Industrial Inorganic Chemistry
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Lecture – 20
Thiosulfates and Dithionite

Welcome back to this class once again. Where we are talking about the different sulfur based salts; that means, inorganic sulfur based salts of not sulfuric acid. But sulfurous acid or any other salt what we can have.

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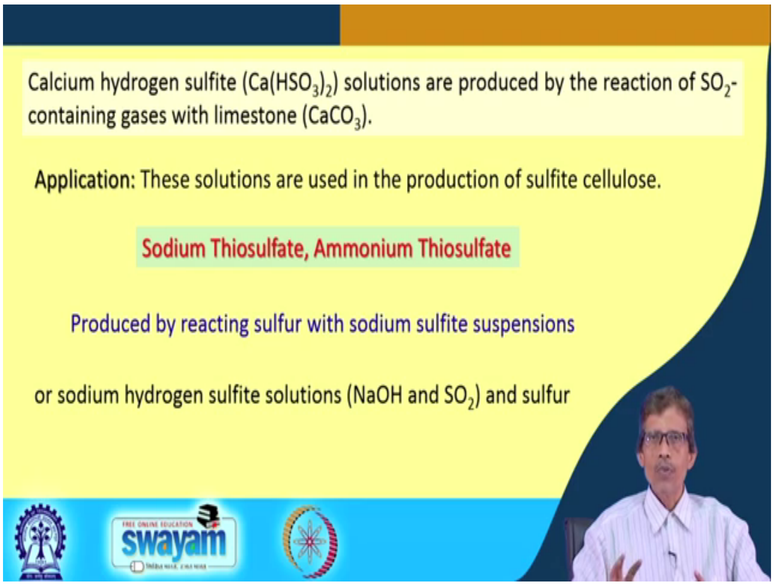

Calcium hydrogen sulfite ($Ca(HSO_3)_2$) solutions are produced by the reaction of SO_2-containing gases with limestone ($CaCO_3$).

Application: These solutions are used in the production of sulfite cellulose.

Sodium Thiosulfate, Ammonium Thiosulfate

Produced by reacting sulfur with sodium sulfite suspensions

or sodium hydrogen sulfite solutions (NaOH and SO_2) and sulfur

So, we have seen that how we can have sodium thiosulfate or sodium bisulfite. So, similarly we can go for calcium hydrogen sulfite. So, as we are talking about the material where we can use it as a safer one for our food material also. So, calcium we all know that this can make no harm sodium and calcium salts are always used as the food preservatives also. So, if we are able to use more amount of bisulfite anion we should go for a corresponding salt where the metal ion is bivalent. That means, instead of your sodium or ammonium salt because ammonium salt we mostly do not use, we use the sodium salt for as a food preservative.

So, calcium can bind 2 of the anions; that means, your Ca HSO 3 whole 2 how we produce it as we have seen already that we can use sodium hydroxide for the preparation of their sodium analogues. So, now, more simpler reaction is possible to use where you can use simple limestone, the calcium carbonate because these calcium carbonate can react with sulfur dioxide containing gases in presence of water because in situ the sulphur dioxide can react with water molecule to giving you the sulfuric acid.

So, in situ production; that means, the material which is being produced in the reaction medium itself can react directly with calcium carbonate. So, calcium carbonate is being decomposed because we know that the calcium carbonate is not a stable one in presence of a very low level of acid concentration it immediately breaks liberating carbon dioxide and living behind with calcium oxide. And that calcium oxide again react with your protons from the medium, from the water molecules giving you calcium hydroxide or simply the calcium ion and the hydroxide ions.

So, the limestone will in the same fashion can directly react with the sulfuric acid in situ produce sulphate as acid; that means, H 2 SO 3. So, the reaction of H 2 SO 3 with calcium carbonate will give you calcium hydrogen sulfite. So, is a example of another typical sulfite salt hydrogen sulfite salt, where we use simple limestone. So, definitely it should be very pure quality, if we are able to use it as a food material, then these compounds sodium salts or the calcium salts have a very useful use in the production of sulfite cellulose.

