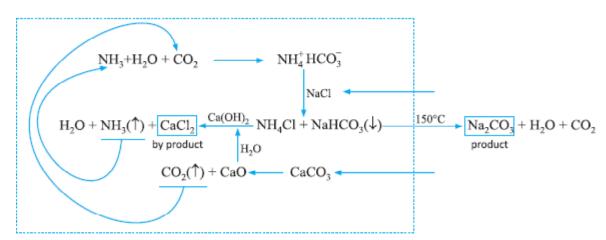
$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

Lime water used above was prepared instantaneously by heating CaCO₃ and passing water through quick lime.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
; $CaO + H_2O \longrightarrow Ca(OH)_2$

The materials consumed are NaCl and CaCO₃ and the useful product is Na₂CO₃. CaCl₂ which is a by product is little used and the rest is wasted. CO₂ and NH₃ formed are used again to continue the process.

The whole process can be diagrammatically shown as:



Properties:

(i) On passing CO₂ through aqueons solution of Na₂CO₃, NaHCO₃ is formed.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3 \downarrow$$

(ii) When aqueous solution of sodium carbonate containing sulphur is treated with sulphur dioxide, sodium thiosulphate is formed.

$$Na_2CO_3 + SO_2 + H_2O \longrightarrow Na_2SO_3 + CO_2 \uparrow$$

 $Na_2SO_3 + S \longrightarrow Na_2S_2O_3$

(iii) On heating washing soda (Na₂CO₃·10H₂O) it forms monohydrate called *heavy ash* or crystal carbonate.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow{\Delta} Na_2CO_3 \cdot H_2O + 9H_2O$$

Uses:

- (i) Used in water softening and cleaning.
- (ii) Used in paper, paint and textile industries

Potassium carbonate (Pearl Ash) is not much important. Its properties resemble closely with Na₂CO₃. It is prepared by carbonation of caustic potash.

$$KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Note: K_2CO_3 cannot be prepared by Solvay's Process because KHCO₃ formed in the reaction is highly soluble and hence cannot be separated form $(NH_4Cl + KHCO_3)$ mixture easily.



Gruop - II

Carbonates are basic salts. BeCO₃ is covalent while other carbonates are ionic. On heating, alkaline earth metal carbonates forms an oxide and carbon dioxide is evolved.

1. Calcium Carbonate [CaCO₃]:

Preparation:

It is mainly extracted from its ores. It can be prepared by these methods also:

(i) It can be prepared by passing limited CO₂ through lime water.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

(ii) It can be obtained by adding sodium carbonate solution to CaCl₂.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Properties:

- (i) It is white powder, almost insoluble in water.
- (ii) On heating at 1200 K, CO_2 is evolved $CaCO_3 \xrightarrow{1200 \text{ K}} CaO + CO_2 (\uparrow)$

(iii)
$$CaCO_3 + HC1 \longrightarrow CaCl_2 + \underbrace{H_2O + CO_2 (\uparrow)}_{H_2CO_3}$$

Uses:

- (i) It used in manufacture of cement and quick lime.
- (ii) Used in Solvay's process in the manufacture of Ca(OH)₂.
- (iii) It is used in toothpaste.

5. Bicarbonates



Gruop - I

Alkali metal are strongly basic and form solid bicarbonates (execpt lithium) while no other melal forms solid bicarbonates LiHCO₃ can exist only in solution. Alkali metal hydrogen carbonates are soulble in water. On heating, they decompose to give carbonates.

The hydrongen bonding in bicarbonates enhances the stability. In NaHCO₃, the HCO₃ ions are linked to form infinite chain while in KHCO₃, a dimeric anion is formed.

$$\begin{bmatrix} O-H-O \\ O-C \\ O-H-O \end{bmatrix}^{2-}$$

As the electropositive character increase down the group, the stability of hydrogen carbonates also increases down the group.

1. Sodium Bicarbonate [NaHCO₃] (Baking Soda)

Preparation:

It is an intermediate product of Solvay's process.

$$NaCl + NH_4^+ + HCO_3^- \longrightarrow NaHCO_3 + NH_4Cl$$

Properties:

On heating, it decomposes to give Na₂CO₃, evolving CO₂ which is used to detect bicarbonates.

$$NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O(\uparrow) + CO_2(\uparrow)$$

Uses:

- (i) It used in fire extinguisher.
- (ii) It is used as baking powder in manufacturing of cake making it fluffy. Backing powder contains NaHCO₃ and Ca(H₂PO₄)₂

$$2\text{NaHCO}_{3} \xrightarrow{50-100^{\circ}\text{C}} \text{Na}_{2}\text{CO}_{3} + \text{H}_{2}\text{O} + \text{CO}_{2} \uparrow$$

$$\text{Ca}(\text{H}_{2}\text{PO}_{4})_{2} + \text{NaHCO}_{3} \longrightarrow \text{CO}_{2} \uparrow$$

The CO₂ produced makes cake or bread rise.

