Industrial Inorganic Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 25
Cryolite and Other Industrially Important Fluoride Salts

Good morning everybody. Welcome back once again to our class where we are talking about the halogen and the different halogen compounds. And we are just discussing about the fluorides how you can utilise the fluorides and how the fluoride compounds are useful for isolation of some industrially important compounds and we were with the sodium aluminium hexafluoride.

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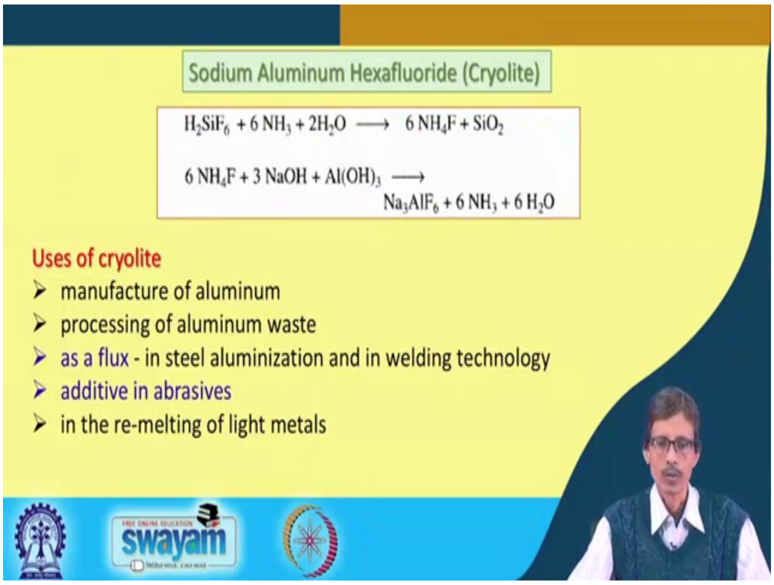

Sodium Aluminum Hexafluoride (Cryolite)

$$H_2SiF_6 + 6\,NH_3 + 2H_2O \longrightarrow 6\,NH_4F + SiO_2$$

$$6\,NH_4F + 3\,NaOH + Al(OH)_3 \longrightarrow Na_3AlF_6 + 6\,NH_3 + 6\,H_2O$$

Uses of cryolite
- manufacture of aluminum
- processing of aluminum waste
- as a flux - in steel aluminization and in welding technology
- additive in abrasives
- in the re-melting of light metals

So, is a commercial name of it is also cryolite where we know that this is the typical isolation procedure for the different cryolite material for the different sources which can give us the corresponding industrial preparation of aluminium, which is a very important one and is typically electrolytic process. But if we consider typically the as a compound how sodium aluminium hexafluoride you can get from the typical raw materials because we were talking about the formation of silicon tetra fluoride and hexafluorosilicic acid. So, earlier we have seen that how hexafluorosilicic acid can be useful for the production of different types of quartz materials or the corresponding processing of the quartz material or the glass surfaces.

Now, we will see how quickly we can see the reaction if we consider that if you allow to react hexafluorosilicic acid; that means, H_2SiF_6 with ammonia in aqueous medium. That means, aqueous ammonia you are trying to react it with hexafluorosilicic acid. So, what should be your reaction products? In a small scale also in the laboratory scale what should be your typical product from that particular reaction.

So, one of the important reaction for this particular purpose one of the pathway for this reaction is that this hexafluorosilicic acid is not very much stable in presence of the water molecule. So, in presence of water the silicon centre which is under the cover of 6 fluoride ions in an octahedral geometry will try to go out; that means, the silicon fluorine bonds will be broken, if you go down from there that means, from the SiF_6 to minus species to SiF_4.

There also you have 4 fluoride groups attached to the silicon centre and that is also in presence of your water molecule is not stable. So, what is happening therefore? If some compound is not stable in aqueous medium in moisture or in presence of water we see that particular compound can go for hydrolysis reaction, we consider it hydrolysis reactions. Large number of inorganic molecules or compounds or the organic molecules or compounds are susceptible to this sort of hydrolysis reaction where that oxygen of the water molecule or the hydroxide group of the water molecule try to attack or hydrolyse the corresponding silicon fluorine bond.

