



- Li, Na, K, Rb, Cs and Fr are called Alkali metals. They are placed in the 1st group of periodic table.
- Francium is highly radioactive.
- > Oxides of these metals dissolve in water giving strong alkalies so the elements are known as alkali metals.

Electronic configuration:

- > These elements belongs to s-block.
- > Valency shell electronic configuration is ns^1 .

Element	Atomic number		Electronic configuration
Li	3	$[He]2s^1$	
Na	11	$[Ne]3s^{1}$	
K	19	$[Ar]4s^1$	
Rb	37	$[Kr]5s^{1}$	
Cs	55	$[Xe]6s^{1}$	
Fr	87	$[Rn]7s^{1}$	

Electronic configuration:

The abundance in earth crust decreases with the increase of atomic weight.

Na> K> Rb> Li> Cs

- > Na and K are 6th and 7th most abundant elements in the earth crust.
- Due to high reactivity, these elements do not occurs in the elementary state.
- > The high reactivity due to the presence of valence electron and lower ionisation potential.
- > Density increases from 'Li' to 'Fr' due to increase in atomic weight.

- > Density order is Li<K<Na<Rb<Cs.
- > The density of potassium is less than sodium due to
 - 1) Sudden large increase in the atomic size
 - 2) Presence of vacant 3d orbital
- > They are soft metals.
- The soft ness increases down the group due to decrease in the strength of the metallic bond.
 - The melting point order is

Li> Na> K> Rb> Cs

• The boiling point order is

Li> Na> K> Cs> Rb

Alkali metals and their salts give flame colouration when heated with conc. HCl, due to absorption of visible light.

- Na Golden yellow
- K Lilac blue
- **Rb Red** violet
- Cs Blue violet
- > The atomic and inoic radii increases with increase in atomic number.
- > The elements have low I.P due to their large atomic size.

> The I.P order of ionization energy is

Li> Na> K> Rb> Cs

- > Lithium is the highest second ionisation potential.
- Electronegativity of the elements decreases down the group, due to increase in atomic size, the electronegative order is.

Li> Na> K> Rb> Cs

Electropositive Nature (or) Metallic Nature:

- > These are most electropositive and further increase down the group.
- > The order of electro positivity is

Li< Na< K< Rb< Cs

- > Most electro positive element is Cs.
- The readily form ionic compounds due to their large atomic size and low ionization potentials.

Valency oxidation states:

The alkali metal atoms show only +1 oxidation state, because their uni-positive ions have the stable.

Inert gas configuration (ns^2np^6) in the valence shell

> These are monovalent elements and readily form M^+ ions.

Conductance:

> They are good conductors of heat and electricity due to the mobility of valence electron.

Hydration of ions:

- All alkali metal salts are ionic [*except lithium*] and soluble in water due to the fact that cations get hydrated by water molecules.
- The amount of heat released when one mole of inoic compound is dissolve in large amount of water is called "hydration energy" (or) heat of hydration. It is exothermic process.
- Smaller the size of cation larger is the extent of hydration and hydration energy.
- > The alkali metal ions exist as hydrated ions $M^+(H_2O)_x$ in the Aqueous solution.

- > In a aqueous solution conductivity increases from $Li^+_{(aq)}$ to $Cs^+_{(aq)}$.
- It is because of the decrease in the size of hydrated cations from Li to Cs.
- > The size of $[Li(H_2O)_x]^+ = 3.40A^0$ and $[Cs(H_2O)_y]^+ = 2.28A^0$
- > The order of hydration enthalpies of alkali metal ions is

 $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

Relative ionic radii:

 $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

Relative ionic radii in water (or) relative degree of hydration.

 $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

NOTE:

> Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated Ex: LiC*l*.2*H*₂O.

Reactivity:

These are highly reactive metals reactivity increase down the group. As they vigorously react with air and water they are stored in inert solvent like kerosene oil. 'Li' is stored by properly packing in paraffin wax coated papers in kerosene.

Action with oxygen (oxides):

- When alkali metals are exposed to air the outer surface is tarnish. It is due to the formation of oxide layer on its surface.
- When alkali metals are heated in air. Li mainly gives Li₂O.
 Sodium mainly gives sodium peroxide (Na₂O₂) and others give super oxides. (KO₂, RbO₂, CsO₂)

- > Sodium forms mono oxides in limited supply of air
 - $4Li + O_2 \longrightarrow Li_2O$ $2Na + O_2 \longrightarrow Na_2O_2$ $K + O_2 \longrightarrow KO_2$ $Rb + O_2 \longrightarrow RbO_2$ $Cs + O_2 \longrightarrow CsO_2$
- The electronic structure of oxide, peroxide and super oxide ions are represented as follows.

$$\begin{bmatrix} \vdots \vdots \vdots \end{bmatrix}^{-2} \qquad \begin{bmatrix} \vdots \vdots \vdots \\ - \vdots \end{bmatrix}^{-2} \qquad \begin{bmatrix} \vdots \vdots \\ - \vdots \end{bmatrix}^{-2} \qquad \begin{bmatrix} \vdots \vdots \\ - \vdots \end{bmatrix}^{-2}$$

> Their oxides dissolve in water to give strong bases.

 $Na_2O + H_2O \longrightarrow 2NaOH \Rightarrow 2Na^+ + OH^-$

> Oxides can be neutralised by acids.

 $Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$

> Peroxides (O_2^{2-}) are the salts of H_2O_2 . There fore metal peroxides will give H_2O_2 on react with water or dil.acids.