6. Sulphates



Gruop - I

Sodium sulphate (Na_2SO_4 . $10H_2O$) is named as Glauber's salt. It is produced as a by-product while manufacturing HCl.

Fomation of hydrated salts of Na₂SO₄:

$$Na_2SO_4 \xrightarrow{T < 32^{\circ}C} Na_2SO_4.10H_2O$$
 ; $Na_2SO_4 \xrightarrow{T < 12^{\circ}C} Na_2SO_4.7H_2O$

It is used in paper industry.



🛓 Gruop - II

Sulphates of the alkaline earth metals are all white solids & stable to heat. Be and Mg sulphate are highly soluble while other alkaline earth metal sulphates are very less soluble. This is due to very high hydration enthalpy of Be^{2+} and Mg^{2+} . Thermal stability of alkaline earth metal sulphates increases down the group while solubility decreases.

1. Magnesium Sulhate [MgSO₄]

It is a colourless soluble salt which decomposes to MgO, SO_2 and O_2 on heating.

 ${\rm MgSO_4}$. ${\rm 7H_2O}$ is called Epsom salt while ${\rm MgSO_4}$. ${\rm H_2O}$ is called Kieserite.

2. Calcium Sulphate [CaSO₄]

Preparation:

It is prepared in lab by adding dil. H₂SO₄ to the solution of calcium salt.

$$CaCl_2 + H_2SO_4 (dil) \longrightarrow CaSO_4 + 2HCl$$

Properties:

In nature it occurs as Gypsum CaSO₄ . 2H₂O.

When powdered plaster of paris $CaSO_4$. 1/2 H_2O is mixed with the correct amout of water it sets into a solid mass of $CaSO_4$. $2H_2O$ (gysum). The process is used in plastering walls and plasters for fractures.

ALUMS

The general representation of alums is $[(M^1)_2 SO_4][(M^{III})_2 (SO_4)_3]$. $24 H_2 O$ where M^I represents the metal with +1 Oxidation state and M^{III} represents the metal with +3 oxidation state. These alums are double salts, which dissolve in water to give $[M^I (H_2 O)_6]^+$, $[M^{III} (H_2 O)_6]^{3+}$ and SO_4^{2-} ions and therefore., the alums are also represented as $[M^I (H_2 O)_6]$, $[M^{III} (H_2 O)_6]$ (SO_4)₂. They form octahedral crystals.

If M^I is K^+ and M^{III} is Al^{3+} , Then the alum is potash alum $\left(K_2SO_4, Al_2(SO_4)_3.24H_2O_4\right)$ or $\left[K(H_2O)_6\right]\left[Al(H_2O)_6\right]\left(SO_4\right)_2M^1$ can be K^+ , NH_4^+ , Rb^+ , Cs^+ , TL^+ and M^{III} can be Fe^{3+} , Al^{3+} , CO^{3+} , Ga^{3+} , Mn^{3+} . $\left(NH_4\right)_2SO_4.Fe_2\left(SO_4\right)_3.24H_2O$ is called ferric ammonium alum while $K_2SO_4.Cr_2\left(SO_4\right)_3.24H_2O$ is chrome alum. Potash alum on heating dissolves in its own water of crystallisation and on further heating forms $K_2SO_4.Al_2\left(SO_4\right)_3$ called *burnt alum*.

Micro Cosmic Salt [Na(NH₄)HPO₄]

Microcosmic salt is a white crystallion solid and is prepared NH₄Cl and Na₂HPO₄ as follows :

$$NH_4Cl + Na_2HPO_4 \longrightarrow Na(NH_4) HPO_4 \downarrow + NaCl$$

On decomposition the following is obtained:

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} NH_4 \uparrow + NaH_2PO_4$$

 $NaH_2PO_4 \xrightarrow{\Delta} NaPO_3(Calgon) + H_2O$

Microcosmic salt can be used as a substitue for borax in the Bead Test

Similar salt are also formed by Magnesium:

$$\begin{split} & \operatorname{MgSO_4} + \operatorname{NH_4OH} + \operatorname{Na_2HPO_4} \longrightarrow \operatorname{Mg}(\operatorname{NH_4})\operatorname{PO_4} \\ & \operatorname{Mg}(\operatorname{NH_4})\operatorname{PO_4} \stackrel{\Delta}{\longrightarrow} \operatorname{NH_3} \uparrow \operatorname{MgHPO_4} \stackrel{\Delta}{\longrightarrow} \operatorname{Mg_2P_2O_7} + \operatorname{H_2O} \end{split}$$

IMPORTANT THINGS TO REMEMBER

Section - 4

Anomalous properties of Lithium:

The anomalour behaviour of lithium is due to the : (i) exceptionally small size of its atoms and ion, and (ii) high polarizing power (i.e., charge/radius ratio). As a result, there is increased covalent character of lithium compounds which is resposible for their solubility in organic solvents. Further, lithium showns diagonal relationship to magnesium which has been discussed subsequently.