So, hydrolysis of that particular one; that means, the corresponding SiF_4 or H_2SiF_6 can undergo for the corresponding hydrolysis reaction. If we consider that in terms of the anionic ligands or anionic parts surrounding your silicon centre; that means, in presence of that particular fluoride ions you can have 6 fluoride groups around the silicon centre.

So, if all of them or partly 4 of them or 2 of them can be substituted by the hydroxide ions, once water molecule can go for is nucleophilic attack to the silicon centre and it can establish new silicon oxygen bonds on the silicon centre. And ultimately that particular hydrolysis reaction giving you silicic acid and at the time passes it goes to the corresponding formation of silicon dioxide or silica or some amount of quartz we consider in a different form.

So, one of them; that means, the silicon the entire silicon what is present in hexafluorosilicic acid will be taken away by water molecules to your silicon dioxide and the ammonium giving rise to that particular protons of the water molecule giving ammonium ion and that ammonium ion will be available to trap or to bind your available fluoride groups which are coming out from the hexafluorosilicic acid. So, as a result in terms of your 6 fluoride groups available on the hexafluorosilicic acid will be taken out by these ammonium ions and ammonium fluoride will be form, so 6 molecules of ammonium fluoride will be formed along with your silicon dioxide. So, you get two product, one is ammonium fluoride and another is your silicon dioxide.

Now, whether this ammonium fluoride can be useful for making your cryolite; that means, how we can make synthetically prepared cryolite because not all the countries are lucky enough or fortunate enough to get this particular natural source of cryolite. But if we can have some other source of aluminium or some aluminium processing industry or the aluminium smelting process or any other sources of aluminium, can give rise to a corresponding compound which is easily available as its hydroxide.

So, aluminium hydroxide is readily available from different sources of aluminium. It may or may not be of bauxite source or it may or may not be your typical the scrap aluminium from the aluminium industry. Anywhere you can have the corresponding very low grade or very poor quality aluminium sample you can convert it by alkali treatment in the basic medium. So, alkaline treatment of that particular one giving simple aluminium hydroxide.

So, now that aluminium hydroxide will be using for the preparation of cryolite. So, your aluminium hydroxide will be the typical source for making your synthetic cryolite because that cryolite will be we can use it for aluminium production, the pure quality of aluminium production through electrolysis. So, that particular reaction; that means, ammonium fluoride here is reacting with aluminium hydroxide and obviously, in presence of some excess amount of sodium hydroxide because that particular reaction between sodium hydroxide and aluminium hydroxide we know that this can also give you the sodium aluminate formations. If we consider that sodium hydroxide and aluminium hydroxide can giving you the sodium aluminate formation and that sodium aluminate is typically reacting with ammonium fluoride giving you Na 3 AlF 6 which is your cryolite.

So, we get the cryolite we get back the corresponding ammonia which were utilised earlier and the water molecule. So, whatever amount now amount of ammonia we were using the aqueous ammonia we are using we are getting back basically from that particular second reaction. So, basically the entire reaction is between the silicic acid and your aluminium hydroxide. So, two components are your having, one is your corresponding hexafluorosilicic acid and another is aluminium hydroxide and from that we you are making cryolite. So, that can be a very good question for you also when you study this particular code that you should always remember the I ask you or if somebody ask you that how will you get cryolite from aluminium hydroxide.

What the other thing you require? You require the hexafluorosilicic acid or how silicic acid or hexafluorosilicic acid is useful for making cryolite in the laboratory or in the industry or in a large scale production, because this cryolite material is commercially very interesting and is very important also industrially because it can be used for the manufacture of aluminium. So, aluminium industry is largely dependent on the regular supply of your cryolite material, whether you get it from your natural source or you get it from some other synthetically prepared cryolite. Just now, what we have seen that from the scrap aluminium or any other aluminium we can make this as your Na 3 AlF 6.

