Main Group Chemistry
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Lecture – 27
Chemistry of Group 13 Elements

Welcome to MSB lecture series on main group chemistry. So, let me begin todays lecture with discussion on aluminium hydrides in my previous lecture, I was discussion about boron hydrides and their preparation and their utility in organic synthesis. So, let me now start discussion on aluminium hydrides, aluminium hydride can be prepared by reacting aluminium trichloride with lithium aluminium hydride in ether, so how that happens.

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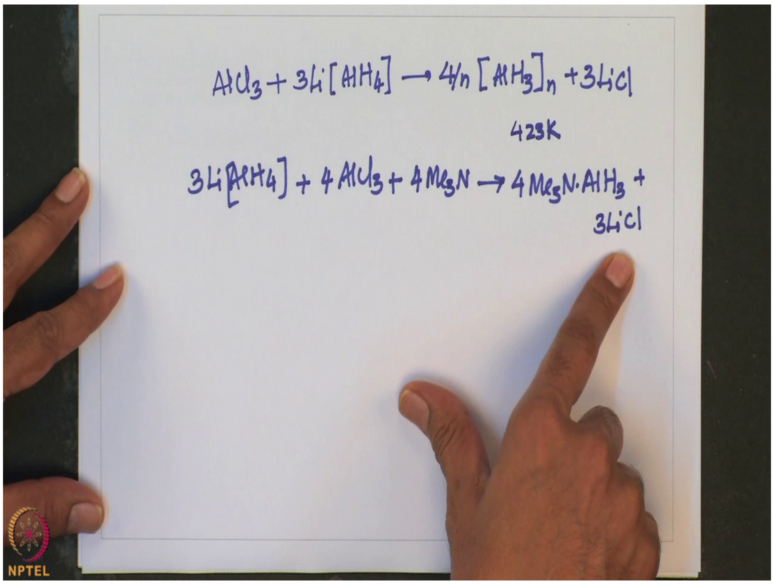

$AlCl_3 + 3Li[AlH_4] \rightarrow 4/n\,[AlH_3]_n + 3LiCl$

423K

$3Li[AlH_4] + 4AlCl_3 + 4Me_3N \rightarrow 4Me_3N{\cdot}AlH_3 + 3LiCl$

So, AlCl 3 plus lithium aluminium hydride it gives so, this how one can make conveniently aluminium hydride or one can also call it as aluminane so; however, the formation of etherate complexes because of electron deficiency complicates the synthesis ok. So, these compounds are highly unstable so, above 423 kelvin. So, these are unstable with respect to decomposition to give the corresponding element that is aluminium and hydrogen. And since this are thermally unstable so, one can think of exploiting their property in generating thin films of aluminium, now this is where a utility of this things comes in fact, volatile p block elements have been used in in generating thin films.

Aluminium hydride reacts with Lewis bases very similar to boron hydride to form the corresponding adducts for example, let us take a lithium aluminium hydride and treat this one with AlCl 3 and so, here this is the another way of making it and then stabilizing them as adducts for example, take lithium aluminium hydride and treat that 1 with aluminium chloride in presence of soft base such as triethylamine it gives an adduct of AlH 3 and LiCl will be precipitating out of course, this reaction can be carried out in a organic solvents such as ether.

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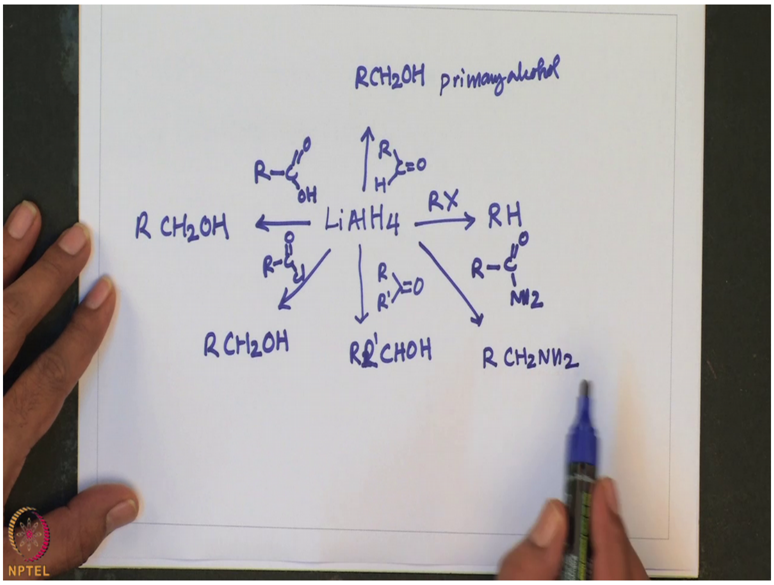

Now, let us look into some reactions of lithium aluminium hydride with organic compounds. So, lithium aluminium hydride so, take this 1 treat this 1 with hydrogen alkane or alkyl halide it gives RH and 1 can also treat this 1 with an aldehyde. So, this gives RCH 2 OH 1 can also treat this 1 with a ketone so, it gives secondary this is primary alcohol. So, in this case what we get is a secondary alcohol R 2 RCH 2 CHOH secondary alcohol we get it. And instead if we take an acid it gives again a primary alcohol, and if I say take an acid chloride acid chloride it gives again primary alcohol if we take an amide 1 can get a primary amine treat.

