Industrial Inorganic Chemistry
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Lecture – 19
Sulfur Dichloride, Thionyl Chloride

Good evening everybody, we are talking about the different sulfur compounds, starting from your sulfuric acid.

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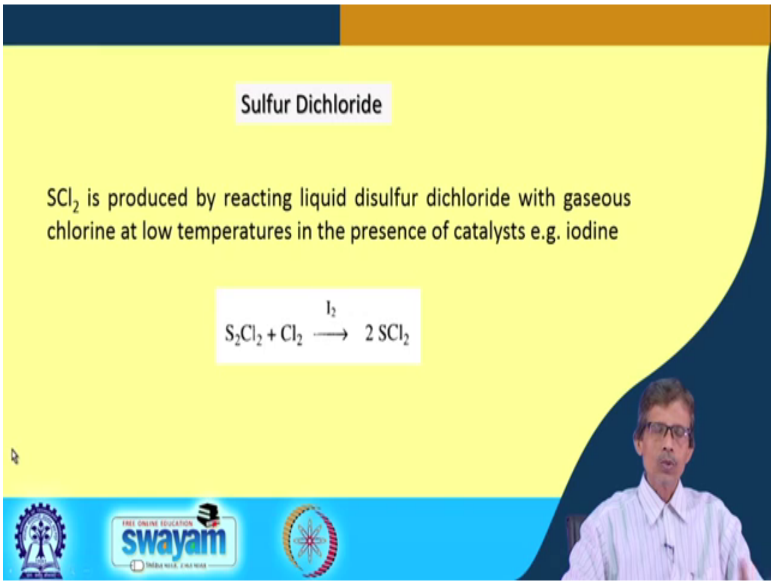

Sulfur Dichloride

SCl_2 is produced by reacting liquid disulfur dichloride with gaseous chlorine at low temperatures in the presence of catalysts e.g. iodine

$$S_2Cl_2 + Cl_2 \xrightarrow{I_2} 2\,SCl_2$$

And now we have moved to some compounds where we can have sulfur and chlorine bonds. And last time what we have seen is that you can have 2 sulfur and on the both 2 ends you can have 2 chlorides; that means, the compound is disulfide dichloride. Now if we see that that also have seen that the sulfur dichloride; that means, it is SCl 2.

So, how we get that particular SCl 2 compound is very important because we have the source of the sulphur, the elemental sulfur and we have the source of chlorine as the chlorine gas. So, this is also produced in a nicer way that by reacting liquid sulfur dichloride disulfide dichloride what we have prepared earlier. So, we have seen that how we can make from direct reaction of chlorine and sit or S 2; that means elemental sulfur for the production of S 2 Cl 2 not SCl 2. So, from there basically if we take out one of the sulfur atom from that molecule we will get SCl 2.

So, what do you do? We do the reaction of sulfur disulfide dichloride with excess of chlorine; that means, you have to either remove sulfur or you add more chlorine in terms of their molecular stoichiometry. So, if we do the same reaction with chlorine gas with S 2 Cl 2 at low temperature in the presence of some catalysts. We all know that here we are converting your SO 2 to SO 3 we have seen some particular type of metal oxide catalysts which is vanadium pentoxide.

Now, we will see the simple iodine the elemental iodine I 2 is useful for this particular conversion. So, we require the presence of that particular catalyst for the typical conversion of disulfur dichloride to sulfur dichloride. So, what do we do we basically taking away of one of the sulfur atom from the S 2 Cl 2 which we have seen also earlier that you have sulfur-sulfur bond and on the 2 ends you have the 2 chloride groups attached to these 2 sulfur.

Now, if we get sulfur dichloride which is very much similar to that of your water molecule; that means, water we have we know that oxygen is present and you have 2 hydrogen atoms attached to that oxygen centre now. Instead of that particular sulfur what we will see afterwards also during the preparation of your hydrogen sulphide, hydrogen sulfide is of similar type that where sulfur is the central atom and you have 2 hydrogen atoms attached to the particular sulfur.