Points of Difference between Lithium and other Alkali Metals:

- (i) Lithium is much harder. Its M.P. and B.P. are higher than the other alkali metals.
- (ii) Lithium is least reactive but the strongest reducing agent among all the alkali metals. On combustion in air it forms mainly monoxide, Li₂O and the nitride, Li₂N while other metals form only oxide.
- (iii) LiCl is deliquescent and crystallizes as a hydrate, LiCl.2H₂O whereas other alkali metal chlorides do not form hydrates.
- (iv) Lithium hydrogencarbonates being unstable is not obtained in the solid form while all other elements form solid hydrogencarbonates.
- (v) Li₂CO₃, LiNO₃, LiOH all form oxide on gentle heating, through the analogus compounds of the rest of the group are stable.

$$4\text{LinO}_3 \longrightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$

 $2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2$

- (vi) Li₂CO₃, LiF and Li₂O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.
- (vii) Lithium is much heavily hydrated than those of the rest of the group.

Points of Similarities between Lithium and Magnesium:

The similarity between lithium and magnesium is particularly striking and arises because of their similar sizes : atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : $Li^+ = 76$ pm, $Mg^{2+} = 72$ pm. The main points of similarity are:

- (i) Both lithium and magnesium are harder and lighter than other element in the respective group.
- (ii) 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, Li₃N and Mg₃N₂, by direct combination with nitrogen.
- (iii) The oxides Li₂O and MgO do not combine with excess oxygen to give any superoxide.
- (vi) The crbonates of lithium and magnesium decompose easily on heating to form the oxides and CO₂. Solid hydrogencarbonates are not formed by lithium and magnesium.
- (v) Both LiCl and MgCl₂ are soluble in ethanol.
- (vi) Both LiCl and MgCl₂ are deliquescent and crystallize from aqueous solution as hydrates. LiCl.2H₂O and MgCl₂.8H₂O

Anomalour Behaviour of Beryll ium:

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

- (i) Beryllium has exceptionally small atomic and ionic sizes and thus does not compare well with other members of the group. Because of high ionization enthalpy and small size it forms compounds which are largely covalent and get easily hydrolysed.
- (ii) The oxide and hydroxide of beryllium, unlike the hydroxides of other elements in the group, are amphoteric in nature.

Diagonal Relationship between Beryllium and Aluminum:

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

- (i) Like aluminium, beryllium is not readily attacked by acids beacuse of the presence of an oxide film on the surface of the metal.
- (ii) Beryllium hydroxide dissolves in excess of alkali to give a beryllate ion, $[Be(OH)_4]^{2-}$ just as aluminium hydroxide give aluminate ion, $[Al(OH)_4]^{-}$.
- (iii) BeCl₂ and AlCl₃ exist in form to chain. BeCl₂ form polymeric chain (chain with a large no. of BeCl₂ molecules) and AlCl₃ forms dimeric chain (chain with two AlCl₃ molecules).
- (iv) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-} , AlF_6^{3-} .

IN-CHAPTER EXERCISE - D

- 1. $NaHCO_3$ and NaOH can not exist together in solution. Why?
- 2. The hydroxide and carbonates of Na and K are easily soluble in water while the corresponding salts of Mg and Ca are sparingly soluble in water. Explain.
- 3. Solvay Process is used to manufacture sodium carbonate but it is not extended to the manufacture of potassium carbonate. Why?
- **4.** Why are MgO and BeO used for the lining of steel making furnance.
- 5. On the treatment with cold water, an element (A) reacted quietly, liberating a colourless, odourless gas (B) and a compound (C). Gas (B) further reacts with element (A) to yield a solid product (D) which reacted with water to give a basic solution (E). (E) is found to be same as (C). When carbon dioxide was bubbled through solution (C) initially a white precipitate (F) is formed, but this redissolved forming solution (G) when more CO₂ was added. Precipitate (F) was heated at 1000°C, a white compound (H) was formed which when heated with carbon at 1000°C, gave a solid (I) of some commercial importance. Name the substances (A) to (I).

HYDROGEN Section - 5

Postion of Hydrogen in the Periodic Table

Hydrogen has electronic configuration 1s¹. On one hand, its electronic configuration is similar to the outer electronic configuration (ns¹) of alkali metals, which belong to the first group of the periodic table. On the other hand, like halogens (with ns² np⁵ configuration belonging to the seventeenth group of the periodic table). it is short by one election to the corresponding noble gas configuration, Helium (1s²). Hydrogen, therefore, has resemblance to alkali metals, which lose one electron to form uni-positive ions, as well as with halogens, which gain one electron to form uni-negative ion. Like alkali metals, hydrogen forms oxides, healides and sulphides. However, unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteistics under normal conditions. In fact, in terms of ionization enthalpy hydrogen resembles more with halogens, $\Delta_i H$ of Li is 520 kJ mol⁻¹, ΔH of F is 1680 kJ mol⁻¹ and $\Delta_i H$ of H

is $1312~{\rm kJ~mol}^{-1}$. Like halogens, if forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds. However, in terms of reactivity, it is very low as compared to halogens. It is always a matter of debate in which group hydrogen should be placed. It is best placed separtely in the periodic table.