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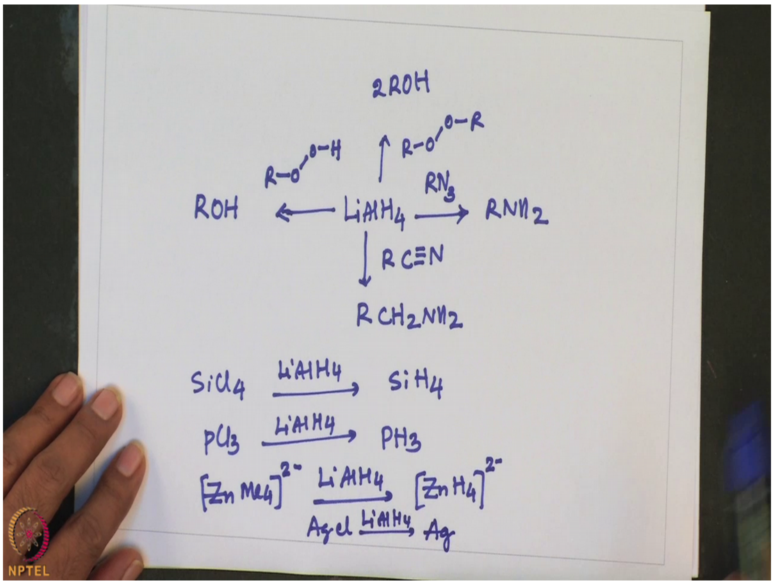

This 1 with an oxide organic oxide RN 3 it gives amine. If you treat with a nitril such as astro nitrile or belzon nitrile it gives primary amine, if it is treated with hydrogen peroxide hydro peroxide, it gives alcohol. If you treat with a peroxide this hydro peroxide and this is peroxide it will give again alcohol.

So, this are few reactions and you can see how effectively 1 can use for a variety of organic transformations and of course, 1 can also do reaction such as this one for example, SiCl 4 when its treated with lithium aluminium hydride it gives the (Refer Time: 07:52) SiH 4. And similarly pCl 3 lithium aluminium hydride gives pH 3, and 1 can also tetra methyl zinc 2 minus. If it is treated with lithium aluminium hydride it can give very unstable species of course, this is very unstable, now as there was 1 can make tetra hydro zincate can be made. And it can also reduce metals for example, AgCl when its treated with lithium aluminium hydride it gives silver. So, these are some of the reactions where you can find the utility of lithium aluminium hydride.

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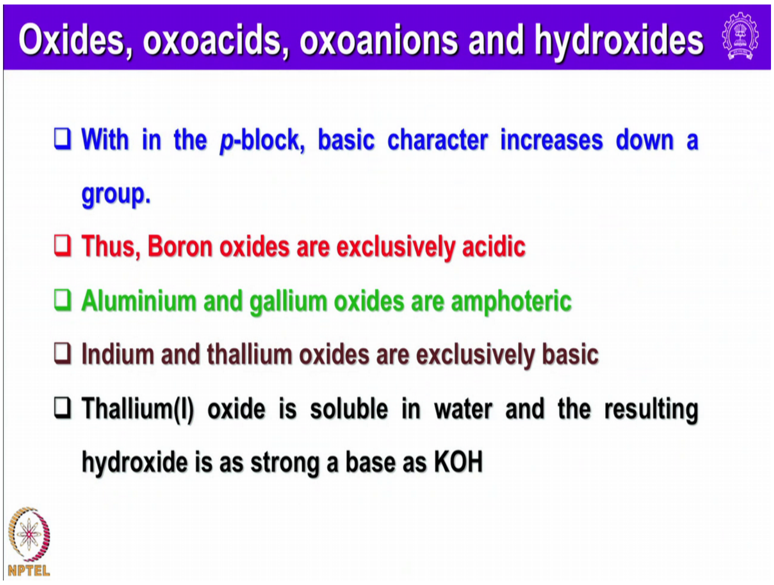

Oxides, oxoacids, oxoanions and hydroxides

- ❑ With in the *p*-block, basic character increases down a group.
- ❑ Thus, Boron oxides are exclusively acidic
- ❑ Aluminium and gallium oxides are amphoteric
- ❑ Indium and thallium oxides are exclusively basic
- ❑ Thallium(I) oxide is soluble in water and the resulting hydroxide is as strong a base as KOH

So, let us look into digalen the simplest gallium hydrate is digalen is nothing, but Ga 2 H 6. And this is prepared starting from gallium trichloride and the product condenses at low temperature as a white solid, but decomposes above 253 kelvin. So, one can conveniently prepare starting from gallium trichloride treating this one with trimethylsilane as a as a source of hydride ions of course, the structure of this one is similar to ethane initially what we get is this one something like this, and this one on further treatment with lithium gallium hydride at 240 kelvin it gives.

So, this how 1 can make digalen 1 can expect reactions of digalen very similar to diborane only thing 1 should remember is all reactions of digallen must be carried out at low temperature. Since it decomposes above 253 kelvin to give gallium and dihydrogen, whatever the reactions I had described in case of diborane can be carried out using digalen probably we maintain the temperature below 253 kelvin.

