

and mine welcome to the lecture series again today i will be talking to you about the chemistry of group two elements that is alkaline earth elements they are also called s two block elements since they have two electrons in their valence shell they are called s two block elements as well as the s two block elements and you know the electronic configuration of alkaline earth elements is ns^2 that means they have two electrons in their valence shell and hence the group of state of alkaline earth metals or alkaline earth elements is pressed to beryllium the first one next magnesium calcium strontium barium and radium of course radium is radioactive and similar to lithium among group one elements beryllium differs from other elements going to its smaller size and very high charge to size ratio but beryllium resembles more of aluminum that means it has a diagonal relationship with aluminum at the end i will be discussing about the diagonal relationship and similarities between beryllium and aluminum and atomic and ionic radii are smaller than those of group one elements because here they have two electrons are there and also there is an increment in the effective nuclear charge as a result what happens the size shrinks ok

So atomic and ionic radii are smaller and they readily form $m+2$ ions the cationic species can be done readily by removing two electrons and $m+2$ ions and $m+2$ ions if you compare between alkali metals and alkaline earth metals $m+2$ ions are smaller than $m+1$ the alkaline earth elements in their free state atomic and ionic radii decreases down the group as the size increases again similarities are there between alkali metals and alkaline earth metals and ionization enthalpies decreases down the group of course due to the increase in the size the first ionization enthalpies are higher than those of the corresponding group one elements and here second ionization enthalpies are lower than the first ionization enthalpies because in the case of first ionization enthalpy you have to remove electron from a paired set that is s^2 ok obviously it requires larger energy and once of removing one electron removal of the second electron would be lot easier that is the reason the second ionization energy or ionization enthalpy is much lower compared to the first ionization enthalpy and again when you compare hydration enthalpy the same trends are followed hydration enthalpy decreases down the group due to increase in ionic size the sequence that followed is very similar to alkali metals hydration enthalpy is highest for beryllium and then magnesium and then calcium strontium

So this is the sequence that is followed as far as hydration enthalpy is concerned and due to the larger size group two elements are more extensively hydrated compared to group one elements example magnesium chloride

So due to the larger size of alkaline earth metals they are more extensively hydrated compared to group one elements example magnesium chloride is hexa hydrated if you recall lithium chloride that is dihydrated that means it it has two molecules of solvated water whereas magnesium fluid has six molecules of solvated water and same thing is true with calcium also ah if you compare those with sodium and potassium chlorides they do not form such hydrates and all these alkaline earth metals are silvery white in color and they are soft but harder than group one elements and again they are all strongly electro positive and this electro positivity trend increases down the group and chemical reactivity of group two elements can be again considered by looking into their interactions with air that is water oxygen hydrogen nitrogen halogens and also its reducing capability and also its behavior in liquid ammonia and also its interaction with organic moieties and if you see again it imparts colors to the oxidizing flame for example beryllium and magnesium do not impart any color because of the high ionization energy associated with them whereas in case of calcium it gives brick red color and in case of strontium it is crimson red color and whereas barium gives characteristic apple green color and the corresponding wavelengths are given here 662 650 and 554.5 nanometers respectively for this emissions and in this case the emission is a result of the electron excited from

So we have ns^2 electronic configuration

So when the s electron is excited we have a electronic configuration of $ns^1 np^1$ electronic configuration that means one of the s electrons is promoted to p one as a result the intense color is observed when this electron returns to the ground state ok ah they emit the radiation in the following region this how the color will be seen and when we look into the reactivity you can see the flame test colors here very nice apple green color can be seen in case of barium and strontium and calcium the corresponding colors of course because of this nice colors they are also used in firework let us look into the chemical reactivity of group two elements and because of smaller size compared to alkali

metals they are strongly hydrated as that we saw in our previous slide that is magnesium and calcium are hexa hydrated having six equivalents of water molecules and they also have high lattice energy and beryllium has a different chemistry compared to magnesium calcium strontium barium and radium and free beryllium two plus does not exist unlike other alkaline earth metals and always it is its compounds are covalent and contain solvated ions such as when you put sodium chloride or potassium chloride into water you can see Na^+ and Cl^- signs whereas in case of beryllium that is not going to happen and instead it always exists as a coordinated complex having this kind of a formulation many of the salts are less soluble in water for example K_2SO_4 is soluble not calcium sulphate or strontium sulphate and beryllium is a rare element ok and that is extracted from this mineral called beryl it has the composition $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