 $Na_2O + 2H_2O \longrightarrow 2NaOH + H_2O$

> Concentrated peroxide solution will give O_2 on reaction water. $Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$

- > Na_2O_2 forms octahydrate crystals (Na_2O_2 . $8H_2O_3$).
- $> Na_2O_2$ is also known as oxone.
- > Even K_2O_2 can be used for the same purpose and it is much better than Na_2O_2 .
- $> Na_2O_2$ can be used as oxidising agent.
- Super oxides are coloured and paramagnetic due to the presence of unpaired electron or odd electron bond.
- > The bond order in super oxide is 1.5

$$\left[\begin{array}{c} \vdots \overrightarrow{\mathbf{0}} \cdots \overrightarrow{\mathbf{0}} \vdots \end{array}\right] \longleftrightarrow \left[\begin{array}{c} \vdots \overrightarrow{\mathbf{0}} \cdots \overrightarrow{\mathbf{0}} \vdots \end{array}\right] \longleftrightarrow \left[\begin{array}{c} \vdots \overrightarrow{\mathbf{0}} \cdots \overrightarrow{\mathbf{0}} \vdots \end{array}\right]$$

- The stability of super oxides increase in the size of alkali metal ion due to an increase in lattice energy.
- > CsO_2 is the most stable superoxide its lattice energy is highest due to high coordination number of Cs^+ .
- > The increasing order of stability of super oxides is.

 $LiO_2 < NaO_2 < KO_2 < RbO_2 < CsO_2$

Alkali metal	Monoxide (M ₂ O)	Peroxide (M ₂ O ₂)	Superoxide (MO ₂)
Li	Li ₂ O (White)	-	-
Na	Na ₂ O(White)	Na ₂ O ₂	-
К	K ₂ O(white)	K ₂ O ₂	KO ₂
Rb	Rb ₂ O (Yellow)	Rb ₂ O ₂	RbO ₂ (brown)
Cs	Cs ₂ O(orange)	Cs ₂ O ₂	CsO ₂ (orange)

Name of oxide	formula	oxidatio n no.of oxygen	No. of valences in oxide ion	Magnetic Nature	colour
Monoxide	MO ₂	-2	10	Diamagnetic	No colour
Peroxide	M ₂ O ₂	-1	18	Diamagnetic	No colour
Superoxide	MO, oxides is du	e to $\frac{1}{2}$	al defect.	Para magnetic	orange`

Action with water:

All the alkali metals readily react with water evolving hydrogen due to

 ve E^o values.

 $2M + 2H_2O \rightarrow 2MOH + H_2$

Where M= Li, Na, K, Rb, Cs

- > Li less vigorously react with water even through it has higher ve E_{red}^0 value. The behavior attribute its small size and high hydration enthalpy.
- The reactivity with water increases down the group from Li to Cs. Due to increase in electropositive character.

- The standard electrode potential of lithium is most negative. This is because of high hydration enthalpy of Lithium cation.
- > The order of reactivity with water is

Li< Na< K< Rb< Cs

- > Fires due to alkali metals cannot be controlled by water.
- Alkali metals also react with proton donors such as alcohol, 1 alkynes, and gaseous ammonia.

Action with Hydrogen: (Hydrides)

Alkali metals (M) react with hydrogen directly at 300 - 600⁰ c to form MH type ionic hydrates or saline hydrates.

 $2M + H_2 \rightarrow 2MH$ Where M=Li, Na, K, Rb, Cs

- > All alkali metal hydrates are conic solids with high MP and BP(saline hydrates).
- As the metallic nature increases, ionic nature of hydrates increases, bond length increases.
- > The order of ionic nature of hydrates is

LiH< NaH< KH< RbH< CsH

- > As the bond length increases, thermal stability and bond enthalpy decreases.
- > The order of thermal stability is

LiH> NaH> KH> RbH> CsH

> Hydrates dissolve in water by evolving hydrogen gas.

 $H^- + H_2 O \to H_2 + O H^{\ominus}$

Action with Halogen (Halides):

- > The alkali metals readily react with halogen to form ionic halides (M_x) .
- > Halides of Na and K are present in sea water.
- > Prepared by the direct combination of the element

 $2M + X_2 \rightarrow 2MX$

- > ΔH_f^0 of fluorides decreases down down the group for Chlorides, Bromides, Iodides
- > They are also produced by the action of hydrogen halides on their hydroxides or carbonates.

NaOH+HC $l \rightarrow$ NaCl+ H_2O

 $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

- > Except cesium halides, other halides have face centered cubic lattice.
- Cesium halides have body centered cubic lattice.
- > They have high MP and BP.
- > All halides expect LiF is due to its high lattice energy.
- **CsI** has less stability in water due to low hydration enthalpy.
- They are good electrolytes and conduct electricity in aqueous or molten states.
- Among lithium halides LiF is ionic. The other lithium halides are some what covalent.

Reducing Nature:

- > The alkali metals are strong reducing agents.
- Among alkali metals lithium is the most powerful and sodium is the least powerful reducing agent.
- > The standard electrode potential (E^{\odot}) measure the reducing power.
- > Greater the hydration enthalpy greater the ve E^{\odot} value and hence greater the reducing power.
- > The order of reducing nature of alkali metals is

Li> Cs> Rb> K> Na

- Lithium has least S.R.P $(E^{\odot} = -3.04 V)$ and
- Sodium has lightest S.R.P ($E^{\odot} = -2.72V$)

Solutions in liquid ammonia:

Alkali metals when dissolved in liquid ammonia in the absence of impurities, form a deep blue coloured solution.