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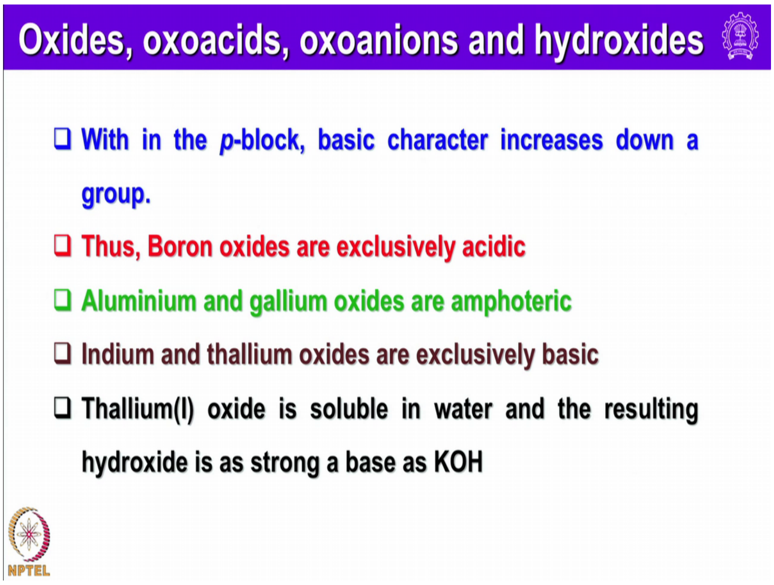

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Now, let us look into oxides oxo acids oxo anions and hydroxides of group 13 elements within the p block basic character increases down a group. This is true with most of the groups as well thus boron oxides are exclusively acidic, but when you go for heavier once of course, aluminium is amphoteric and gallium also to an extent amphoteric, whereas indium and thallium oxides are exclusively basic and thallium oxide thallium 1 oxide is soluble in water and the result in hydroxide is a strong base and its bassicity can be compared to potassium hydroxide.

So, boron forms B 2 O 3 and also several poliborates and also borosilicate glasses, borosilicate glasses are very important in glass industry boron oxide B 2 O 3 is acidic and is prepared by dehydration of boric acid. So, alkali metal and alkaline earth metal oxides are basic whereas p block oxides are acidic and boron oxide is no exception, and 1can prepare boron oxide by simply performing dehydration of boric acid.

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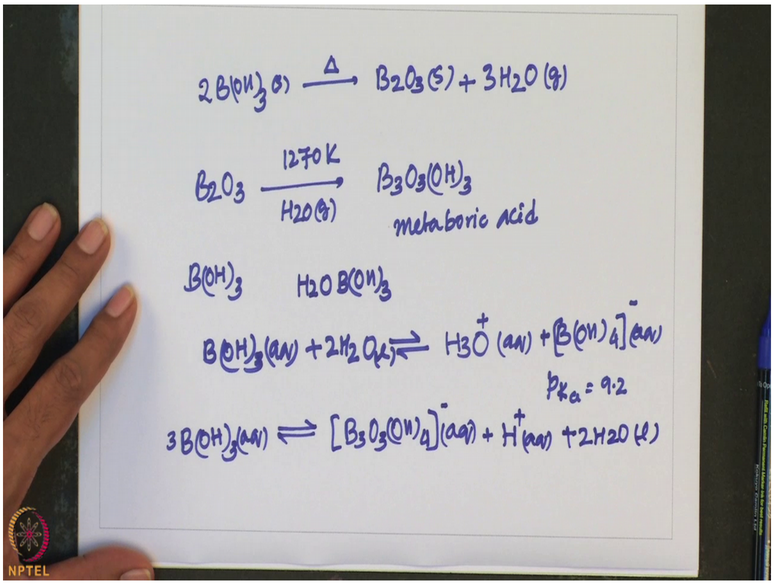

$2B(OH)_3(s) \xrightarrow{\Delta} B_2O_3(s) + 3H_2O(g)$

$B_2O_3 \xrightarrow[H_2O(g)]{1270K} B_3O_3(OH)_3$

metaboric Acid

$B(OH)_3$ $H_2O\,B(OH)_3$

$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons H_3\overset{+}{O}(aq) + [B(OH)_4]^-(aq)$

$pK_a = 9.2$

$3B(OH)_3(aq) \rightleftharpoons [B_3O_3(OH)_4]^-(aq) + H^+(aq) + 2H_2O(l)$

For example 2B OH thrice solid on heating it gives B 2 O 3 plus 3H 2 O the principal oxide of boron is B 2 O 3, and it is obtained by dehydration of boric acid at red heat. So, that is what I showed you. So, water is taken up slowly by B 2 O 2 giving back B OH thrice that is called orthoboric or boric acid B OH thrice is also called orthoboric acid or simply it can be called as boric acid, but above 1270 kelvin molten B 2 O 2 reacts rapidly with steam to give reacts rapidly with steam to give so, this is called meta boric acid.