Then, obviously, the second thing that means, the processing of aluminium waste because the industrial waste or any other thing where we are consuming aluminium. So, this aluminium basically can be a waste material and that can be processed for very useful cryolite preparation. Sometime it can also be used as a flux as we have seen in the terms of a metallurgical component that this flux when steel aluminization; that means, if we consider that some aluminium is also present in some steel material because we know the nickel is present, iron is present and the carbon is present from the stainless steel to any other kind of steel.

But some aluminium based steel material we can put this particular material as a flux for steel aluminization and in welding technology because it can reduce the corresponding fusion temperature for the welding purpose. Then it can be a very good additive for making abrasives. So, abrasive industry is also dependent on cryolites. And in the remelting of light metals, again some kind of material like that of your flux, we can use cryolite to go for the typical melting process the fusion process basically what we see that for melting of gold we know that we use borax which is a very good material.

Similarly, for re-melting of light metal not the heavy metals the light metals we can use this particular compound; that means cryolite directly for that particular process.

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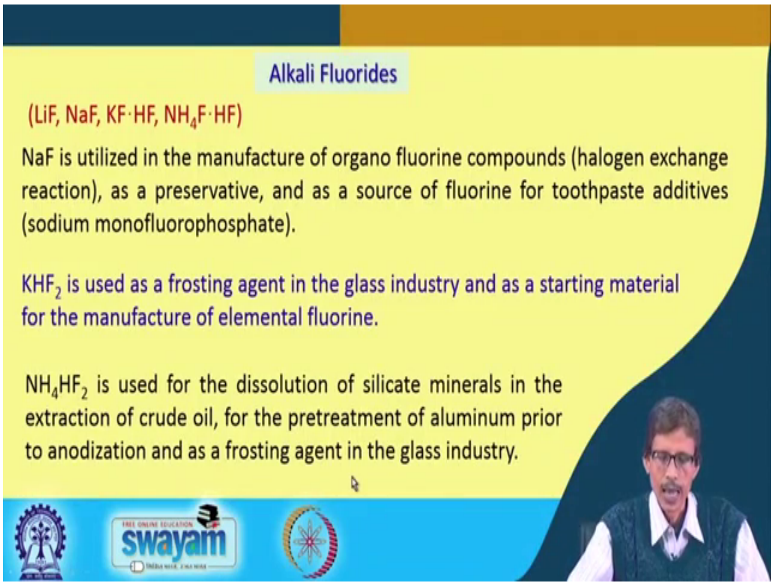

Alkali Fluorides

(LiF, NaF, KF·HF, NH_4F·HF)

NaF is utilized in the manufacture of organo fluorine compounds (halogen exchange reaction), as a preservative, and as a source of fluorine for toothpaste additives (sodium monofluorophosphate).

KHF_2 is used as a frosting agent in the glass industry and as a starting material for the manufacture of elemental fluorine.

NH_4HF_2 is used for the dissolution of silicate minerals in the extraction of crude oil, for the pretreatment of aluminum prior to anodization and as a frosting agent in the glass industry.

Then we move from alkali fluorides, just now what we have seen that ammonium fluoride we can make directly from hexafluorosilicic acid, now that alkali fluorides are nothing but alkali metal ion fluorides; that means, you have can have lithium, sodium, potassium and all these alkali metal ions and the fluoride ions as its good salts. So, two of them are very small; that means, if we consider that we are talking about the lithium as the lithium fluoride.

So, is a very small species both cation and anions are very small, and as we have seen that in case of aluminium that hexafluorosilicic acid or AlF 6 3 minus lF 6 3 minus basically is utilising for your electrolysis. That means, for electrochemistry the other industry which is dependent on electrochemistry can have some good usefulness of these compounds like this fluoride based different alkali metal ions.