So I briefly discuss about the extraction of beryllium from this mineral first it has to be treated with sodium hexafluorosilicate that leads to the formation of a fluorinated compound having formula Na_2BeF_4 this one on treatment with sodium hydroxide forms beryllium hydroxide beryllium hydroxide when treated with ammonium hydrogen difluoride a very strong fluorinating agent it forms NH_4BeF_4 from which one can get BeF_2 simply by heating once after getting pure beryllium fluoride it can be reduced using magnesium to get elemental beryllium

So this is how beryllium is extracted from beryl and simple anhydrous compounds of beryllium are covalent in nature when crystallized from water as I said salts are formed like hexagon beryllium two plus are formed hydrated beryllium ion that is a tetra aqua beryllium two plus is very similar to hydrated aluminum and both are acidic in nature as a result of high polarizing power of the small highly charged beryllium two plus ion which results in hydrolysis the other hydrated group two cations are not acidic going to their lower charge densities for example if you take it gives $\text{Be}(\text{OH})_2$ three times plus plus H_3O^+

So therefore what you can call as tetra aqua beryllium two plus only exist in strong acid solutions on increasing the pH hydroxide ions such as $\text{Be}(\text{OH})_3^-$

So on increasing the pH hydroxide ions such as OH^- will form and eventually that leads to the formation of $\text{Be}(\text{OH})_2$ in excess hydroxide BeO and $\text{Be}(\text{OH})_2$ dissolved to give beryllite iron that is Be_2O_3 demonstrating the amphoteric nature of beryllium as this primary structure will appear like this

So this indicates the amphoteric nature of beryllium very similar to aluminium hydroxide and combustion of group 2 metals in oxygen gives mono oxide species like strontium oxide barium oxide will absorb oxygen under pressure to give peroxides that means under normal circumstances all of them will form mono oxides but only in case of strontium and barium under high pressure one can prepare the corresponding peroxides M_2O_2 peroxides and superoxides are not formed by combustion and tend to be unstable because the smaller M^{2+} ions are highly polarizing and cause the peroxide and superoxide salts to decompose to MO which have high lattice energies

So you can see here the lattice energy is in the close to in case of beryllium oxide is minus four two nine eight kilo joules per mole in case of magnesium oxide it is three thousand eight hundred kilo joules per mole and in case of calcium oxide is 3419 kilojoules per mole strontium oxide it is 3222 whereas in case of barium it is

So it is steadily decreasing nevertheless they show very high lattice energies and also that is also reflected in the melting point if you see the melting point case of beryllium oxide is 2500 whereas it drops to about 1475 in case of barium oxide and this calcium hydroxide it can react with hydrogen peroxide and water to form calcium oxide

So calcium hydroxide reacts with hydrogen peroxide aqueous hydrogen peroxide to form calcium peroxide and calcium oxide itself when treated with water forms the calcium hydroxide and similarly magnesium two plus reacts with hydroxides to form corresponding magnesium hydroxide and barium hydroxide is the most stable and most soluble hydroxide among all hydroxides of group two elements and the carboxylate salts of the metals magnesium to barium of the type all normal salts ok however beryllium hydroxide reacts with carboxylates to give basic carboxylates

So basic carboxylates have the formula Be_4O_6 carboxylate group surrounds that means there is a difference in the reactivity with carboxylates with magnesium to barium you get simply corresponding carboxylates as normals are similar to palladium acetate sodium acetate whereas in case of beryllium hydroxide it reacts to give a basic carboxylate which has four beryllium atoms one oxygen atoms and six carboxylate groups

are there and let us look into the structure how it looks

So you can see here an oxygen is coordinated to four beryllium atoms sitting at the center of the tetrahedron and now these carboxylate groups are essentially bridging ligands what they do is they bridge in this fashion to stabilize this tetrahedral beryllium moiety if you just look into the acetate group this is something like this

