

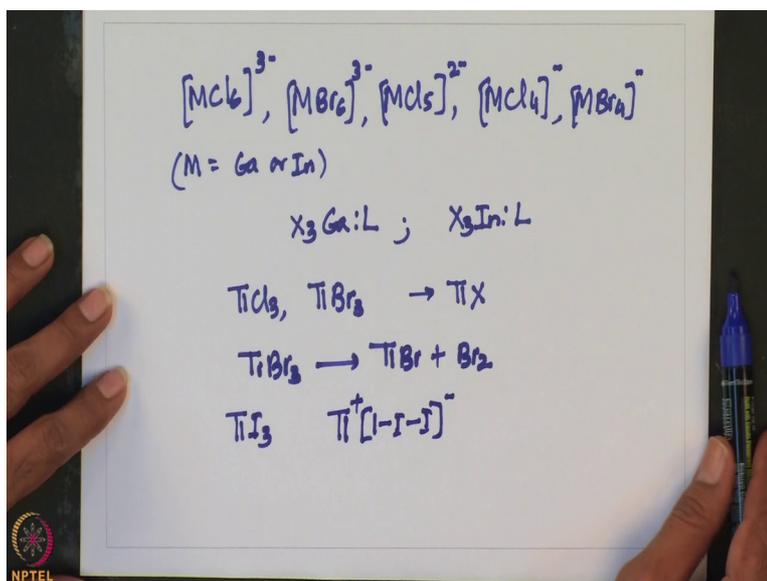
Main Group Chemistry
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Lecture – 29
Chemistry of Group 13 Elements

Welcome to MSB lecture series on main group chemistry. In my last lecture I was discussing about group 13 halides, let me continue from where I had stopped. I was discussing about trihalides of boron as well as aluminium, say let us look into other 3 elements in the series. Gallium and indium tri chlorides and tri bromides also form adducts very similar to aluminium as well as boron halides, but with coordination numbers greater than 3.

So, here one can anticipate coordination numbers of 4, 5 or 6 for example.

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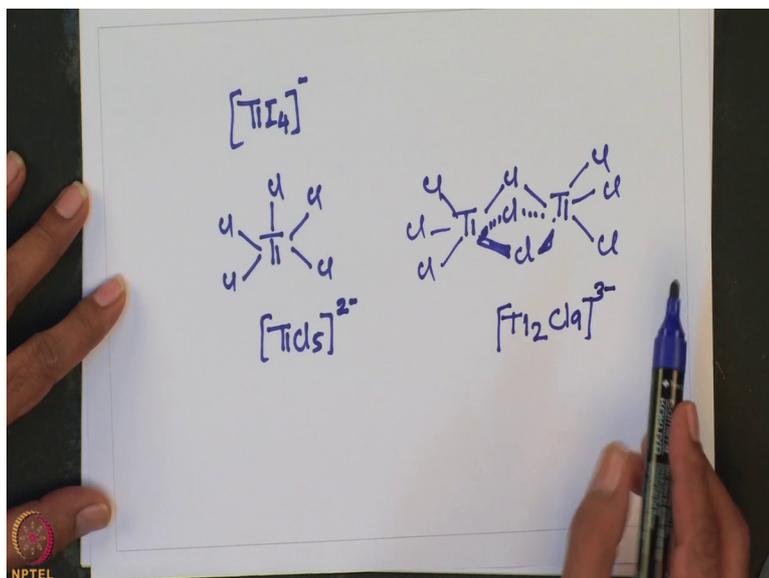


MCl_6^{3-} or MBr_6^{3-} MCl_5^{2-} MCl_4^{-} and also MBr_4^{-} . So, these are the possibilities where m is essentially gallium or indium and also one can also form simple adducts of this type for example, $X_3Ga:L$; L is a Lewis base and also $X_3In:L$. So, they are essentially neutral Lewis bases such as trimethylamine or ether. Thallium tri halides are less stable than those of the earlier group 13 elements. In fact, thallium trichloride and thallium tribromide are unstable with

respect to conversion to the corresponding mono halides. So, that means in fact, when you make thallium trichloride or thallium tribromide they are oxidizing in nature.