And of course, when we look into the property boric acid is a very weak (Refer Time: 14:03) acid in aqueous solution. In fact, boric acid primarily a weak Lewis acid and the complex it forms with H 2 O essentially is looks this way. So, and this the actual source of proton comes here, so I can you can see this one from this reaction so proton. So, Pk a for this 1 is 9.2 a as is typical of many of the lighter elements of p block there is a tendency for the anion to polymerize by condensation with the loss of water thus in concentrated neutral or basic solution equilibrium the 1 I am going to show will exist for example, ok.

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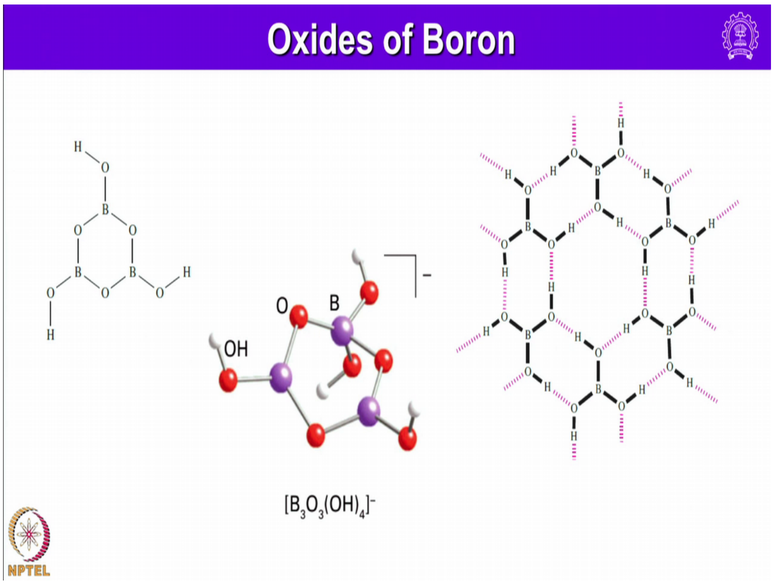

Oxides of Boron

$[B_3O_3(OH)_4]^-$

Some oxides of boron are shown in this slide you can see here . So, B 3 O 3 OH thrice will be something like this and also B 3 O 3 OH 4 times will be having something like this cyclic structure and of course, through hydrogen bonding interaction it can have a 2 dimensional sheet like structure.

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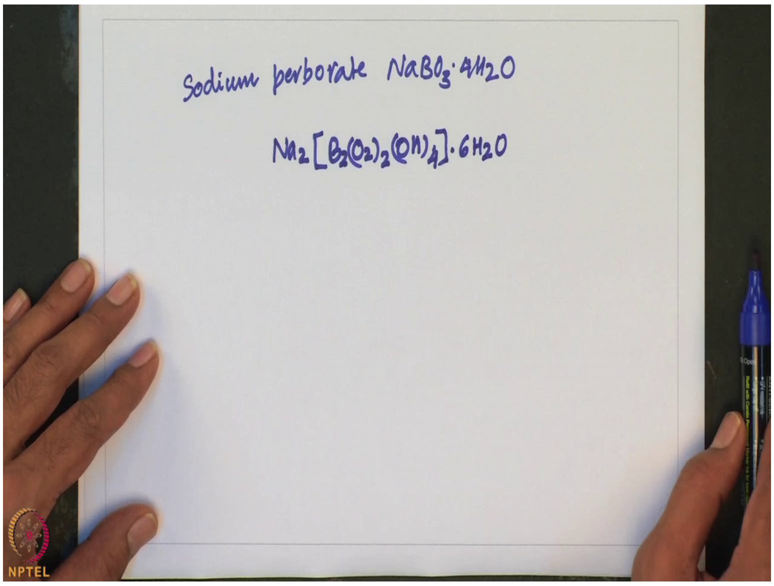

Sodium perborate $NaBO_3 \cdot 4H_2O$

$Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$

Sodium per borate so, another interesting molecule . So, this is a NaBO 3 4H 2 O this is N aBO 3 4H 2 O. So, this is used as a bleach in laundry powders automatic dish washed powders and also whitening toothpaste. So, although the formula is often given as NaBO

3 4H 2 O, the compound contains the peroxide anion O 2 2 minus. So, and is more accurately described in this way.

So, it is appropriate to describe in this way instead of showing as if it is solvated with 4 equivalents of water. So, 1 should conveniently precisely write in this way Na 2 B 2 O 2 2 this we have to peroxides OH. So, this is where its utility comes as a bleach plus 6 the correct description of sodium perborate is this one, the compound is preferred to hydrogen peroxide in many applications, because it is more stable and liberates oxygen only at elevated temperatures. So, occidental spileach does not leads to any complications that we come across with respect to hydrogen peroxide especially when it is stored in larger quantities from, that point of view this sodium perborate is preferred over hydrogen peroxide.