So this comfortably bridges as a mono anionic ligand

So we have six such carboxylate groups they are bridging four beryllium atoms to give this structure to basic carboxylate lead also forms similar basic carboxylate and magnesium reacts with nitrogen on heating to form magnesium nitride and of course magnesium nitride is very reactive on treatment with water it undergoes hydrolysis very similar to lithium nitride to form ammonia and magnesium hydroxide and group two metals dissolve in liquid ammonia to form blue solutions containing solvated electrons similar to alkali metals however their solubilities are much lower all of the group two metals except beryllium form an ionic dihydride MH_2 on heating the metal in hydrogen because of high ionization energy associated with beryllium it does not react as a result using simple method one cannot make beryllium dihydride instead one has to go for drastic conditions for example beryllium hydride can be prepared starting from beryllium chloride which on interaction with lithium aluminium hydride gives ok

So this is one method and if you want to prepare very pure beryllium hydride there is an indirect method is there in this one one has to make first a tributyl beryllium compound that is beryllium chloride has to be treated with Grignard reagent such as tertiary butyl magnesium chloride this gives initially ditertbutyl beryllium plus two equivalents of magnesium chloride ditertbutyl beryllium on heating it forms beryllium hydride plus two equivalents of propene

So you may be wondering how a di-tert-butyl beryllium compound gives beryllium hydride plus two equivalents of propene basically what happens when you have some beta hydrogen atoms they have a easy pathway for decomposition and one such mechanism can be seen here that is called beta hydrogen elimination just if you look into the slide I have shown here you can see here this is we have an ethyl group on metal this ethyl group are some organic group having beta hydrogen can be written in this fashion when you write in this fashion you can see this is the beta hydrogen atom and due to this coming very close to metal you have this four membered intermediate here and this intermediate takes hydrogen on to metal and formation of ethylene is seen and this ethylene bond bridges and eventually this decomposes to give metal hydride and an alkene is formed

So this is essentially the decomposition pure beryllium hydride can be prepared starting from di-tert-butyl beryllium ok using beta hydrogen elimination method for example here let me show for the formation of one beryllium hydrogen bond the same can be repeated with another one let me write in this fashion as I had mentioned earlier it forms a four membered ring and then eventually this bond breaks here and this bond breaks here leading to the formation of $plus$

So here two methyl propane is formed similarly this tertiary butyl group also undergoes beta hydrogen elimination to form this again undergoes another beta hydrogen elimination to form H_2

So here one more this group is formed here

So and reactions with halogens are very similar to alkali metals directly one can react with halogens to prepare the corresponding MX_2 species ok and thermal decomposition of dibutyl beryllium tetrafluoride is the best method for the preparation of Bef_2 that I showed you while showing the metallurgical extraction of beryllium from beryllium ore beryl

So if you take here one can get pure beryllium difluoride one can also prepare using carbon reduction using beryllium oxide of course this reaction happens only at a temperature of six hundred to eight hundred kelvin ok and Bef_2 beryllium dichloride is a covalent polymer in the solid state anhydrous beryllium halides are soluble in many solvents going to the formation of complexes other alkaline earth metal chlorides such as magnesium chloride calcium chloride strontium and barium chloride are ionic water soluble salts but fluorides are only slightly water soluble going to the high lattice energy for M^{2+} ion and small F^{-} ion in fact that is true with most of the fluorides whether we consider sodium fluoride are in general alkali metal fluorides or alkaline earth metal fluorides or even aluminum fluorides they are all having high lattice energy going to the same charge cations and small F^{-} ions let us look into further the chemical reaction as I said the calcium chloride has fcc structure one

can see from this one and this is very similar to sodium chloride structure in case of beryllium chloride as it has polymeric structure why it has polymeric structure okay in solid state it has a polymeric structure with two chlorides bridging the adjacent beryllium atoms