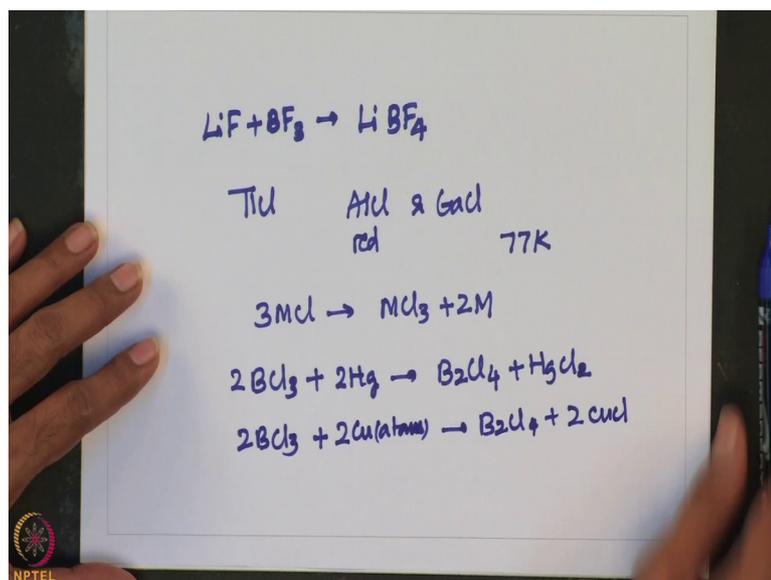
Here one can anticipate this kind of reaction. So, the compound thallium tri iodide is isomorphous with alkali metal tri iodides, and it's really a thallium mono tri iodide. So, sometime people get confused with this formulation indicating that the thallium is in plus 3 state, it is not so, still thallium is in plus one state and its I₃ represents here I₃⁻. So, that one can conveniently write this one as plus and I I I minus. This is the correct representation of thallium iodide tri iodide and when thallium tri iodide is treated with excess of iodine, an interesting redox reaction occurs with the formation of tetra iodide of this type.

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And thallium 3 also exhibits coordination numbers higher than 4, I had already mentioned in complex chlorides prepared by the addition of chloride to TlCl₃. For example, one can also see thallium having this kind of geometry this is thallium 2 minus or it can also have an octahedral geometry in this fashion, where we have 3 bridging chlorides. So, this is essentially thallium 2, you have 9 Cl 9 and then it is 3 plus 3 3 minus. So, all the halides that is tri halides are powerful Lewis acids and they readily form m x 3 l often b f 3 used as an adduct of diethyl ether. The formation of anion such as m x 4 minus from m x 3, a by addition of halides can also be viewed as Lewis acid base complex formation for example.

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If you say LiF and if you had BF₃, it essentially it forms LiBF₄ and this is also essentially formation of a Lewis acid Lewis base complex, and for aluminium and other heavier group members more than one legant is able to be added up to a maximum of 6 coordination that you saw ok.

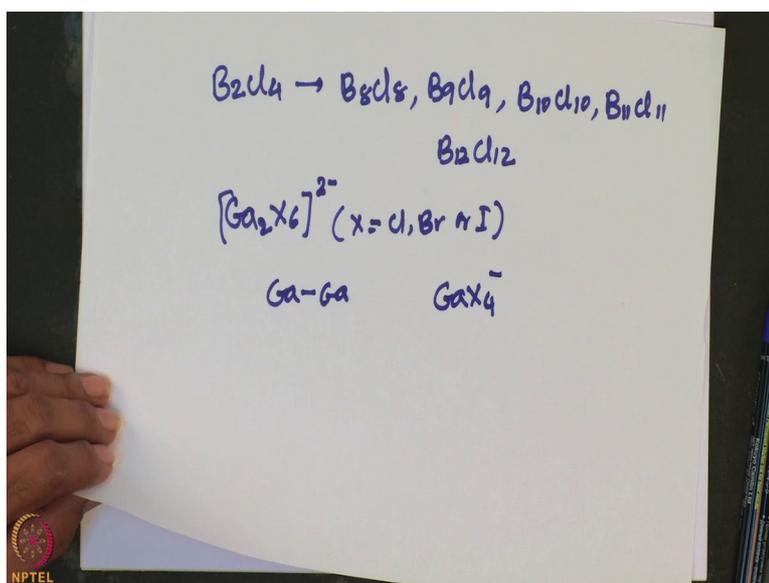
And when you come to the lower axis states, all group 13 elements do form (Refer Time: 06:29) halides; however, except thallium all are unstable towards disproportionation to the metal and the trivalent halides. Even gaseous thallium chloride is unstable to disproportionation. So, aluminium Cl and gallium chloride monochloride can be formed by the reaction of aluminium or gallium metal with h c l at high temperatures and low pressure, that essentially gives red this one aluminium chloride or gallium chloride, which are condensed at low temperature that is at 77 Kelvin one can think of on warming; what would happen is, they undergo disproportionation to give the corresponding MCl₃ plus 2M.

