Main Group Chemistry
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Lecture - 22
Chemistry of Group 2 elements

This is my 22 lecture on the chemistry of main group elements, in my 21 lecture, I started discussing on the chemistry of main group elements and I had stopped while discussing the chemistry of main group oxides, let me continue from where I had stopped; these metal oxides that means, the metal oxides of group 2 elements are basic in nature, when they react with water they give the corresponding hydroxides.

Similarly when you treat calcium hydroxide with hydrogen peroxide in aqueous medium, it forms calcium peroxide. That so this calcium oxide on treatment with water gives calcium hydroxide, if calcium hydroxide is treated with hydrogen peroxide in aqueous medium it gives calcium peroxide.

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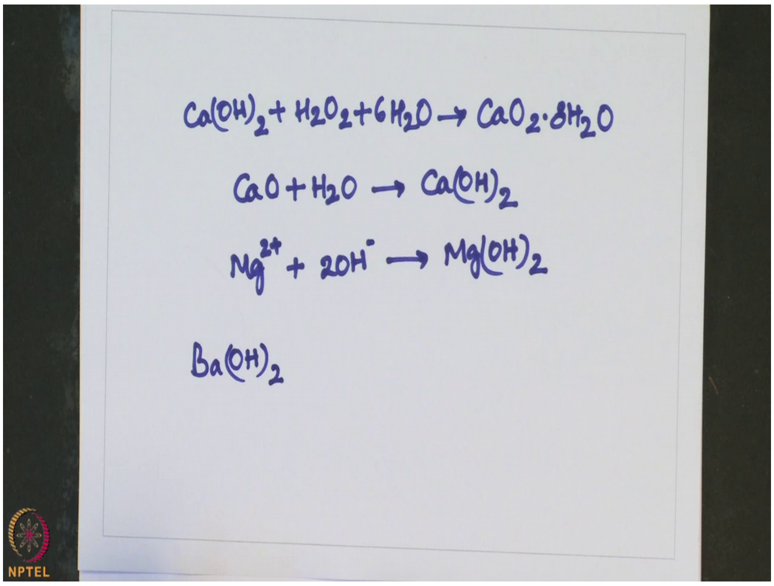

$$Ca(OH)_2 + H_2O_2 + 6H_2O \rightarrow CaO_2\cdot 8H_2O$$

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

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

$$Ba(OH)_2$$

As I already mentioned calcium oxide reacts with water to give calcium hydroxide, similarly if we take magnesium 2 plus ions and react with hydroxide ions leads to the formation of magnesium hydroxide and of course among all hydroxides of group 2 elements barium hydroxide is the most stable and most soluble hydroxide.

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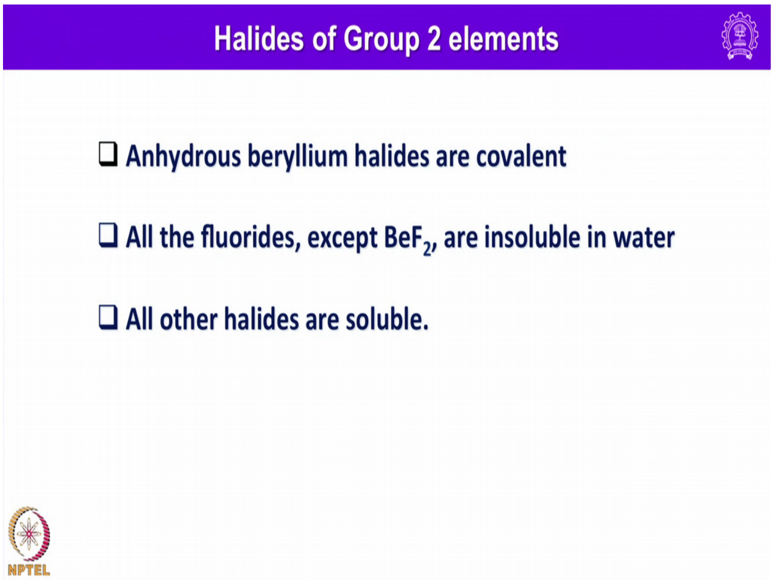

Halides of Group 2 elements

☐ Anhydrous beryllium halides are covalent

☐ All the fluorides, except BeF_2, are insoluble in water

☐ All other halides are soluble.

So, now let me move on to halides of group 2 elements, of course when we talk about halides of group 2 elements anhydrous beryllium halides are always covalent, whether we talk about fluorides chlorides bromides or iodides; all the fluorides except beryllium fluoride are insoluble in water; that means, all the fluorides of group 2 elements except beryllium fluoride are insoluble in water and rest of the halides of group 2 elements are all soluble.

Then the question is why fluorides are sparingly soluble? So, all though solubility increases slightly more down the group, the radius of the cat ion increases from beryllium to barium. So, as a result the cat ion coordination number also increases from 4 to 8.