Sulfide based cellulose are produced for different purposes that we will also see in some cases when we will talk about the carbon disulfide production that how we get the cellophanes or some other material from the typical cellulose. Similarly this cellulose having some alcohol functions is a polymeric function of or polymeric part of your glucose molecule cellulose is nothing, but your polymeric glucose having some useful CH 2 OH groups.

So, CH 2 OH group can be converted to sulfate or the sulfite function giving you a corresponding sulfite cellulose. Now we will move slowly to that of your thing what we just now told you that how you make Na 2 S 2 O 3 or its ammonium version or the ammonium salt. That means, you have to make thiosulfate which is very useful from analytical point of view, which is useful also industrially large amount of sodium thiosulfate or ammonium thiosulfate is produced industrially and there is a huge demand.

So, several tonnes of all these annually produced by all these industries in organic chemistry industries, how they produced? They simply produced by reacting sulfur. So, again we consume elemental sulfur what we get from the natural sources. So, the natural sources of sulfur are still very useful for making not only sulfuric acid war, but for different other types of compounds which are industrially important.

One such example is for making sodium thiosulfate. So, already we have seen that how sulphur dioxide can be consumed for making sodium bisulfite or hydrogen sulfite as well as sodium sulfite which is Na 2 SO 3. Now as I told you in case of your tunnel chloride preparation or sulfonyl chloride preparation that you have the sulfur center and your mono sulfur dichloride compound, sulfur having 2 Cl bonds which can be converted to SO giving you SOCl 2 or which can be converted to SO 2. That means, SO 2 Cl 2 can be formed one is thermal fluoride and other is sulfuryl fluoride.

That means what do you see now that like thioether also I told you that thioether sulfur, that sulfur group has a lone pair of electron and that lone pair of electron can form very good coordinate bond; that means, that 2 electrons on sulfur can donate to the oxygen forming sulfur oxygen bond.

Similarly, if the same type of reaction can take place between one sulfur to the other sulfur meaning you a terminal SS bond. So, that terminal SS bond is present in S 2 O 3 2 minus that is why whatever sulfite you have in your hand; that means, sulfite means your bisulfite or SO 3 2 minus. So, SO 3 2 minus is sulfur having 3 sulfur oxygen bonds. Now what will you do? We will just simply put one sulfur on the sulfur; that means, we are trying to make one sulfur sulfur bond which will be coming from your elemental sulfur that is where you go for this reaction.

That means reacting sulfur with sodium sulfite suspensions or sodium hydrogen sulfite solutions which are nothing, but a mixture of sodium hydroxide and sulfur dioxide as well as some extra amount of sulfur. So, if that particular alkaline solution is very easy to dissolve that particular excess sulfur we get a direct reaction of the 2 anionic parts, one is that corresponding S O 3 2 minus and other is simply s; that means, sulfur S 0.

So, elemental sulfur is providing you sulfur atoms which is attached to it converting your SO 3 2 minus 2 S 3 O 3 O 3 2 minus.

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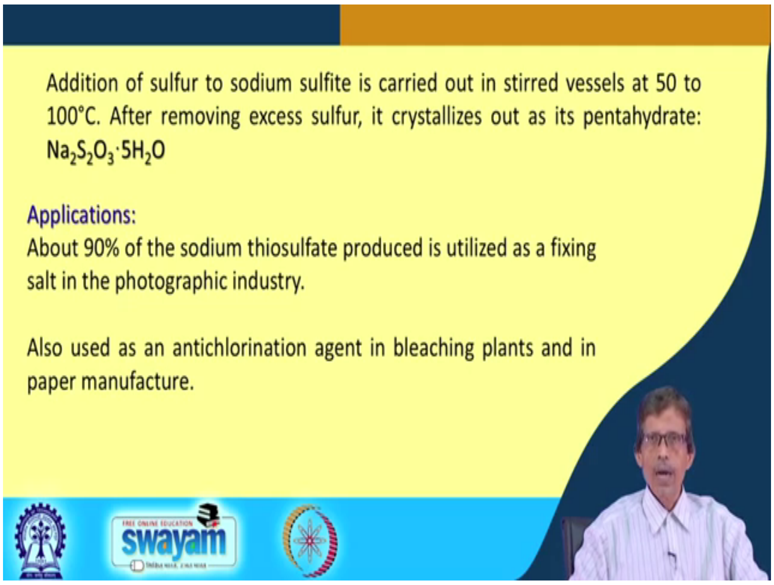