So, we can have typically lithium fluoride, we can make sodium fluoride, we can have potassium fluoride but it can be a bi salt with the acid the free acid the hydro fluoric acid. That means, KF dot HF what is that? It is nothing but you are K HF 2 by fluoride ions. Instead of typical fluoride ions sometimes we find that bi-fluoride ions are much more stable in the solution medium compared to your typical fluoride ion, if the protons or the acidic medium is available to you.

So, instead of typical calcium fluoride it can be stabilized further with the addition of the stoichiometric amount of hydrofluoric acid such that you get K HF 2 because this HF, one H another F and you can have the typical electronegativity difference. So, the fluoride centre can attract the hydrogen ion end; if the hydrogen ion is available, so the fluoride from both two ends one side you have ion H another side you have another H; that means, F H 2 or H that is a HF two molecule. So, this is HF two molecule can have to be stabilized in presence of the potassium ion and you get the potassium bi-fluoride. Similarly, you get the corresponding ammonium bi-fluoride in your hand also these are all bi salts.

So, the second one; that means, sodium fluoride can be utilized further in the manufacture of different organ of fluorine compound, that you have the organic compound in our previous classes, we have also discussed or seen that you can have in the organic molecule backbone that carbon hydrogen bond. That means, CH functions are there and we can substitute those CH functionality to CA functionality, and that can be achieved very easily through the use of sodium fluoride as the typical inorganic source. So, it gives you the corresponding halogen exchange reactions what is that that hydrogen can be substituted hydrogen atom on the carbon centre can be substituted by the fluorine.

And as a source of fluorine for toothpaste additives, because as we have seen that appetite is the material the building material for your teeth for your bone etcetera, and for your teeth enamel if you can go for a corresponding fluoride derivative that not instead of hydroxyapatite you can have the corresponding fluoro appetite which is much stronger than hydroxyapatite. And that fluoro appetite can be obtained if you go for slow fluorine release or the fluoride ion release rather is basically through the top process of your toothpaste. If you have sodium fluoride, some amount of little bit amount of sodium fluoride in your toothpaste that slow release of that fluorides while you brush your teeth can be attacked by that of your fluoro appetite formation from the hydroxyapatite on the bone enamel.

So, what do we use basically? Sodium monofluorophosphate because the phosphate is also required for your teeth material. So, instead of directly using sodium fluoride we cannot use sodium fluoride, but sodium monofluorophosphate the other end is also phosphate is also getting supplemented. So, these are the material for bio mineralization of your teeth. So, alkali fluorides in terms of your sodium monofluorophosphate because that can also be prepared from your sodium fluoride can be the corresponding supply for your bi mineralization process, because all these things; that means, the phosphate the phosphate derivatives, the fluoro derivatives and the fluoro appetite derivative they are all mineral like material. So, in (Refer Time: :15:28) on the teeth surface we can make this molecules or this material for your protection of your teeth.

Then, the potassium bi-fluoride. So, the other one that KF dot HF or KF K HF 2 is used as a frosting agent in the glass industry. We know that the fluorides will be attacking your silicon dioxide surface of the glass; that means, the silicon centre can be attacked by your fluoride but we cannot use directly the hydro fluoric acid for processing or very easy etching process on the glass surface and sometimes if you require a frosted glass you require that surface is basically attacked by only potassium bi-fluorides. So, potassium bi-fluorides a simple painting also some time can be helpful to give you the frosted glass formation. So, the glass industry is using huge amount of this particular fluorine base compound or this material, and it can be also a very good material for the manufacture of elemental fluorine or the fluorine gas; that means, from K HF 2 the fluoride part we can go for its corresponding oxidation to make the elemental fluorine.

Then, similarly the other one the 4th one the 4th compound what we have seen that we are talking about 1 2 3 4, the 4th compound which is your ammonium bi-fluoride instead of potassium because all this cations have important role to play when it has some application. Particularly the industrial application it has some different goal definitely instead of the simple presence of ions in presence of the potassium it is giving some other information's or other reactions which is not able to get it we not able to get it through this corresponding ammonium salts. Ammonium salt is your ammonium bi-fluoride. And which is use useful also for the dissolution of silicate minerals in the extraction of crude oil.

