Main Group Chemistry
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Lecture - 21
Chemistry of Group 2 elements

Welcome to MSB lecture series on main group elements, let me begin today s lecture with group 2 element hydrides. Let me start the discussion on the hydrates of group 2 elements.

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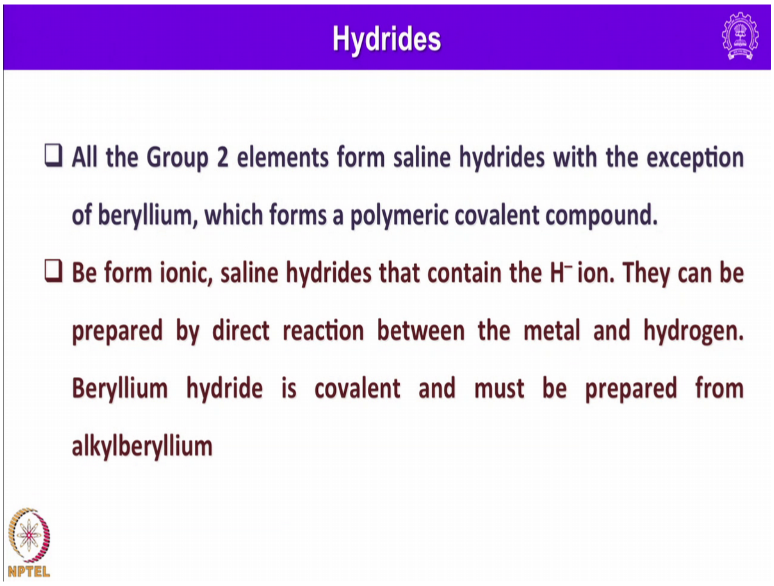

Hydrides

- All the Group 2 elements form saline hydrides with the exception of beryllium, which forms a polymeric covalent compound.
- Be form ionic, saline hydrides that contain the H^- ion. They can be prepared by direct reaction between the metal and hydrogen. Beryllium hydride is covalent and must be prepared from alkylberyllium

All the group 2 elements form saline hydrides that is ionic hydrides, with exception of beryllium and in fact, which forms a polymeric covalent compound, it forms a one dimensional a polymeric beryllium hydride chain. And beryllium form ionic saline hydrides that contain H minus ion, they can be prepared by direct reaction between the metal and hydrogen. So, beryllium hydride is a covalent and must be prepared from alkyl beryllium. So, because of its covalent nature, it is very difficult to prepare starting from beryllium and hydrogen gas. In fact, it can be conveniently prepared in its purest form starting from alkyl beryllium that method I will show you later.

So, for example, the stable beryllium hydride can be prepared by pyrolysis of (Refer Time: 01:32) tertiary butyl beryllium, and I would tell you later how to make that one.

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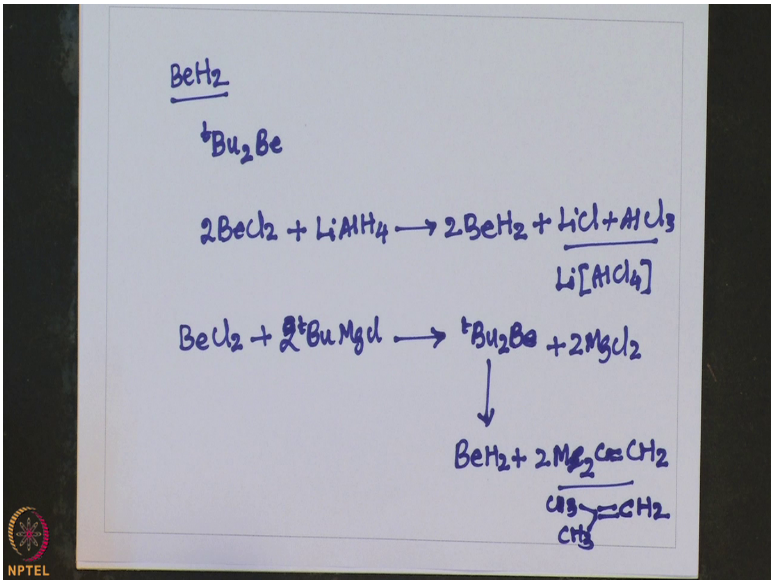

$\underline{BeH_2}$

${}^tBu_2Be$

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + \underbrace{LiCl + AlCl_3}_{Li[AlCl_4]}$$

$$BeCl_2 + 2\,{}^tBuMgCl \longrightarrow {}^tBu_2Be + 2MgCl_2$$

$$BeH_2 + 2Me_2C{=}CH_2$$

So, in order to prepare beryllium hydride, one should use this argenometallic compound such as bis tertiary butyl beryllium. And of course, one can also prepare starting from beryllium chloride, treating that one with a reducing agent such as lithium aluminum hydride. So, beryllium chloride on treatment with lithium aluminum hydride, it gives plus LiCl plus AlCl 3 or they should be conveniently written as AlCl 4. So, here one should remember when you are making these hydrides, they are extremely reactive and react readily with water as a result these reactions has to be carried out in non aqueous medium, and in dry organic solvents reaction has to be carried out and if the incorporation of moisture and oxygen should be excluded at all stages.

So, let me show you how to prepare this di tertiary butyl beryllium, BeCl 2 should be treated with the Grignard reagent, it forms plus 2 Mg Cl 2 and this one on decomposition gives Be H 2 plus CH 2. So, this is nothing, but.