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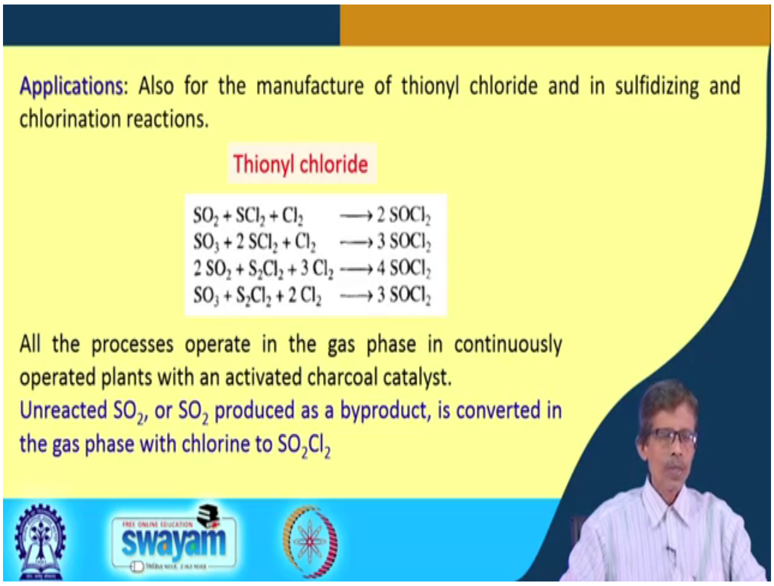

Applications: Also for the manufacture of thionyl chloride and in sulfidizing and chlorination reactions.

Thionyl chloride

$$SO_2 + SCl_2 + Cl_2 \longrightarrow 2\,SOCl_2$$
$$SO_3 + 2\,SCl_2 + Cl_2 \longrightarrow 3\,SOCl_2$$
$$2\,SO_2 + S_2Cl_2 + 3\,Cl_2 \longrightarrow 4\,SOCl_2$$
$$SO_3 + S_2Cl_2 + 2\,Cl_2 \longrightarrow 3\,SOCl_2$$

All the processes operate in the gas phase in continuously operated plants with an activated charcoal catalyst.

Unreacted SO_2, or SO_2 produced as a byproduct, is converted in the gas phase with chlorine to SO_2Cl_2

Here the sulfur is attached to 2 chloride. So, you get that particular sulfur dichloride and it has also different kinds of applications and that is why we prepare it for say different purposes and sometime for the introduction of sulfur we use some sulfur bearing compounds for the introduction of that sulfur in some big backbone; that means, big structure of organic molecules or some polymeric structures.

So, here we use we will take the example of one application for the manufacture of thionyl chloride and in sulfidizing and chlorination reactions what have seen also earlier in case of your S 2 Cl 2 molecule. So, why we produce another kind of this particular molecule is also interesting to know because the reactivity pattern for these 2 compounds; that means, S 2 Cl 2 SCl 2 can the different and one such application is the thionyl chloride preparation because we use huge amount of thionyl chloride for the laboratory purpose also.

For organic transformations, for the chlorination reactions simple chlorination reactions sometime we also use that for your acid chloride preparations. So, COOH if you have RCOOH, it can be directly converted to RCOCl with the use of thionyl chloride and also in sulfidizing and chlorination reaction; that means, introduction of sulfur or introduction of chlorine in some reactions. So, here now we will see that, what is that particular thionyl chloride. So, we have S 2 Cl 2 already we have seen.

Now, we today is SCl 2, now it is thionyl chloride; that means, you get some compound where compound is SOCl 2. So, you have S 2 Cl 2, SCl 2 now we get some compound which is a SOCl 2. So, what is this now? That instead of that the molecular formula why they are also very similar; that means, instead of 1 sulfur in S 2 Cl 2 we have 1 oxygen and 1 sulfur. But the connectivity wise it is completely different it is very much similar to that of your sulfur dichloride with extra sulfur oxygen bond.

So, if you consider there are many pathways or many reactions which can ultimately lead to this particular sulfur oxychloride we can say or we can consider is that the thionyl chloride. So, because one other version of this type of molecule you know that is also known as the sulfuric chloride that we will also see which is a SO 2 Cl 2. So, sulfur is there, if you have 2 sulfur oxygen bond, you get sulfuric chloride, if you have one sulfur oxygen bond or particular one end and other end, you have the 2 chloride groups starting from your SOCl SCl 2.