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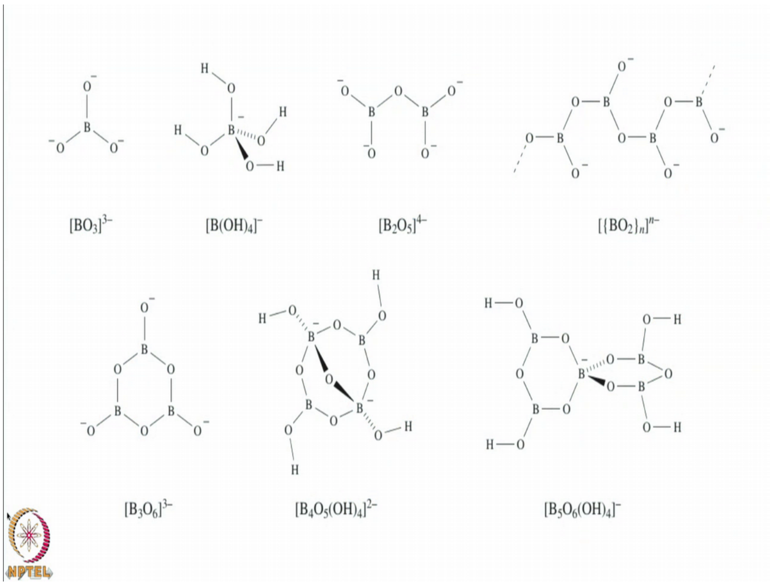

$[BO_3]^{3-}$ $[B(OH)_4]^{-}$ $[B_2O_5]^{4-}$ $[\{BO_2\}_n]^{n-}$

$[B_3O_6]^{3-}$ $[B_4O_5(OH)_4]^{2-}$ $[B_5O_6(OH)_4]^{-}$

So, in this slide I have shown some of the boron oxide and hydroxide peroxides and all those things you can see here ok.

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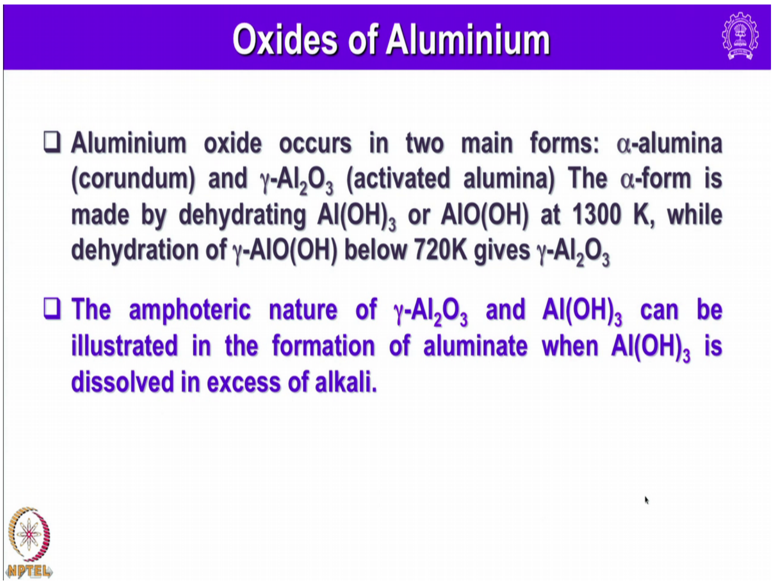

Oxides of Aluminium

- ❑ Aluminium oxide occurs in two main forms: α-alumina (corundum) and γ-Al_2O_3 (activated alumina) The α-form is made by dehydrating $Al(OH)_3$ or AlO(OH) at 1300 K, while dehydration of γ-AlO(OH) below 720K gives γ-Al_2O_3
- ❑ The amphoteric nature of γ-Al_2O_3 and $Al(OH)_3$ can be illustrated in the formation of aluminate when $Al(OH)_3$ is dissolved in excess of alkali.

So, now let us look into the oxides of aluminium. Aluminium oxides occur in mainly 2 forms, one is alpha alumina that is also called corundum and also gamma alumina that is called activated alumina the alpha form is made by dehydrating aluminium hydroxide or aluminium oxy hydroxide at 1300 k while dehydration of gamma aluminium oxy hydroxide below 720 kelvin gives, gamma or activated alumina the amphoteric nature of alumina and trihydroxy aluminium can be illustrated in the formation of aluminate, when AlOH thrice or aluminium hydroxide is dissolved in an excess of alkali. So, I can I will show you I will write down all the equations for you.

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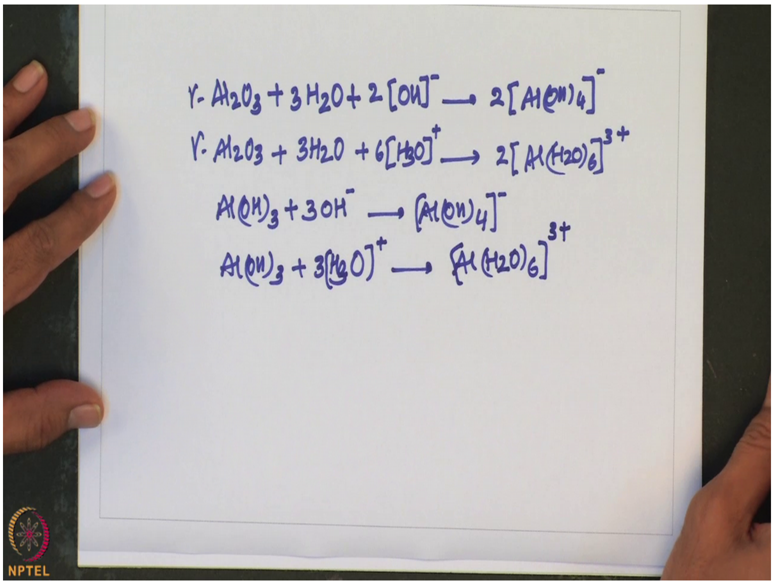