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\mathsf{M}+(x+y)NH_3 \to [M(NH_3)_x]^+
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The blue colour of the solution is due to ammoniated (solvated) electrons.

Note:

- In concentrated solution, the blue colour changes, bronze colour and becomes diamagnetic due to cluster formation.
- The solution are paramagnetic and on standing slowly liberated hydrogen resulting in the formation of amide.

$$M^+_{(am)} + e^- + NH_{3_{(liq)}} \rightarrow MNH_{2_{(am)}} + \frac{1}{2} H_{2_{(g)}}$$

- The electrical conductivity of these solutions is by the movement of ions as well as electrons. Hence they are called mixed conductors.
- Due to the presence of free electrons, these solution act as powerful reducing agents.
- From Li to Cr the electropositive nature increases and the reducing nature also increases.

Hydroxides:

• Alkali metals form hydroxides with the formula MC hydroxides are formed when the metals or their oxides react with water.

 $2M + 2H_2O \rightarrow 2MOH + H_2$

 $M_2O + H_2O \rightarrow 2MOH$

M = Li, Na, K, Rb, Cs

- These are strongly basic. Among alkali metal hydroxide. LiOH is a weak base, while the others are strong bases. The strongest of all the bases is CsOH.
- The solubility of the hydroxides increases from LiOH to CsOH.
- The order of basic nature, solubility is

LiOH< NaOH< KOH< RbOH< CsOH

- These are colourless and hydroscopic substances.
- They readily absorb moisture and CO₂ from atmosphere forming white carbonates.

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

• They form alkoxides with alchols. (Alkoxide – "RO")

Salts Of Oxo – acids :

• Oxo – acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom.

Example:

- Carbonic acid H_2CO_3 ; $[OC(OH)_2]$.
- Alkali metals form salts with all the oxo acids, they are generally soluble in water and thermally stable.

• Thermal stability of oxo acids salts of alkali metals increases down to the group as the electro positive character increases.

Anomalous Behaviour:

- The deviation in properties of element when compared to the properties of elements of the same group is known as anomalous behaviour.
- In alkali metals Li exhibits anomalous behaviour due to
 - 1. small atomic and inoic size
 - 2. High polarising power (i.e., charge / radius ratio)
 - 3. Absence of vacant d- orbitals
 - 4. High electronegativity

Anomalous Behaviour of Lithium:

- Lithium is much harder, while other alkali metals are soft and can be cut with knife.
- Its M.P and B.P are higher than the other alkali metals.
- Most of the Lithium compounds are covalent but other compounds are ionic.
- Lithium is least reactive.
- Lithium compounds are less soluble in water.
- Lithium is the strongest reducing agent among all the alkali metals in aqueous solutions.

- LiOH is a weak base.
- In air 'Li' forms mainly monoxide, $(Li_2 O)$ and the nitride, $(Li_3 N)$. $6 Li + N_2 \rightarrow 2 Li_3 N$, $4 Li + O_2 \rightarrow 2Li_2 O$
- LiCl is deliquescent (absorbs more moisture and turns to liquid) and crystallises as a hydrate salt (LiCl $\cdot 2H_2O$) where as other alkali metal chlorides do not form hydrates.
- *LiHCO*₃ is not obtained in the solid form while all other elements form solid hydrogen carbonates.
- Li can not form acetylide on reaction with acetylene where as other elements can form acetylides.

• Lithium nitrate when heated gives lithium oxide, *Li*₂*O*, where as other alkali metal nitrates decompose to give the corresponding nitrate.

 $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ $2NaNO_3 \rightarrow 2NaO_2 + O_2$

- LiF and *Li*₂*O* are comparatively much less soluble in water.
- Directly combines with carbon to form carbide.
- Li_2CO_3 on heating decomposes to Li_2O and CO_2 while other carbonates are thermally more stable do not decompose.

 $Li_2CO_3 \rightarrow Li_2O + CO_2$

Diagonal relationship with magnesium:

• Lithium shows diagonal relationship with magnesium.

The similarity in properties between lithium and magnesium arises because of their similar sizes, polarising power.

Atomic radii	ionic radii
Li=152 pm,	$Li^+ = 76pm$
Mg=160 pm,	$Mg^{2+} = 72pm$
The main points of similarity are:

- Both lithium and magnesium are harder and lighter than other elements in the respective groups.
- Lithium and magnesium react slowly with water and liberate hydrogen gas.

 $2Li + 2H_2O \rightarrow 2LiOH + H_2$ Mg+2H₂O \rightarrow Mg(OH)₂ + H₂

- Oxides and hydroxides are much less soluble.
- Their hydroxides decompose on heating.
- Both form a nitride, Li_3N and Mg_3N_2 by direct combination with nitrogen.

 $6Li + N_2 \rightarrow 2Li_3N$

 $3Mg + N_2 \rightarrow Mg_3N_2$

- The oxides *Li*₂*O* and MgO do not combine with excess oxygen to give any superoxide.
- The carbonates of lithium and magnesium de compose easily on heating to form the oxides and *CO*₂.

 $Li_2CO_3 \rightarrow Li_2O + CO_2$

 $MgCO_3 \rightarrow MgO + CO_2$

- Both elements can not form solid bi carbonates.
- Both LiCl and MgCl₂ are soluble in ethanol.
- Both LiCl and $MgCl_2$ are deliquescent and crystalise from aqueous solution as hydrates.