So, what we see that if you have SCl 2. So, the sulfur is here and the 2 Cl 2 Cl. So, sulfur is forming one bond over there; that means, it is the corresponding addition of sulfur; that means, it is basically a sulfoxide formation. So, this is sulfoxide formation and for the other compound it is the sulfone formation. So, if we consider that your SCl 2 molecule the sulfur dichloride molecular is similar to that of our any organic molecule, where you have a sulfur as the centre and 2 carbons are attached to that particular centre.

We considered that particular molecule as the thioether. So, very interestingly that particular thioether, having 2 lone pair of electrons on it that particular thioether sulfur you can add or you can transfer oxygen from some other source like hydrogen peroxide or hydroxy benzene or metachrome or benzoic acid we can transfer that oxygen to the sulfur centre making it a SOCl 2. So, these are all the different types of reactions or the reactivity pattern on say simple SCl 2 type of molecules.

So, if you consider that our goal is that converting this SCl 2 to SOCl 2. So, it is basically a question posing to you that how you can convert the first 2 examples which are sulfur dichloride and the second, third and fourth examples are the conversion of the disulfur dichloride, the first this is what we discussed last time in our previous class.

So, these 2 how you convert to SOCl 2 so we should supply something which can transfer oxygen to that particular centre. So, in the first case it is a simple reaction of sulfur dioxide gas with that of your sulfur dichloride, that only will not give you the desired product; that means, your. So, Cl 2 because you require more amount of Cl 2. So, you have to use corresponding chlorine gas as the extra source.

So, in between what you can have you can have one end you have the source of oxygen donor or the oxygen donor molecule should be available and some other end you can have the corresponding Cl 2; that means, the source of the chlorine. So, the reaction of these 2 along with your SCl 2 or S 2 Cl will give you 4 different ways of making thionyl chloride. So, sulfur dioxide plus S Cl 2, in presence of chlorine will giving you 2 molecules of thionyl chloride.

In the second case more oxygen bearing molecules that in sulfur trioxide, because if we considered that some industry is producing some excess of sulfur dioxide or we are burning some amount of sulfur to sulfur dioxide or trioxide. So, that gas outlet or the excess amount of that particular 2 gases; that means, sulfur dioxide and trioxide can be consumed in presence of your extra chlorine gas by sulfur dichloride, mono sulfur dichloride to make your time thionyl chlorides.

So, first 2 reactions are therefore, is a direct reaction of conversion of sulfur dichloride to thionyl chloride and the next 2 again we are using either sulfur dioxide or sulfur trioxide. But now our substrate is disulfur dichloride in presence of chlorine again giving you 4 molecules of thionyl chloride in the first case and 3 molecules of thionyl chloride in the second case.

So, the basic strategy for all these 4 different types of reactions are same in all these cases either we are using sulfur dichloride monosulfur dichloride or disulfur dichloride, you would have to have some oxygen donor. So, we are using 2 types of oxygen donor molecules which one is sulfur dioxide and sulfur trioxide and in presence of some excess or the required amount of chlorine gases. So, this process is basically if we considered that you have 4 different processes and the reactions are all in taking place in gas space in continuously operated plants with an activated charcoal as the catalyst.

So, in all this reactions, particularly all the industrial important conversions or all the industrial important reactions what we see to increase the yield of the reaction or the amount of conversion for a particular type of reaction if the reaction is not very useful in going towards the maximum side or the right. That means, the percentage conversion is less we always use the catalyst such that, we can have a good amount of conversion from the left to right; that means, say 70 percent or 80 percent conversion will take place when we go for the reactions of 2 component or 3 component reactions.

So, earlier we have seen that vanadium pentoxide your can be your catalysts, iodine can be a catalysts now your charcoal. So, the charcoal powder or the charcoal dust so you have a huge surface on it and if the gas is also flowing on the surface of that charcoal. So, charcoal powder is basically giving you something where you have the activated surface area and the gas molecules are absorbed on it and you get the required conversions. So, on that particular surface each and every carbon centre is basically trapping that particular SO 2 or SO 3 molecules and 2 other species basically 3 component reactions it is a plus b plus c giving you only one product which is your d.

So, charcoal catalyzed reactions for all these 4 cases can be useful for producing thionyl chloride. So, what we can see that depending upon your activity of that particular catalyst we have a particular amount of conversion where you do not expect that all the sulfur dioxide whatever we are using in terms of your molecular stoichiometry.