This is a typical disproportionation reaction, and in case of boron one can start from BCl₃ and treat this one with mercury it forms B₂Cl₄ plus HgCl₂ or one can take 2 BCl₃ and treat with copper atom generate B₂Cl₄ through the formation of 2 equivalents of cuprous chloride.

So, some atoms of the same element are oxidized, and others reduce in the same reaction is called as disproportionation reaction. Disproportion reaction is nothing, but a reaction

in which the same element is oxidized as well as reduced and of course, B_2Cl_4 decomposes at room temperature to form progressively higher analogs such as can give B_8Cl_8 or B_9Cl_9 and also large clusters such as $B_{10}Cl_{10}$ or $B_{11}Cl_{11}$ or even $B_{12}Cl_{12}$.

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And gallium to occurs in the species $Ga_2X_6^{2-}$. So, where x equals chlorine bromine or iodine and essentially this is formed by the electrolysis of gallium metal in strong acid. So, these essentially contain a gallium to gallium bond, as a result this accounts for plus 2 oxy state, but are readily oxidised by halogens to give GaX_4^- species.

Now, let us look into the compounds of boron with nitrogen. So, that is a popular well known compound series that is called boron nitrides ok.

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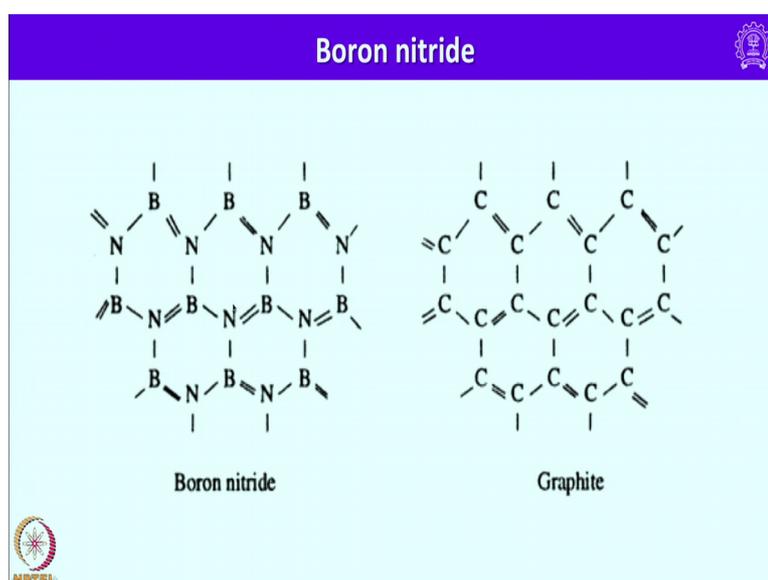
Compounds of boron with nitrogen: Boron nitride

- ❑ Boron nitride (BN) consists of planar sheets of atoms
- ❑ Boron nitride is a white crystalline solid, resembles graphite in its structure.
- ❑ A boron atom bonded together with a nitrogen atom has 8 valence electrons, 3 from boron and 5 from nitrogen (The same number of electron as are present in two adjacent carbon atoms in graphite)



So, boron nitride consists of planar sheets of atoms very similar to the graphite. Boron nitride is a white crystalline solid, resembles graphite in its structure a boron atom bonded together with a nitrogen atom that has 8 valence electron. So, for example, 8 valance electrons are coming 3 from boron and 5 from nitrogens, that will make 8 electrons and similarly in case of 2 adjacent carbons if we take, we have a total of 8 electrons $s^2 p^2 s^2 p^2$. So, that we have 8 electrons, and similar in case of boron nitride also b and n accounts for a total of 8 electrons ok.

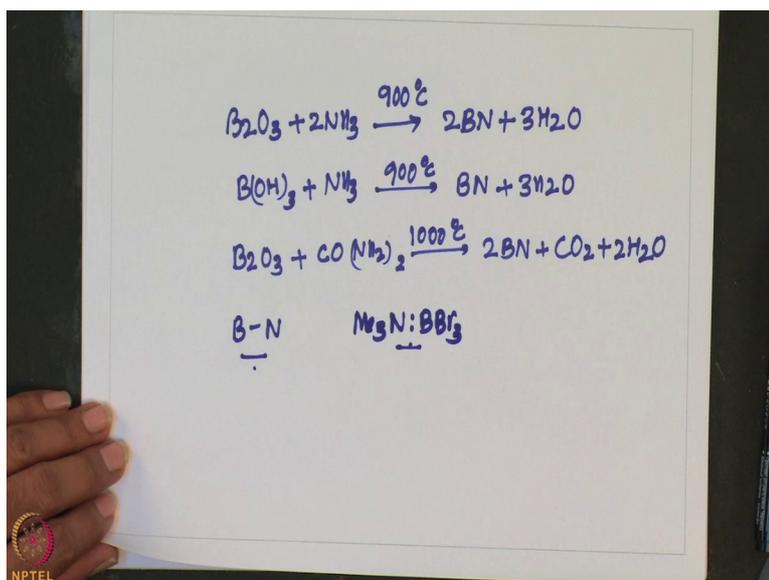
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So, this is how the boron nitride layer structure looks like and we have alternative double bonds, and this is very similar to the graphite. And how to prepare this boron nitrides one conveniently prepare starting from boron oxide, and its interaction with ammonia at high temperature.