So, strontium fluoride and barium fluoride out of fluoride structure fluoride is nothing but calcium fluoride it has FCC face centered cubic structure, the remaining fluorides that is strontium fluoride, if you consider or barium fluoride they adopt calcium fluoride structure the other halides of group 2 form layer structures reflecting the increasing polarizability of the halide ions and how to prepare this fluorides; beryllium fluoride can be conveniently prepared from the thermal decomposition of ammonium tetra fluoro berrylite that is n h 4 twice b e f 4.

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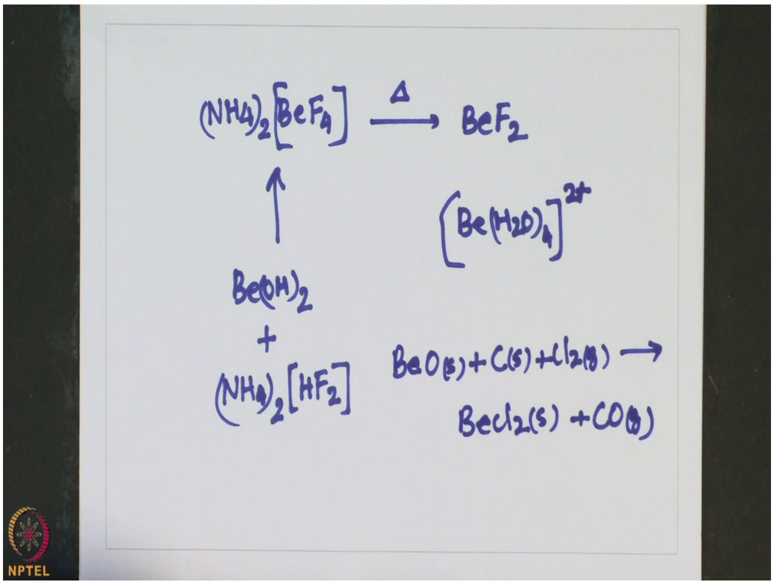

Of course this itself can be prepared starting from beryllium hydroxide plus ammonium hydrogen di fluoride, this we saw in the extraction of beryllium from beryl. So that means, 1 can conveniently make beryllium tetra fluoride the ammonium tetra fluoro berylate starting from beryllium hydroxide and it is reaction with this compound shown here and then the thermal decomposition of this 1 will give BeF2 and beryllium di fluoride is a glossy solid that exists in several temperature dependent phases similar to SiO2 and it is soluble in water forming the hydrate.

That means, when you take BeF2 and add water immediately it forms a complex having 4 water molecules, in it is coordination sphere having a tetra hedral geometry and of course beryllium chloride can be made from the corresponding beryllium chloride can be made starting from beryllium oxide, using carbon as a reducing agent beryllium oxide plus carbon that is coal as reducing agent causing chlorine gas leads to the formation of ok. So, this is how 1 can conveniently prepare beryllium chloride.

So, similarly beryllium chloride beryllium bromide beryllium iodide it can also be prepared from the direct reaction of the elements at elevated temperature using the corresponding halogen dimmers; the structure of solid BeCl2 is a polymeric chain very similar to beryllium hydride that already I showed you in 1 of my last lectures. Magnesium chloride adopts the cadmium chloride type layer structure in which the layers are arranged. So, that Cl minus ions are cubic close packed both magnesium I2 and calcium I2, that is magnesium iodide and calcium iodide adopt the closely related cadmium iodide structure in which the layers of iodide ions are hexagonal close packed ok.

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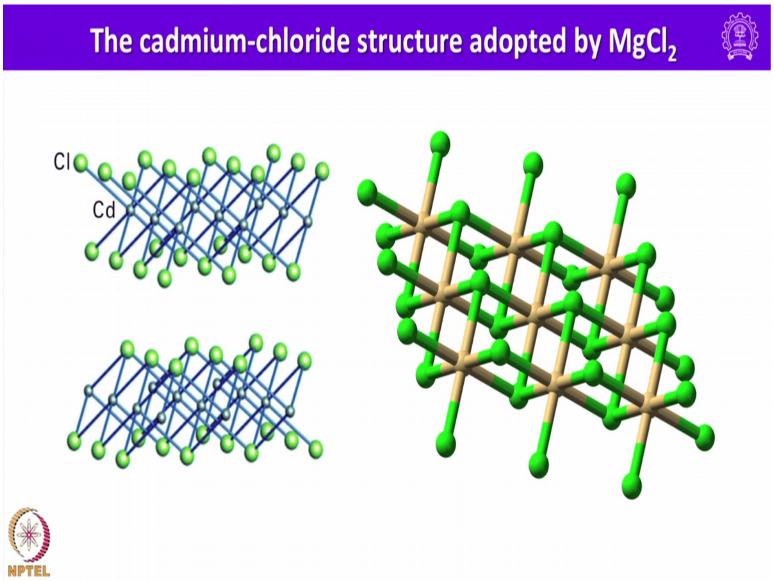

The cadmium-chloride structure adopted by $MgCl_2$

So, I have shown here for your reference the cadmium chloride structure, you can see here cadmium chloride structure; that means, here essentially metal ions are coordinated by 6 chloride ions each metal ion. So, in this process all of them are sharing here for example, you all of them are acting as tri bridging ligands all halides are acting as tri bridging ligands and then the metal ions show octahedral geometry here. So, this is a typical cadmium chloride structure that is adopted by magnesium chloride as well and the green 1 represent halide or chloride and the brown 1 represent metal ions divalent metal ions such as magnesium ok.