LiCl.2 H_2O and $MgCl_2.8H_2O$

• Alkyl lithium (Li^+R^-) are similar to grignald reagents in organic synthesis.

Sodium Carbonate:

- Anhydrous sodium carbonate (Na_2CO_3) is called soda ash (or) soda.
- Sodium carbonate deca hydrate (Na_2CO_3) is called washing soda or salt soda.
- It is prepared by.

1. Solvay or ammonia soda process

Solvay process (or) Ammonia soda process:

Raw materials: Brine, Lime stone, Little NH₃.
 By – product : CaCl₂
 Intermediate products: NaHCO₃
 Recycled products : NH₃ and CO₂
 Impurities in brine solution: Calcium & magnesium salts

- They are removed in the form of carbonate precipitate.
- Precipitation of NaHCO₃ in carbonation tower is due to common ion effect.

Solution from carbonation tower.

Consists of : NaHCO₃ & NH₄Cl

Recovery of *NH*₃:

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

Principle:

Reactinos: $NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$ $NH_3HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$ $2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$

- It is suitable method to prepare Na_2CO_3 .
- K_2CO_3 can not be manufactured by solvay's process because $KHCO_3$ is more soluble in water.

Properties of *Na*₂*CO*₃**:**

- It is a white crystalline solid.
- It loses its water of crystallization when exposed to atmosphere of crumbles to powder i.e., efflorescent nature.

It loes water in four stages.

 $Na_{2}CO_{3}.10H_{2}O \longrightarrow Na_{2}CO_{3}.7H_{2}O \longrightarrow Na_{2}CO_{3}.4H_{2}O$ $Na_{2}CO_{3}.H_{2}O \xrightarrow{\Delta} Na_{2}CO_{3}$ $Na_{2}CO_{3}.H_{2}O \xrightarrow{\Delta} Na_{2}CO_{3}$

- Anhydrous sodium carbonate is thermally stable.
- It dissolves in water with the liberation of heat.
- It aqueous solution is basic due to anionic hydrolysis of CO_3^{2-} .

 $CO_3^{2-} + H_2O \longrightarrow HCO_3^{-} + OH^{-}$

$$CO_3^{2-} + 2H_2O \longrightarrow H_2CO_3 + 2OH^-$$

Note:

• 1 mole Na_2CO_3 gives 2 moles OH^- ions during hydrolysis.

Its aqueous solution gives pink colour with phenolphthalein indicator and yellow colour with methyl orange indicator.

Uses of Na_2CO_3 :

- It is used in the manufacture of glass, caustic soda and water glass, Borax, Soap powder.
- It is used for softening of hard water.
- It is used in laundries, paper and dye industry.
- It is used in sizing of paper.
- It is used in petrolium refining.
- It is used in the preparation of ultramarine.
- It is used in the qualitative and quantitative analysis.

Sodium chloride NaCl:

- The most abundant source of sodium chloride is sea water which contains 2.7 to 2.9% by mass of the salt.
- If the form of rock salt it exists as mineral.
- Crude sodium chloride, generally obtained by crystallisation of brine solution, contains sodium sulphate, calcium chloride and magnesium chloride as impurities.
- It is slightly hygroscopic due to presence of impurities like $CaCl_2$ and $MgCl_2$.
- To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered.

- The solution is then is then saturated with HCl gas.
- Crystals of pure NaCl separate out calcium and magnesium chloride being more soluble than sodium chloride remain in solution.
- NaCl melts at 1081 K. it has a solubility of 36gr in 100gr of water at 273K. The solubility does not increase appreciably with increase in temperature.

Uses :

- It is used as a common salt (or) table salt for domestic purpose.
- It is used for the preparation of Na_2O_2 , NaOH and Na_2CO_3 .

Sodium Hydroxide (or) Caustic soda:

• It is manufactured by

Castner – Kellner process (or) Mercury cathode process

- NaOH obtained by the electrolysis of brine solution.
- A rectangular iron tank, divided into three compounds by two slate suspended partitions which do not touch the bottom in electrolytic cell.
- The bottom of the tank is covered with mercury.
- NaCl solution is taken in the outer compartments and dil NaOH is taken in the central compartments.

- Two graphite electrodes are placed in the outer compartments act as anode.
- Hg acts as cathode in the outer compartments and anode in the central compartment. Hg is the intermediate electrode by induction effect.
- A series of iron rods suspended in the central compartment act as anode.
- In the outer compartments Cl^- ions are oxidised and Cl_2 is liberated at the graphite electrodes.
- Na^+ ions gain the electrons at the Hg cathode to form sodium amalgam.
- After reaching the central compartment sodium amalgam reacts with H_2O to produce NaOH and H_2 which is liberated at iron cathode.

• 20% NaOH is formed in the central compartment reactions during electrolysis.

In the outer compartment:

Ionisation of brime: $2NaCl \rightarrow 2Na^+ + 2Cl^-$

At graphite Anode: $2Cl^- \rightarrow Cl_2 + 2e^{\ominus}$

At Hg Cathode: $Na^+ + e^{\ominus} + Hg \rightarrow NaHg$

In the middle compartment:

At Hg anode: $NaHg \rightarrow Na^+ + e^{\ominus} + Hg$ At iron cathode: $2Na^+ + 2e^{\ominus} + 2H_2O \rightarrow 2NaOH + H_2$ • In stand of H₂ gas, Sodium is formed in the outer compartments because the discharge potential of sodium is lowered in presence of Hg cathode.