So, let me write down few reactions that are available to make boron nitride.

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B_2O_3 plus 2NH_3 900°C since the ratio is one is to one, they are essentially written as BN or one can also write B₂N₂. One can also prepare starting from boric acid of course, at same temperature 900°C can give BN plus $3\text{H}_2\text{O}$; one can also treat B_2O_3 with urea, but at 1000°C , the common form of boron nitride has an order layer structure that I showed you in the previous slide containing hexagonal rings with alternate boron and nitrogen atoms, and boron BN bonds are shorter than in adducts such as tri methyl amine BBr_3 or others. So, the BN bonds in boron nitrides are shorter than those observed in adducts such as. So, this distance is shorter than this one, this distance is longer than this one. So, in boron nitrides BN bonds are shorter.

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So, you can see in this slide the layers of graphite, and essentially the layers of graphites are separated by a distance of 335 picometre and here carbon carbon distance is 154 picometre.

In case of boron nitride the layers are separated by little short distance of 330 picometre and here boron nitrogen bond distance is 145 picometre. So, this how the boron nitride layer looks like. So, that hexagonal B₃N₃ motive in this layered form of boron nitride appears in a group of compounds called borazines.

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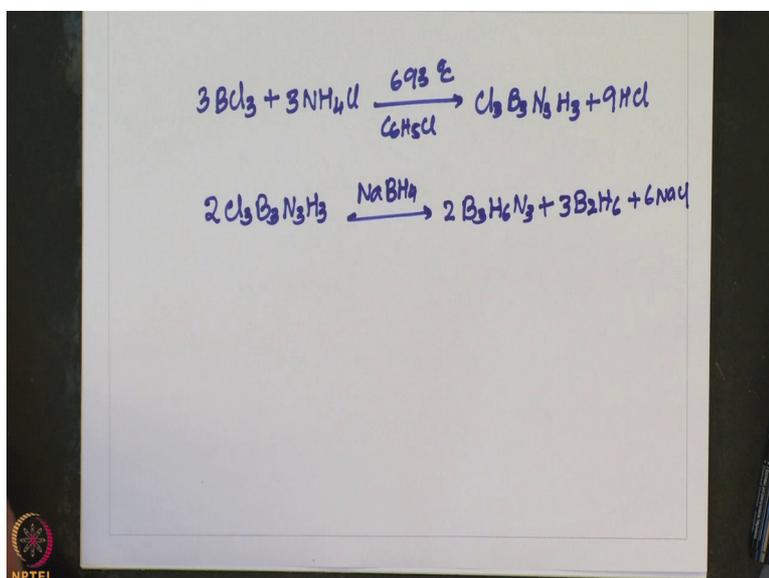
Compounds of boron with nitrogen: Borazine

- The hexagonal B₃N₃-motif in the layered form of boron nitride appears in a group of compounds called *borazines*.
- It is isoelectronic and isostructural with benzene.
- Borazine is a colourless liquid (mp 215 K, bp 328 K) with an aromatic odour and physical properties are similar to those of benzene.
- Borazine was first prepared by Alfred Stock in 1926 by the reaction between diborane and ammonia

$$3\text{B}_2\text{H}_6 + 6\text{NH}_3 \xrightarrow{250-300\text{ }^\circ\text{C}} 2\text{B}_3\text{H}_6\text{N}_3 + 12\text{H}_2$$

They are also known as porazines, essentially a borazine molecule is isoelectronic with benzene. Borazine is a colourless liquid I have shown here melting point is 215 Kelvin and boiling point is 328 Kelvin with an aromatic odour, and physical properties are essentially similar to those of benzene and. In fact, borazine was first prepared by Alfred Stock in 1926 by reacting B_2H_6 with excess of ammonia, heated to a temperature of 250 to 300 degree centigrade. You can see that equation is shown here $3 B_2H_6 + 6 NH_3$ gives $B_3H_6N_3$ plus $12 H_2$ and one can also prepare using other methods, for example, BCl_3 when it's treated with ammonium chloride at 693 degree centigrade using chlorobenzene as a solvent.