Isotpes of Hydrogen

Hydrogen has three isotopes: Protium $({}^1_1H)$, Deuterium $({}^2_1H)$ or D and Tritium $({}^3_1H)$ or T. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen, Protium, has no neutrons. Deuterium (also know as Heavy Hydrogen) has one and Tritium has two neutrons in the nucleus.

The predominant form is Protium. Terrestrial hydrogen contains 0.156% of Deuterium mostly in the form of HD. The Tritium concentration is about one atom per 10^{18} atoms of Protium. Of these isotopes, only Tritium is radioactiver and emits low energy β^- Particles ($t_{1/2}=12.33$ years).

Since the isotopes have the same electronic configuration, they have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthyalpy of bond dissociation.

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10 ⁻¹⁵
Relative atomic mass (g mol ⁻¹)	1.008	2.014	3.016
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.0
Density (g L ⁻¹)	0.09	0.18	0.27

Prepartion of Dihydrogen, H₂

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

Laboratory Preparation of Dihydrogen

1. It is usually prepared by the reaction granulated zinc with dilute hydrochloric acid.

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

2. It can also be prepared by the reaction of zinc with aqueous alkali.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

Sodium Zincate

Commercial Production of Dihydrogen:

1. Electroysis of acidified water using platinum electrodes gives hydrogen. This method gives very pure H₂ but it is very expensive

$$2H_2O(1) \xrightarrow{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

2. It is obtained as a by product in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solutionn. During electrolysis, the reactions that take place are:

At anode:
$$2Cl^{-}(aq) \longrightarrow Cl_{2}(g) + 2e^{-}$$

At cathode:
$$2H_2O(1) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$$

The overall reaction is

$$2Na^{+}\left(aq\right)+2Cl^{-}\left(aq\right)\\ +2H_{2}O\left(l\right) \longrightarrow Cl_{2}\left(g\right)+H_{2}\left(g\right)+2Na^{+}\left(aq\right)+2OH^{-}\left(aq\right)$$

3. Reaction of steam on hydrocarbons or coke at high temperatures in the presence of catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow{1270K} nCO + (2n+1)H_2$$

$$CH_4(g) + H_2O(g) \xrightarrow{Ni} CO(g) + 3H_2(g)$$

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

$$C(s) + H2O(g) \xrightarrow{1270K} CO(g) + H2(g)$$

It is difficult to obtain pure H_2 from water gas, since CO is difficult to remove. Still CO may be liquified at a low temperature under pressure. Thus seperating it from H_2 . One more thing that can be done is the gas mixture can be mixed with steam, cooled to 400° C and passed over iron oxide to give H_2 and CO_2 .

$$CO + H_2O \xrightarrow{Fe} CO_2 + H_2$$

This is called Water - gas shift reaction. This reaction increases the amount of H_2 and gives a method to extract H_2 easily. CO_2 in mixture of CO_2 and H_2 can be removed by dissolving mixture in water under pressure, or reacting mixture K_2CO_3 solution giving KHCO₃, or by scrubbing mixture with sodium arsenite solution.

Physical Properties:

Dihydrogen is a colouless, odourless, tasteless, combustible gas. It is lighter than air and insoluble in water.

Chemical Properties:

The chemical behaviour of dihydrogen (and for that matter any molecule) is determined, to a large extent, by bond issociation enthyalpy. The H-H bond dissociations enthalpy is the highest for a single bond between two atoms any element. It is because of this factor that the dissociation of dihydrogen into its atoms is only $\sim 0.081\%$ around 2000K which increases to 95.5% at 5000K. Also, it is relatively inert at room temperature due to the high H-H bond enthalpy.

1. Reaction with halogens: It reacts with halogens, X_2 to give hydrogen halides, HX.

$$H_2(g) + X_2(g) \longrightarrow 2HX(g)$$
 (X = F, Cl, Br, I)

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

2. Reaction with Dioxygen: It reacts with dioxygen to form water. The reaction is highly exothermic.

$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst of heating}} 2H_2O(l); \quad \Delta H = -285.9 \text{ kJ mol}^{-1}$$

3. Reaction with dinitrogen: It reacts with dinitrogen to form ammonia.

$$3H_2(g) + N_2(g) \xrightarrow{673K, 200atm} 2NH_3(g); \quad \Delta H = -92.6 \text{ kJ mol}^{-1}$$

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

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

$$H_2(g) + 2M(g) \longrightarrow 2MH(s)$$
; where M is an alkali metal

5. Reaction with metal ions and metal oxides: It reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

$$H_2(g) + Pd^{2+}(aq) \longrightarrow Pd(s) + 2H^+(aq)$$

 $yH_2(g) + M_xO_y(s) \longrightarrow xM(s) + yH_2O(1)$

6. Reaction with organic compounds: It reacts with many organic compounds in the presence of catalysts to give useful hydrogenated products of commercial importance. For example: Hydrogenation of vegetable oils using nickel as catalyst give edible fats (margarine and vanaspathinghee).

