Topic: S – Block Elements

Lecture No. 02

STUDY MATERIAL

For

Bachelor's of Science

(Ist Semester)

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Solubility of Alkali Metals in Ammonia

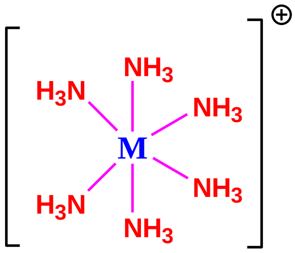
Alkali metals dissolve in liquid ammonia to give highly conducting solution with blue colour. Dilute solutions of alkali metals in liquid ammonia are blue due to solvated electrons and solvated metal ions. When the concentration of ammonia solution becomes above 3M, metals ion cluster are formed, the solutions are copper-coloured with metallic lustre. The solutions are good conductors of electricity and are paramagnetic in nature. The paramagnetic character decreases as concentration increases.

Explanation:

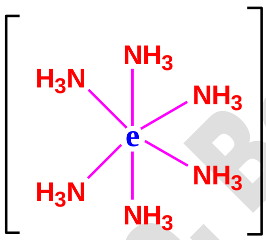
When an alkali metal is dissolved in liquid NH_3, ionisation of alkali metal takes place

$$M(s) \xrightarrow{\text{Liquid } NH_3} M^{\oplus} + \bar{e}$$

Both metal cation (**M^+**) and electron (**e^-**) are solvated by NH_3 forming ammoniated metal cation **$[M(NH_3)_x]^+$** and ammoniated electron **$[e(NH_3)_y]^-$**



Ammoniated metal cation



Ammoniated electron

It is the ammoniated electron which is responsible for the blue colour of the solution and the electrical conductivity is due to the ammoniated cation **$[M(NH_3)_x]^+$** as well as due to the ammoniated electron **$[e(NH_3)_y]^-$**. The values of x and y depends on the extent of solvation by NH_3. Dilute solutions are paramagnetic due to free electrons. In concentrated solutions ammoniated electrons associate to form electron-pairs and their paramagnetic character decreases.

$$[e(NH_3)_y]^- + [e(NH_3)_y]^- \longrightarrow [e(NH_3)_y]_2^{2-}$$

Electron pair

The blue colour of the solution is attributed to the fact that when light falls on the ammoniated electrons, they absorb energy corresponding to red colour and the transmitted light has blue colour. In concentrated solutions the colour changes from blue to bronze. The blue solution is paramagnetic in nature while the concentrated solutions are diamagnetic in nature. The presence of free ammoniated electrons makes the blue solution reducing in nature. The solutions on standing slowly liberate hydrogen resulting in formation of amide. When dry ammonia gas is passed over heated metals, amides are formed and hydrogen is evolved.

$$2M + 2NH_3 \longrightarrow 2MNH_2 + H_2$$

Alkali metal — Metal amide

Alkali metal amides are powerful reducing agents due to the presence of amide (NH_2^-) ions.

General Chemical Characteristics of Compounds of Alkali Metals

Oxides

An oxide is a chemical compound that contains at least one oxygen atom in combination with other metal or non-metal atom in its chemical formula. Among alkali metals Lithium forms monoxide (**Li_2O**), Sodium forms peroxide (**Na_2O_2**) while the rest of elements **(K, Rb, Cs)** of this group form super oxides (MO_2). A few important characteristics of the oxides are as follows:

- Monoxides are least stable while superoxides are maximum stable.
- Oxides readily dissolve in water to form hydroxides which are basic in nature.
- Both oxides and superoxides are colourless when in pure state. However superoxides are yellow or orange in colour.
- Peroxides are diamagnetic as all the molecular orbitals (MO) in peroxide ion (O_2^{2-}) are filled. The superoxides are paramagnetic in nature because all the molecular orbitals in the superoxide ion (O_2^-) are not filled.