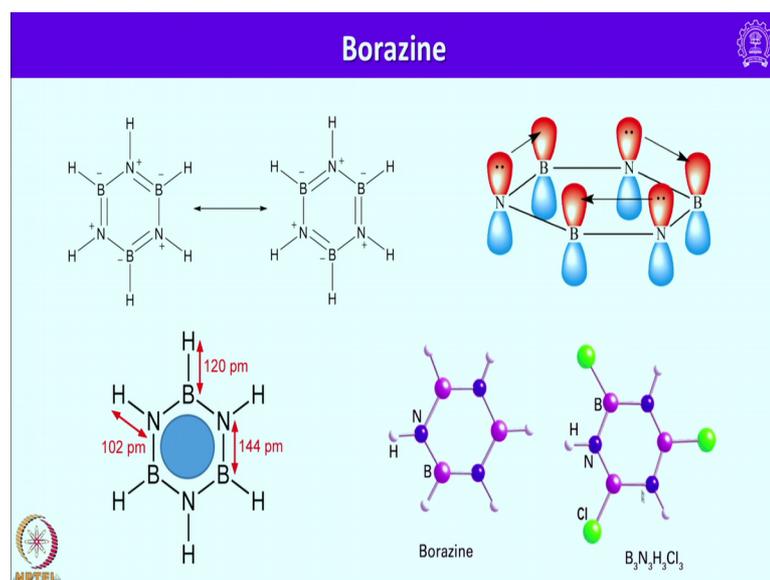
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If you take this chloroborane nitrate and treat this one with sodium borohydride, it gives back borazine along with B_2H_6 the 6 equivalents of NaCl. So, the BN distances in the planar BN ring, essentially equal all are equal and that is 144 picometre. The delocalisation of the lone pair electrons of nitrogen to vacant p orbital of boron is responsible for making these BN bonds equal; that means, you have delocalisation very similar to that we see in benzene, and because nitrogen has a lone pair and boron has an empty orbital.

So, there is a delocalisation of these electrons. Borazine is known as inorganic benzene because of its similarity in structure and physical properties to benzene. So, this is how one can write the borazine structure here.

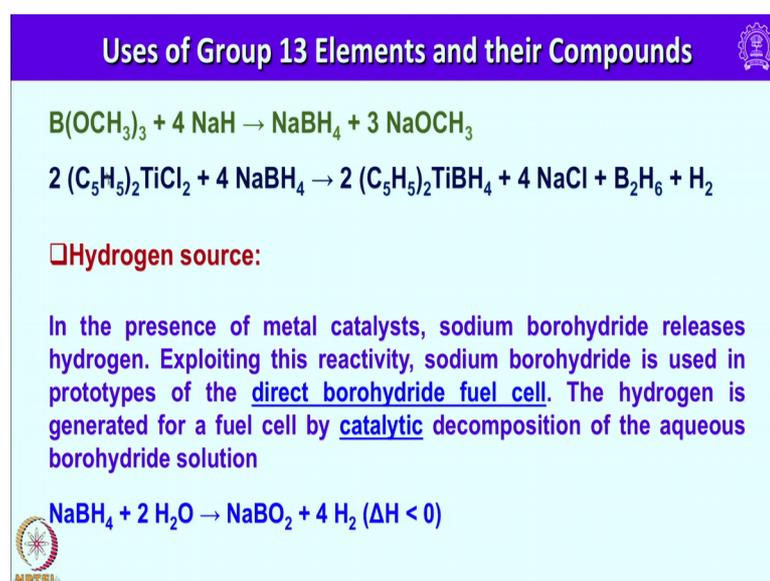
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Of course one can write alternate structure and also one can write a resonance structure, this kind of interactions with nitrogen lone pairs with empty B orbitals of boron responsible for multiple bond character here and of course, here some bond parameters I have given here and this is the analogous trichloro compound. So, the boron hydrogen bonds are replaced by boron chlorine bonds here.

So, let us look into the some reactions of borazine.

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So, when it is treated with water, it forms BH_3NH_2 which in turn gives hydroxy borazine and if you treat with a little excess of water, it gives boric acid on treatment with hydrochloric acid, it forms chloro borazine. Of course, the reaction of boron trichloride with ammonium chloride can also give this compound, and this one on treatment with methyl magnesium bromide can give you the corresponding methyl derivative that is $\text{Me}_3\text{B}_3\text{N}_3\text{H}_3$. This is planar structure whereas this one does not have a planar structure this has a cyclohexane type structure. So, something like this structure is there of course, they are having. So, it continues like this and of course, N has H it continues like that.