The most important fluoride of the group 2 is calcium fluoride, it is also called fluoride it is mineral form fluoride is the only large scale source fluorine. In fact, hydrogen fluoride is prepared by the treatment of sulphuric acid on calcium fluoride or flurosphar.

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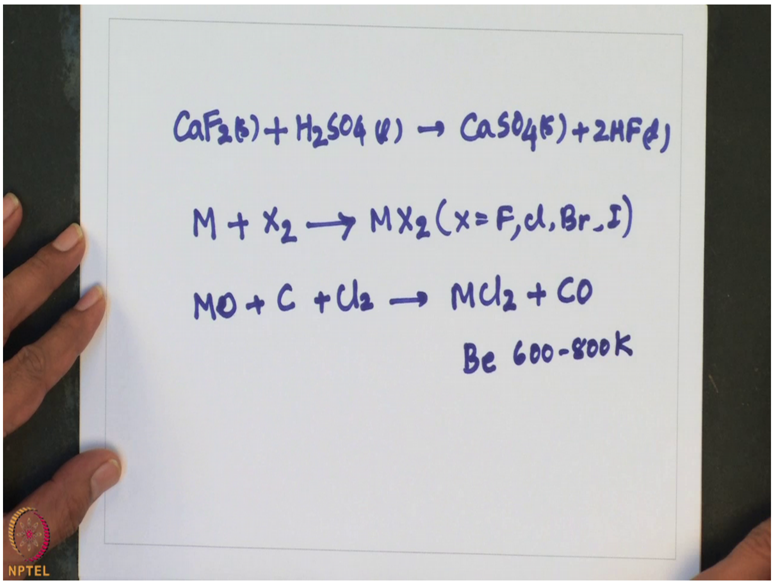

$CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2HF(g)$

$M + X_2 \longrightarrow MX_2 \, (X = F, Cl, Br, I)$

$MO + C + Cl_2 \rightarrow MCl_2 + CO$

Be 600-800K

So, calcium fluoride on treatment with concentrated sulphuric acid leads to the formation of calcium sulphate plus hydrogen fluoride. So, this is how hydrogen fluoride is generated starting from calcium fluoride or fluoride. So, let us look into the reactions of halogens and the properties of halogens. So, in general if I take consider this as group 2 element. So, a typical halogen where x is fluoride, chloride, bromide or iodide or MO plus carbon plus Cl 2 gives MCl 2 plus CO of course, in case of beryllium the temperature required is about 600 to 800 Kelvin.

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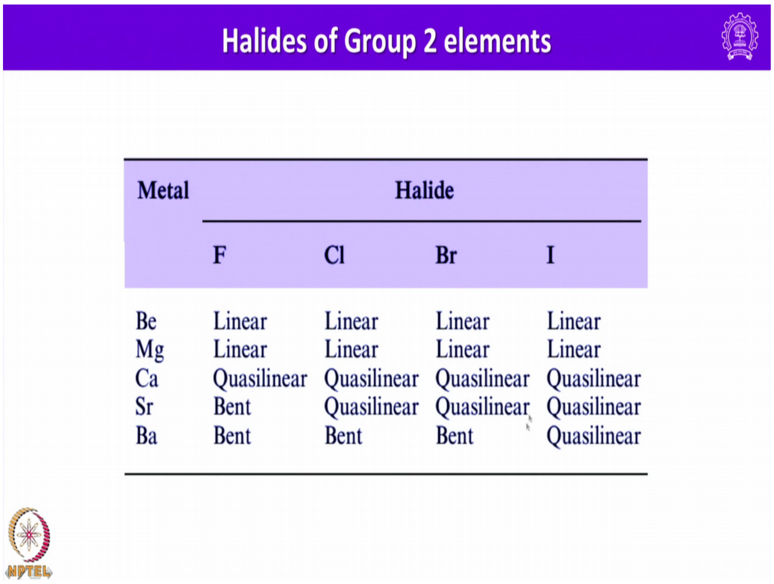

Halides of Group 2 elements

Metal	Halide			
	F	Cl	Br	I
Be	Linear	Linear	Linear	Linear
Mg	Linear	Linear	Linear	Linear
Ca	Quasilinear	Quasilinear	Quasilinear	Quasilinear
Sr	Bent	Quasilinear	Quasilinear	Quasilinear
Ba	Bent	Bent	Bent	Quasilinear

I have listed some of the halides, here you can see in this slide beryllium forms linear structure in all the cases 2 coordinated and whereas magnesium also linear whereas, calcium shows quasilinear structure in case of all 4 halides and same whereas in case of strontium with fluoride it is a bend structure; whereas, in case of chloride bromide and iodide it shows quasilinear structure, similarly barium shows bend structure with all halides except in case of iodine, in case of iodine it shows quasilinear structure and what is quasilinear?