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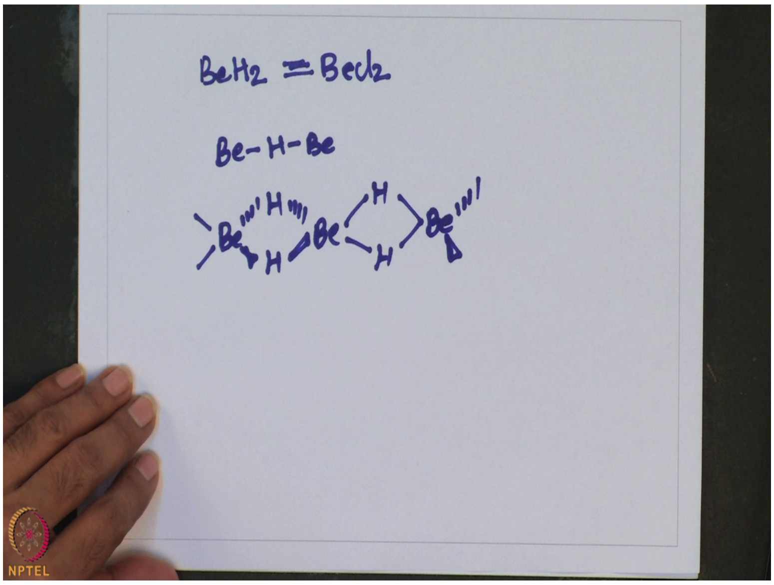

So, beryllium hydride structure is very similar to BeCl 2. In fact, in both the cases beryllium species whether its beryllium hydride or beryllium chloride act as Louis acid as well as Louis, base as a result what happens they form (Refer Time: 04:42) having this bridges Be H e Be H Be bridge, and they form the association to form one dimensional chain like this. So, it goes like this similar structure one can show for beryllium chloride as well in solid state.

So, now let us look into the decomposition of di tertiary butyl beryllium. So, how it is giving beryllium hydride?

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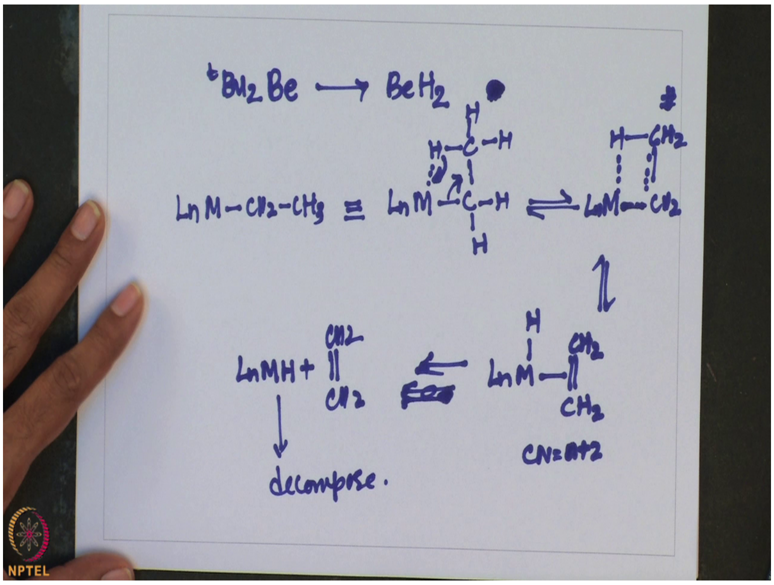

So, here we should talk about the kinetic path way, that is available for the decomposition of no alkyl beryllium to give beryllium hydride. So, this pathway that is used for the decomposition of alkyl beryllium or in general argenometallic compounds is called beta hydrogen elimination. And here it its although beryllium to carbon bond is quite stable compared to any other bonds having the energy very similar to nitrogen carbon or phosphorous carbon, here because of free coordinate sites that are available on the metal. So, this beta hydrogen elimination takes place and here I will show you how that happens using a general method of our beta hydrogen elimination, let us have a molecule like this let us assume we have one CH 2 CH 3 group here, and this I would preferably write in this fashion.

So, now basically what happens? So, this comes to very close to and it forms a 4 member intermediate of this type. So, here of course, I can also show this one this moves here, and this will come here as a result what we get is. So, so all and preferably I can call it as this one as intermediate, and then this one leads to the formation of M 2 hydrogen meta hydrogen bond and hence here we get a unsaturated species, and then here a coordination number increases by coordination number will be n plus 2 increases by 2, and then eventually this gives rise to. So, and of course, later this can also decompose. So, this kind of beta hydrogen elimination makes the argenometallic compounds unstable, and here most of the compounds if they are coordinatively unsaturated, there is a scope for the increase of the coordination (Refer Time: 09:04) by 2.

As a result this kind of rearrangement takes place and that results in the elimination of one of the hydrogen, and eventually this compound decomposes of course, this method is exploited in the formation of a beryllium hydride here. So, in case of beryllium hydride first let me write one group here.