Hydroxides

When oxides of the alkali metals are dissolved in water, they form corresponding hydroxides. They have following important features:

- The hydroxides are white crystalline solids.
- Hydroxides such as NaOH and KOH are deliquescent in nature i.e; when exposed to atmosphere, they absorb moisture and change to liquid form.
- Hydroxides are strong bases and in solution readily release OH^- ions. The basic strength of hydroxides increase down the group.
- The hydroxides in general have a strong and corrosive action on skin and are therefore known as **Caustic Alkalis.**
- Alkali metal hydroxides have strong affinity for water. They dissolve in water releasing large amount of heat i.e; Dissolution process is highly exothermic in nature.
- Basic strength of hydroxide increases with the increasing electropositivity of metal
  CsOH > RbOH > KOH > NaOH > LiOH
- Solubility of hydroxides increases with increasing ionic character.
  CsOH > RbOH > KOH > NaOH > LiOH

Halides

Alkali metals combine directly with halogens to form corresponding halides (MX). They can also be prepared by the action of aqueous solution of HX on corresponding oxides, hydroxides and carbonates.

$$2M(s) + X_2(g) \xrightarrow{\text{Heat}} 2MX(s)$$

$$M_2O(s) + 2HX(aq) \longrightarrow 2MX(aq) + H_2O(aq)$$

$$MOH(aq) + HX(aq) \longrightarrow MX(aq) + H_2O(aq)$$

$$M_2CO_3(aq) + 2HX(aq) \longrightarrow 2MX(aq) + H_2O(aq) + CO_2(aq)$$

- The halides are colourless, crystalline solids with high melting points.
- The halides of Lithium are generally covalent while the rest of halides are ionic in nature.
- All the halide have negative enthalpy of formation and becomes less negative from fluorides to iodides.
- The melting and boiling points of the halides of the alkali metals follow the order:
  Fluorides > Chlorides > Bromides > Iodides

- All the halides are water soluble. However LiF is only slightly soluble in water due to high lattice energy. Similarly, CsI is also very little soluble in water because both Cs^+ and I^- ions are large in size have and have also smaller hydration enthalpy.
- Halides of Lithium being covalent in nature dissolve in organic solvents such as, ethyl alcohol, ethyl acetate etc. LiCl also dissolves in pyridine.

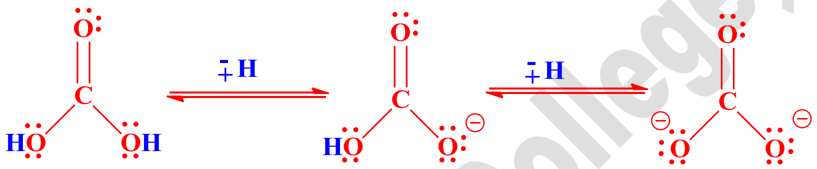
Carbonates

In chemistry, carbonate is a salt of carbonic acid (H_2CO_3), characterized by the presence of a carbonate ion, a polyatomic ion with the formula of CO_3^{2-}.

- Formula of Carbonate ion: CO_3^{2-}
- Formula of Bicarbonate ion: HCO_3^- (It is also referred as Hydrogen-carbonate ion in IUPAC system).
- These anions are formed from carbonic acid (H_2CO_3) by removing H^+ ions successively as follows:

$$\underset{\text{Carbonic acid}}{H_2CO_3} \rightleftharpoons \underset{\text{Bicarbonate ion}}{HCO_3^- + H^+} \rightleftharpoons \underset{\text{Carbonate ion}}{CO_3^{2-} + H^+}$$

The structural relationships can be represented as:



Their shapes are **trigonal planar** with 120° of bond angles at carbon atom. The central carbon atom possess sp^2 hybridization.

Compounds containing Carbonate ion

- All these metals from M_2CO_3 type carbonates, (Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3,Cs_2CO_3)
- Li_2CO_3 is least stable out of all these carbonates, because it is covalent and decomposes to Li_2O and CO_2 at low temperature. Order of their stability is as follows

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$$

- Stability of carbonates of IA group metals > stability of carbonates of IIA group metals
- The thermal stability of carbonates increases on moving down the group as:

$$Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$$

- Usually carbonates are formed when small amounts of carbon dioxide is passed through alkaline solutions.

$$2NaOH + \underset{\text{small amount}}{CO_2} \longrightarrow Na_2CO_3 + H_2O$$

- Bicarbonates are eventually formed when excess of carbon dioxide is passed through the alkaline solutions.