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Uses of Group 13 Elements and their Compounds

$\text{B}(\text{OCH}_3)_3 + 4 \text{NaH} \rightarrow \text{NaBH}_4 + 3 \text{NaOCH}_3$

$2 (\text{C}_5\text{H}_5)_2\text{TiCl}_2 + 4 \text{NaBH}_4 \rightarrow 2 (\text{C}_5\text{H}_5)_2\text{TiBH}_4 + 4 \text{NaCl} + \text{B}_2\text{H}_6 + \text{H}_2$

Hydrogen source:

In the presence of metal catalysts, sodium borohydride releases hydrogen. Exploiting this reactivity, sodium borohydride is used in prototypes of the direct borohydride fuel cell. The hydrogen is generated for a fuel cell by catalytic decomposition of the aqueous borohydride solution

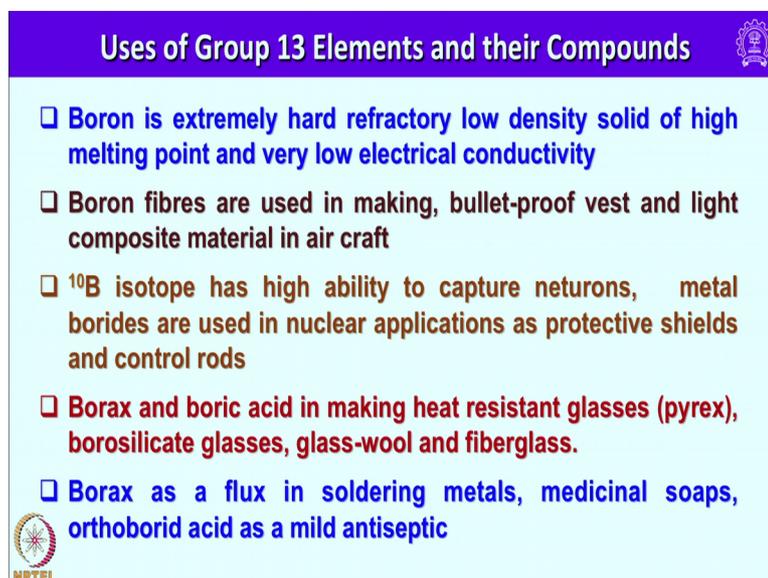
$\text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4 \text{H}_2 \quad (\Delta H < 0)$

So, let me look into the uses of group 13 elements and their compounds, very useful sodium borohydride can be prepared from boron trimethoxy derivative, on treatment with sodium hydride it gives sodium borohydride. And (Refer Time: 20:07) in dichloride on treatment with boron hydride, sodium borohydride gives this compound and in the presence of metal catalysts sodium borohydride releases hydrogen, exploiting this reactivity sodium borohydride is used in prototypes of direct borohydride fuel cell.

So, the hydrogen is generated for fuel cell by catalytic decomposition on the aqueous boron hydride solution, that I have shown here. So, essentially NaBH_4 plus $2 \text{H}_2\text{O}$ gives NaBO_2 plus 4H_2 comes out. So, this is what we used; that means, you can just

store it as and when it is required, one can react with water to generate H₂ and so; that means, one can think of using it as a hydrogen source in direct borohydride fuel cells ok.

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Uses of Group 13 Elements and their Compounds

- ❑ Boron is extremely hard refractory low density solid of high melting point and very low electrical conductivity
- ❑ Boron fibres are used in making, bullet-proof vest and light composite material in air craft
- ❑ ¹⁰B isotope has high ability to capture neutrons, metal borides are used in nuclear applications as protective shields and control rods
- ❑ Borax and boric acid in making heat resistant glasses (pyrex), borosilicate glasses, glass-wool and fiberglass.
- ❑ Borax as a flux in soldering metals, medicinal soaps, orthoboric acid as a mild antiseptic

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So, boron is extremely hard refractory low density solid of very high melting point and very low electrical conductivity that is important. And boron fibres are used in making bullet proof vest, and light composite material in aircraft, and ¹⁰ boron isotope has high ability to capture neutrons. So, metal borates are used in nuclear applications as protective shield and control rods. Essentially boron metal borates having ¹⁰ boron isotope. So, borax and boric acid in making heat resistant glasses that is Pyrex glass and also borosilicate glasses, and also they are used in glass wool and fibreglass manufacturing. Borax as a flux in soldering metals, medicinal soaps, orthoboric acid as a mild antiseptic are some of the uses ok.