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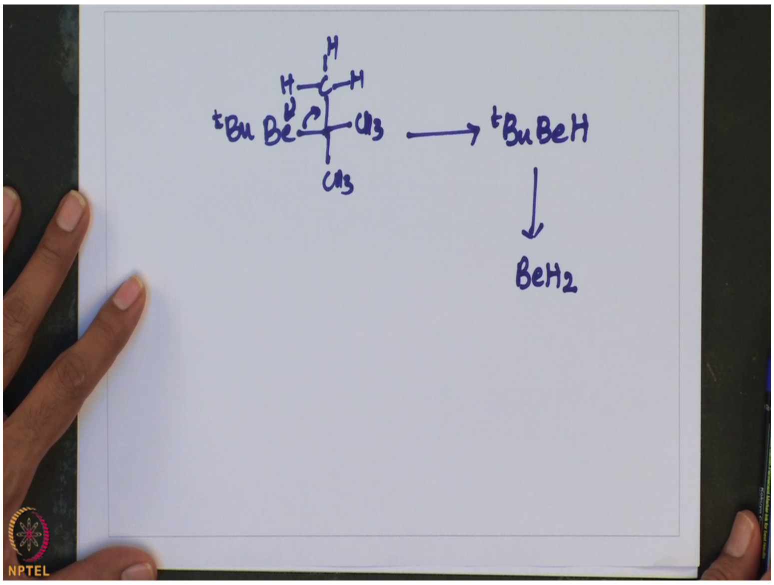

Intact and then let me write here tertiary butyl group like this. So, in the same fashion you can write here. So, this eventually leads to the formation of mono beryllium hydride species, and if I repeat this again this eventually gives to beryllium hydride. So, this is how beryllium hydride in its pure form can be prepared starting from di tertiary butyl beryllium. And these reactions can also be reversible; this is where utility of this type of compounds comes in hydrogenation reactions.

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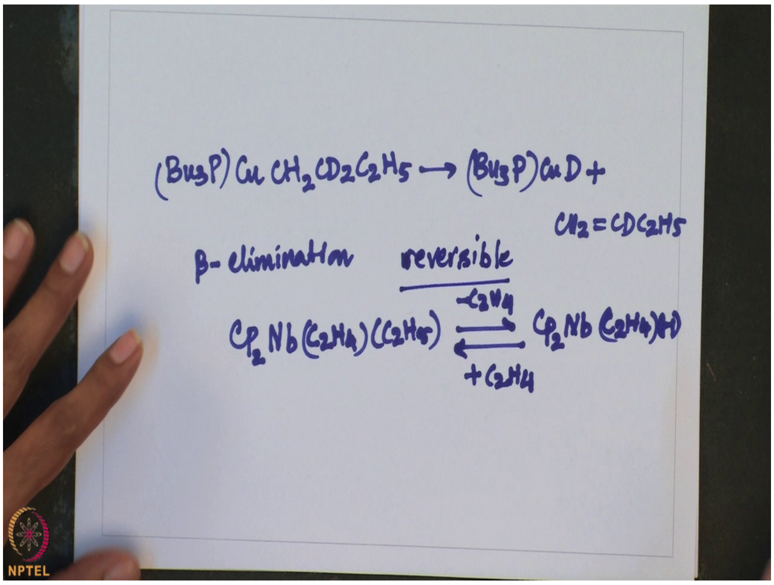

For example I will also write for your information (Refer Time: 10:28) tri tertiary butyl (Refer Time: 10:30) copper complex, with a labeled organic moiety.

So, beta hydrogens are replaced by deuterium. So, here the product is P, D and of course, this can be verified from one H and M r spectrum. So, here this beta is labeled so; that means, we have replaced hydrogen with deuterium, as a result one can expect the formation of (Refer Time: 11:19) instead of hydride C u H, and this can be verified by n m r and also through the formation of this one by analyzing the compound that is coming as a byproduct, one can confirm that the reaction that is responsible is beta hydrogen elimination. And as I said this can also be reversible one can also make beta elimination reversible. I will show one example here let us consider this cyclo pentadinyl dimer having a C 2 H 4 group ethylene, as well as an ethyl group this cyclo pentadinyl (Refer Time: 12:10) ethylene ethyl compound, this one on heating it loses C 2 H 4 to form CP 2 Nb, C 2 H 4 and H; that means, hydride bond and of course, on addition of ethylene, one can regenerate the ethyl and ethylene complex. So, this shows the these reactions can be made reversible. Of course, some of these reactions come very handy in catalytic organic transformations.

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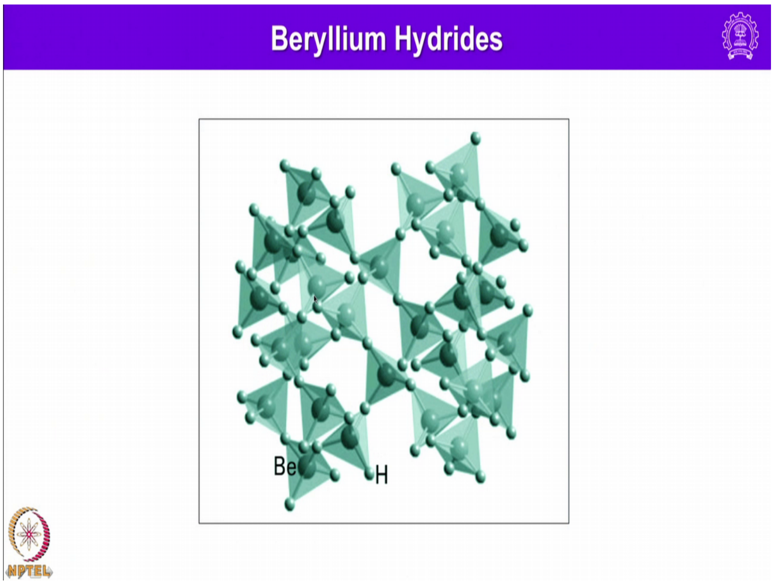

Beryllium Hydrides

So, this is how beryllium hydride structure looks like, you can see here we have 4 bond I can one can also explain this one using valence bond theory using hybridization concept let me do that one.