So, if we have the crude oil and it has some contamination of the silicate mineral in it we cannot pass or we cannot allow that silicate mineral to be still there in the crude oil. So, we have to take out that through the attack by your fluoride ions. So, ammonium bi-fluoride will be the choice, for attacking your silicate mineral to remove it as your silicon tetra fluoride. For the treatment pre-treatment of the aluminium prior to anodization and as a frosting agent as like that of your potassium bi-fluoride ammonium bi-fluoride is also helpful for as a frosting agent and some time since it can also go for attacking your aluminium. So, solid aluminium by the formation of your aluminium tri-fluoride or the corresponding ammonia aluminium hexafluoride you can go for your corresponding anodization of the corresponding aluminium metallic surface.

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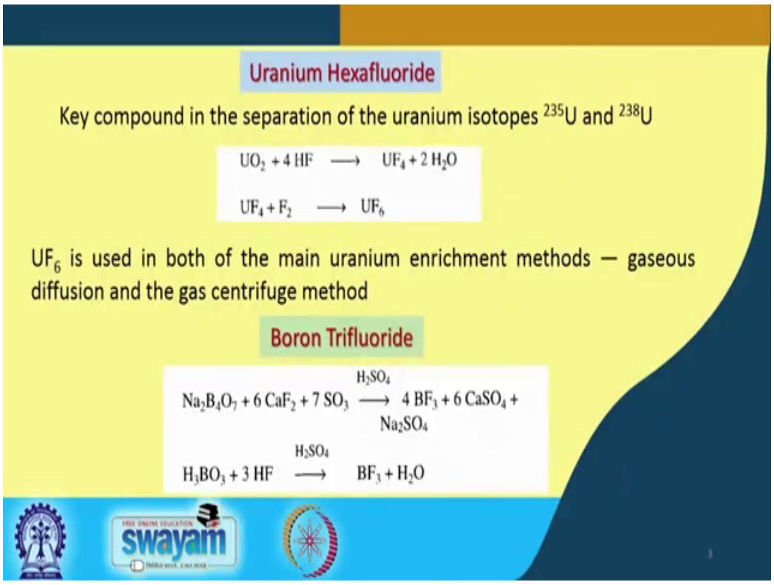

Uranium Hexafluoride

Key compound in the separation of the uranium isotopes ^{235}U and ^{238}U

$$UO_2 + 4\,HF \longrightarrow UF_4 + 2\,H_2O$$

$$UF_4 + F_2 \longrightarrow UF_6$$

UF_6 is used in both of the main uranium enrichment methods — gaseous diffusion and the gas centrifuge method

Boron Trifluoride

$$Na_2B_4O_7 + 6\,CaF_2 + 7\,SO_3 \xrightarrow{H_2SO_4} 4\,BF_3 + 6\,CaSO_4 + Na_2SO_4$$

$$H_3BO_3 + 3\,HF \xrightarrow{H_2SO_4} BF_3 + H_2O$$

Then we move to some radioactive material because we know that uranium processing and all this thing we get it from our natural sources. So, uranium oxides some other material as the oxides we get. So, the processing of these uranium material if we are able to get the corresponding formation of its fluoride compound quite easily, we can process that basically for the uranium processing. So, basically this particular compound; that means, your UF 6 uranium in the hexavalent state remember it that is UF 6 uranium will be in the hexavalent state unlike your aluminium or silicon.

So, is basically the most important compound in the separation of uranium isotopes we get two isotopes, one is 235 and 238. So, you can get the corresponding hexafluorides and we can separate it from their typical properties; that means, your physical properties will be the different for these two isotopes and we can separate it out. So, if you can have other than this; that means, UO 2 uranium dioxide which is a tetravalent compound that compound or some other uranium oxide source in your hand which can be directly allowed to react with hydrofluoric acid only not any other salt. Giving you like silicon tetra fluoride you again gate uranium tetra fluoride and water and that uranium tetra fluoride can further be oxidized by elemental fluorine to uranium hexa fluoride.