So that you have a spirocyclic beryllium continues in one dimension leading to the formation of a polymeric chain whereas in case of gas phase it exists as both monomeric form that is $BeCl_2$ and also dimeric form Be_2Cl_4 the sulfates are also known solubility of these sulfates of alkaline earth metals decreases going from beryllium to barium and all the group two metal sulphates lose SO_3 to form the oxide on strong heating if you take a typical alkaline earth metal sulphate on heating it forms the oxide plus SO_3 is released this is very similar to carbonates giving the oxide plus carbon dioxide this is true in case of magnesium calcium and strontium and whereas barium carbonate is much stable to heat and it does not decompose readily and in liquid ammonia alkaline earth metals dissolve to give deep blue color solution similar to alkali metals again this is very similar to alkali metals in liquid ammonia

So here the colour is more intense it is essentially because of this kind of reaction that happens

So it forms two kinds of complex ions

So here as due to the presence of divalent cation surrounded by ammonia and also electron free electron surrounded by ammonia you have two sets of complexes in liquid ammonia with carbon as one can make different types of carbides for example magnesium calcium strontium and barium form ethanoids that means acetylides when treated with acetylene and to make compounds of the type $M-C \equiv C$ ok

So essentially if you look into this formula it appears like C_2^{2-} ion is present example calcium carbide beryllium and magnesium also form two other type of carbides

So beryllium on diuretic combination with carbon forms beryllium carbide at high temperature and in this case ok in most of this carbides of highly electro positive elements on hydrolysis the corresponding hydrocarbon is liberated whereas in this case beryllium carbide on hydrolysis it gives methane and another carbide is Mg_2C_3 or it can also be written in this function and of course as beryllium carbide has this ok So this is how as you can satisfy the valency and write the correct structure ok the most important argumentally compounds of group 2 metals are the grignard reagents as grignardians are simply prepared by treating alkyl halides with magnesium in a polar solvent such as ether ok

So this grignard reagent $R-Mg-Cl$ are always solvated by ether giving tetrahedral geometry to magnesium

So widely used for the formation of carbon carbon bonds in organic synthesis ok and these compounds grignard reagents are very similar to organolithium in terms of their reactivity towards other halides to form carbon carbon bonds and in case of grignard reagent one has to carry out the reaction in a polar solvent such as diethyl ether that diethyl ether will give essentially a tetrahedral geometry through coordination of oxygen to magnesium in this fashion

So in absence of any interaction or association if you prepare grignard reagents such as $R-Mg-Cl$ that essentially get coordinated with the two equivalents of ether to have a tetrahedral geometry and this one will give temporarily coordinative saturation to magnesium and it stabilizes this grignard reagents that is the reason the the solvent is very very important and one has to choose a polar solvent while performing grignard reaction to generate a species of the type $R-Mg-Cl$ the organometallic compounds of R to Mg are also known but much less studied than the grignard reagents both dimethyl beryllium and dimethyl magnesium have the polymeric structure similar to beryllium hydride or beryllium chloride

So that I would show you later as how one can explain the polymeric structure using even as simple as valence bond concept and the about the utility of wigner reagents in organic reactions just I want to show you one reaction here for example take $R-Mg-Cl$ and treat this with a ketone initially it forms and this one under acidic condition forms the corresponding alcohol through the elimination of magnesium chloride

So that means treatment of grignard reagent to ketone leads to the formation of tertiary alcohol not only that one one can also use in various other p block element organo compounds for example treatment of grignard reagents such as ethyl magnesium bromide with PCl_3 phosphorous dichloride leads to the formation of very important as phosphine

ligand triethyl phosphine ok

So one can use a variety of reagents of magnesium with general formula R_2MgX and use it extensively one can extensively use it in organic chemistry or with p block elements to make element to carbon bonds you can see here i have shown some structures of organomagnesium compounds here they can have a dimeric structure you can see here they can have dimeric structure with the two alkyl groups bridging or one can also have primary structure like this two such units bridging or one can also have a cyclic structure in this fashion or simply they can exist in monomeric form if the solvent is available to satisfy its coordinative saturation and when we have this kind they are essentially three center two electron bonds i will show you how three center two electron bonds can be realized in case of an beryllium carbon compounds or beryllium hydride compounds i am taking here dimethyl beryllium compound