Addition of sulfur to sodium sulfite is carried out in stirred vessels at 50 to 100°C. After removing excess sulfur, it crystallizes out as its pentahydrate: $Na_2S_2O_3 \cdot 5H_2O$

Applications:

About 90% of the sodium thiosulfate produced is utilized as a fixing salt in the photographic industry.

Also used as an antichlorination agent in bleaching plants and in paper manufacture.

So, we will add sulfur to sodium sulfite and in a vessel we take where the standing arrangements should be there, it can be laboratory level vessel or it can be huge one for the industry one. Industry level we can also use and the vessel can be heated to 50 degree to 100 degree centigrade and when sulfur is being consumed by your sodium sulfite, we get the corresponding sodium thiosulfate in the solution.

And if you evaporate the excess water from the medium we get a saturated solution of sodium sulphate (Refer Time: 08:46) thiosulfate. So, the saturated sodium thiosulfate solution along with some water of crystallizations which are very important, because we all know that good amount of water of crystallizations are present when we allow to crystallize some inorganic salts like copper sulphate which is also pentahydrate. Copper acetate which is monohydrate; then ferric chloride which is heptahydrate.

Why these hydrates are there because these hydrates will crystallize it from the medium giving you good crystals or single crystals where water is present without water you will not get those crystals. So, water is present forming huge number of hydrogen bonds and those hydrogen bonds are responsible for your crystallization. So, one particular crystal if you are able to detect that from the knowledge of your known crystal safe and morphology of that particular sodium thiosulfate, it has to have the corresponding 5 water molecules.

So, it will always be crystallized at a pentahydrate. So, application wise you can have about 90 percent of it is used in the photographic industry earlier definitely, but now that particular one is not we are using photographic industry has been changed typically, is the digital photography era has come but earlier this particular one for the fixing salt in the photographic industry.

So, the same knowledge that wow we use this particular thiosulfate for the reduction or the removal of silver bromides; that means, the solubilization of the sodium bromide crystals by sodium thiosulfate due to the formation of the complexation reaction between the silver ions and the thiosulfate anions.

Giving you the corresponding thiosulfate complexes of silver ions so that information is always be useful whether you have the photographic industry still present of that type or not. And also it is used like in the previous cases where we have seen that it is used also for the anti chlorination reaction as a useful reagent for anti chlorination and in bleaching plants and in paper manufacture also, that in also paper industry it is a bleaching agent and is also a very useful reducing agent.

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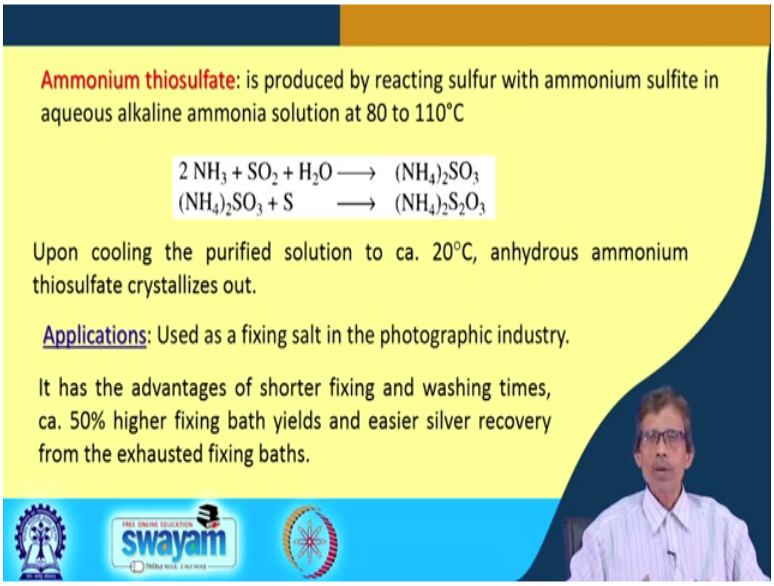