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

spraingly soluble in water

- Carbonates and bicarbonates are solids at room temperature. Carbonates of Group-1 and Group-2 elements are colourless. Whereas, the carbonates of transition elements are generally coloured.
- The polarizing power of the Group-1 metal ions (**M^+**) is less than the polarizing power of Group-2 metal ions (**M^{2+}**). Hence Group-2 carbonates are more covalent than the carbonates of Group-1. The polarizing power *decreases* down the group with increase in the size of metal ion. Hence the ionic nature increases down the group.
- $NaHCO_3$ and $KHCO_3$ can exist in the solid state. But the bicarbonates of Group-2 elements are only known in aqueous solutions.
- Except Li_2CO_3, the Group-1 carbonates are fairly soluble in water. The solubility *increases* down the group as the ionic nature increases.
- Carbonates are decomposed to carbon dioxide and oxide upon heating. Whereas bicarbonates give carbonate, carbon dioxide and water.

$$CO_3^{2-} \xrightarrow{\text{Heat}} CO_2 + O^{2-}$$

$$2HCO_3^{-} \xrightarrow{\text{Heat}} CO_3^{2-} + CO_2 + H_2O$$

- Thermal stability of Group-1 and Group-2 carbonates (also of bicarbonates) *increases* down the group as the polarizing power of the metal ion decreases.
- Carbonates of Group-1 are more stable than those of Group-2.
- Small and highly charged metal ions possess more polarizing power and hence facilitate the decomposition of carbonate ion into carbon dioxide and oxide ion.

Lithium Carbonate (Li_2CO_3)

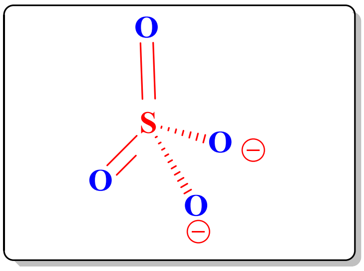
- Lithium carbonate is a colourless salt with polymeric nature.
- It is sparingly soluble in water and its solubility decreases with increase in temperature, but it dissolves in presence of carbon dioxide due to the formation of $LiHCO_3$.
- It is used in psychiatry to treat mania. The lithium ions interfere the sodium pump and inhibit the activity of protein Kinase C (PKC).
- It is also used in the preparation of lithium cobalt oxide - which is present in lithium ion battery cathodes.

Sodium Carbonate (Na_2CO_3)

- It is fairly soluble in water
- It is also called as washing soda.
- It is used mainly in laundries and in softening hard water.
- It is also used in making glass.
- used as laboratory reagent
- Sodium carbonate is a colourless salt.

Sulphates

The Sulphate ion is a polyatomic anion with the empirical formula SO_4^{2-}. Sulphate is basically a chemical compound that is composed of sulphur and oxygen atoms. Sulphate forms salts with a variety of elements including potassium, sodium, calcium, magnesium and barium. In sulphate ion, sulphur is the central atom and is surrounded by four oxygen atoms which are located at equal distances in the plane. Two of the oxygen atoms form S=O bonds and the other two oxygen atoms form S-O bonds. The molecule possesses **Tetrahedral geometry**.



- Basic character, ionic character, melting point, boiling point, solubility, thermal stability and reactivity increases from Li to Cs
  $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$
- Li_2SO_4 is insoluble in water whereas other sulphates, i:e., **Na_2SO_4, K_2SO_4** are soluble in water.
- **$Na_2SO_4 . 10H_2O$** is called **Glauber's salt**

General Chemical Characteristics of Compounds of Alkaline Earth Metals

Oxides and Hydroxides

- Alkaline earth metals generally react with oxygen to form metal oxides. Beryllium is reluctant to react with oxygen unless it is in the form of powder. Beryllium has a very strong layer of beryllium oxide on its surface and this prevents any new oxygen to react with it.

  $$2M\,(s) + O_2\,(g) \longrightarrow 2MO\,(s)$$

  Thus all alkaline earth metals form normal oxides of formula (MO). However Barium form peroxide.

  $$Ba\,(s) + O_2\,(g) \longrightarrow BaO_2\,(s)$$

- BeO is amphoteric in nature while all other oxides are basic in nature and yield hydroxides in aqueous solution. Basic strength of the hydroxides increases while going down the group
- Oxides are highly stable due to large ionic crystal lattice energies. The values are so high in case of oxides of Be and Mg that these compounds are almost insoluble in water. BeO is insoluble in water but dissolves in acid and alkali and is thus amphoteric in nature

  $$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

  $$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

  sodium beryllate

- CaO combines with solid acidic oxides at high temperature

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

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

- MgO is not very reactive, especially if it has been ignited at high temperature and for this reason it is used as a refractory. BeO is also used as a refractory.
- Solubility of hydroxides increases while going down the geoup
  $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- $Ca(OH)_2$ is called **Lime Water or Slaked Lime** and $Ba(OH)_2$ is called **Baryta Water**, Lime water or Baryta water turns milky by CO_2.

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

$$Ba(OH)_2 + CO_2 \longrightarrow \boxed{BaCO_3} + H_2O$$

Milky

- $Ba(OH)_2$ show milkyness even on exhaling breath on it.