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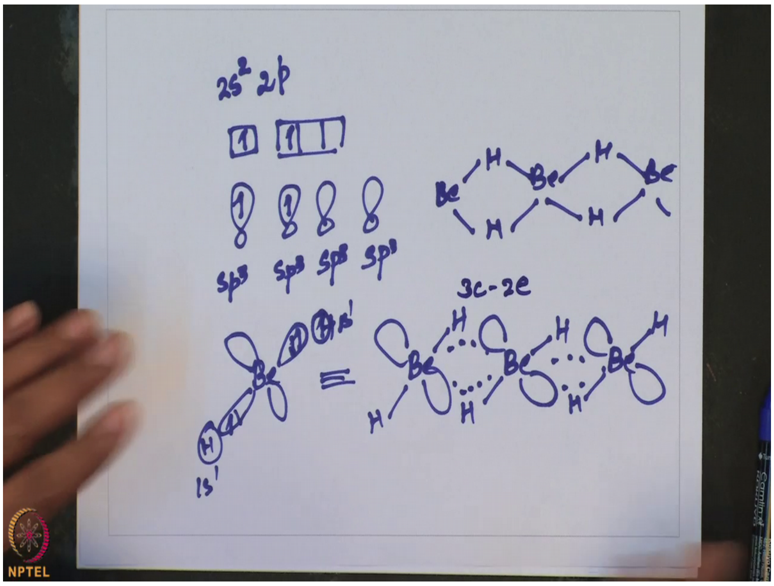

For example, in case of beryllium, what we have is 2 S 2 electronic configuration, and of course, 2 P orbital is empty. So, prior to the formation of hydride, what it does is it promotes one of the electron to the P; that means, now we have a situation like this and now this S and 3 Pp orbitals will combine to form 4 S P 3 and out of 4 S P 3 we have 2 S

P 3 with one electron each and other 2 with 0 electrons. So, now, they orient in this fashion. So, we have one electron here one electron here no electron here now H comes here H with one electron and then H with another electron here.

So, we have a situation like this now. So, here we have 2 covalent bonds are formed here, because this hydrogen is giving one electron from its 1 S 1, 1 S 1 and here 1 S 1. So, and now these 2 are empty, now we have a situation like this it can be written like this and here still we have empty one empty S P 3 orbitals. So, another beryllium atoms comes here and another beryllium atoms comes here. So, it can continue in this way what happens now? This is empty and we have 2 electrons are there now interaction takes place here. So, that essentially results in. So, it goes. So, this is how one can explain the polymeric chain that is formed in beryllium hydride to overcome electron deficiency, and if you consider here now this bond acts as a Louis base it gives electron whether this bond this one acts as a Louis as it so; that means, each beryllium essentially acts as a Louis base as well as a Louis acid and hence you see the formation of products in which we have this 3 centered 2 electron bonds are formed ok.

So, they find a method of overcoming the coordinative unsaturation, through this unsaturated electronically unsaturated 3 centered bonds. This is what exactly happens in case of (Refer Time: 16:15) B 2 H 6 also of course, I will be elaborating more when I look into the chemistry of group13 elements. So, the ionic hydrates of the heavier elements react violently with water to produce hydrogen.

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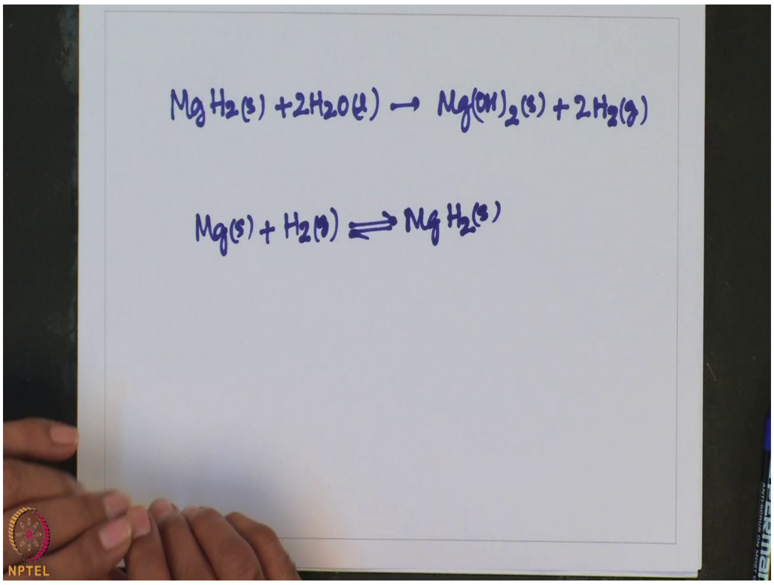

$$MgH_2(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + 2H_2(g)$$

$$Mg(s) + H_2(g) \rightleftharpoons MgH_2(s)$$

For example, let us consider magnesium hydride, if I treat this one with water it forms readily magnesium hydroxide plus H 2 is liberated. So, as this reaction is not violent as that for the group one elements, can be used as a source of hydrogen in fuel cell; that means, although they react violently the violence is considerably less compared to the group 1 element hydrates reaction with water.