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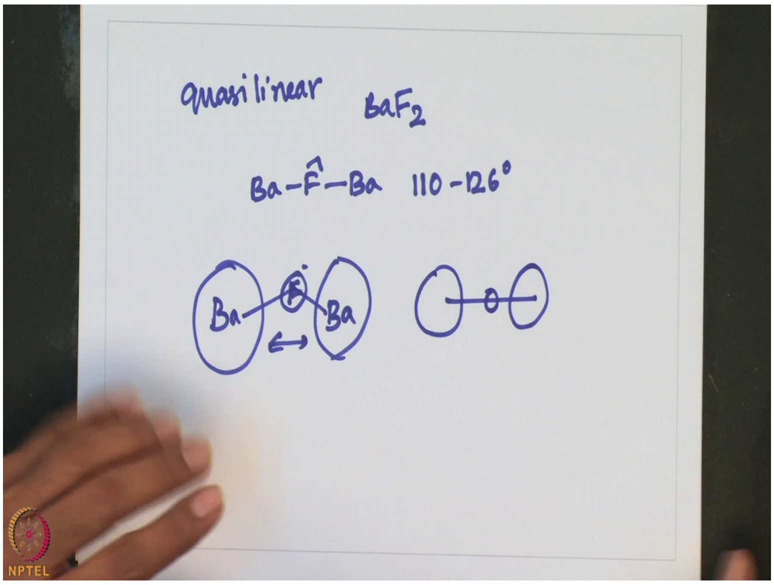

The term quasilinear refers to a species for which the calculated energy difference between linear and bend structure is less than 4 kilo joules per mole, the most bend of the di halides is barium fluoride ok. It has a bond angle in the range of 110 so in case of barium.

So, what we are talking about is this 1 this angle is in the range of 110 to 126 degree ok. The preference for bend structures for the heaviest metals combined with fluorine chlorine or bromine has been explained in terms of inverse polarization and the participation of the atomic orbitals for calcium strontium and barium.

I do not know to what extent it is true the incorporation or brining in d orbital’s to enhance it is coordination number, it appears like it is hyper valiancy; however, since the energy of d orbital’s is very high it is not appropriate to consider the participation of the atomic orbital. In fact, molecular orbital diagram will give you a clear picture about actually what is happening in this type of bonding. So, inverse polarization occurs when the metal ion is polarizable and is polarized by fluoride or chloride or to a lesser extent by bromide ions, the polarization is termed inverse to distinguish it from the polarization of a large polarizable anion by a cat ion.

So, another convincing explanation about the bending or linear structure can also be given by looking into the relative size of the ions; for example, if we consider say barium relatively large divalent ion and if it prefers to have a bent structure with fluoride something like this, it so happens that these 2 come very close to establish a bent structure this angle will shrink to establish a covalent bond between them or ionic bond. So, they come very close to each other in this process what happens these 2 positively charged ions will start repelling each other, as a result what happens this type of bent structure is destabilized; on the other hand if we look into this kind of structure where they are linear.

So, no such inconveniency is caused here both the cat ions are kept conveniently away from each other, as a result what happens most of the main group elements as well as elements. When they are combined with fluorine they always have linear structure to minimize the inter electron repulsion between the positively charged metal ions, that is true in case of we take beryllium fluoride or we consider aluminum fluoride. For example, aluminum fluoride if you consider it has a bent structure something like this, whereas when we look into the aluminum fluoride it is tetrameric structure; of course I can give more details when I go to the group 13 chemistry I would elaborate more on these aspects then.

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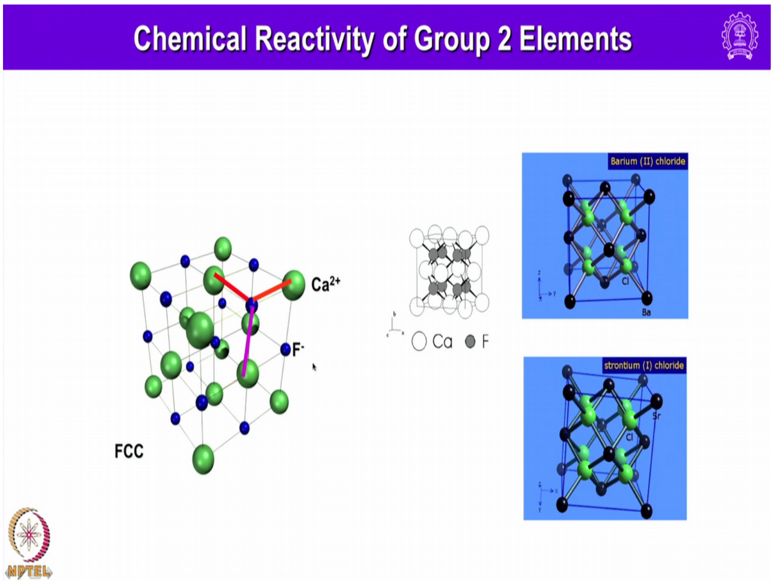
Chemical Reactivity of Group 2 Elements

I was telling this is the structure of calcium fluoride it shows space 100 cubic structure a strontium chloride also has the same structure.