$$\gamma\text{-}Al_2O_3 + 3H_2O + 2[OH]^- \longrightarrow 2[Al(OH)_4]^-$$

$$\gamma\text{-}Al_2O_3 + 3H_2O + 6[H_3O]^+ \longrightarrow 2[Al(H_2O)_6]^{3+}$$

$$Al(OH)_3 + 3OH^- \longrightarrow [Al(OH)_4]^-$$

$$Al(OH)_3 + 3[H_3O]^+ \longrightarrow [Al(H_2O)_6]^{3+}$$

So, these reactions I am going to write essentially depict the amphoteric nature of oxides of aluminium same reaction, but with H plus that is acidic condition it gives hexa aqua aluminium compound. Similarly aluminium hydroxide if it treated with base it gives soluble aluminium hydroxide or aluminate. Similarly if you stated with some of these reactions simply show the amphoteric nature of aluminium oxide and as well as aluminium hydroxide. Now, let us look into the oxides of gallium indium and thallium.

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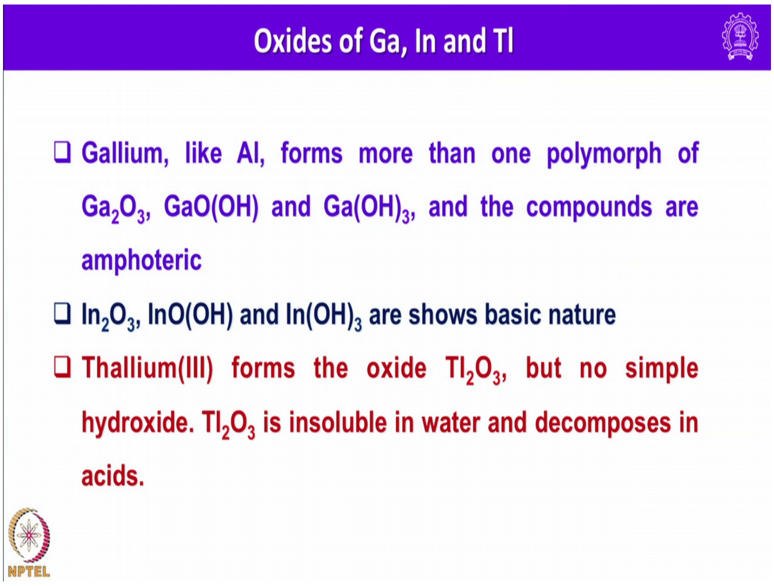

Oxides of Ga, In and Tl

- Gallium, like Al, forms more than one polymorph of Ga_2O_3, GaO(OH) and $Ga(OH)_3$, and the compounds are amphoteric
- In_2O_3, InO(OH) and $In(OH)_3$ are shows basic nature
- Thallium(III) forms the oxide Tl_2O_3, but no simple hydroxide. Tl_2O_3 is insoluble in water and decomposes in acids.

So, a gallium if you see gallium like aluminium forms more than one polymers of oxides for example, Ga 2 O 3 is known and g a gallium oxy hydroxide is known and also gallium hydroxide very similar to aluminium. And the compounds are again amphoteric very similar to aluminium analogous, aluminium compounds, indium oxide, indium oxy hydroxide, and indium hydroxide or essentially basic in nature and thallium 3 compounds of course, you should remember thallium forms both thallium one compound and as well as thallium 3 compounds ok.

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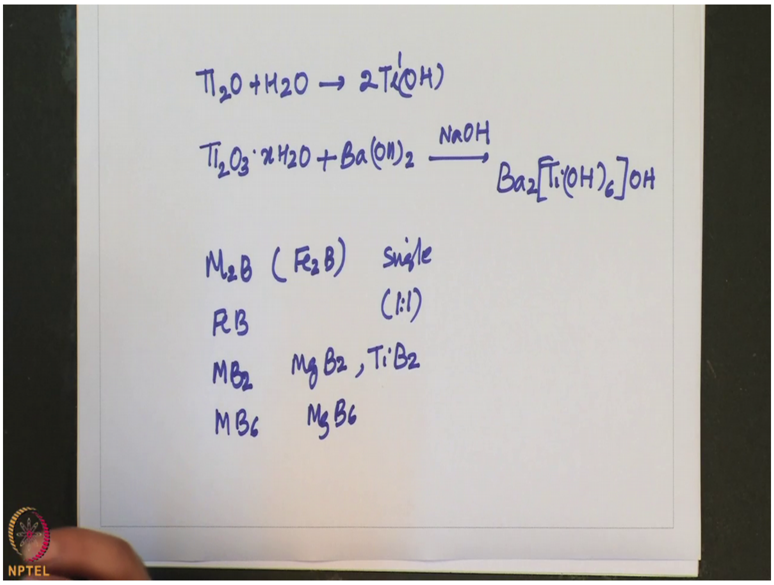

$Tl_2O + H_2O \rightarrow 2\overset{1}{Tl}(OH)$

$Tl_2O_3 \cdot xH_2O + Ba(OH)_2 \xrightarrow{NaOH} Ba_2[Ti(OH)_6]OH$

M_2B (Fe_2B) single

RB (1:1)

MB_2 MgB_2, TiB_2

MB_6 MgB_6

So, thallium 3 forms the oxide Tl 2 O 3, but no simple hydroxide is known for that 1 and this thallium oxide is insoluble in water, and decomposes in under acidic condition or in acidic medium it decomposes thallium oxide on treatment with water it gives thallium hydroxide thallium one hydroxide.