So, since this reactions are not so violent, one can think of using magnesium or alkaline metal hydrides as source of hydrogen in fuel cells and for hydrogen storage a reversible reaction involving up take of hydrogen in room temperature is needed. So that means, essentially one should look for this kind of property, this reaction should be reversible yeah. If you achieve reversibility then this alkaline metal hydrates can be used as source of hydrogen in fuel cells.

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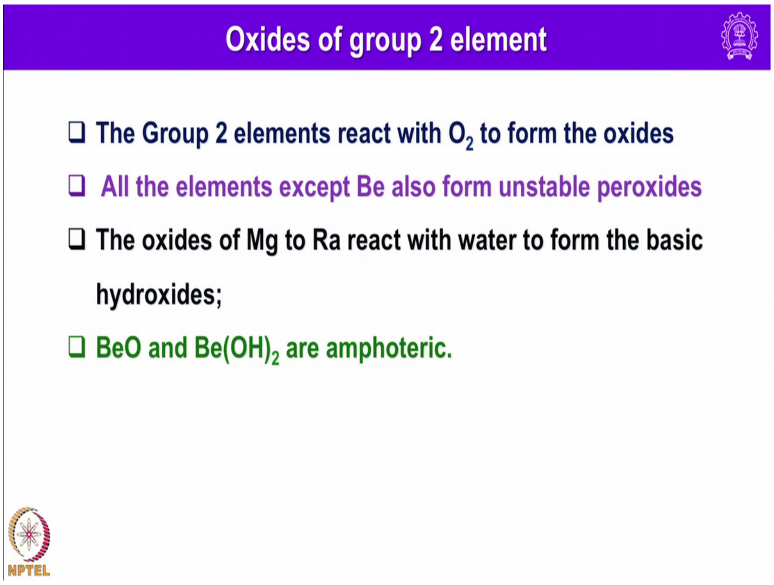

Oxides of group 2 element

- ☐ The Group 2 elements react with O_2 to form the oxides
- ☐ All the elements except Be also form unstable peroxides
- ☐ The oxides of Mg to Ra react with water to form the basic hydroxides;
- ☐ BeO and $Be(OH)_2$ are amphoteric.

So, group 2 elements react with oxygen to form oxides, now, lets me look into the oxides of group 2 elements. Group 2 elements react with oxygen to form oxides all the elements except beryllium also form unstable peroxides. The oxides of magnesium to radium react with water to form basic hydroxides very similar to alkali metal oxides and beryllium oxide and beryllium hydroxide are essentially amphoteric in nature, and beryllium oxide is obtained by ignition of the metal in oxygen.

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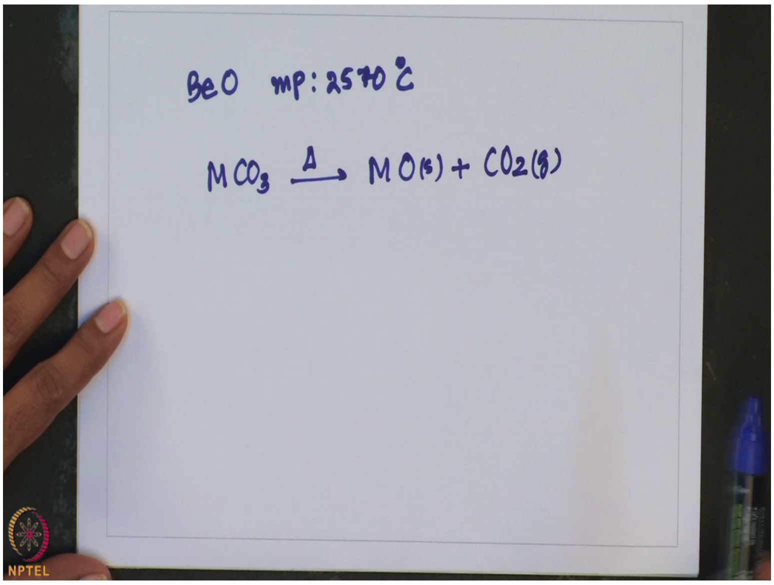

BeO mp: 2570 °C

$$MCO_3 \xrightarrow{\Delta} MO(s) + CO_2(g)$$

It is a white insoluble solid with melting point 2570 degree centigrade, and is insoluble solid the oxides of other group 2 elements can be obtained by direct combination of elements, but they are more commonly obtained by decomposition of the carbonates; that means, on heating carbonates, they give the corresponding oxides along with the liberation of CO 2 gas.

So, this is the general and convenient method used for the preparation of oxides, except in the case of beryllium simply by taking the carbonate and heating, will leads to the formation of oxide through the liberation of carbon dioxide. So that means, when it comes to the structure all oxides from magnesium to barium adopt rock salt structure or sodium chloride structure their melting point decrease down the group as the lattice enthalpy decreases with increase in cation radius, because of mismatch what happen? The lattice energy decreases as a result melting point decreases down the group, and calcium oxide also known as lime or quick lime is used in large quantities in the steel industries to remove phosphorous silicon and Sulphur impurities of course, I will be discussing more about their uses later when heated calcium oxide is thermo luminescent, and emits a bright white light hence is called lime light of course, melting points I have shown here.