By molar ratio is not fully converted to the product side. So, you can have some unreacted sulfur dioxide or some sulfur dioxide produced as a by product in some other reactions not this particular reaction is converted in the gas phase with chlorine to a. So, 2 Cl 2 now which is little bit more easier because you directly use chlorine gas to trapt it as a. So, 2 Cl 2 which is your sulfuryl fluoride trying. So, we cannot lose or we should not allowed to go the excess amount of sulfur dioxide or sulfur dioxide from all other sources in the air.

We should try it for some value added compound which is your sulfuryl chloride and direct the action of chlorine of that particular sulfur dioxide can give you very quickly your sulfuric chloride.

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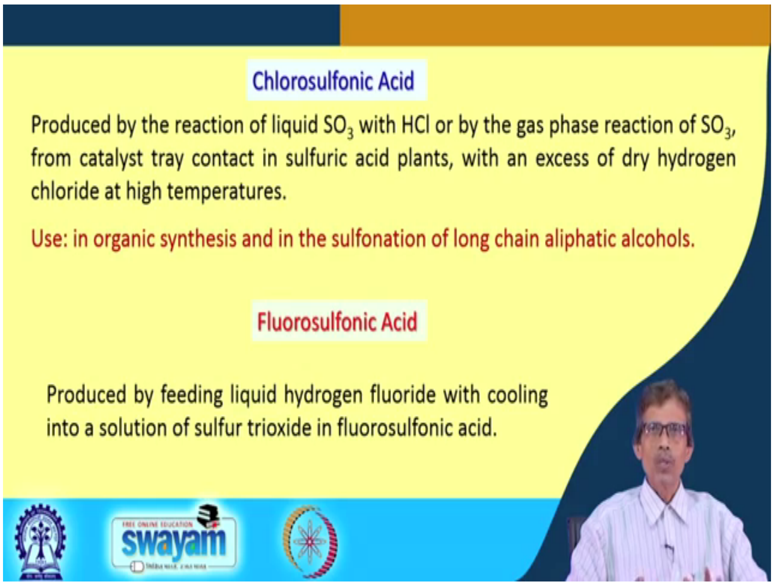

Chlorosulfonic Acid

Produced by the reaction of liquid SO_3 with HCl or by the gas phase reaction of SO_3, from catalyst tray contact in sulfuric acid plants, with an excess of dry hydrogen chloride at high temperatures.

Use: in organic synthesis and in the sulfonation of long chain aliphatic alcohols.

Fluorosulfonic Acid

Produced by feeding liquid hydrogen fluoride with cooling into a solution of sulfur trioxide in fluorosulfonic acid.

So, what you see then that the different types of other particular reactions that you can have this thionyl chloride or sulfuryl chloride for the chlorination reactions or some other reactions also then we just introduced something the halogenated sulfuric acids clothes.

So, if you have the sulfuric acid then the corresponding sulfonic acid function which is your SO 3 H function then if we attach it to some halogen x. So, we get the chlorosulfonic acid, and how we get that particular reactions? So, just now we have seen how we make a SO Cl 2 how we make a SO 2 Cl 2 now instead of that now we have Cl Cl is now attached to that particular part and is produced by the reaction of liquefied sulfur trioxide with HCl or the gas phase reaction of SO 3 from a catalyst tray contact in sulfuric acid plants.

Because the in the sulfuric acid plants we are handling sulfur dioxide for making sulfur trioxide which is absorbed by water. So, there are catalyst trays and those catalyst trays contact can be utilized for this particular conversion also, only thing that you have introduce HCl as a gas and with an excess of dry hydrogen chloride at high temperature. So, the reaction for this particular conversion is high enough and at high temperature you must have the dry no moisture no water vapour in it.

So, dry hydrogen chloride can react with sulfur dioxide giving you chlorosulfonic acid, where we use this particular chlorosulfonic acid? In organic synthesis and now in sulfonation earlier we have seen that thionyl chloride or sulfuric chloride can be used for chlorination of your carboxylic acids, but now we can go for sulfonation of long chain aliphatic alcohols. Previously we have seen that we can have some useful molecule which are industrially important which can produce in a large scale and it has a huge market also like that of your different surfactant molecules, the detergent different types of detergents which are long chain aliphatic molecules.