Ammonium thiosulfate: is produced by reacting sulfur with ammonium sulfite in aqueous alkaline ammonia solution at 80 to 110°C

$$2\,NH_3 + SO_2 + H_2O \longrightarrow (NH_4)_2SO_3$$
$$(NH_4)_2SO_3 + S \longrightarrow (NH_4)_2S_2O_3$$

Upon cooling the purified solution to ca. 20°C, anhydrous ammonium thiosulfate crystallizes out.

Applications: Used as a fixing salt in the photographic industry.

It has the advantages of shorter fixing and washing times, ca. 50% higher fixing bath yields and easier silver recovery from the exhausted fixing baths.

Then we just move to the other salt; that means, not from sodium you gave for the ammonium salt which can be produced again directly from reacting sulphur with ammonium sulfite instead of sodium sulfite it is now ammonium sulfite in aquas alkaline ammonia; that means, ammonium hydroxide only at 80 to 110 degree centigrade. So, this is the typical reaction protocol where you are able to make ammonium thiosulfate.

But now, instead of sodium hydroxide you just simply use ammonia. So, ammonia or ammonium hydroxide will take care of the reaction producing your ammonium thiosulfate. So, the reaction is very simple, the first one is for the formation of your ammonium sulfite from your resolution of sulphur dioxide by water and reacting it with ammonia giving you ammonium sulfite. And that ammonium sulfite when it is reacting with excess sulfur the elemental sulfur the sulfur in the 0 oxidation state giving you S 2 or 3 2 minus an ion; that means, the thiosulfate anion giving you that ammonium thiosulfate.

So, these 2 simple reactions can be useful for not only trapping sulfur dioxide, but also trapping ammonia as a gas and elemental sulfur for the production of some useful compound, which is your ammonium thiosulfate. And when it is formed in the solution a saturated solution will be getting and from that saturated solution if you cool the solution because your temperature or reaction was a little bit higher which was around 100. So, a solution at 100 degrees should be cooled to room temperature or below that; that means, at about 20 degree centigrade where anhydrous ammonium thiosulfate crystallizes out.

Because cooling basically taking out that particular salt which is already dissolved in your water medium should go out because at low temperature your solubility of the corresponding salt is less. So, to get that saturated solution and beyond that the supersaturated solution will give you or we remove the excess amount of that salt which is already present in it at higher temperature. So, crystallization is therefore, there and that crystallization will give you the solid ammonium thiosulfate separated from that particular reaction medium.

And sometimes we get these as very good and very beautiful crystals out of that. So, as already I told you that is for your sodium thiosulfate thing, similarly ammonium thiosulfate is also useful for fixing salt; that means, for dissolution of any silver bromide based crystals.

So, if we just go if you work on some area where you are using some silvers, like silver nano particles making or silver bromide preparation. And if you want to remove those silver bromide or dissolution of silver bromide you can directly use this particular sodium thiosulfate which is also industrially important material for us.

And if you compare this ammonium thiosulfate with that of our previously discussed sodium thiosulfate this time it has some advantage because of sort of fixing and washing times because you can save time earlier days people were trying to get some other compound by changing only that sodium ion by ammonium ion. And it can have 50 percent higher fixing bath yields, because the reaction always we can go for those reactions which are easier to achieve and the yield for whether we can talk in terms of the fixing of that particular photography or we can go for the baths of their the dissolution of silver ion and easier for silver recovery.

That means we take those silver bromides as silver thiosulfate complexation and ultimately if we reduce that particular silver thiosulfate for some chosen reducing agent, some specific reducing agents are there which can be added to that silver thiosulfate solution to give you silver 0 as the metallic silver or silver powder to your hand. So, silver recovery because silver is a very expensive material. So, silver recovery process is also very much useful through this particular process; that means, this particular second compound not the previous one; that means, use of your sodium thiosulfate.