So, uranium tetra fluoride UF 4 is susceptible to oxidation by fluorine, you cannot go for a direct reaction of UO 2 with fluorine to get the UF 6. You have to go through that UF 4 UF 4 formation is important, which is nothing but the corresponding addition of the fluoride group to the uranium centre which is in tetravalent state. So, the formation of these is used both in the main uranium enrichment method; that means, whether you require for uranium 238 because for the corresponding processing for your nuclear chemistry or a reactions you required some of these isotopes should have the corresponding enrichment whether you go for uranium 238, for the fission reaction or something for the reactors and all other places we required the enrichment.

So, this particular one because uranium hexafluoride you are forming here and if you have the two isotopes uranium 235 and 238, so you will be getting depending upon the percentage of uranium 235 and uranium 238 you get two of these compounds which are isotopically different. But if you go for a diffusion process; that means, the gaseous diffusion and the gas centrifuge method for the separation process because one will be heavier than other will be you can allow for your separation.

Then, one more important compound what we see from organic chemistry point of view to the industrial sector is nothing but simple boron tri-fluoride. So, at one end you have uranium hexafluoride which is the heaviest one uranium is a corresponding actinides and heaviest elements and heaviest element also forms fluorides. And the lightest one is your boron in the periodic table. So, periodic table from boron to uranium you can think of its reaction with the fluoride ions, you can think of about this oxidation and you can get some useful compound based on the fluoride industry only.

So, how you get this boron tri-fluoride? Is again a very simple; straight (Refer Time: 22:15) reaction because we are always interested to know the basic inorganic chemistry reactions because you should know the reaction how these reactions can the balance because on the left-hand side most of the time you will find that these are the ores are the minerals. So, the first component for this is your nothing but your Na 2 B 4 O 7. What is that? Your Na 2 B 4 O 7 is nothing but your borax which is again available naturally. So, you can have huge borax source and that borax we all know that the borax can be utilised for the formation of boron oxide or the boric acid which is H 3 BO 3.

Now, this is in your hand, and again the fluoride the calcium fluoride. So, that is also a mineral material, so that is also available. Now, you can supply some amount of sulphur trioxide that we have seen our in a while we are talking about your sulphur chemistry that sulphur industrial chemistry all the sulphur compounds we know that how we can get sulphur trioxide. So, sulphur trioxide calcium fluoride and borax in presence of sulphuric acid. So, is a typically a acidic reaction acidic medium reaction where we get the boron present in the borax will be reacting with the fluoride available from calcium fluoride to give you the boron tri-fluoride.

So, is basically is in some kind of simultaneous double metathesis reaction is happening, so calcium fluoride is giving you the boron tri-fluoride basically. So, calcium will take up the sulphate ion from sulphuric acid as well as from sulphur trioxide because these sulphur trioxide is also available to trap your corresponding oxygen from the borax and that oxygen will give you for its conversion from sulphur trioxide to again sulphate anion. So, that sulphate anion will be therefore, separated as sodium sulphate because sodium salt of that particular anionic part; that means, your B 4 O 7 2 minus is your borax.

So, those sodium ions available from the borax will be converted to sodium sulphate and the remaining as your calcium sulphate because these two are your by products. And these two by product; that means, your calcium sulphate and sodium sulphate if we are able to separate them from the boron tri-fluoride we can have these two material also as a typical material which can be useful industrially if you can prepare a large amount of calcium sulphate. Because we know that is nothing but your plaster of Paris type of thing from the gypsum we get and your sodium sulphate which we also prepare from sulphur, elemental sulphur.