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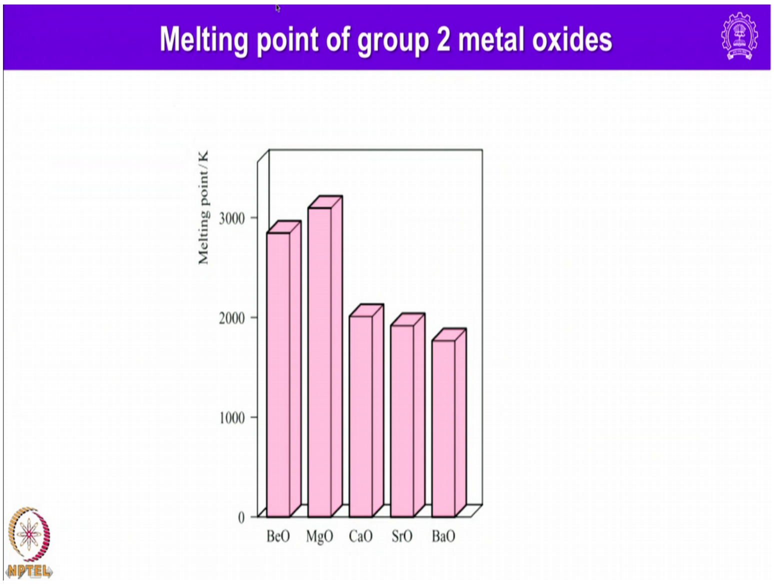

Melting point of group 2 metal oxides

In this slide, you can see the trends melting point is little higher in case of magnesium oxide, and steadily decreases down the group. And you can see here I have given the lattice energy and the melting point.

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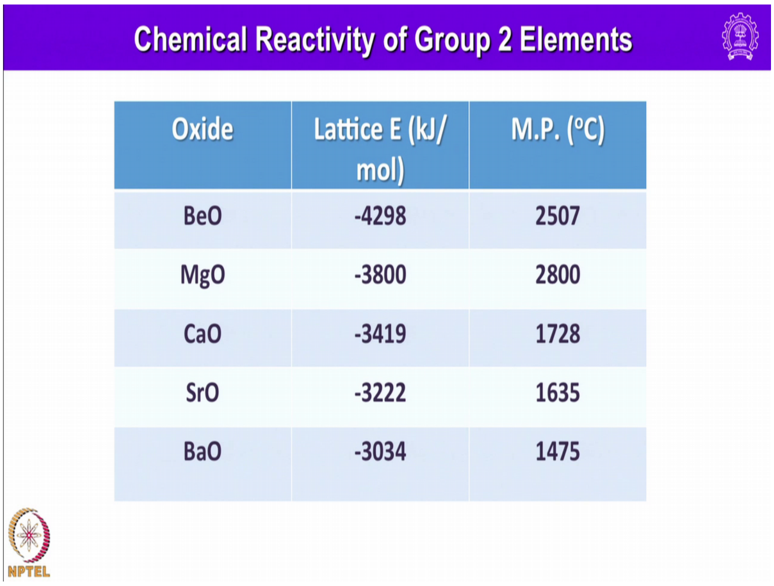

Chemical Reactivity of Group 2 Elements

Oxide	Lattice E (kJ/mol)	M.P. (°C)
BeO	-4298	2507
MgO	-3800	2800
CaO	-3419	1728
SrO	-3222	1635
BaO	-3034	1475

So, they complement each other beryllium oxide with very high lattice energy of 4298 shows highest melting point, and as the lattice energy decreases one can expect the decrease in the melting point as well. So, those trends are very clear, and that can be seen from this table here. And barium oxide with lattice energy of 3034 kilo joules per mole, shows melting point among alkaline earth metals with 1475 degree centigrade as its melting point. And sulphides of group 2 elements also adopt rock salt structure and have application as phosphorous. Beryllium sulphide adopts zinc blend structure that in zinc sulphide structure, and sulphides of heavier elements all crystallize with rock salt structure and barium sulphide produced by reducing the naturally occurring (Refer Time: 21:37) that is BaSO 4 with coke.

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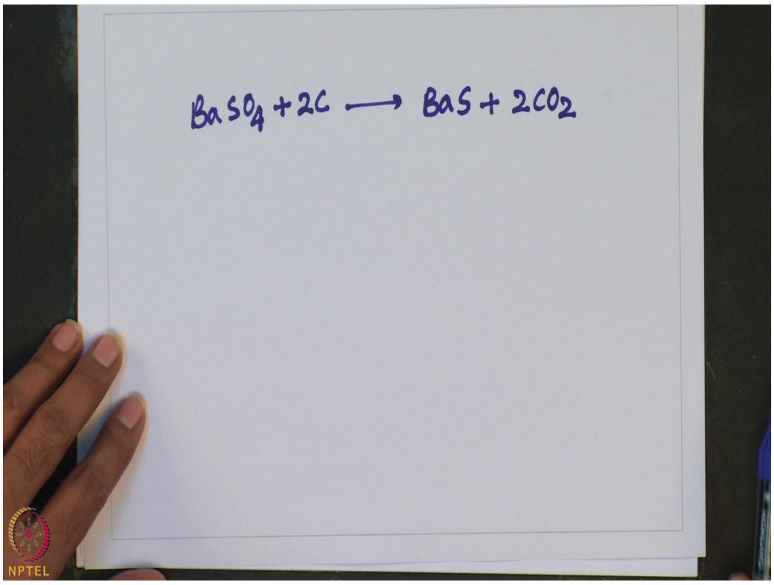

$$BaSO_4 + 2C \longrightarrow BaS + 2CO_2$$

For example one can reduce conveniently BaSO 4 into BaS by simply treating with coke.