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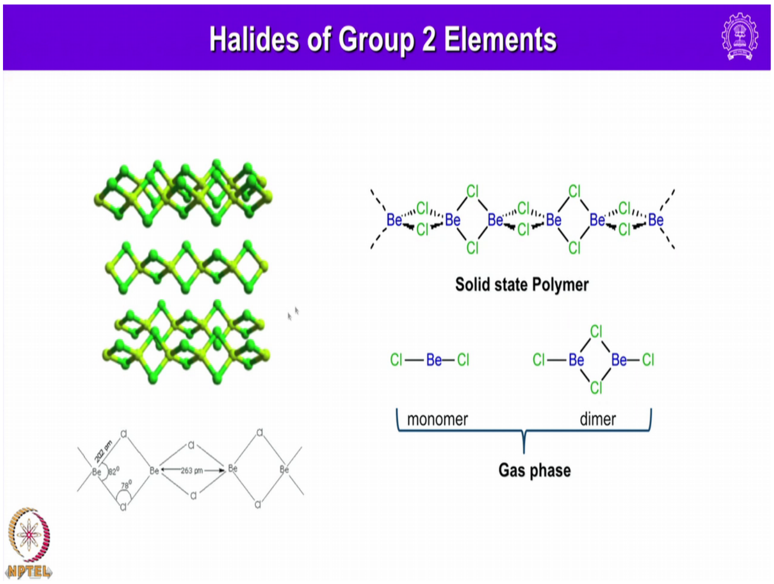
Halides of Group 2 Elements

In case of beryllium as I mentioned it shows in solid state a 1 dimensional polymeric structure, the structure is very similar to the structure, I explained in case of beryllium hydride and in the gas phase it shows both monomerically with angle 180 and also this can also undergo dimeration to give a compound of this type. So, both are possible whereas, in solid state it shows exclusively one dimensional chain like structure here and of course here I already described the structure of this one using by using valence bond theory using sp3 hybridization.

If you consider sp 3 hybridization beryllium centre, we have 4sp3 hybrid orbital with 2sp3 hybrid orbital having 1 electron each and 2sp3 hybrid orbital's having no electron, essentially these are disposed in at tetrahedral angles and they make bonds with chloride and now the chloride lone pair will interact with 1 of the empty sp3 orbital to establish a coordinate bond this is how we have the linear structure that I have shown there.

So that means, you say it is a essentially a 1 dimensional polymer. So, let us look into the reactions with other elements such as nitrogen, magnesium burns in nitrogen to form greenish yellow compound having composition Mg3N2.

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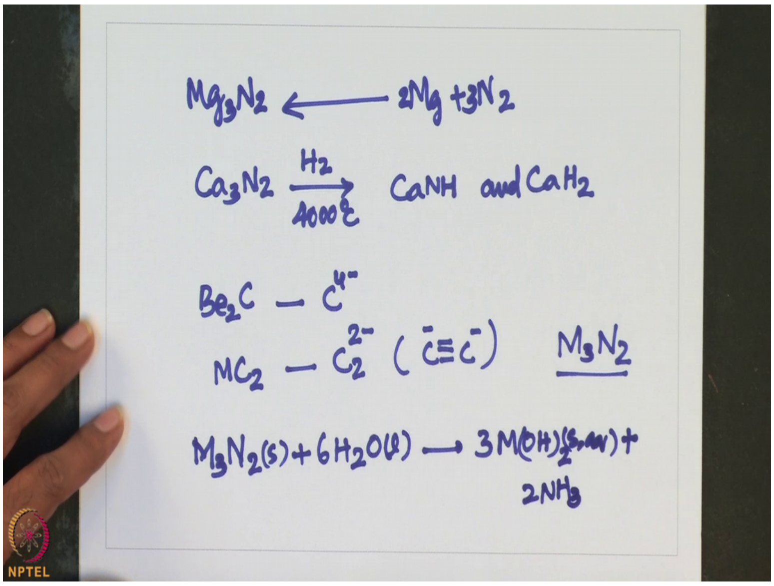

$Mg_3N_2 \longleftarrow 2Mg + 3N_2$

$Ca_3N_2 \xrightarrow[4000^\circ C]{H_2}$ CaNH and CaH_2

$Be_2C - C^{4-}$

$MC_2 - C_2^{2-}\ (\bar{C}\equiv\bar{C})$ $\underline{M_3N_2}$

$M_3N_2(s) + 6H_2O(l) \longrightarrow 3M(OH)_2(s, aq) + 2NH_3$

So that means it can be conveniently prepared by burning magnesium under nitrogen, which has been used as a catalyst for preparing cubic boron nitrite, calcium nitrate reacts with hydrogen gas at 4000 degree centigrade to produce a compound like this. So, calcium nitrate also one can prepare directly combining calcium with nitrogen N2. So, this one reacts with hydrogen gas at 4000 degree centigrade to form CaNH and CaH2 as well calcium hydride and beryllium nitrate melts at 2200 degree centigrade and is used as a refractory material; beryllium carbide formally contains essentially the moment we look into this 1 we should be able to speculate that this contain C4 minus ion so; that means, this 1 readily reacts with water to give methane, the carbides of magnesium calcium strontium and barium have a different formula they form preferably this kind of species and contain this indicates they contain C2 2 minus ion here essentially an acetylide ion this is nothing, but acetylide ion.