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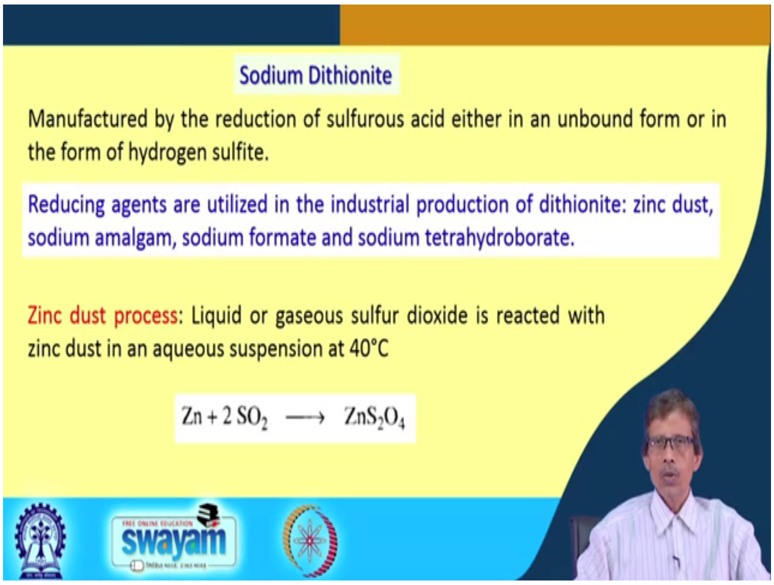

Sodium Dithionite

Manufactured by the reduction of sulfurous acid either in an unbound form or in the form of hydrogen sulfite.

Reducing agents are utilized in the industrial production of dithionite: zinc dust, sodium amalgam, sodium formate and sodium tetrahydroborate.

Zinc dust process: Liquid or gaseous sulfur dioxide is reacted with zinc dust in an aqueous suspension at 40°C

$$Zn + 2\,SO_2 \longrightarrow ZnS_2O_4$$

Then we just go for another most important compound or very interesting compound is dithionite compound. So, we have seen from our sodium salts of sulfite, sodium bisulfites then sodium thiosulfate. Now we go for a dithionite type of thing and it has some other special applications or the special reactivity pattern. But now we try to understand only, what is that dithionite anion even dithiol; that means, 2 sulfur groups are there, but your oxygen content is different, but how we make it? It is again manufactured by the reduction of sulfuric acid.

So, whatever we are doing we are going down further that is already we know that your sulfur dioxide is the reducing agent and your corresponding sulfurous acid salts; that means, the sodium sulfite or sodium bisulfite or the sodium thiosulfate they are all reducing in nature, but the reduction equivalent is restricted to their potential up to sulfur dioxide. That if we consider that sulphur dioxide is a moderately enough or moderately good enough reducing agent, we will get the same effect out of all these discussed salts.

But we cannot go beyond that, but now we will see that we are able to make some other compound which is the powerful reducing agent compared to sulfur dioxide based salts and alpha dioxide itself which is dithionite. So, preparation technique will also be different. What we have to do? We have to reduce that particular sulfur dioxide further such that the product what you will be getting is the stronger reducing agent compared to your that sulfur dioxide based molecules or the sulfur dioxide based salts in your hand.

So, this sulfurous acid either as the free acid or in an unbound form; that means, your free acid in the form of hydrogen sulfite; that means, it can get it as your sodium hydrogen sulfite and we can go for other stronger reducing agent because we have to reduce it to some other species; that means, sulfite bisulfite to dithionite. So, what are those reducing agents are utilized for industrial production or dithionite. So, zinc dust we will simply take the zinc dust because zinc dust all we know is a stronger reducing agent many organic reactions or so many other type of reactions we use zinc dust.