Now, let us look into the hydroxides of group 2 elements.

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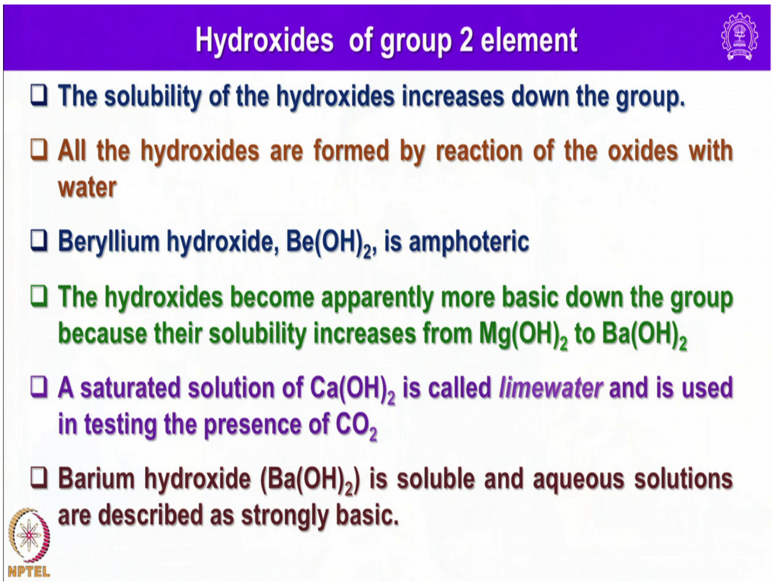

Hydroxides of group 2 element

- The solubility of the hydroxides increases down the group.
- All the hydroxides are formed by reaction of the oxides with water
- Beryllium hydroxide, $Be(OH)_2$, is amphoteric
- The hydroxides become apparently more basic down the group because their solubility increases from $Mg(OH)_2$ to $Ba(OH)_2$
- A saturated solution of $Ca(OH)_2$ is called *limewater* and is used in testing the presence of CO_2
- Barium hydroxide ($Ba(OH)_2$) is soluble and aqueous solutions are described as strongly basic.

Again the solubility of hydroxides increases down the group, all the hydroxides are formed by reaction of the oxides with water here there should not be any confusion. Hydration enthalpy decreases down the group, but the solubility of the hydroxides increases down the group. All the hydroxides are formed by reaction of the oxides with water, you take any of these alkaline earth metal oxides and treat with water the corresponding hydroxide will be formed and beryllium hydroxide is amphoteric in nature.

The hydroxides become apparently more basic down the group because of their solubility increases from magnesium hydroxide to barium hydroxide a saturated solution of calcium hydroxide is called lime water and used in testing, the presence of CO 2; that means, it readily reacts with CO 2, barium hydroxide is soluble and aqueous solutions are described as strongly basic; that means, barium hydroxide is quite strong base as I said if carbon dioxide is bubble through the lime water, a white precipitate of calcium carbonate is formed which then disappears on further reaction with carbon dioxide to form hydrogen carbonates.

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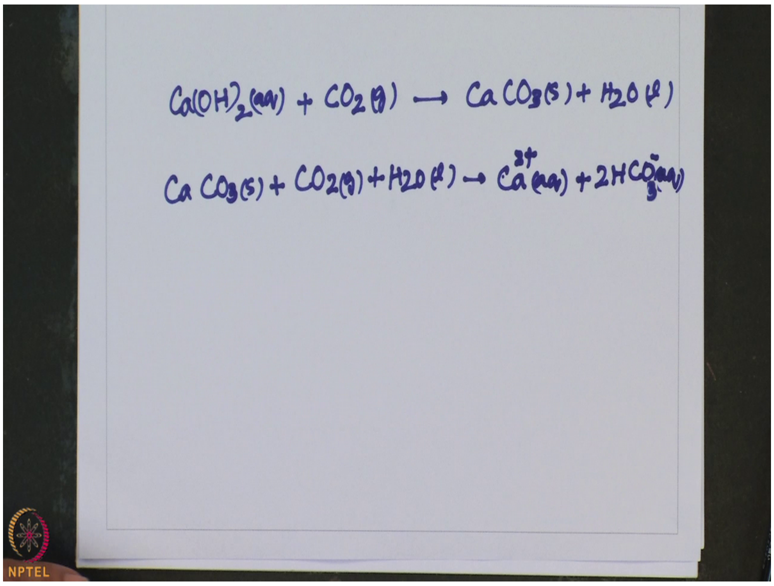

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$

$$CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

You take calcium hydroxide in aqueous medium, treat this one bubble carbon dioxide it forms calcium carbonate plus H 2 O comes out ok.

