ALKALI METALS

SYNOPSIS

* Lithium (Li), Sodium (N1), Potassium (K), Rubidium (R2), Cesium (Cs) and Francium (Fr) are called Alkali metals.
* Francium is highly radioactive. Its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes.
* Oxides of these metals dissolve in water giving strong alkalis. So these elements are known as alkali metals.
* Abundance: The abundance in earth crust decreases with the increase in atomic weight.
* Electronic configuration: These elements belong to s-block and their valence shell configuration is ns^1.
* No element contains 18 electrons in their (n-1) shell.
* Atomic volume: Atomic volume of alkali metals is highest in each period and goes on increasing down the group

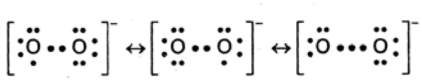
Element	Li	Na	K	Rb	Cs
GMV in cm^3	13	24	46	56	71

* Density: These elements have low densities when compared with the other metals.
* Potassium is less dense than sodium due to
  1. Sudden large increase in the atomic size from Na to K.
  2. The presence of vacant d-orbitals
  3. Large inter0atomic distances in the crystal lattice.
* Most electro positive element is Cs.
* Hardness: These are soft metals. Softness further increases down the group due to decrease in the strength of metallic bond.
* Valency & oxidation states: The alkali metal atoms show only +1 oxidation state, because their unipositive ions have the stable inert gas configuration $\left(s^2 or\ s^2P^6\right)$ in the valence sheall.
* Nature: Alkali metal ions (in the form of salts) are colorless and diamagnetic, since all the electrons are paired. Some of their compounds like $K_2Cr_2O_4, KMnO_4$ are colored which is due to their oxyanions.
* Second ionization potential values of alkali metals are very high, because the second electron is to be removed from the ion with stable inert gas configuration.
* Flame test: Alkali metals and their salts give flame colouration when heated with conc. HCl in Bunsen flame.
* Exhibit colour due to absorption of visible light.
* The characteristic flame colours of alkali metals are

Metal	**Colour**	λ **in** A^0
LI	Crimson red	6708
Na	Golden Yellow	5890
K	Lilac Blue	4404
Rb	Red-Violet	4202
Cs	Blue-Violet	4556

* The melting points order is
  $Li > Na > K > Rb > Cs$
* The boiling points order is
  $Li > Na > K > Cs > Rb$
* The increasing order of SRP values of alkali metals is $Li < Cs < Rb < K < Na$ (SRP values –ve)

* The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes.
  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
* Alkali metals when dissolved in liquid Ammonia in the absence of impurities form a deep blue colored solution.
  $M + (x+y)NH_3 \rightarrow \left[M(NH_3)_x\right]^+ + \left[e(NH_3)_y\right]^-$
* The blue colour of the solution is due to ammoniated (solvate4) electrons. (Note: In concentrated solution, the blue colour changes to bronze colour and become diamagnetic due to cluster formation).
* The solutions are paramagnetic and on standing slowly liberated hydrogen resulting in the formation of amide.
  $M^+_{(am)} + e^- + NH_3(liq) \rightarrow MNH_{2(am)} + 1/2H_2(g)$
* 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 solutions act as powerful reducing agents.
* The reactivity with water increase on descending the group from Li to Cs and Li<Na<K<Rb<Cs due to increase in electropositive character in the same order.
* Ionic nature, reducing nature, solubility, basic nature increases from LiH to CsH.
* LiH is thermally more stable
  $LiH > NaH > KH > RbH > CsH$
* With oxygen (Oxides): When alkali metals are heated in air, Li mainly gives Li_2O, sodium mainly gives sodium peroxide (Na_2O_6) and others give super oxides. (KO_2, RbO_2, CsO_2).
* Peroxides (O_2^{2-}) are the salts of H_2O_2. Therefore metal peroxides will give H_2O_2 on reaction with water or dil.acids.
  $Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$
* Concentrated peroxide solutions will give O_2 on reaction with water
  $2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$
* Na_2O_2 forms octahydrate crystals $Na_2O_2.8H_2O$
* 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 is used in qualitative analysis in the identification of chromium salts as it forms yellow colored chromate salts.
  $3Na_2O_2 + 2Cr(OH)_3 \rightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$
* Super oxides are coloured and paramagnetic due to the presence of unpaired electron or odd electron bond.
  Resonance structures of superoxide ion (O_2^-):



* Super Oxides are paramagnetic in nature.
* LiO_2 and NaO_2 are yellow in colour and are highly unstable.