Sometimes you can go for a moderate reducing agent or reducing behavior from the zinc dust in presence of ammonium chloride. Even we can reduce the nitro function or the nitro group or the nitro group present in some organic molecule by zinc dust. So, here basically this reduction is done by zinc dust; that means, the dithionite some amount of that particular stronger ability of reduction is coming from your zinc dust reaction. So, zinc dust, if zinc dust is the strongest one and is the corresponding sulfur dioxide is the moderate one you will get in between the corresponding ethanoate ion.

Then sodium amalgam; that means, sodium dissolved in mercury. So, is amalgam Na Hg x or sodium formate, sodium if will take the help of some organic molecule organic reducing agent which is sodium formate or sodium tetrahydroborate Na BH4. So, boron based, hydride based boron hydride based which is tetrahydroborate anion pH 4 minus can also be utilized for this reduction.

So, the first process where you use simple zinc dust and in that zinc dust process the liquid or gaseous sulfur dioxide is reacted with zinc dust. So, either we take the liquefied or liquid form of that sulfur dioxide or if we dissolved in water is reacted with zinc dust in an aqua suspension. That means, in water medium at 40 degree only, not very much. So, at this temperature your simple chemical reaction what is being achieved over there is your zinc plus SO 2 giving you zinc S 2 O 4; that means, zinc dithionite.

So, salt also you will be getting directly from the zinc as the cation because zinc is the reducing agent itself is oxidizing to the corresponding bivalent zinc cation Zn 2 plus. So, these zinc 2 plus as Zn 2 plus is present in the medium and SO 2 is fixed basically in the form of S 2 O 4 2 minor. That means, you have sulfur sulfur bond formation, like organic chemistry we all know that when we go for a typical oxidation reaction on thiol based some proteins or polypeptides where you have 2 thiolends.

If you go for oxidation you can have a sulfur sulfur bond, similarly some thiol molecule; the organic thiol molecule to a minor thiol phenol or some only thiol phenol. If you oxidize it with hydrogen peroxide or any other oxidizing agent you get and you end up with a sulfur sulfur bond. So, those sulfur groups are the anionic function because it is a thiol function whether it is coming from the amine acid that cysteine molecule or it is coming from some thiol function or amino thiol function these are s minus.

But here your SO 2 molecule is the neutral molecule and from that neutral molecule which is already tetravalent a state is getting reduced and we are forming a new sulfur sulfur bond such that your molecule is SS and other end you have 2 oxygen atoms on the sulfur and on the other end also you have 2 oxygen atoms attached to the terminal sulfur. So, basically what you are doing you are bringing 2 SO 2 molecule together forming SS bond. So, reduction is also giving you some formation of your SS bond to making you or giving S 2 O 4 2 minus.

As it is forming as the anion because 2 electrons are being transferred from zinc center to that particular center of those anion. So, zinc is becoming the cation so you saturate it you try to isolate, it you try to crystallize it from the medium you will be getting the zinc dithionite salt from the reaction medium.

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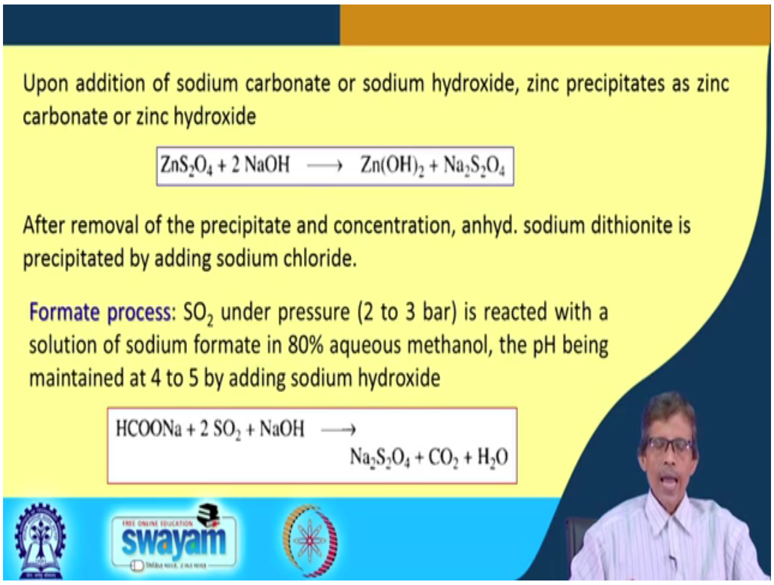