And at the end you have the sulfate functions such as your SDS molecules sodium dodecyl sulfate. So, this is a sodium salt and sulfite is your typical corresponding an ionic part and is a dodecyl part; that means, dual carbon bearing long chain aliphatic chain is there with is obtained from a typical alcohol which is also readily available which is your lauryl alcohol.

So, sulfonation of all these long chain aliphatic alcohols can be achieved by chlorosulfonic acid. Now the next example of this particular chlorosulfonic acid is the flouro 1; that means, instead of Cl attached to the sulfur end of the sulfuric acid function now you have the fluorine end which is attached to the sulfonic acid group and that sulfonic acid group now can be attached to the fluorine as a corresponding part. So, it is produced by feeding now liquid hydrogen fluoride like your HCl the hydrochloric acid

Now, your hydrofluoric acid is introduced with cooling into a solution of sulfur trioxide in some amount of flourosulfonic acid. So, what do you do we take sulfur trioxide which is dissolved in already available flourosulfonic acid for producing more amount of flourosulfonic acid such that we react basically that sulfur trioxide. So, sulfur trioxide is on the already available flourosulfonic acid. So, flourosulfonic acid is your base or your solvent and that flourosulfonic acid containing sulfur trioxide, excess sulfur trioxide will be directly reacting with hf giving you the corresponding chlorosulfonic acid.

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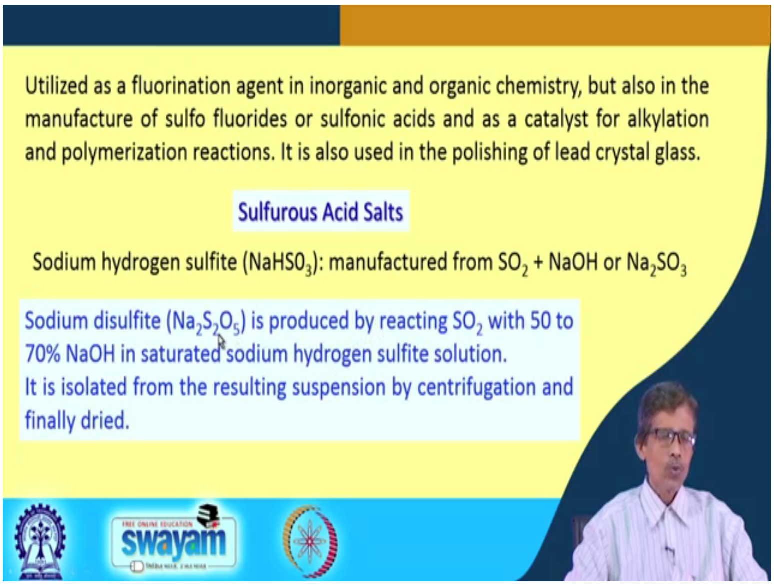

Utilized as a fluorination agent in inorganic and organic chemistry, but also in the manufacture of sulfo fluorides or sulfonic acids and as a catalyst for alkylation and polymerization reactions. It is also used in the polishing of lead crystal glass.

Sulfurous Acid Salts

Sodium hydrogen sulfite ($NaHSO_3$): manufactured from SO_2 + NaOH or Na_2SO_3

Sodium disulfite ($Na_2S_2O_5$) is produced by reacting SO_2 with 50 to 70% NaOH in saturated sodium hydrogen sulfite solution.
It is isolated from the resulting suspension by centrifugation and finally dried.

So, that is forming in a nicer way that will be a very useful reagent; that means, chlorosulfonic acid chlorosulfonic acid your flourosulfonic acid for some other purpose not for sulfonation because the chlorosulfonic acid we have seen it is utilized for sulfonation. Earlier we have seen that you di sulfur dichloride or sulfur dichloride utilized for chlorination or thionyl chloride is also another product from there.

Thinoyl chloride or sulfuryl chloride is used for the chlorination of organic carboxylic acids or long chain carboxylic acids. Now a useful reaction mechanism what gives you the flourination of typical inorganic or organic molecules because the fluorine is a very useful molecular atom to be introduced in some complex pharmaceutical molecules in dry and drug and medicinal industry, pharmaceutical industry we get the corresponding molecules and some of the molecules are fluorinated.