Uses of Dihydrogen

- The largest single use of dihydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers.
- Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soyabean, cotton seeds etc.
- It is used in the manufacture of bulk organic chemicals, particularly methanol.

$$CO(g) + 2H_2(g) \xrightarrow{cobalt} CH_3OH(l)$$

- It is widely used for the manufacture of metal hydrides.
- It is used a rocket fuel in space research.
- Dihydrgoen is used in fuel cells for generating electrical energy. If has many advantages over the conventional fossil fuels and electric power. It does not produce any pollutions and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

Hydrides

Binary compounds of the elements with hydrogen are called hydrides. The type of hydride which an element forms depends upon its electronegativity and hence on the type of bond formed. Hydrides are conveniently studied under three classes.

- (i) Ionic or salt like hydrides
- (ii) Covalent or molecular hydrides
- (iii) Metallic or interstitial hydrides
- **lonic or salt like hydrides:** These are formed by metals of low electronegativity, i.e. alkali and alkaline earth metals by direct reaction with H₂ and some highly positive members of lanthanide series with the exception of Be and Mg whose hydrides show significant covalent character.

Te stability of the hydrides decreases as the size of the cation increases.

$$LiH > NaH > KH > RbH > CsH$$

 $CaH_2 > SrH_2 > BaH_2$

CaH, is called *Hydrolith*.

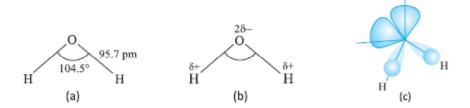
- **Covalent or Molecular hydrides:** These hydrides are formed by all the true non-metals (except zero group elements) and the elements like Al, Ga, Sn, Pb, Sb, Bi. Po, etc., which are normally metallic in nature. The simple hydride of B and Ga are dimeric materials B₂H₆ (diborane) and Ga₂H₆ respectively and the hydride of aluminium is polymeric in nature, (AlH₃)_n.
- Metallic or interstitial hydrides: Many transition and inner-transition elements at elevated temperatures absorb hydrogen into the interstices of their lattices to yield metal-like hydrides, often called the interstitial hydrides. These hydrides are often non-stoichiometric and their composition vary with temperature and pressure. Formulae of some of the hydrides of this class are:

$$TiH_{1.73}$$
, $CeH_{2.7}$, $LaH_{2.8}$, $PdH_{0.60}$, $ZrH_{1.92}$

The interstitial hydrides have metallic appearance and their properties are closely related to those of the parent metal. They posses reducing properties probably due to the presence of free hydrogen atoms in the metal lattice.

Water

In the gas phase water is a bent molecule with a bond angle of 104.5°, and O-H bond length of 95.7 pm. It is a highly polar molecule. Its orbital overlap is shown in figure below. In liquid phase, water molecules are associated together by hydrogen bonds. In ice each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.



Chemical Properties of Water:

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

1. Amphoteric Nature: It has the ability to act as an acid as well as a base i.e., it behaves as an amphoteric substance. In the Bronsted sense it acts as an acid with NH₃ and a base with H₂S.

$$H_2O(1) + NH_3$$
 (aq) $\Longrightarrow OH^-(aq) + NH_4^+(aq)$
 $H_2O(1) + H_2S$ (aq) $\Longrightarrow H_3O^+(aq) + HS^-(aq)$

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

2. Redox Reactions Involving Water: Water can be easily reduced to dihydrogen by highly electropositive metals.

$$2H_2O(1) + 2Na(s) \longrightarrow 2NaOH(aq) + H_2(g)$$

Water is oxidised to O₂ during photosynthesis.

$$6CO_2(g) + 12H_2O(1) \longrightarrow C_6H_{12}O_6(aq) + 6H_2O(1) + 6O_2(g)$$

With fluorine also it is oxidized to O_2 .

$$2F_2(g) + 2H_2O(1) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

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

$$\begin{aligned} &P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4 \text{ (aq)} \\ &\operatorname{SiCl}_4(l) + 2H_2O(l) \longrightarrow \operatorname{SiO}_2(s) + 4HCl(aq) \\ &N^{3-}(s) + 3H_2O(l) \longrightarrow NH_3(g) + 3OH^- \text{ (aq)} \end{aligned}$$

- 4. **Hydrates Formation:** From aqueous solutions many salts can be crystallised as hydrated salts. Water of hydration are water molecules attrached to a compound that can be removed on heating. Such an association of water is of different types viz.,
 - (i) Coordinated water e.g., $\left[Cr(H_2O) \right]^{3+} 3Cl^{-}$
 - (ii) Interstitial water e.g., $BaCl_2$. $2H_2O$
 - (iii) Hydrogen-bonded wate e.e., $\left[\mathrm{Cu}\left(\mathrm{H}_{2}\mathrm{O}\right)_{4}\right]^{2+}\mathrm{SO}_{4}^{2-}$. $\mathrm{H}_{2}\mathrm{O}$ in CuSO_{4} . $\mathrm{5H}_{2}\mathrm{O}$

Here in ${\rm CuSO_4}$. ${\rm 5H_2O}$, four water molecules of hydration are coordinate bonded and one is hydrogen bonded.