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Uses of Group 13 Elements and their Compounds

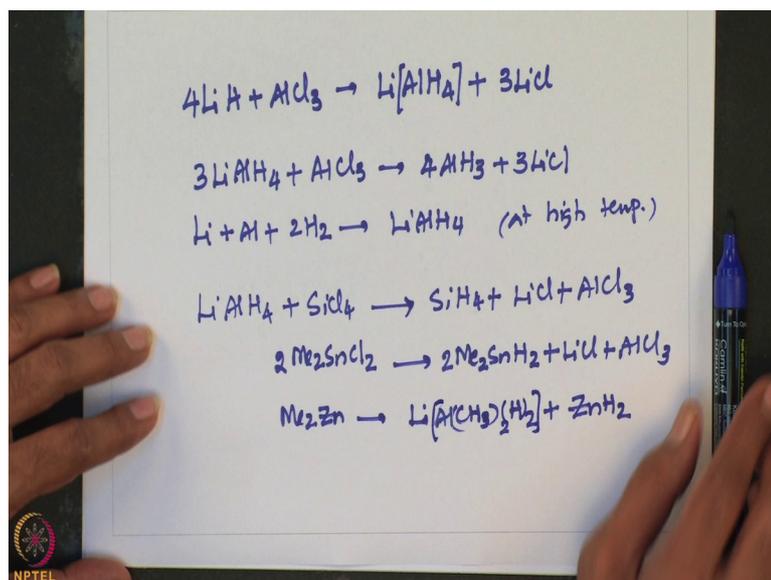
- ❑ **Al is a bright silvery-white metal with high tensile strength**
- ❑ **Has high electrical and thermal conductivity**
- ❑ **Electrical conductivity is twice that of Copper by wt-to-Wt basis**
- ❑ **To make alloy with Cu, Mn, Mg, Si and Sn**
- ❑ **Can be made into thin wires, plates, foils, sheets- used in packing, utensil making, construction, air craft.**



And aluminium is a very bright silvery white metal, with very high tensile strength. So, as a result it poses very high electrical and thermal conductivity.

In fact, electrical conductivity of aluminium is twice that of copper by weight to weight basis, because of this one and also its light metal. So, one can make conveniently alloy with copper, manganese, magnesium, silicon and tin, and also aluminium can be made into thin wires, plates, foils, sheets used in packing, utensil making, construction and also in aircraft engineering. Two important compounds of group 13 elements in organic synthesis are essentially aluminium hydride and lithium aluminium hydride.

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So, one can prepare these things conveniently starting from aluminium chloride, and lithium hydride. For example, lithium hydride on treatment with aluminium trichloride gives very useful lithium aluminium hydride. And if we use excess of lithium aluminium hydride, one can get aluminium hydride as well.

One can also prepare by directly reacting lithium with aluminium in presence of hydrogen gas. To prepare lithium aluminium hydride, but this requires very high temperature. And of course, the usefulness of aluminium lithium aluminium hydride can be seen in the following few reactions or one can also treat his one with dimethyl zinc. So, this are the some of the applications of lithium aluminium hydride, and B₂O₃ a finds important application in glass industry, the glass industry in western Europe and US account for about half the B₂O₃ consumed ok.

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B₂O₃ in the glass industry

- ❑ The glass industry in Western Europe and the US accounts for about half the B₂O₃ consumed.
- ❑ Fused B₂O₃ dissolves metal oxides to give metal borates. Fusion with Na₂O or K₂O results in a viscous molten phase, rapid cooling of which produces a glass; fusion with appropriate metal oxides leads to coloured metal borate glasses
- ❑ Borosilicate glass is of particular commercial importance. It is formed by fusing B₂O₃ and SiO₂ together.
- ❑ Borosilicate glasses include *Pyrex* which is used to manufacture most laboratory glassware as well as kitchenware. It contains a high proportion of SiO₂ and exhibits a low linear coefficient of expansion. *Pyrex* glass can be heated and cooled rapidly without breaking.



And fused B₂O₃ dissolves metal oxides to give metal borates, fusion with sodium oxide and potassium oxide results in viscous molten phase, rapid cooling of which produces glass. Fusion with appropriate metal oxides leads to coloured metal borate glasses, and borosilicate glass is of particular commercial importance, it is formed by fusing B₂O₃ with silica. Borosilicate glasses include Pyrex which is used to manufacture most laboratory glassware as well as kitchenware, it also contains high proportion of silica and exhibits a low linear coefficient of expansion, as a result it can tolerate very high temperature and on cooling rapidly it does not break. The refractive index of Pyrex is 1.47, the Pyrex glass is 1.47.