So, a say for way of going for this fluorination reaction is using that fluorosulfonic acid not by your sodium chloride or ammonium chloride or not by direct hydrochloric acid, but why this particular sulfonic acid. So, it will be useful for both organic as well as inorganic substrate, but also in the manufacture of sulfo fluorides, some more complex sulfur fluoride molecules or sulfonic acids you can have. And those sulfonic acids can also be prepared from your flourosulfonic acid and as a catalyst for alkylation and polymerization reaction some very low concentration of this flourosulfonic acid can also be utilized for alkylation reaction. That means, alkene can go for some alkylation reactions of polymerizations or some long chains organic molecule formation.

So, this can involve function as a good catalyst, not as your flouro acetic acid or any other fluorine bearing acid, but is the different type of acid which can be considered as a typical inorganic acid inorganic mineral acid which is your flouro sulfonic acid and also it is used in polishing of lead crystal glasses, because the fluorine we know that which can reach the surface. So, its polishing that, but your concentration of this available fluorine is also less unlike your sodium fluoride or hydrofluoric acid.

So, this can also be utilized for polishing your lead crystal glasses. Now we will go for sulfurous acid bearing different salts. So, we have seen that how we can get sulfuric acid you can also see when sulfur dioxide is being trapped by water molecules we get H 2 SO 3 which is nothing, but your sulfurous acid. Now, how we can convert it to some corresponding acids; that means, sulfurous acid salts whether you can get the sodium salt of sulfurous acid, potassium salt or ammonium salts.

Because sometimes we will find that these are not produced directly from the free acids. Whether you should go for preparing sulfurous acid first and then go for the different salts because these salts are very useful for making more and more complex other sulfur bearing inorganic salts. So, sulfurous acid solved one search example is sodium hydrogen sulphite, it is as a huge application for typical laboratory base reactions in organic and inorganic chemistry laboratories as well as in the food chemistry or sometimes it can also be useful in some agriculture also.

So, is a hydrogen sulphite, that Na plus HSO 3 minus. So, it is bisulfite ion bearing salt; that means, we are getting it from sulfurous acid. So, sodium hydrogen sulphite, how you make it? We can make it either from a mixture of sulfur dioxide is sodium hydroxide or we can get it from sodium sulfite because bisulfite is a bi salt we can get rid from simple sodium sulfite or the direct reaction of sulfur dioxide with sodium hydroxide or we can also produce this type of salt the sodium bisulfite is Na 2 S 2 O 3 not 5 O 5 is also another category.

But the first thing what we can go like that sodium bisulfite or sodium thiosulfate we considered and disulfite is also if we consider is that some more number of oxygen groups are attached. Is produced also by reacting sulfur dioxide is 50 to 70 percent of NaOH in saturated sodium hydrogen sulfite solution. So, again just now what we have seen that if we can use the product material as the corresponding base or as the corresponding solvent or as the medium we can go some simple reactions where the reactant is reacting with some amount of acid or the base.

So, if you have a hydrogen sulfite solution; that means, your Na HSO 3 solution on it you can go with the same reaction; that means, the reaction of SO 2 with NaOH and when the reaction is over you go for saturation it is a concentrated solution you have to make. And it is isolated from the resulting suspension if the product is forming over there by centrifugation; that means, you use for using the centrifugal force for that. So, you use for that particular purpose or centrifuge.

So, the centrifugation and finally, it is dried in a dry atmosphere in desiccator or in (Refer Time: 24:36).

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Applications in - photographic industry
- paper industry
- textile industry
- leather industry

Sodium sulfite is produced by reacting SO_2 containing gases with sodium hydroxide in a saturated sodium sulfite solution at 60 to 80°C

Use as a reducing agent, in the manufacture of $Na_2S_2O_3$, as an oxidation prevention agent for developer solutions in the photographic industry, as an antichlorination agent in the paper and textile industries, for the preservation of food and for the treatment of boiler water.

So, this salts basically starting from your sulfurous acid or any other thing; that means, you can have a bisulfite salt, which can be produced from a bisulfite salt or a S 2 O 5 or we can see also we can produce it for thiosulfate which is S 2 O 3 type of salt. So, S 2 O 5 type of salt S 2 O 5 2 minus an ion bearing salt or SO 2 O 3 minus an ion bearing salt, where you have more and more number of oxygen, but you can have 2 sulfur sulfur bonds present in it.