Note: You will learn about hyrates later in Coordination Compounds.

*Hard and Soft Water:

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

Hard water forms scum/precipitate with soap. Soap containg sodium strearate ($C_{17}H_{35}COONa$) reacts with hard water precipitate out Ca/Mg strearate.

$$2RCOONa(aq) + M^{2+}(aq) \longrightarrow (RCOO)_2 M \downarrow +2 Na^+(aq)$$
; M is Ca/Mg

e.g.,
$$2C_{17}H_{35}COONa(aq) + Ca^{2+}(aq) \longrightarrow (C_{17}H_{35}COO)_2 Ca \downarrow + 2Na^+(aq)$$

It is, therefore, unsuitable for laundry.

The hardness of water is of two types:

(i) Temporary hardness, and (ii) Permanent hardness.

Temporary Hardness:

Temporary hardness is due to the presence of magnesium and calcium hydrogen-carbonates. It can be easily removed by:

1. **Boiling**: During boiling, the soluble Mg(HCO₃)₂ is converted into insoluble Mg(OH)₂ and Ca(HCO₃)₂ changed to insoluble CaCO₃. These precipitates can be removed by filteration.

$$Mg(HCO_3)_2 \xrightarrow{Heating} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
 $Ca(HCO_3)_2 \xrightarrow{Heating} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$

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

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

 $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$

Note: Temporary hardness such as $Ca(HCO_3)_2$ can also be removed by adding Na_2CO_3 .

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow +2 NaHCO_3$$

Permanent Hardness:

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

1. Treatment with washing soda (Sodium carbonate):

$$MCl_2 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + 2NaCl$$
 $(M = Mg, Ca)$
 $MSO_4 + Na_2CO_3 \longrightarrow MCO_3 \downarrow + Na_2SO_4$
(Washing soda)

2. **Calogen's method**: Sodium hexametaphosphate (Na₆P₆O₁₈), commercially called 'Calgon' or Graham' salt', when added to hard water, the following reactions take place:

$$Na_6P_6O_{18} \longrightarrow 2Na^+ + Na_4P_6O_{18}^{\ 2^-}$$
 $(M = Mg, Ca)$
 $M^{2+} + Na_4P_6O_{18}^{\ 2^-} \longrightarrow [Na_2MP_6O_{18}]^{2^-} + 2Na^+$

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

3. **lon-exchange method**: This method is also called zeolite/permutit process. Hydrated sodium aluminium silicate is zeolite/permut process. For the sake of simplicity, sodium aluminum silicate (NaAlSiO₄) can be written as NaZ. When this is added in hard water, exchange reactins take place.

$$2\text{NaZ}(s) + \text{M}^{2+}(aq) \longrightarrow \text{MZ}_2(s) + 2\text{Na}^+(aq)$$
 (M = Mg,Ca)

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

$$MZ_2(s) + 2NaCl (aq) \longrightarrow 2NaZ(s) + MCl_2 (aq)$$

4. **Synthetic Resins Methods**: It is used in the prodcution of deionised water and more efficient than the Zeolite process.

Water is passed through two differnt ion-exchange columns:

1st Column (Cation Exchange Coloumn):

The resin exchange H⁺ with Na⁺, Ca²⁺ and Mg²⁺

$$\underbrace{re \sin - SO_3H}_{\text{sulphonic acid}} + M^+ \longrightarrow re \sin - SO_3M + H^+$$

2nd Coloumn (Anion Exchange Column):

The resin exchanges OH^- with Cl^- , HCO_3^- , SO_4^{2-}

$$\underbrace{re \sin - NR_4^+OH^-}_{re \sin \text{ with basic}} + X^- \longrightarrow re \sin NR_4^+X^- + OH^-$$

When all reactive sites on resins have been used they can be regenerated by treating first one with dil. H_2SO_4 and second one with Na_2CO_3 solution.

Heavy water, D₂O

It 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:

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$

 $SO_3 + D_2O \longrightarrow D_2SO_4$
 $Al_4C_3 + 12D_2O \longrightarrow 3CD_4 + 4Al(OD)_3$

DEGREE OF HARDNESS

Section - 6

Concentration of Solute in Terms of Parts per Million (or ppm) :

Concentration of solute (in ppm) = mass of solute (in gms) in 10^6 ml solution It is used in determining the hardness of water which is due to the presence of bicarbonates (temporary hardness), chlorides and sulphates (permanent hardness) of Calcium and Magnesium. Degree of Hardness is defined as the number of parts of CaCO₃ or equivalent to other calcium and magnesium salts present in a million (10^6) parts of water.

$$Degree of Hardness = \frac{Mass \ of \ CaCO_3}{Mass \ of \ water} \times 10^6 \ ppm$$