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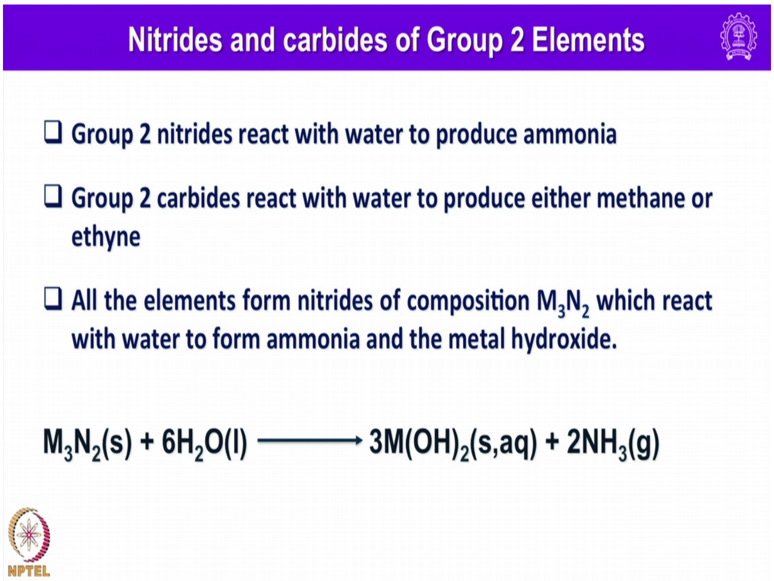

Nitrides and carbides of Group 2 Elements

- ☐ Group 2 nitrides react with water to produce ammonia
- ☐ Group 2 carbides react with water to produce either methane or ethyne
- ☐ All the elements form nitrides of composition M_3N_2 which react with water to form ammonia and the metal hydroxide.

$$M_3N_2(s) + 6H_2O(l) \longrightarrow 3M(OH)_2(s,aq) + 2NH_3(g)$$

So, group 2 nitrites react with water to produce ammonia, group 2 carbides react with water to produce either methane or ethane. So, all the elements form nitrate that means, all the elements of group 2 element form nitrates of composition M3N2 and which readily react with water to form ammonia and the metal hydroxide corresponding hydroxide will be formed.

So, 1 can write a general equation for the reaction of metal nitrate with water, of course this is in aqueous medium plus 2NH3. So, all metal nitrates of group 2 elements react with water to form the corresponding metal hydroxide plus ammonia is formed ammonia is liberated.

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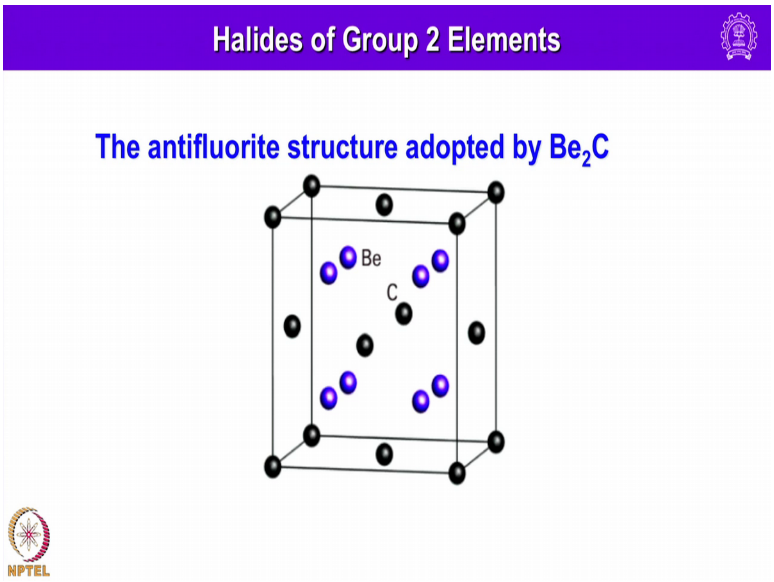

Halides of Group 2 Elements

The antifluorite structure adopted by Be_2C

The structure of beryllium carbide is similar to anti fluoride structure that I have shown here and the carbides of calcium strontium and barium can be prepared simply by heating the beryllium oxide or carbonate, with carbon in a furnace maintained at around 2000 degree centigrade.