Properties of NaOH

- * It is white crystalline solid with soapy touch.
- It is highly deliquescent (absorb moisture turns to liquid)
- It dissolves in water with the liberation of heat due to the formation of hydrates. NaOH.nH₂O. (n = 1, 2, (or) 7
- * It decomposes the body proteins and makes a paste. Hence it is called caustic soda .

Uses of NaOH

- * It is used in soap, paper, artificial silk and textile Industries.
- ✤ It is used in the purification of Bauxite.
- ***** used in the preparation of NaClO, NaClO₃, Na₂CO₃ etc
- ✤ It is used in the petroleum refining.
- ✤ It used for mercerizing cotton.
- * It is used in the preparation of alumina, phosphates and silicate glass etc.
- * It is used to absorb SO_2 from atmosphere near power generation.
- ✤ It is used in cleaning glass ware in the laboratory.

NaHCO₃ sodium bi carbonate (or) Baking soda

- * It is preparation by Solvay's' process
- ★ It is also obtained by saturating Na_2CO_3 solution with CO_2 $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$
- ✤ It is slightly soluble in water
- It's aqueous solution is slightly basic due to less extent of hydrolysis of HCO₃.
- NaHCO₃ solution gives Yellow colour with methyl orange indicator and it does not give any colour with phenolphthalein indicator. Which is used to distinguish Na₂CO₃ & NaHCO₃.

* On heating it decomposes to give Na_2CO_3 2 $NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$

Uses

- > It is used as a fire extinguisher
- Used as an antacid, mild antiseptic for skin infections.
- It is used in making baking powders.
- > It is used in the preservation of butter.
- It is used in the effervescent drinks.

Biological importance of Na⁺ & K⁺ : -

- ➢ Na⁺, K⁺ helps in maintaining the osmotic pressure in the cell
- The transport activity Na⁺ ions is known as Sodium pump. But K⁺ ions are not pumped out. The emery required for pumping out of Na⁺ ions or taking K⁺ ions or H+ is provide by the hydrolysis of ATP to ADP.
- ➢ Na⁺ ions are useful for the movement of glucose into the cell
- ➤ The K⁺ ions are essential for the metabolism of glucose in the cell
- K+ ions are also useful in the synthesis of proteins and activation of certain enzymes.



Ionization Enthalpy and Electropositive or Metallic Character

- a) Since the atomic size decrease along the period and the nuclear charge increase and thus electrons are more tightly held towards nucleus. It is therefore alkaline earth metals have higher ionisation energy (IE₁) in comparison to alkali metals but lower ionisation energies in comparison of corresponding p block elements.
- b) The ionisation energy of alkaline earth metals decrease from Be to Ba due to increase size.

Alkaline earth metal	Ве	Mg	Са	Sr	Ва	Ra
First ionization energy (KJ mol ⁻¹)	899.5	737.7	589.8	549.5	502.9	509.4
Second ionisation energy (KJ mol ⁻¹)	1757.1	1450.7	1145.4	1064.3	965.2	979.06

(c) No doubt first ionisation energy of alkaline earth metals are higher than alkali metals but a closer look on 2nd ionisation energy of alkali metals and alkaline earth metals reveals that IE2 of alkali metals are higher than alkaline earth metals.

Li Be 1st ionisation energy (kJ mol⁻¹) 520 899 2nd ionisation energy (kJ mol⁻¹) 7296 1757 It may be explained as : Li : $1s^2$, $2s^1$ Removal of 2s electron Li⁺ : $1s^2$ Removal of 1s electron Li²⁺ : $1s^1$ Be : $1s^2$, $2s^2$ Removal of 2s electron Be⁺ : $1s^2$, $2s^1$ Removal of 1s electron Be⁺ : $1s^2$, $2s^1$ Removal of 1s electron Be²⁺ : $1s^2$ The removal of 2nd electron in alkali metals takes place from (n-l)th subshell which is more closer to the nucleus and thus more energy is required to remove the electron, whereas removal of 2nd electron from alkaline earth metals takes from ns-subshell.

- (d) All these possess strong electropositive character which increases from Be to Ba.
- (e) These are less electropositive than alkali metals as the later have low ionisation energy.
- (f) Thus, for alkaline earth metals Be < Mg < Ca < Sr < Ba < Ra

Increasing order of electropositive character,

metallic character and reactivity

Reaction with liquid NH₃₍₁₎

(a) Like alkali metals, alkaline earth metals also dissolve in NH3(ij giving bronze coloured solution, when concentrated, and bright blue solution, when dilute. Bright blue colour is due to ammoniated electrons while bronze colour is due to formation of metal ion clusters.

M + (x + 2y)NH₃→ [M(NH₃)X]²⁺ + 2[e(NH₃)_y]⁻
[e(NH₃)_y]⁻ → NH₂⁻ +
$$\frac{1}{2}H_2$$
 + (y - 1)NH₃

(b) These solutions are unstable and decompose slowly to give amides and H₂. Reaction is accelerated by transition metal atoms/ions. On evaporation, these solutions give hexa-ammoniates (Unlike solutions of alkali metals which give metal), which are decomposed to amides.