Illustrating the Concept:

How to calculate degree of hardness in a water sample containing 111 ppm of $CaCl_2$?

$$E_{CaCO_3} = \frac{100}{2} = 50$$
 ; $E_{CaCl_2} = \frac{111}{2} = 55.5$

which means 50 gm of $CaCO_3 \equiv 55.5$ gm $CaCl_2$

or
$$55.5 \text{ gm CaCl}_2 \equiv 50 \text{ gm of CaCO}_3$$

$$\Rightarrow$$
 111.0 gm CaCl₂ = 100 gm of CaCO₃ = 100 ppm

Illustration - 1 Calculate the weight of CaO required to remove hardness of 10^6L of water containing 1.62 gm of $Ca(HCO_3)_2$ in 1.0 litre.

Solution:

Consider the reaction between CaO and Ca(HCO₃)₂.

$$CaO + Ca(HCO_3)_2 \longrightarrow 2 CaCO_3 + H_2O$$

From stoichiometry, we have:

1 mole of
$$Ca(HCO_3)_2 \equiv 1 \text{ mole of CaO}$$

$$\equiv$$
 2 moles of CaCO₃

Now moles of bicarbonate in 1.0 L of sample

$$= \frac{1.62}{162} = 0.01 \quad [M_0 \text{ of } Ca(HCO_3)_2 = 162]$$

- \Rightarrow moles of CaO required for 1.0 L of sample = 0.01 (from stoichiometry)
- \Rightarrow moles of CaO required for 10^6 L of water = $0.01 \times 10^6 = 10^4$ moles.
- \Rightarrow grams of CaO= $10^4 \times 56 = 5.6 \times 10^5$ gm.

Illustration - 2 A particular water sample is found to contain 96.0 ppm of SO_4^{2-} and 122.0 ppm of

 HCO_3^- , with Ca^{2+} as the only cation. How many ppm of Ca^{2+} does this water contain?

Solution:

$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

$$Ca(HCO_3)_2 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Every mol of $CaSO_4$ has equal mol of

$$Ca^{2+}$$
 and SO_4^{2-} but every mole of

$$Ca(HCO_3)_2$$
 has Ca^{2+} half the mol of HCO_3^- .

96 ppm =
$$96 \text{ g SO}_4^{2-}$$
 in $10^6 \text{ mL H}_2\text{O}$
= $1.0 \text{ mol of SO}_4^{2-} = 1.0 \text{ mol of Ca}^{2+}$

122 ppm = 122 g
$$HCO_3^-$$
 in 10^6 mL H_2O
= 2.0 mol of HCO_3^- = 1.0 mol of Ca^{2+}

Total
$$Ca^{2+} = 1+1 = 2.0 \text{ mol of } Ca^{2+}$$

$$=80 \,\mathrm{g} \, \ln 10^6 \, \mathrm{mL} \, \mathrm{H}_2\mathrm{O}$$

$$\therefore$$
 Ca²⁺ = 80 ppm

Illustration - 3 A sample of hard water contains 1 mg $CaCl_3$ and 1 mg $MgCl_3$ per litre. Calculate the hardness of water in terms of $CaCO_3$ present in per 10^6 parts of water.

Solution:

55.5 gm
$$CaCl_2 \equiv 50$$
 gm $CaCO_3$ \Rightarrow 1 mg $CaCl_2 \equiv \frac{50}{55.5}$ mg $CaCO_3 \equiv 0.9$ mg $CaCO_3$

47.5 gm MgCl₂ = 50 gm CaCO₃
$$\Rightarrow$$
 1 mg MgCl₂ = $\frac{50}{47.5}$ mg CaCO₃ = 1.05 mg CaCO₃

$$\Rightarrow \qquad \text{Hardness in CaCO}_3 \text{ ppm} = \frac{(0.9 + 1.05) \times 10^{-3} \text{ gm}}{1/1000} = 1.95 \text{ ppm}$$

Illustration - 4 A sample of hard water contains 244 ppm of HCO_3^- ions. What is the minimum mass of CaO required to remove ions completely from 1 kg of such water sample?

Solution:

244 ppm
$$HCO_3^- \equiv 244 \text{ gm } HCO_3^- \text{ in } 1000 \text{ L} \equiv 244 \text{ mg } HCO_3^- \text{ in } 1.0 \text{ L} \equiv 4 \text{ mmoles } HCO_3^- \text{ in } 1.0 \text{ L}$$

$$\equiv 2 \text{ mmoles } Ca(HCO_3)_2 \text{ in } 1.0 \text{ L}$$

$$CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O \implies \equiv 2 \text{ mmoles } CaO \text{ in } 1.0 \text{ L} \equiv 2 \times 56 \equiv 112 \text{ mg } CaO$$

lllustration - 5 250 ml of hard water is treated with 100 ml of 0.1 N Na₂CO₃ to remove temporary hardness. Excess of Na₂CO₃ required 40 ml, 0.1 N HCl for complete neutralization. Calculate degree of hardness of water.