So, in photographic industry they are very useful, also they are useful in paper industry in textile industry and in leather industry in leather industry this sulfur bearing salts are useful for removing the hairs of the animal skin. And in textile industry also you can have something for as a reducing agent or some time for getting the sulfur dyes, the sulfur bearing dyes we can make and that sulfur bearing dies can be utilized for your incorporation of the dying for that particular textile.

Then paper industry is also it is bleaching or sometimes it is simply reducing the material for that particular purpose and photographic industry also we know that the silver thiosulfate type of thing we know it for the fixing material. So, when sodium sulfite directly; that means, Na 2 SO 3 is produced by reacting that sulfur dioxide containing gases is sodium hydroxide in a saturated again sodium sulfite solution at 60 to 80 degree centigrade. So, if you can go for direct conversion of sulfur dioxide to your sodium sulfite.

So, whatever sulfur dioxide you can have you can get it by burning your sulfur as sulfur dioxide and that sulfur dioxide can be converted to your typical sodium sulfite which is a very useful reducing agent for some reduction reactions in all industrially available reactions where we use sodium sulfite. So, it can be used as a very good reducing agent and also in the manufacture of thiosulfate, manufacturing procedure for the thiosulfate as an oxidation prevention agent; that means, again you can maintain a reducing atmosphere for that particular purpose and this oxidation prevention agent for developer solutions in the photographic industry.

So, is a very good fixing material for reduction reactions. So, we have to see now that how we get this that SO 2 you have which can be very easily converted to SO 3. That means, sulfur is there and you can attach 3 oxygen atoms on that particular sulfur for making you SO 3 minus which is your sulfite ion if one hydrogen is still present in it, we get bisulfite ion HSO 3 minus. Now in case of your S 2 O 3 2 minus which will be the anion of your sodium thiosulfate by the introduction of some extra sulfur centre or extra sulfur atom to your thiosulfate unit we get it.

And it is also prepared as anti chlorination agent; that means, if you have some extra chlorine in it or you have to remove some amount of chlorine in the paper and textile industry always we know that in paper and textile industry some material is always used as a bleaching agent, like your sodium hypochlorite. So, this bleaching agents are mostly chlorine based agents. So, you have to go for this anti chlorination or dechlorination reaction; that means, you have to remove the chlorine from that particular material; that means, which is being trapped in paper or which is being trapped in the textile.

So, we can get it out of that so if you just simply go for a typical reaction it is a reduction reaction using this sulfur based corresponding salts and also for the preservation of food material that is why it is useful in the food industry or doing some good amount of food chemistry and in the treatment of boiler water; that means, if you have something present as the oxidizing agent. So, that particular oxidizing agent; that means, if we have some excess oxygen or some peroxides or some chlorine, chlorine is also a oxidizing agent which is also a bleaching agent that is why it is going for bleaching action on paper and textile which is destroying or decaying that particular dye or colorization which is unwanted.

So, that can be removed by simply going for a reduction reaction using all this sulfur dioxide based salts, so these sulfur based solve that nothing, but your sulfur dioxide based salt and as we all know the sulfur dioxide gas itself is a reducing agent and that sulfur dioxide gas. If you just simply parts that particular sulfur dioxide gas because in all these cases in slightly acidic medium in very dilute acid condition or in water medium it can produce sulfur dioxide. So, that sulfur dioxide is a very good bleaching agent for decolorization even for the petal of the flowers or any other things. So, if you can produce these. So, you can remove the chlorine, you can go for removal of excess chlorine from this paper and the textile industry.

And also preservation of the food because food is getting spoiled by the presence of its oxidation oxidizing (Refer Time: 30:33) equivalent, that means oxygen or any other oxidizing agent. So, if you are able to remove those as a reducing agent your food material will be safe. So, your reduction, so this can also be sodium bisulphite can be a very good food preservative, which is allowed food preservative and for the treatment of boiler water if the boiler water has dissolved chlorine or if the boiler water by the boiler water has some other oxidizing agent which can corrode the corresponding mechanism for your boiler life or some other procedure while using the boiler water that can be destroyed.

So, your boiler water should also be safe from your oxidizing agent. So, you are all this sulfur based salts; that means, your sulfite salts or the thiosulfate can be used. So, in the next class we just see how we can synthesize sodium thiosulfate ok.

Thank you very much.