Carbonates

- Carbonates of all alkaline earth metals are ionic in nature, due to excessive hydration of Be^{2+}, $BeCO_3$ is unusual because it contains hydrated ion **$[Be(H_2O)_4]^{2+}$** .
- $BeCO_3$ decomposes at low temperature and is thus placed in atmosphere of CO_2.

$$BeCO_3 \longrightarrow BeO + CO_2$$

- Thermal stability increases with increase in cationic size down the group.
  $BeCO_3 < MgCO_3 < CaCO_3 <$ SrCO3 $< BaCO_3$
- All of these carbonates are highly soluble in a solution of CO_2 than in water due to formation of bicarbonates.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

- $SrCO_3$ is used in the manufacture of glass for colour TV picture tube.

Sulphates

- Solubility of sulphates in water decreases down the group. Higher solubilities of $BeSO_4$ and $MgSO_4$ are due to the higher enthalpy of hydration of the smaller Be^{2+} and Mg^{2+} ions, which dominates the lattice energy factor.
  $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
- Sulphates decomposes into oxides and SO_3

$$MSO_4 \xrightarrow{Heat} MO + SO_3$$

- Thermal stability of sulphates increases down the group as indicated by their decomposition temperatures.

$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$
500°C	845°C	1149°C	1374°C

- **$MgSO_4.7H_2O$** is called Epsom Salt and is used as mild laxative and correct formulation is **$[Mg(H_2O)_6]SO_4.H_2O$**. $MgSO_4$ is deliquescent and readily soluble in water. It forms double salt with alkali metal sulphates. **$K_2SO_4.MgSO_4.6H_2O$** is sold as fertilizer under the name **"Potash Magnesia"**

- **$CaSO_4.2H_2O$** is called **Gypsum**. Gypsum on heating can be converted into a variety of compounds depending on temperature.

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} \xrightarrow{150^oC} \underset{\text{Plaster of Paris}}{CaSO_4.1/2\ H_2O} \xrightarrow{200^oC} \underset{\text{Dead Plaster}}{CaSO_4} \xrightarrow{1100^oC} CaO + SO_3$$

- Plaster of Paris (POP) is used for plastering walls, as sculptural material and encasing limbs so that broken bones are set straight.
- **$CaSO_4.H_2O$** is called **Alabaster**, a shiny like marble used for making ornaments.
- **BaSO4** is used in medicine as a contrast medium for stomach and intestinal X-rays.

Halides

- Halides of type (**MX_2**) of alkaline earth metals can be prepared by heating the metal or its carbonate with halogen acid.

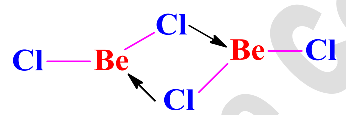
$$M + 2HCl \xrightarrow{\text{Heat}} MCl_2 + H_2$$

$$MCO_3 + 2HCl \longrightarrow MCl_2 + H_2O + CO_2$$

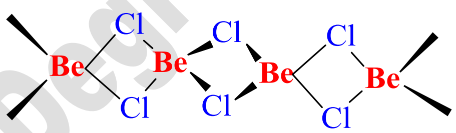
- Beryllium halides are covalent, hygroscopic and fumes in air due to hydrolysis

$$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl\ (\text{fumes})$$

- Anhydrous $BeCl_2$ is polymeric in nature and possess three centre two-electron bonds. Vapours exist as monomer $BeCl_2$ and dimer $(BeCl_2)_2$



Dimer



Polymer $(BeCl_2)_n$

- $BeCl_2$ forms complexes **$M_2[BeCl_4]$** with alkali metal chlorides but are decomposed by water.
- BeF_2 is highly soluble in water due to the high solvation energy of Be^{2+} in forming **$[Be(H_2O)_4]^{2+}$**,while other fluorides MF_2 (**M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}**) are all almost insoluble.
- The chlorides, bromides and iodides of Mg, Ca, Sr and Ba are ionic and are readily soluble in water.
- The halides form hydrates and are hygroscopic in nature.
- $CaCl_2$ is widely used for treating ice on roads, particularly in very cold countries to prevent ice formation even upto -55°C.
- Mixed chloride hydrides of formula (**MClH**) which have layer lattices, are formed when the hydrides and chlorides of alkaline earth metals are heated together.

$$CaH_2 + CaCl_2 \longrightarrow 2CaHCl$$

Hydrides

Compounds of hydrogen with less electronegative elements are known as Hydrides. When hydrogen reacts with any other element the product formed is considered to be a hydride. If we closely observe the periodic table hydride formation is not seen from VA group elements and this condition is known as **Hydride Gap**. Hydrogen molecule usually reacts with many elements except noble gases to form hydrides. However, the properties may vary depending on the type of intermolecular force that exists between the elements, its molecular masses, temperature and other factors.