Solution:

Meq of
$$Na_2CO_3$$
 = meq of $Ca(HCO_3)_2$ + meq of HCl in hard water

Meq of $CaCO_3$ formed = meq of $Ca(HCO_3)_2$ = meq of Na_2CO_3 + meq of HCl in hard water

= $100 \times 0.1 - 40 \times 0.1 = 6$

mmoles of $CaCO_3$ formed = $\frac{6}{2}$ = 3 (in factor of $CaCO_3$ = 2)

Mass of CaCO₃ formed =
$$3 \times 10^{-3} \times 100 = 0.3$$
 gm
Mass of hard water sample = 250 gm (Assuming density of water = 1 gm/ml)
Degree of Hardness = $\frac{\text{Mass of CaCO}_3}{\text{Mass of water}} \times 10^6$ ppm
= $\frac{0.3}{250} \times 10^6$ ppm = 1.2×10^3 ppm

IN-CHAPTER EXERCISE - E

- 1. How can the dihydrogen be obtained from coal gasification method? How is its production enhanced?
- **2.** Arrange the following:
 - (i) CaH_2 , BeH_2 and TiH_2 in order of increasing electrical conductance.
 - (ii) LiH, NaH and CsH in order of increasing ionic character.
 - (iii) H H, D D and F F in order of increasing bond dissolciation enthalpy.
 - (iv) NaH, MgH_2 and H_2O in order of increasing reducing property.

NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

SOLUTION TO IN-CHAPTER EXERCISE - D

- 1. $NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$
- 2. It is because hydration energy of group 1 hydroxides and carbonates is higher than lattice energy where as in group 2 hydroxides and carbonates lattice energy dominates hydration energy.
- 3. K_2CO_3 can't be prepared from soluay's process because KHCO₃ formed in the reaction is highly soluble and hence can't be separated from NH₄Cl + KHCO₃ mixture easily.
- 4. MgO and BeO are used for lining of steel making furnance because they are less reactive, have high melting point, good conductivity towards heat and bad conductivity towards electricity.
- 5. Note: Read the question as this:

On the treatment with cold water, an element (A) reacted quietly, liberating a colourless, odourless gas (B) and a compound (C). Gas (B) further reacts with element (A) to yield a solid product (D) which reacted with water to give a basic solution (E). (E) is found to be same as (C). When carbon dioxide was bubbled through solution (C) initially a white precipitate (F) is formed, but this redissolved forming solution (G) when more CO_2 was added. Precipitate (F) effervesced when moistened with conc. HCl acid and gave deep red colouration to the burner flame. When (F) was heated at 1000° C, a white compound (H) was formed which when heated with carbon at 1000° C gave a solid (I) of some commercial importance. Name the substances (A) to (I).

SOLUTION:

(A) is calcium metal which reacts with water and evolves hydrogen (B) and Ca(OH)₂ solution (C).

$$\begin{array}{c} \text{Ca} + 2\text{H}_2\text{O} & \longrightarrow \text{Ca}(\text{OH})_2 + \text{H}_2 \\ \text{(C)} & \text{(B)} \end{array} \text{"Colourless and Odourless gas"} \\ \text{Ca} + \text{H}_2 & \longrightarrow \text{CaH}_2 \\ \text{(B)} & \text{CD)} \end{array} \quad \text{Solid product} \\ \text{CaH}_2 + 2\text{H}_2\text{O} & \longrightarrow \text{Ca}(\text{OH})_2 + 2\text{H}_2 \\ \text{(E)} \\ \text{Ca}(\text{OH})_2 + \text{CO}_2 & \longrightarrow \text{CaCO}_3 & \xrightarrow{\text{CO}_2} & \text{Ca}(\text{HCO}_3)_2 \\ \text{(F)} & \text{(G)} \end{array}$$

$$\text{CaCO}_3 + 2\text{HCl} & \longrightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \qquad \text{"Gives deep red colouration to flame"} \\ \text{CaCO}_3 & \xrightarrow{\Delta} \text{CaO} & \xrightarrow{C} \text{CaC}_2 \\ \text{(F)} & \text{(I)} \end{array}$$

SOLUTION TO IN-CHAPTER EXERCISE - E

1. Reaction of steam on coal at high temperatures in presence of catalyst yields hydrogen. This process is called as coal gasification.

$$C(s) + H_2O(g) \xrightarrow{1270K} CO(g) + H_2(g)$$

Mixing this CO and H_2 gas mixture with steam, cooling to 400° C and passing over iron oxide gives $CO_2 + H_2$ which finally increases the amount of H_2 .

$$CO + H_2 \xrightarrow{Fe} CO_2 + H_2$$

The above reaction is also called as water gas shift reaction.

- 2. (i) $BeH_2(covelent) < TiH_2 < CaH_2$
 - (ii) LiH < NaH < CsH
 - (iii) F F < H H < D D
 - (iv) $H_2O < MgH_2 < NaH$