 $M(NH_3)_6 \rightarrow M(NH_2)_2 + 4NH_3 + H_2$

NOTE :

- SO₂ on passing through limewater of barya wáter also gives white ppt. Of CaSO₃ and BaSO₃.
- Bicarbonates of alkali metal are found in solid state whereras bicarbonates of alkaline earth metals exists only insolution state. Bicarbonates of other metals are not known.
- The

ALKALI METALS

OBJECTIVES QUESTIONS PREVIOUS COMPETATIVE QUESTIONS

- 1) White metal is an alloy of
 - 1) Na, Mg
 - 2) Na, Pb
 - 3) Li, MgJ Li, Pb

- Assertion(1): Alkali metals are soft and have low melting and boiling points Reason(R): This is because interatomic bonds are weak (AP EAMCET-2015)
 - 1) Both A and R are true and R is the correct explanation of A
 - 2) Both A and R are true and R is not the correct explanation of A
 - 3) A is true but R false



3) Which lithium halide is soluble in Pyridine TS- M -2015

LiF
 LiCl
 Lil

- *5)* En
- 4) LiBr

4) The correct statement for the molecule Csl₃, is : [JEE MAINS – 2014]
1) It is covalent molecule
2√It contains Cs⁺ and I₃⁻ ions
3) It contains Cs³⁺ and I⁻ ions
4) It contains Cs⁺, I⁻ and lattice I₂ molecule

Solution :

It Contains $Cs^+ \& I_3^-$ ions

5) KO₂ exhibits paramagnetic behaviour. This is due to the paramagnetic nature of : [E – 2014]

1) K⁺

2) O_2 $\checkmark O_2^-$

4) KO⁻

Solution :

 O_2^- contains unparied e^-

6) The solubility order for alkali metal fluoride in water is : .. (JEE MAINS ONLINE - 2013)
1) LiF > NaF < KF > RbF
→ RbF < KF < NaF < LiF
3) LiF < RbF < KE < LiF
4) LiF < NaF < KF < RbF

Solution :

The solubility order is RbF < KF < NaF < LiF

7) Which one of the following elements reduces NaOH to Na ? (E- 2012)

Si
 Pb
 C
 Sn

Solution :

Carbon reduces NaOH to Na

3) F_2 + NaOH (conc.) \rightarrow 4) Zn + NaOH(aq) \rightarrow

Solution :

- 1) $2AI + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
- 2) Carbon cannot liberate ' H_2 ' gas
- 3) $F_2 + 6 \text{ NaOH} \rightarrow 5 \text{NaF} + \text{NaOF} + 3H_2$
- 4) $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$
9) Which one of the following order represents the correct sequence of the increasing basic nature of the given oxides.. (A- 2011)
1) K₂O < Na₂O <Al₂O₃ <MgO
Al₂O₃ <MgO <Na₂O <K₂O

 $3) MgO < K_2O < Al_2O_3 < Na_2O$

4) $Na_2O < K_2O < MgO < Al_2O_3$

Solution :

Al₂O₃ is Amphoteric nature Alkaline earth metal oxides are weak bases (MgO) Alkaline earth metal oxides are strong bases (Na₂O, K₂O) 10) In which of the following reactions hydrogen is not liberated ? (E- 2011)
1) Reaction with fused NaOH with C
S Reaction of NaOH with sulphur
3) Heating the Conc. NaOH with Si.

4) Reaction with Zn with NaOH

Solution :

NaOH with sulphur 'H₂' gas is not liberated

 $4S + 6NaOH \rightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$ Sodium thio sulphate 11) Solvay process is used in the manufacture of : ... (E- 2010)
1) K₂CO₃
2) KHCO₃
3) Na₂CO₃
4) CaCl₂

Solution :

Solvay process is used in the manufacture of Na₂CO₃

- 12) Which one of the following is formed apart from sodium chloride when chlorine reacts with hot concentrated sodium hydroxide ? (E- 2010)
 - 1) NaOCI 2) NaClO₃ 3) NaClO₃ 4) NaClO₄ Solution :

 $Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

13) The set representing the correct order of ionic radius is ...(A- 2009)

4) $Li^+ > Be^{+2} > Na^+ > Mg^{+2}$

Solution :

 $Na^+ > Li^+ > Mg^{+2} > Be^{+2}$

- 14) Aluminum reacts with NaOH and forms compound 'X'. If the co-ordination number of Al in 'X' is 6, the correct formula, of X is ... (E- 2009)
 - 1) $[Al(H_2O)_4(OH)_2]^+$
 - 2) $[Al(H_2O)_3(OH)_3]$
 - $\mathbf{\mathcal{J}}[Al(H_2O)_2(OH)_4]^{-1}$
 - 4) $[Al(H_2O)_6](OH)_3$

15) The correct order of stability for the following superoxides is ... (M- 2008)
1) KO₂ > RbO₂ > CsO₂
2) RbO₂ > CsO₂ > KO₂
3) CsO₂ > RbO₂ > KO₂
4) KO₂ > CsO₂ > RbO₂
Solution :

size of cation increase stability of oxide is also increases.

- 16) Which of the following statements are correct for alkali metal compounds.. (M- 2008)
 - i) Superoxides are paramagnetic in nature
 - ii) The basic strengths of hydroxides increases down the group
 - iii) The conductivity of chlorides in their aqueous solutions decreases down the group
 - iv) The basic nature of carbonates in aqueous solutions is due to cationic hydrolysis
 - 1) i, ii and iii only2) i and ii only
 - 3) ii, iii and iv only4) iii and iv only

Solution :

The basic nature of carbonates in aqueous solutions is due to anionic hydrolysis

KEY: 2

17) Which of the following is not correct? (M- 2007)
1) In Nelson method of NaOH preparation Cl₂ is liberated anode
With hot and concentrated NaOH, Cl₂ gas gives NaOCl
3) NaOH reacts with white phosphorous giving phosphine
4) NaOH is used in rayon industry

Solution :