* KO_2 and CsO_2 are orange but RbO_2 is brown coloured.
* Li_2O_2 is white, Na_2O_2 and Cs_2O_2 are yellow coloured. Rb_2O_2 is dark brown, K_2O_2 is orange coloured.
* The monoxides of Li, Na and K are colourless. But the monoxides of Rb and Cs are coloured. Rb_2O -Yellow: Cs_2O -Orange.
* The solubility of the hydroxides increases from $LiOH$ to $CsOH$
* Cesium halides have body centered cubic lattice.
* Li^+ has maximum degree of hydration and for this reason lithium salts are mostly hydrated E.g. LiCl. 2 H_2O
* The solubilities of bicarbonates in water is less than that of the carbonates.
* $NaHCO_3$ is sparingly soluble in water while Na_2CO_3 is water soluble.
* Except Li_2CO_3 the other carbonates are stable and they decomposing only at very high temperatures.
  $Li_2CO_3 \rightarrow Li_2O + CO_2$
* The stability increases from Li_2CO_3 to Cs_2CO_3
* Thermal stability of alkali metal carbonates increases from Li_2CO_3 to Cs_2CO_3. It is because of an increase in the size of cation.
* In alkali metals Li exhibit anomalous behavior. Due to
  1. exceptionally small atomic and ionic size and
  2. high polarizing power (i.e. change/radius ration)
  3. Lack of presence of vacant d-orbitals
* Lithium shows diagonal relationship with magnesium.
* Alkyl litiums are similar to Grignard reagents
* Sodium: It is the most abundant element in 1-A group.
* It is used in the preparation of compounds like $Na_2O_2, NaNH_2, NaCN$ etc.
* Na-Pb alloy is used in the preparation of tetraethyl lead (TEL) which is used as antiknocking agent in petrol.
* Potassium (K)
* Na^+ and K^+ play important role in Biology.
* 20% NaOH is formed in the central compartment.
  Reactions during electrolysis:
  Ionisation of brine: $NaCl \rightarrow Na^+ + Cl^-$
  At graphite anode: $2Cl^- \rightarrow Cl_2^- + 2e^-$
  At Hg cathode: $Na^+ + e^- + Hg \rightarrow Na - Hg$
  At Hg anode: $Na - Hg \rightarrow Na^+ + e^- + Hg$
  At Fe cathode: $2Na^+ + 2e^- + 2H_2O \rightarrow 2NaOH + H_2$
  Instead of H_2 gas, sodium is formed in the outer compartments because the discharge potential of sodium is lowered in presence of Hg cathode.

Sodium Carbonate:

* Decahydrated sodium carbonate $(Na_2CO_3.10H_2O)$ is called washing soda or salt soda.

* Anhydrous sodium carbonate is called soda ash or soda.
* It is prepared by
  1. Solvay or ammonia soda process.
* Solvay process or Ammonia soda process:
  Raw materials: Brine, limestone, little NH_3
  By-product: $CaCl_2$
  Intermediate product: $NaHCO_3$
  Recycled products: NH_3 and CO_2
  Impurities in Brine solution: Calcium & Magnesium salts.
  These are removed in the form of carbonate precipitates.
  Precipitation of $NaHCO_3$ in Carbonation tower is due to common ion effect.
  Solution from carbonation tower Consists of: $NaHCO_3$ and NH_4Cl
* It is suitable method to prepare Na_2CO_3 because of low solubility of $NaHCO_3$.
* K_2CO_3 can not be manufactured by Solvay's process because $KHCO_3$ is more soluble in water.
* $Na_2CO_3.10H_2O \rightarrow Na_2CO_3.7H_2O \rightarrow Na_2CO_3.H_2O$
* It's aqueous solution is basic due to hydrolysis of CO_3^{2-}
  $CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$
  $CO_3^{2-} + 2H_2O \rightarrow H_2CO_3^- + 2OH^-$
* It liberates CO_2 when treated with mineral acids stronger than H_2CO_3 acid.
* $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
  $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$
* It reacts with sulphur and SO_2 to give hypo
  $Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$
  $Na_2SO_3 + S \rightarrow Na_2S_2O_3$
* When fused with silica it gives sodium silicate or water glass.
  $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$
* It causes the precipitation of salt solution as their carbonates.
  $MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaCl$
  $ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$
* It is used in the manufacture of glass, caustic soda and water glass, Borax, Soap power.
* It is used for softening of water.
* It is used in laundries, paper and in dye industry.
* It is used in sizing of paper.
* It is used in petroleum refining.
* It is used in preparation of ultramarine.
* Sodium bicarbonate or Baking soda $(NaHCO_3)$
* It is prepared by Solvay's process.
* It is also obtained by saturating Na_2CO_3 solution with CO_2

* It is a white crystalline substance preparation
  $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$
* $NaHCO_3$ Solution gives yellow colour with methyl orange and it does not give any colour with phenolphthalein.
* It is used as a fire extinguisher.
* It is used as an antacid.
* It is used in making baking powders.
* It is used in the preservation of butter.
* It is used in the treatment of wool and silk.
* It is used in effervescent drinks.