And this particular thing that means, another indirect way that if you go for from this particular, this corresponding your borax that if you can go for your borax thing; that means, borax if you convert this borax to boric acid instead of direct going for your boron tri-fluoride. So, if you can have a procedure or if you can have industry, where borax is utilised for making your boric acid. So, that boric acid can be a store house for that material and if you required the 50 percent of that will be used for making your boric acid and remaining 50 percent you can go for your boron tri-fluoride preparation. So, you directly in that particular case you have to react with simple acid base reaction. Because if you react it with HF that H 3 BO 4 can directly react with your that boric acid to give you your BF 3 and the water molecule. So, via boric acid also you will be able to make your boron tri-fluoride.

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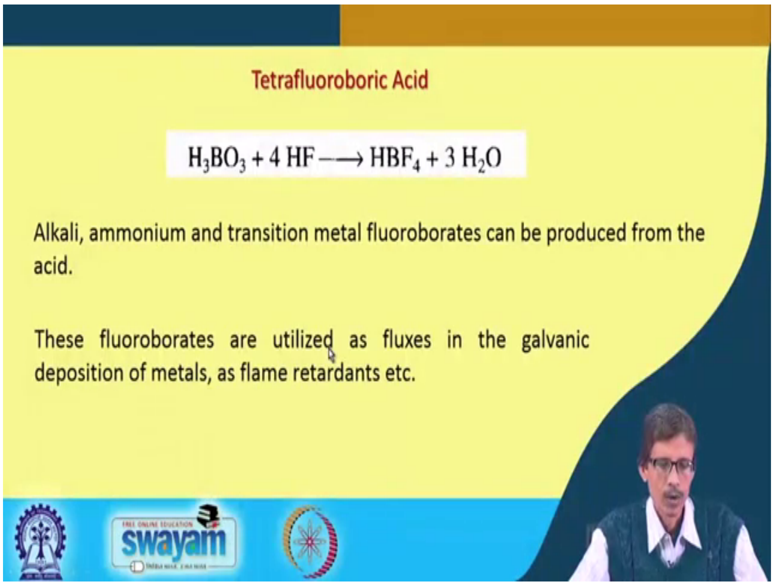

Tetrafluoroboric Acid

$$H_3BO_3 + 4\,HF \longrightarrow HBF_4 + 3\,H_2O$$

Alkali, ammonium and transition metal fluoroborates can be produced from the acid.

These fluoroborates are utilized as fluxes in the galvanic deposition of metals, as flame retardants etc.

Then from that another boron based compound which is also useful that boron tri-fluoride is a Lewis acid we all know it has 3 fluorine centres on the boron, if you apply another fluoride ion to attach it to this particular centre making it as a BF 4 minus ion. So, tetrafluoroboric acid which can also be prepared from your directly from the boric acid with a different stoichiometric reaction with hydrochloric acid, now you have the 4 molecules of HF reacting with the corresponding one giving you the free boric acid because that free boric acid can immediately be converted to its corresponding salt as the sodium salt which is sodium tetrafluoroborate because this particular thing is the acid.

If you react with sodium hydroxide then H BF 4 reaction of it with corresponding sodium hydroxide or any other sodium salt it can be a sodium bicarbonate also to giving you the corresponding Na BF 4 which is sodium tetrafluoroborate, which is a very good source of fluoride ion as well as it is the catalyst sometime and it also a very good anion that is BF 4 minus the fluoro borate anion of a different shape. That means, a small tetrahedral anionic structure it can have for different types of solid state synthesis or solution synthesis.

Then if you substitute this H by alkali metal ion or ammonium ion any other transition metal ion you get the corresponding fluoro borates. So, this fluoro borates can be prepared from use of the corresponding acids and these fluoro borates are utilised as fluxes in the galvanic deposition of metals.