So, in concentrated sodium hydroxide solution and in the presence of barium hydroxide the hydrated oxide forms. So, hydrated oxide of thallium O 2 thallium oxide forms a complex of this type so; that means, essentially Tl 2 O 3, so plus barium hydroxide in sodium hydroxide gives a complex ion of this type B a 2 TiOH 6 times O H . So, in the solid state this anion tri anion is connected to barium 2 atoms and OH minus ions to give a structure that is related to that of k 2 Pt Cl 6 potassium hexa chloroplatinate.

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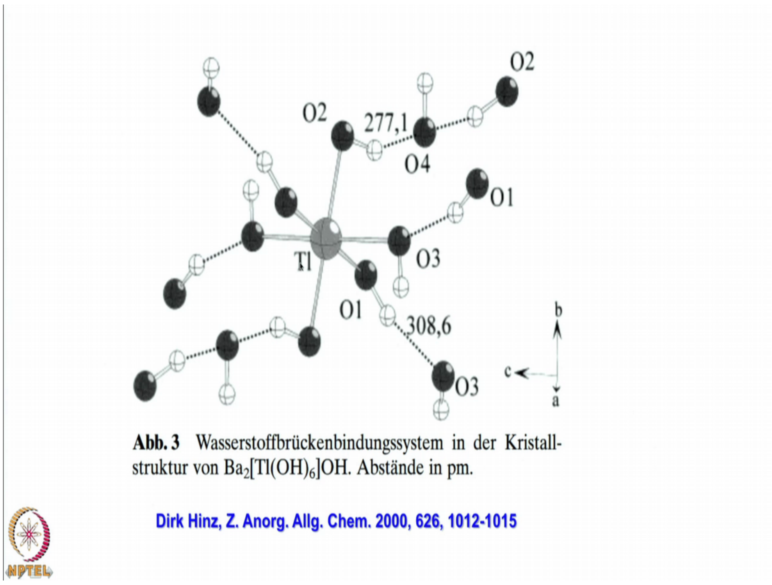

Abb. 3 Wasserstoffbrückenbindungssystem in der Kristallstruktur von $Ba_2[Tl(OH)_6]OH$. Abstände in pm.

Dirk Hinz, Z. Anorg. Allg. Chem. 2000, 626, 1012-1015

So, I have shown here so, just I will show in the next one how they are connective for example, here you can see this is the hexa hydroxy thalate thaliates. So, here you can see all OH groups are octahedral and disposed here, this is taken from this paper here I have sighted here.

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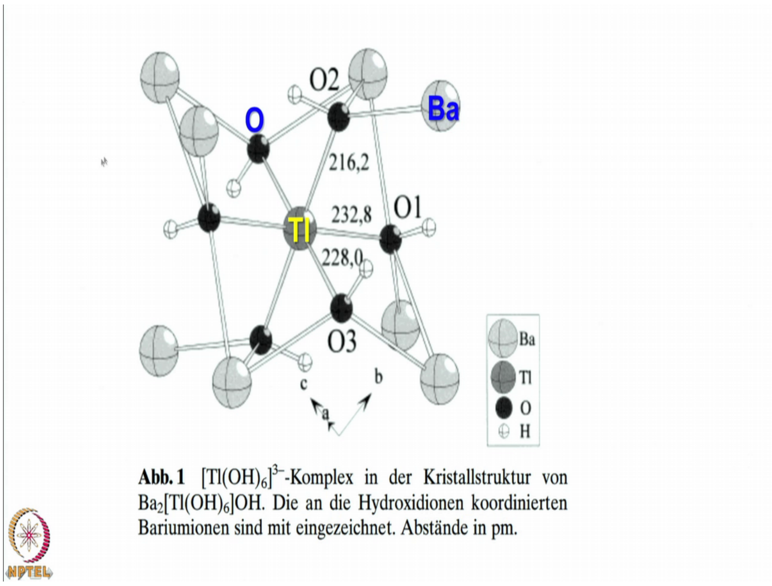

Abb. 1 $[Tl(OH)_6]^{3-}$-Komplex in der Kristallstruktur von $Ba_2[Tl(OH)_6]OH$. Die an die Hydroxidionen koordinierten Bariumionen sind mit eingezeichnet. Abstände in pm.

And of course, here you can see the coordination pair of thallium and how this 6 hydroxy groups are surrounding, and again in each hydroxy group lone pair this is interactive with barium I have shown barium here, one of them I have labelled and this oxygen this is the monomeric unit ok.