So well beryllium you have s two electron that is you have two electrons here and you have no electrons in p orbital

So during the formation of compound what we get is s and p together they combine together to form four hybrid orbital after promoting this s electron to one of the p orbital and now we have four s p three orbitals with two having one electron and two having no electrons

So now here something like this is there

So that means i am considering an a situation like this here you have one here one here now another beryllium atom it comes now basically what you have is if you consider hydrogen one can consider one s one electron here one s one electron here electron is not here

So electron is here

So now basically here no electron is there here here one electron is there and this is one electron is there

So one two three three centered two electron bond is formed and same thing is two in case of here also here one electron is there here no electron is there and you have three centered two electron bonds

So essentially you have two three center two electron bonds are i would discuss more about these aspects when i go to group thirteen elements and discussing the hydrides of boron ok

So let us look into the uses of group two elements and their compounds beryllium is used in making alloys for example copper beryllium alloy used in making high strength springs metallic beryllium is used in making windows of x-ray tubes and magnesium alloys with aluminum zinc and tin are also used in lot of materials and magnesium alloy because of its lighter and strength used in aircraft construction and magnesium powder and ribbon is also extensively used in flash powders bulbs incendiary bombs and signals and suspension of magnesium hydroxide in water that is called milk of magnesia used in antacid magnesium carbide carbonate is used in toothpaste and calcium is used in extraction of metals from oxides which are otherwise difficult to reduce with carbon

So when you have some metals which are very difficult to be reduced from the corresponding metal oxides using carbon one can comfortably conveniently use calcium of course reactions has to be carried at a higher temperature and calcium and beryllium metals going to their reactivity with oxygen and nitrogen at elevated temperature used to remove a small quantity of air from vacuum tubes for effective vacuum it has to be thoroughly evacuated to remove the trace amount of air and essentially air containing oxygen and nitrogen

So since they have high affinity at very high temperature for oxygen and nitrogen by purging at high temperature calcium and barium one can conveniently eliminate all traces of oxygen and nitrogen to get pure vacuum and then one can seal to generate vacuum tubes So radium salts are used in radiotherapy that is in cancer treatment

So now let us look into the diagonal relationship between beryllium and aluminium if you just look into the ionic radius of beryllium $2+$ plus that is about 31 picometer and charge to size ratio is very high and that can be compared to the size of aluminum $3+$ plus since both of them have very comparative are very similar ionic radius you can anticipate similarities in their properties aluminum forms an oxide film and as a result resistant to acid attack this called passivation and beryllium does the same and once when pure beryllium is exposed it immediately forms a thin coating of beryllium oxide and that prevents from further oxidation and even that can even prevent and in the acid attack or it can resist acid attack

So beryllium hydroxide dissolves in alkali to form beryllites that is BeO four times two minus aluminum does the same

So aluminium also under strong alkaline condition aluminium trihydroxide which is insoluble forms aluminum tetrahydroxide that is soluble and chlorides of both beryllium and aluminum have bridged structure if you look into aluminium trichloride that is dimeric having two chloro bridges having the composition Al_2Cl_6 and similarly beryllium dichloride is also unstable it undergoes dimerization to form Be_2Cl_4 or it can have a polymeric network chlorides of both beryllium and aluminium have bridge structures and of course both are used in federal crop reaction for making C-C bonds and both have strong tendency to form complexes letting beryllium f^4 two minus and also hexafluoro eliminate three minus now let us look into few questions like suggest a structure for dimer of BeCl_2 and explain how its formation illustrates BeCl_2 acting as a lewis acid