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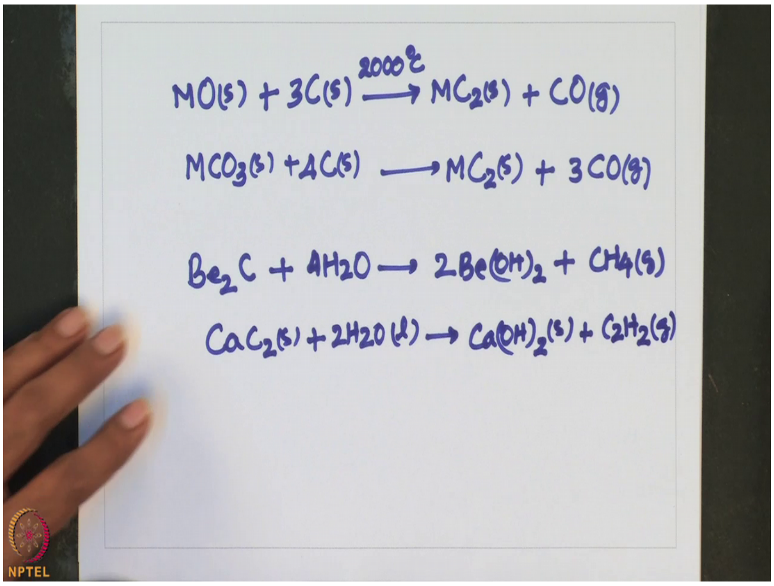

$$MO(s) + 3C(s) \xrightarrow{2000^\circ C} MC_2(s) + CO(g)$$

$$MCO_3(s) + 4C(s) \longrightarrow MC_2(s) + 3CO(g)$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4(g)$$

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$$

For example we take oxide and treat this 1 with carbon around cross metal around 2000 degree centigrade, 1 can also start from corresponding carbonates; so as I mentioned beryllium carbide is different from the carbides of rest of the main group 2 elements. So, beryllium carbide on hydrolysis or on reaction with water forms methane, whereas in case of other carbides such as calcium carbide, it also gives calcium hydroxide but it gives acetylene instead of ethane. So, this is a difference. So, it forms beryllium carbide of this type whereas, calcium carbide of preferably in this composition; let us look into the carbonates and hydrogen carbonates of group 2 elements.

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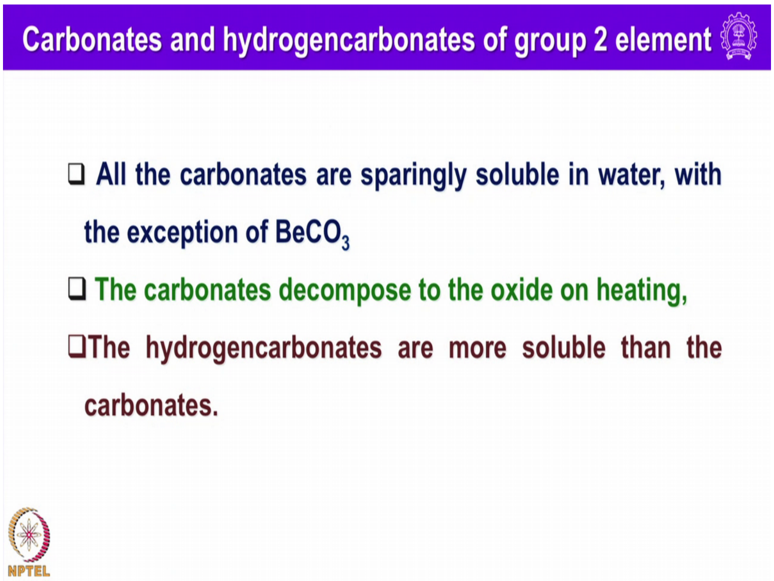

Carbonates and hydrogencarbonates of group 2 element

❑ All the carbonates are sparingly soluble in water, with the exception of $BeCO_3$

❑ The carbonates decompose to the oxide on heating,

❑ The hydrogencarbonates are more soluble than the carbonates.

Again all the carbonates of group 2 elements are sparingly soluble in water with an exception of beryllium carbonate, the carbonates decomposes to oxide on heating; for example, if you take simply MCO3 on heating they form MO plus co 2 ok.

The hydrogen carbonates are more soluble than the carbonates, the carbonates of other elements are all sparingly soluble and are decomposed to the oxide on heating very similar; the group 2 carbonates have similar thermal stability to the group 1 carbonates and these trends can be explained in terms of trends in enthalpies. The powdered limestone is known as agricultural lime, is essentially used to neutralize acidic soil how they do it?