Upon addition of sodium carbonate or sodium hydroxide, zinc precipitates as zinc carbonate or zinc hydroxide

$$\boxed{ZnS_2O_4 + 2\,NaOH \longrightarrow Zn(OH)_2 + Na_2S_2O_4}$$

After removal of the precipitate and concentration, anhyd. sodium dithionite is precipitated by adding sodium chloride.

Formate process: SO_2 under pressure (2 to 3 bar) is reacted with a solution of sodium formate in 80% aqueous methanol, the pH being maintained at 4 to 5 by adding sodium hydroxide

$$\boxed{HCOONa + 2\,SO_2 + NaOH \longrightarrow Na_2S_2O_4 + CO_2 + H_2O}$$

So, what we do basically in this particular reaction we add sodium carbonate or sodium hydroxide. If we try to avoid to get the corresponding zincs dithionite, we will have to have the corresponding sodium salt.

What will happen then addition of sodium carbonate or sodium hydroxide zinc will be precipitated as either zinc carbonate or zinc hydroxide because in alkaline medium whatever zinc ions is present with the zinc dithionite Zn 2 plus will be reacting with carbonate anion. Or the hydroxide ion giving you precipitations which are highly insoluble in material because the ksp values are very less, solubility product values are very less. So, immediately they separate from the reaction medium as precipitate.

So, they go for the formation of zinc carbonate or zinc hydroxide from the medium. So, you have the zinc that dithionite reacting with sodium hydroxide and that is giving you zinc hydroxide formation and your sodium dithionite which is comparatively having higher solubility compared to your zinc dithionite. So, that is why we most of the time we will using zinc dithionite for practical purposes, because your solubility the water solubility or in aqueous solubility is more compared to your zinc dithionite.

And also some concern is there for the use of the corresponding zinc salt compared to your sodium salt. So, if you remove this particular precipitate what is getting over there either your carbonate precipitate or hydroxide precipitate from there. So, after removal of the precipitate and then you go for concentrating system, you go for anhydrous sodium dithionite is precipitated by adding sodium chloride. So, you get a saturated solution of sodium dithionite, but still it has some good solubility in it.

So, we add some common ion; that means your sodium ion. So, in terms of that we add some saturated solution of say sodium chlorides say. So, common ion effect will now play into the role. So, supply of more and more sodium ion will allow you to precipitate out your sodium dithionite what is being formed through the precipitation of zinc as zinc hydroxide. So, it is precipitated out from there, again it can be redissolved and can be recrystallized once again to enhance or to increase the purity of that particular salt.

So, the first category of this particular reaction for reduction of sulfur dioxide is your zinc process or zinc dust process, second is the typically organic process is the format process. So, in the format process now SO 2 under pressure of 2 to 3 bar is reacted with a solution of sodium formate in 80 percent aqueous methanol. That means, 80 percent aqueous methanol, the 20 percent of that water and 80 percent of the methanol is there, and pH is maintained at 4 to 5; that means, its typically alkaline medium. So, in that alkaline medium the formate is a very good reducing agent for your sulfur dioxide what we have seen in case of your that particular previous one; that means, your zinc dust.

So, here we just see that what is happening there, that sodium formate the formic sodium salt of formic acid. So, is HCOONa. So, is used in presence of sodium hydroxide for the reduction of sulfur dioxide. So, if we consider that the yield of this particular reaction is more and we can manipulate this particular reaction quite nicely. Because in the previous case where we used the zinc we have the problem of getting the zinc as the another salt as zinc hydroxide or zinc carbonate we have to remove that particular zinc carbonate or zinc hydroxide from the reaction medium.