So the question is BeCl_2 forms dimer

So that means how you can evoke the acidic and basic properties or lewis acidic property of BeCl_2 that can facilitate the bridging formation or formation of our facilitation of the dimeric or one dimensional chain structure the next another question i will be answering that one shortly why does the solubility of alkaline earth metal hydroxides in water increases down the group

So first let us look into one can write BeCl_2 like this

So now as i mentioned here ah if beryllium has undergone sp^3 hybridization we have four sp^3 hybrid orbitals are there out of that one two sp^3 have one electron each and two sp^3 do not have any electron and those which have one electron can combine with Cl to form two BeCl bonds other ones are m^t now another beryllium is there in the same way i can write the situation is same here

So now this chlorine has if you just remember or recall the lewis dot structure it has eight electrons are there and two electrons are participate in making BeCl bond

So these electrons can be given here and this electron can be given here and then this repeats

So because of this one here ah beryllium acts as a lewis acid and takes two electrons from beryllium and in that fashion ah one beryllium when it is acting as lewis acid this beryllium acts as a lewis base and when you go to the next one

So that means basically there is a tandemness is there in its behavior acting as lewis acid and lewis base that results in the formation of this bridging ah bonds eventually that leads to the formation of a one dimensional chain

So this is how one can explain the lewis acidity of beryllium that leads to the formation of one dimensional chain and why does the solubility of alkaline earth metal hydroxide in water increases down the group that means among alkali earth metal hydroxides the iron being common the cationic radius will influence the lattice enthalpy since the lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size the solubility increases as we go down the group and then if you look again why does the solubility of alkaline earth metal carbonates and sulphates in water decreases down the group in fact BaCO_3 highly insoluble and is stable it does not decompose readily the size of anions being much larger compared to cations the lattice enthalpy will remain almost constant within a particular group since the hydration enthalpies decreases down the group solubility will increase as found for alkaline earth metal carbonates and sulphates

So next the the question if i go back ah to this one there is a question here ah reaction of magnesium carbide with water gives propane also just look into the question carefully reaction of a magnesium carbide with water gives propane suggest a formulation of the carbide and give an example of a common gaseous molecule with which the carbide ion is isoelectronic that means if the the statement given clearly states that there is a magnesium carbide and which on treatment with water gives propane propane means there should be three carbons if three carbons are there and magnesium carbide is there one can think of MgC_3 because propane is there ah and then if it is giving

So what kind of ah reaction you can see what kind of binding can be anticipated here

So if it gives propane it should be something like this this is propane ok

So one can now write and compute the reaction

So now if you just see this equation is balanced now

So $\text{MgC}_3 + 2\text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_8 + \text{MgO}$

So now that means this one one can write ok

So suggested formation of the carbide

So carbide is M_2C_3 and this is isoelectronic with carbon dioxide

So just by analyzing this statement one can conveniently write the right equation and arrive at the right answer

So with this I complete the chemistry of alkaline earth metals in my next lecture I would be discussing about group 13 elements that is the boron group

So we have in group 13 we have boron aluminum gallium indium and thallium

So I shall discuss the chemistry of those in my next lecture

So let me summarize the salient features of the group 2 elements. In case of group 2 elements plus two oxygen state dominates the chemistry of all group 2 elements

So in case of group 2 elements plus two of state dominates all alkaline earth metals show very low first and second ionization enthalpies and are most electro positive elements in the periodic table

So beryllium Be^{2+} due to its very small size forms either covalent compounds or contain solvated ions these features are not seen with rest of the elements the group 2 metals form more stable coordination complexes compared to the group 1 metals and alkaline earth metals form basic oxides with beryllium due to its smaller size beryllium oxide is amphoteric that means all alkaline earth metals form basic oxides except beryllium in case of beryllium due to its smaller size BeO acts as a amphoteric oxide very similar to aluminum oxide

So this completes the discussion on the chemistry of group 2 elements in my next lecture I will be discussing on the group 13 elements starting from boron and aluminum gallium indium and thallium

So thank you very much you