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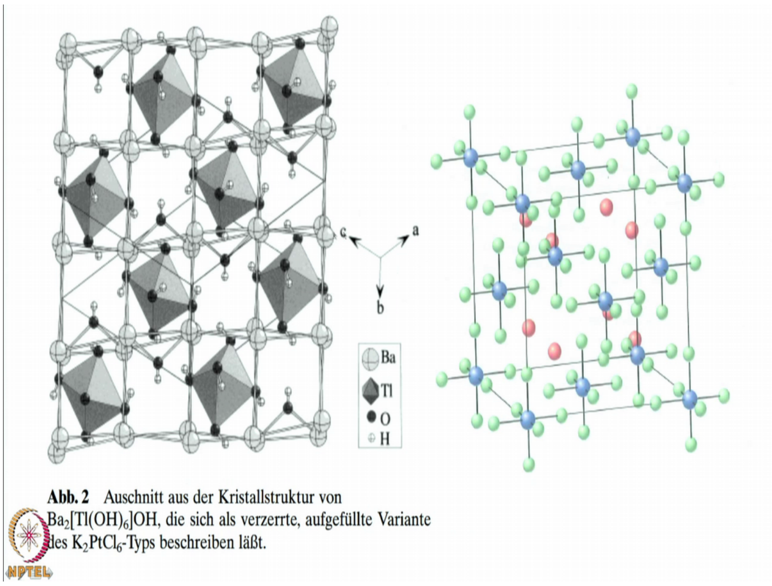

Abb. 2 Auschnitt aus der Kristallstruktur von $Ba_2[Tl(OH)_6]OH$, die sich als verzerrte, aufgefüllte Variante des K_2PtCl_6-Typs beschreiben läßt.

And then this is how in the lattice it looks like and this structure is very similar to potassium hexa chloroplatinate here. So, lastly before I conclude my talk let me show you about borides. So, when boron is heated with most metals metal borides are formed, similar to the carbides or silisides or hydrides we come across respectively the reaction with a carbon silicon or hydrogen.

The structure of these bore hydrides are dependent on the metal to boron ratio and contains single pairs chains double chains sheets or cluster of boron atoms. So, compounds with composition M 2 B, we come across composition with M 2 B for example, Fe 2 B have single boron atoms with those of Fe 2 B we have here, single boron atom and here, in this case the ratio is 1 is to 1, and here in this case basically what happens we have a single chain of boron atoms running through the metal lattice.

So, in MB 2 we also have another type of boride that is called MB 2 so, in this one what happens material has a sheet structure; that means, 1 borane layer is there and above and below metals are there it continues alternate arrangement of boron as well as metal a sheets. So, example Mg B 2 or titanium B 2. So, we also have another 1 boride having composition 1 is to 6. So, for example, magnesium is there. So, there are clusters of 6 boron atoms have arranged in the octahedral fashion, within the cube of a metal atom in a typical CsCl type structure that is FCC structure in MB 12 another the last one we have MB 12 in this one for example, aluminium. So, in this 1 basically what happens we have an icosahedral b twelve clusters surrounded by aluminium in the lattice.

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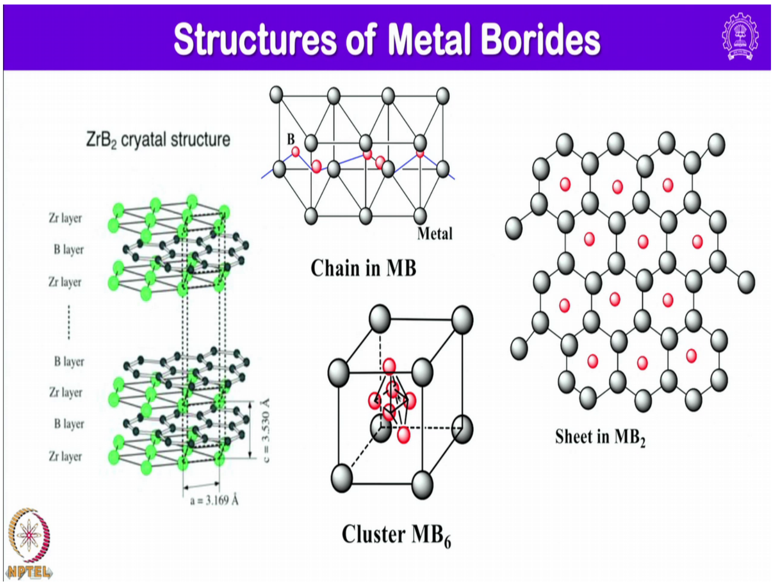

Structures of Metal Borides

So, I will try to show you some of them here you can see here a single chain is running here, where the ratio is 1 is to 1 and here a ratio is 1 is to 2 here. So, between 2 sheets of metal 1 boron sheet is there and here, again example is zirconium boride you can clearly see between the 2 layers of metal this boron sheet is there and here. Where the ratio is 1 is to 6 you can see a typically in a cube aat the centre boron cluster is there in which 6 boron atoms are essentially disposed towards 6 corners of an octahedron.

So, their arrangement is octahedron, and also one can also see similar one where icosahedral will be there in case of a MB 12 boron hydrates. So, let me stop here in my next lecture I will be discussing about the halides of group thirteen elements. So, thank you very much and have a present reading of inorganic chemistry until I return with my next lecture.

Thank you very much.