Then we get the neat sodium dithionite in your hand, but in this particular case the product of the reaction, the byproduct rather of this reaction is your CO 2 and H 2 O. So, the reaction is a very straight cut one, that is why it you have advantage of using format anions over zinc dust is that, you only you are producing water molecule and carbon dioxide. Because you are reducing equivalent from your format anion H CO 2 minus is transferred to your sulphur dioxide molecule to give you your sodium dithionite anion and producing carbon dioxide and water molecule.

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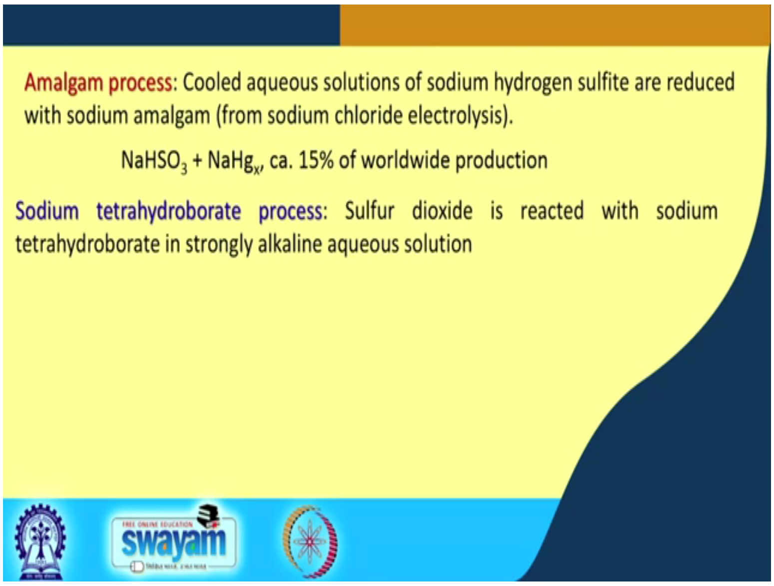

Amalgam process: Cooled aqueous solutions of sodium hydrogen sulfite are reduced with sodium amalgam (from sodium chloride electrolysis).

$NaHSO_3 + NaHg_x$, ca. 15% of worldwide production

Sodium tetrahydroborate process: Sulfur dioxide is reacted with sodium tetrahydroborate in strongly alkaline aqueous solution

So, it will be a little bit very neat reaction where you get this particular reduction and the third process is your amalgam; that means, sodium amalgam; that means, you are using a reduction reaction in presence of sodium metal, sodium dissolved in mercury. So, cooled aqueous solutions of sodium hydrogen sulfite; that means, your sodium bisulfite is reduced to sodium amalgam where we get sodium amalgam? Because we will find when we see when we study the sodium chloride electrolysis we will find the chlor alkali process we will find somewhere when we study the halogens.

So, from sodium chloride electrolysis we produce this sodium amalgam and that sodium amalgam can be directly used for this particular reduction reaction and the straightway this reaction between NaHSO 3 plus Na Hg x which is your sodium amalgam. So, about 15 percent of your production, that worldwide production of sodium dithionite is being achieved by this particular process. So, definitely it will have some advantages and some companies are basically fund of handling this one because already they have all the set up all the mechanism and all the knowledge and the manpower for doing this reaction. They use 15 percent of these they are using this particular amalgam process.

So, today we will not be able to finish it the today tomorrow or next class we will just continue the last one; that means, where we will be using the organic reducing agent, because it is well known that the sodium borohydride process the sodium borohydride is a well known reducing agent is a very strong reducing agent where it can reduce your organic functional groups like aldehyde or any other carboxylic acid or any other groups also sometimes the amine functions.

So, is a very strong reducing agent, but they are based on the hydride ions or the hydride groups or H minus is coming from the boron center giving you that particular reduction reaction and that borohydride; that means, the hydride deduction, we have seen zinc reduction, we have seen the corresponding amalgam reduction.

Now, we will see the hydride reduction for the preparation of sodium dithionite ok. So, next day we will just see how you can use the sodium borohydride for making sodium dithionite ok.

Thank you very much.