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B₂O₃ in the glass industry

- ❑ The refractive index of *Pyrex* is 1.47, and if a piece of clean *Pyrex* glassware is immersed in a mixture of MeOH/C₆H₆, 16/84 by weight, it seems to 'disappear'; this gives a quick way of testing if a piece of glassware is made from *Pyrex*.
- ❑ Fibreglass falls into two categories: textile fibres and insulation fibreglass. Of the textile fibres, alumina-borosilicate glass has the most widespread applications. The fibres possess high tensile strength and low thermal expansion, and are used in reinforced plastics. Insulation fibreglass includes glass wool which contains ~55–60% SiO₂, ~ 3% Al₂O₃, ~ 10–14% Na₂O, 3–6% B₂O₃ plus other components such as CaO, MgO and ZrO₂.



And if a piece of clean *Pyrex* glass where is immersed, in a mixture of methanol and benzene in 16 by 84 weight. It seems to disappear. This gives a quick way of testing if a piece of glass where is made from *Pyrex* or not you should remember that one. The refractive index of *Pyrex* is 1.47, and if you take a mixture of methanol and benzene in 16 by 84 weight, its refractive index also will be 1.47 as a result what happens in a container made up of *Pyrex* if we start adding, what happens? It appears like glass where is disappearing or dissolving and sometimes people use this in magic tricks also, that is an indication of checking whether the glass we are using is *Pyrex* or not.

Fibre glass falls into 2 categories one is textile fibres and insulation fibreglass of the textile fibres alumina borosilicate glass has most widespread application, the fibres poses very high tensile strength and low thermal expansion and are used in reinforced plastic. Insulation fibreglass includes glass wood which contains about 55 to 60 percent of silica and 3 percent aluminium oxide, and 10 to 40 percent of sodium oxide, and 3 to 6 percent of boron oxide plus other components such as calcium oxide magnesium oxide and zirconium oxide ok.

And also this boron nitride finds application in aerospace industry, and also it is an excellent thermal insulator, and also its used in cosmetics and also personal care industries and In fact, hexagonal boron nitride was first developed to meet the needs of

the aerospace industry, it is stable in oxygen and is not attacked by steam below 900 degree centigrade. This hexagonal boron nitride I am talking about.

It is a good thermal insulator and has low thermal expansion, and is resistant to thermal shock. So, these applications have lead to its use in industry to make high temperature crucibles. Boron nitride nanotubes have been formed by depositing boron and nitrogen (Refer Time: 29:52) tungsten surface under high vacuum. These nanotubes could be suitable for high temperature conditions under which carbon nanotubes would burn. The softness and shine of powered boron nitride has lead to its widest application in the cosmetics and personal care industries, it is a non toxic and presents no known hazard and is added to many products up to around 10 percent, it adds a pearlescent shine to products such as nail polish and lipsticks, and is added to foundations to high wrinkles. Its light reflective properties scatter the light making wrinkle less noticeable.

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Aluminium alloys: lightening the load

- ❑ It is light, has high electrical and thermal conductivity, high reflectance, and is easily machined.
- ❑ Alloys strength is achieved by using Al
- ❑ The greatest use of aluminium alloys worldwide is in building and construction
- ❑ Al/Cu/Mg alloy is used in aircraft
- ❑ Al/Cu alloy is used in satellites and space vehicles
- ❑ Al alloys in cars is increasingly prevalent and they are used to make body panels, engine blocks, wheels, bumpers, radiators, and trims
- ❑ aluminium alloys are used to make cooking utensils, refrigerator bodies, air conditioning units, toys, tools, and collapsible toothpaste and cosmetic tubes.

 NPTEL

So, aluminium alloys also find lot of application, and it is light has high electrical and thermal conductivity, high reflectance and is easily machined. So, alloy strength is achieved by using aluminium. So, the greatest use of aluminium alloys worldwide is in building and construction for example, aluminium copper magnesium alloys is used in aircraft, aluminium and copper alloys used in satellites and space vehicles, aluminium alloys in car is increasingly permanent and they are used to make body panels, engine blocks, wheels, bumpers, radiators and trims. Aluminium alloys are also used to make

cooking utensils, refrigerator bodies, air conditioning units, toys, tools and collapsible toothpaste and cosmetic tubes.

The chemical and physical properties of aluminium makes it the most widely used non ferrous metal it is light has high electrical and thermal conductivity, high reflectance and is easily machined. These products are enhanced by the previous oxide layer on the surface which makes it resistant to corrosion; that means self protection through the formation of a layer that is called passivation that also gives extra resistance towards corrosion. So, I will stop at this stage, and in my next lecture I would introduce wades rule to explain boron hydrides and then look into some problems based on group 13 elements.

So, thank you very much have a very pleasant reading of inorganic chemistry see you in my next lecture.