Similarly, if calcium carbonate is taken and treated with CO 2 in presence of water. So, this leads to the formation of hydrogen carbonate. So, simple anhydrous compounds of beryllium are covalent in nature, when crystallized from water a salt containing tetra aqua beryllium cation is formed for example.

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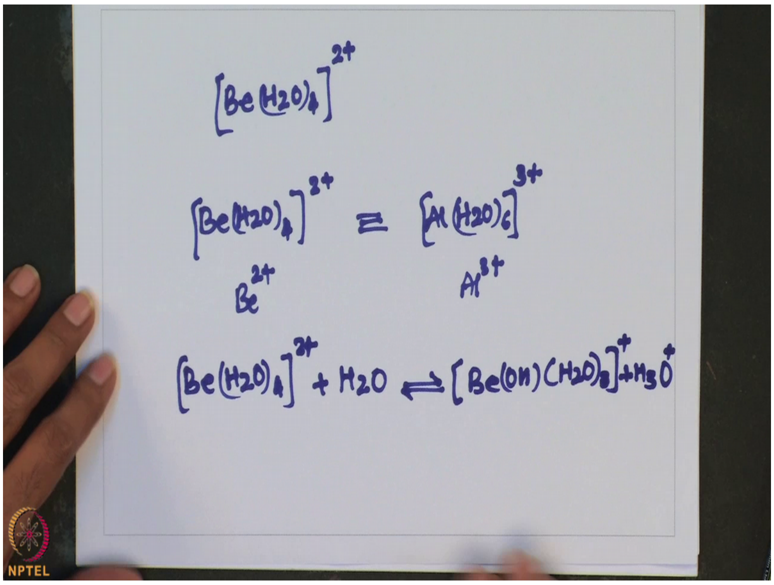

$[Be(H_2O)_4]^{2+}$

$[Be(H_2O)_4]^{2+} \equiv [Al(H_2O)_6]^{3+}$

Be^{2+} Al^{3+}

$[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(OH)(H_2O)_3]^{+} + H_3O^{+}$

So, this is essentially due to the large hydration enthalpy of beryllium compared to other group 2 elements. And this beryllium tetra aqua beryllium cation is very similar to the aluminum complex of course, aluminum forms hexa aqua compound and. So, similar to this hexa aqua aluminum 3 plus, this tetra aqua beryllium is acidic as a result of the high polarizing power of the small beryllium 2 plus ion, of course, here we have the small 3 plus ion which results in hydrolysis. The other hydrated group 2 cations are not acidic owing to their low charge to size ratio or charge density ok.

So; that means, except beryllium other alkali metal compounds do not show amphoteric properties. So, this acidic property of hexa aqua can be shown from this reaction also. For example, this hexa aqua compound when it is treated with water is formed here so; that means, this indicates this reaction indicates that tetra aqua beryllium 2 plus only exists in strong acid solution on increasing the PH hydroxide bridged ions.

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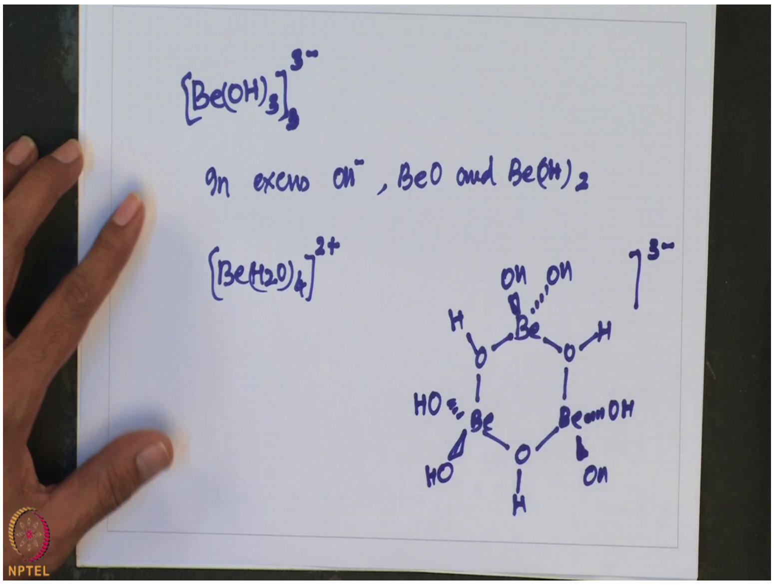

$[Be(OH)_3]_3^{3-}$

In excess OH^-, BeO and $Be(OH)_2$

$[Be(H_2O)_4]^{2+}$

Such as before the precipitation of Be OH twice so; that means, on increasing the p H beryllium hydroxide is formed prior to the precipitation of beryllium hydroxide, this species is formed. So, in excess hydroxide B e o and BHO 2 will be formed. So, in excess hydroxide OH minus. So, both B e O and B e O H twice, dissolve to give berylyte ion that is again comes back to hexa aqua berylate ion, demonstrating the amphoteric nature of beryllium.

So, if you are curious to know the structure of this one this has a cyclic structure, let me write the structure before I conclude this talk. It has a 6 membered cyclic structure with alternate beryllium and oxygen atoms. So, this is the structure of the cyclic beryllium hydroxide anion. So, let me stop here, in my next lecture I will be discussing more about reactions of hydroxides and then the chemistry of alkali metals with respect to their interaction with halogens and other species so.

Thank you very much.