 $3Cl_2 + 6NaOH(con3) \rightarrow 5NaCl + NaClO_3 + 3H_2O$

18) Which of the following pair cannot exist together in solution ? (E- 2007)
1 NaHCO₃ + NaOH
2) Na₂CO₃ + NaOH
3) Na₂CO₃ + NaCl
4) NaHCO₃ + NaCl

Solution :

NaHCO₃ has replaceable hydrogen

19) Which of the following carbonates decompose readily at low temperatures ? (M- 2007)
1) Na₂CO₃
2) K₂CO₃
3) Li₂CO₃
4) Rb₂CO₃
Li₂CO₃ △ Li₂O + CO₂

20) The ionic mobility of alkali metal ions in aqueous solution is maximum for .. (A- 2006)

1) Li⁺
 2) Na⁺
 3) K⁺
 4 Rb⁺

Solution : Due to decrease in hydration enthalpy

21) Based on lattice energy and other considerations which one of the following alkali metal chlorides is expected to have the highest melting point ? (A - 2005)

KbCl	2) KCl		
3) NaCl	4) LiCl		

Solution :

RbCl had highest melting point

22) Which one of the following will react most vigorously with water ..

1) Li 2) Na 3) K 4 Rb

Solution :

Down the group electro positive character increases so reactivity also increases

23) Based on lattice energy and other considerations, which one of the following alkali metal chloride is expected to have the highest melting point ? ..

1) NaCl	2) LiCl		
🐳 RbCl	4) KCl		

Solution :

RbCl has high melting point due to strong electrostatic force of attraction

- 24) Fire extinguishers contains H₂SO₄ and which one of the following.....
 - a) NaHCO₃
 - **VaHCO**₃ and Na₂CO₃
 - $3) Na_2CO_3$
 - 4) CaCO₃

Solution :

Fire extinguishers contains H₂SO₄ and a mixture of NaHCO₃ & Na₂CO₃

- 25) Which of the following statement about Na_2O_2 is not correct?
 - 1) It is diamagnetic in nature
 - 2) It is a derivative of H_2O_2
 - 3) Na_2O_2 Oxidises Cr^{3+} to CrO_4^{2-} in acid medium
 - **W** It is super oxide of sodium

26) Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compounds with the greatest and the least ionic character, respectively are :

1) LiCl and RbCl
 RbCl and BeCl₂
 3) MgCl₂ And BeCl₂
 4) Rbcl And MgCl₂

ALKALINE EARTH METALS

OBJECTIVE QUESTIONS OF PREVIOUS COMPETETIVE QUESTIONS

1) Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ?

(JEE MAINS-2015) 1) CaSO₄ 3) BeSO₄ 3) BaSO₄ 4) SrSO₄ Solution :

BeSO₄ has greater hydration energy than lattice energy

2) The correct order of thermal stability of hydroxide is: (JEE MAINS-2015)
1) Ba(OH)₂ <Sr(OH)₂ <Ca(OH)₂ <Mg(OH)₂
2) Ba(OH)₂ <Ca(OH)₂ <Sr(OH)₂ <Mg(OH)₂
3) Mg(OH)₂ <Ca(OH)₂ <Sr(OH)₂ <Ba(OH)₂
4) Mg(OH)₂ <Sr(OH)₂ <Ca(OH)₂ <Ba(OH)₂

Solution :

The thermal stability of hydroxides increases down the group

3) Which of the alkaline earth metal halides given below is essentially covalent in nature? (JEE MAINS-2015)



4) Equimolar solutions of the following compounds are prepared separately in water. Which will have the lowest pH value ?.. (JEE MAINS ONLINE -2013)

1) **BeCl₂**

2) SrCl₂

3) CaCl₂

4) MgCl₂

Solution :

pH will be highest for $BeCl_2$ as it produces strong acid HCl and weak base $Be(OH)_2$.

Down the group basic nature increases.

As a result acidic strength decreases due to neutralization of acid by base Higher the hydrogen ion concentration lower the pH.



5) In which of the following exothermic reactions, the heat liberated per mole is the highest ?

1) $CaO + H_2O \rightarrow Ca(OH)_2$

2) SrO + H₂O \rightarrow Sr(OH)₂

3) $BaO + H_2O \rightarrow Ba(OH)_2$

4) MgO + H₂O \rightarrow Mg(OH)₂

Solution :

All the reactions are exothermic w.r.t. to dissolution of IIA group oxides. Down the group atomic size increases.

Hence hydration energy decreases. BeO and MgO are not soluble in water under ordinary conditions due to their high lattice energies. BeO is amphoteric while MgO is weaky basic and down the group basic nature increases. The solubility of hydroxides increases down the group.

6) Which of the following on thermal decomposition yields a basic as well as an acidic oxide ? (E-2012)

 $4 \text{ (CaCO}_3 \quad 2) \text{ NH}_4 \text{NO}_3 \quad 3) \text{ NaNO}_3 \quad 4) \text{ KClO}_3$

Solution :

$$\begin{array}{c} \mathbf{CaCO}_{3} \xrightarrow{\Delta} \mathbf{CaO} + \mathbf{CO}_{2} \\ & \text{Basic} \\ & \text{oxide} \end{array} \xrightarrow{Acidic} \\ & \text{oxide} \end{array}$$

7) Which of the following is NOT correct ?