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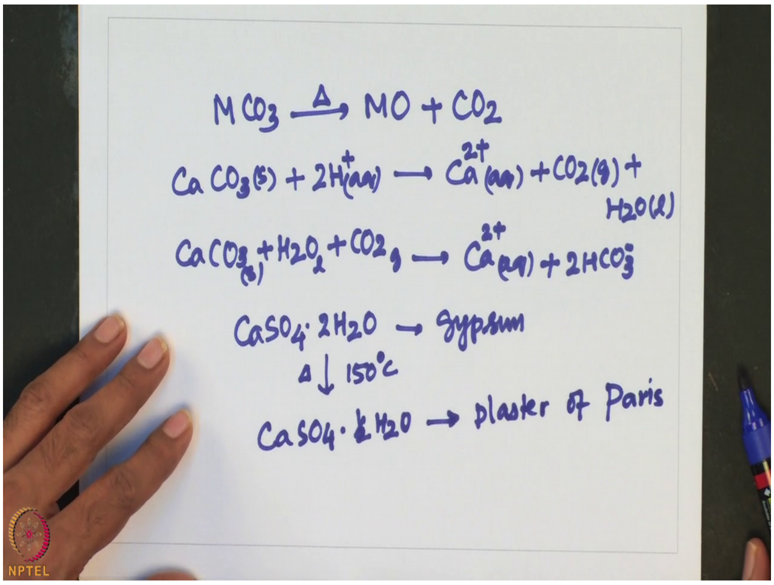

$MCO_3 \xrightarrow{\Delta} MO + CO_2$

$CaCO_{3(s)} + 2H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$

$CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \rightarrow Ca^{2+}_{(aq)} + 2HCO_3^-$

$CaSO_4 \cdot 2H_2O \rightarrow$ gypsum

$\Delta \downarrow 150°C$

$CaSO_4 \cdot \frac{1}{2}H_2O \rightarrow$ plaster of Paris

For example You take calcium carbonate use so like this, so essentially 1 can conveniently neutralize calcium carbonate is sparingly soluble in water, but it is solubility is increased CO2 is dissolved in the water as in rain water. So, what would happen here is again so calcium carbonate plus H2O plus CO2 liquid yes and this is solid ok. So, similarly 1 can also conveniently make sulphates and nitrates of group 2 element.

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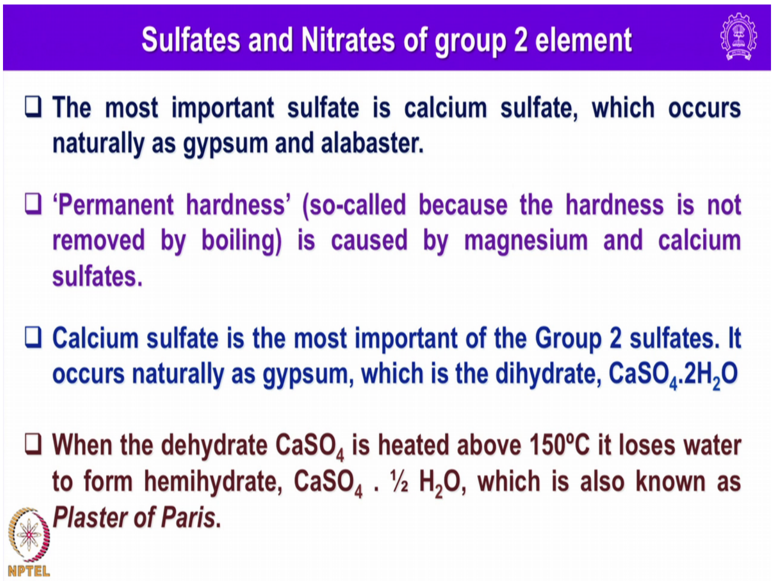

Sulfates and Nitrates of group 2 element

- ❑ The most important sulfate is calcium sulfate, which occurs naturally as gypsum and alabaster.
- ❑ 'Permanent hardness' (so-called because the hardness is not removed by boiling) is caused by magnesium and calcium sulfates.
- ❑ Calcium sulfate is the most important of the Group 2 sulfates. It occurs naturally as gypsum, which is the dihydrate, $CaSO_4.2H_2O$
- ❑ When the dehydrate $CaSO_4$ is heated above 150°C it loses water to form hemihydrate, $CaSO_4$. ½ H_2O, which is also known as *Plaster of Paris.*

The most important sulphate is calcium sulphate which occurs naturally as gypsum and alabaster the permanent hardness, so called the hardness is not removed by boiling; that means, the when you simply heat water and if you cannot remove the hardness by boiling, that is because of permanent hardness it is essentially caused by magnesium and calcium sulphide present in water.

So, calcium sulphate is the most important of the group 2 sulphates, it occurs naturally as gypsum; gypsum is nothing but calcium sulphate di hydride. I will be elaborating more about it is utility and also how 1 can make plaster of paris starting from gypsum and all those things; essentially gypsum is nothing but calcium sulphate di hydride is called gypsum.

When the di hydride calcium sulphate is heated above 150 degree centigrade it loses water to form hemi hydrate; that means, it will be having only half equivalent of water per calcium sulphate molecule that is known as plaster of paris. That means, if you heat this 1 to about 150 degree centigrade it forms hemi hydrate this is called plaster of paris. So, let me continue more on this sulphates and nitrates and the remaining chemistry of main group elements in my next lecture.

Thank you very much.