Classification of Hydrides

Hydrides are mainly divided into three major types or groups. These groups are based on the nature of chemical bonding. The three types of hydrides are:

- **Ionic Hydrides**
- **Covalent Hydrides**
- **Metallic Hydrides**

Ionic Hydrides or Saline Hydrides

- These types of hydrides are formed when hydrogen molecule reacts with highly electropositive S-block elements (Alkali Metals and Alkaline Earth Metals).
- All ionic hydrides are solids, have high melting points, non-conducting and non-volatile.
- However, in liquid state, they conduct electricity.
- Ionic hydrides on electrolysis liberate hydrogen gas at the anode.
- Saline or ionic hydrides do not dissolve in conventional solvents and they are mostly used as bases or reducing reagents in organic synthesis.

Example of Ionic Hydrides: **LiH**, **NaH, KH, CaH_2,** etc. These contain hydrogen as the negatively charged hydride ion (H^-).

Covalent Hydrides

- Covalent hydrides are formed when hydrogen reacts with other similar electronegative elements like **Silicon (Si), Carbon (C), Nitrogen (N)** etc. The most common examples are **SiH_4, CH_4 and NH_3**.
- In general, compounds that are formed when hydrogen is reacted with non-metals are called Covalent Hydrides. The compounds share covalent bonds and are either volatile or non-volatile. Covalent hydrides are also either liquids or gases.
- Some covalent hydrides are unstable in presence of air, such as **SnH_4**.

Example of Covalent Hydrides: **SiH_4 (silane), CH_4, GeH_4 and SnH_4.**

Metallic Hydrides

- Metal hydrides are also known as **Interstitial Hydrides**. They are formed when hydrogen molecule reacts with d or f-block elements. The bond is mostly covalent type but sometimes the hydrides are formed with ionic bonds.
- These are usually formed by transition metals and are mostly non-stoichiometric being deficient in hydrogen,

Example of Metallic Hydrides: **$TiH_{1.5-1.8}$, $VH_{0.56}$, $CrH_{1.7}$, $LaH_{2.87}$, $TaH_{2.76}$** etc.

Some Important Compounds

- **KNO_3** is used in gun powder.
- **KO_2** is used to obtain oxygen on high monutains.
- **$BaCO_3$** is a medicine for killing rats.
- **$CaOCl_2$** is a germicide and a bleaching agent.
- **$BaSO_4$** is insoluble in water and is used in detecting obstruction in the digestive system by technique known as **Barium Meal**. Presence of BaSO4 in stomach helps in getting X-ray.
- **$MgCl_2.5MgOH.\ xH_2O$** is called **Sorel's Cement or Magnesia Cement**, which is used for the filling up cavities in the teeth.
- **$CaCN_2$** is a fertilizer.
- **$Na_2B_4O_7.10H_2O$** is called **Borax**, which is a mineral of Na.
- Complex compounds of Mg and Fe are Chlorophyll and Haemoglobin, respctively.
- Na and K is kept in kerosene because they are highly reactive.
- Li is hard and cannot be cut by knife. Na, K and Rb are soft solids and Cs is a liquid.
- Order of stability of alkali metals is **$M_2O > M_2O_2 > MO_2$**.
- Hydration energy of Li^+ is maximum. Therefore, its conductivity is low.
- Formulae and constituents of portland cement are : **$Ca_3SiO_5 + CaSiO_4 + Ca_3Al_2O_6$**
- Formula of superphosphate of lime is : **$Ca(H_2PO_4)_2.H_2O + CaSO_4.2H_2O$**
- Stability of hydrides is : **LiH > NaH > KH > RbH > CsH**
- **H_2SO_4, Na_2CO_3 and $NaHCO_3$** are used as fire extinguisher.
- **$LiCO_3$** is used in mental disorders.
- **$LiNO_3$ and $NaNO_3$** melt on absorbing moisture in air, KNO_3 does not have this character, therefore, it is used in gun powder.
- **CaH_2** is called **Hydrolith.** It is used in the transportation of H_2. In case of emergency it can be used as a portable source of Hydrogen.