LiOH is a weaker base than NaOH
Salts of Be undergo hydrolysis
Ca(HCO₃)₂ is soluble in water
Hydrolysis of beryllium carbide gives acetylene

(E-2012)

Solution :

 $Be_2C + 4HOH \rightarrow 2Be(OH)_2 + CH_4\uparrow$

8) The no. of types of bonds between carbon atoms in calcium carbide is .. (A-2011)



3) Two sigma, one pi

2) One sigma, one pi

4) Two sigma, two pi

Solution :



- 9) The reactivity of Ca, Sr, Mg and Ba with water follow the order.... (E-2011)
 - 1) Sr > Ba > Mg > Ca
 - $\mathbf{A} \mathbf{B} \mathbf{a} > \mathbf{S} \mathbf{r} > \mathbf{C} \mathbf{a} > \mathbf{M} \mathbf{g}$
 - 3) Ca > Mg > Ba > Sr
 - 4) Sr > Ca > Mg > Ba

Solution :

Order of Reactivity is Be < Mg < Ca < Sr < Ba

10)Which of the following metal ions plays an important role in muscle contraction... (M-2011)



2) Na⁺





Ca⁺² helps in muscle contraction

11) Match the following.

List-1(Minerals)				List-2 (Composition)					
1) Dolomite				1) CaCO ₃					
2) Fluorapatite			2) 2BeO.SiO ₂						
3) Phen	acit	e		3) SrS	SO ₄				
4) Celes	site			4) Ca	CO ₃	. Mg	CO ₃		
The correct answer is		5) 3Ca ₃ (PO ₄) ₂ . CaF ₂							
Α	B	C	D	Α	B	C	D		
1) 4	5	3	2	3) 4	5	1	2		
2) 5	4	2	3	4) 4	5	2	3		

Solution :

CaCO₃. MgCO₃ ------ dolomite $3Ca_3(PO_4)_2$. CaF₂ ------ Fluorapatite $2BeO. SiO_2$ ------ phenacite $SrSO_4$ ------ celesite Key: 4

- 12) The set representing the correct order of ionic radius is ... (A-2009)
 - 1) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
 - $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
 - 3) $Li^{2+} > Na^+ > Mg^{2+} > Be^{2+}$
 - 4) Mg²⁺>Be²⁺>Li⁺>Na⁺


- 14) Which one of the following is the correct statement..... (A-2008)
 - 1) Beryllium exhibits coordination number of six
 - Chlorides of both beryllium and aluminum have bridged chloride structure in solid phase
 - 3) B₂H₆. 2NH₃ is known as inorganic benzene
 - 4) Boric acid is protonic acid

 15) The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K⁺, Ca²⁺, Mg²⁺, Be²⁺? (A-2007)

1) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

2) $Mg^{2+} < K^+ < Ca^{2+} < Mg^{2+}$

3) Be²⁺ < K⁺ < Ca²⁺ < Mg²⁺

 $\sqrt{K^+} < Ca^{2+} < Mg^{2+} < Be^{2+}$

- 16) Among the following which is water insoluble ? (E-2007)
 - 1) Sodium fluoride
 - 2) Potassium fluoride
 - 3) Beryllium fluoride
 - **Magnesium fluoride**

Solution :

Except BeF₂; all alkaline earth metal fluorides are insoluble in H_2O .

17) Element with atomic number 38, belongs to ... (M-2007)
11 A group and 5th period
2) II A group and 2nd period
3) V A group and 2nd period
4) III A group and 5th period

Solution :

Sr – belong to 5th period & 2nd A group

18) What are the metal ions present in carnallite... (E-2006)

Solution :

KCl.MgCl₂.6H₂O -----carnallite



20) One mole if magnesium nitride on the reaction with an excess of water gives : (A-2004)



2) One mole of nitric acid

3) One mole of ammonia

4) Two moles of nitric acid

Solution :

 $2Mg_3N_2 + 12H_2O \rightarrow 6Mg(OH)_2 + 2NH_3\uparrow$

One mole of Mg_3N_2 on Reaction with excess of H_2O release "2" moles of NH_3 gas.

21) In curing cement plasters water is sprinkled from time to time. This helps in ... (A-2003)

WDeveloping interlocking needle-like crystals of hydrated silicates

2) Hydrating sand and gravel mixed with cement

3) Converting sand into silicic acid

4) Keeping cool

22) The substance not likely to contain CaCO₃ is (A-2003) Calcined gypsum

2) Sea shells

3) Dolomite

4) A marble statue

Solution :

CaSO₄; CaCl₂ in H₂O gives permanent Hardness.

- 23) The solubilities of carbonates decrease down the magnesium group due to a decrease in ... (A-2003)
 - **W**Hydration energies of cations
 - 2) inter-ionic attraction
 - 3) Entropy of solution formation
 - 4) Lattice energies of solids

Solution :

Solubility ∝ Hydration energy of cation

24) Which one of the following processes will produce hard water.... (A-2003)

1) Saturation of water with MgCO₃

Saturation of water with CaSO₄

3) Addition of Na₂SO₄ to water

4) Saturation of water with CaCO₃

Solution :

CaSO₄; CaCl₂ in H₂O gives permanent Hardness.

25) A metal M readily forms its sulphate MSO₄ which is water soluble. It forms its oxide MO which becomes inert on heating. It forms an insoluble hydroxide M(OH)₂ which is soluble in NaOH solution. Then M is (A-2002)

Mg
 Ba
 Ca

4) Be

Solution :

BeSO₄ ------water soluble BeO ------inter towards Heating BeO + HOH \rightarrow Be(OH)₂ Amphoteric (Insoluble) Be(OH)₂ + 2NaOH \rightarrow Na₂BeO₂ + 2H₂O Sodium Beryllote





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