So, again from the metallurgical point of view we now know that what are the different types of fluxes and how these fluxes are also useful. So, if we go can go for the deposition of some important metal ions as metals. So, galvanic deposition; that means, you have a galvanic cell and you go for a corresponding reduction of the metal ion and those metal ions are coming out nothing but from your transition metal. If we go for the transition metal deposition it is transition metal ion fluoro borates. So, transition metal ion fluoro borates in corresponding electrolysis bath, you take it and you can go for is corresponding electrolysis or sometime this fluoro borates are also useful as a flame retardant material. So, they can reduce the flame and they can extinguish the flame for some useful purposes.

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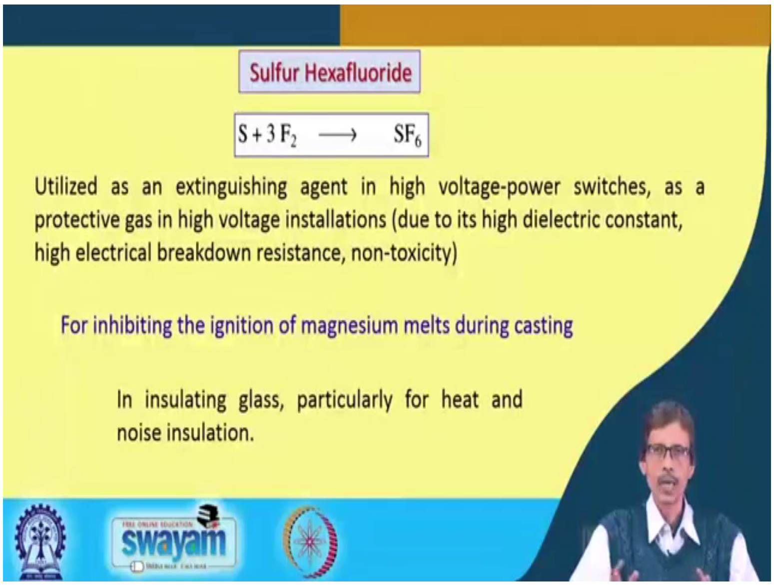

Sulfur Hexafluoride

$S + 3F_2 \longrightarrow SF_6$

Utilized as an extinguishing agent in high voltage-power switches, as a protective gas in high voltage installations (due to its high dielectric constant, high electrical breakdown resistance, non-toxicity)

For inhibiting the ignition of magnesium melts during casting

In insulating glass, particularly for heat and noise insulation.

Then we can have the sulphur hexafluoride. So, like your uranium hexafluoride. So, now, you can get it in terms of your corresponding non-metallic part. That means, sulphur you have and as we have seen that we can know we know sulphur dioxide sulphur trioxide, but we never discussed it in terms of a sulphur compound but it is also a important compound based on sulphur but we are discussing this in the presence of your typical corresponding hexafluoride as the corresponding useful fluoride compound. So, sulphur is taken but it is basically useful fluoride compounds. So, your SF 6, so SF 6 again you can directly use from the elemental reaction between the elemental sulphur and the fluorine giving you the sulphur hexafluoride compound in your hand.

And again, unlike your front retardant material but it is extinguishing agent, it can extinguish the flame. So, flame extinguishing agent in the high voltage power switches, in the transformers and all other cases because sulphur hexafluoride is basically using that basically utilize that particular gas as a high voltage power switch in different high voltage power switches. It is also a protective gas in high voltage installations in the transformers also, due to its high dielectric stand based on a typical physical property having a high dielectric constant value it can be used and high electrical breakdown resistance is also very high and is also is non-toxic and is also not environmentally so dangerous like other material which we consider that environmentally they are not useful.

And it is also useful for inhibiting the ignition of magnesium melts during casting. If we go for a casting material or casting process, and if we go for the inhibition because magnesium, we know that quickly it can burn in presence of oxygen. So, burning of magnesium can be stopped in presence of this sulphur hexafluoride, and in insulating glass particularly for heat and noise insulations. If we can go for insulation of these two quantities heat as well as noise we can make the corresponding insulating glass made up of silicon hexafluoride. So, silicon hexafluoride will be the raw material for making the special type of insulating glasses.

Thank you very much.