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

Lecture - 21
Sodium Hydroxyl Methanesulfinate and Hydrogen Sulfide

Good morning everybody. So, we are talking about the different sulfur compounds and how we can produce industrially those compounds which are also important in different reactions and other industrial processes.

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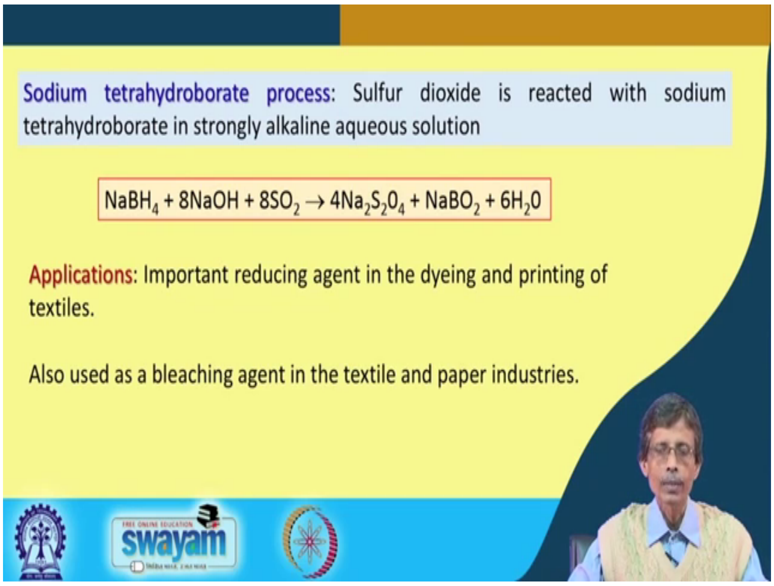

Sodium tetrahydroborate process: Sulfur dioxide is reacted with sodium tetrahydroborate in strongly alkaline aqueous solution

$$\boxed{NaBH_4 + 8NaOH + 8SO_2 \rightarrow 4Na_2S_2O_4 + NaBO_2 + 6H_2O}$$

Applications: Important reducing agent in the dyeing and printing of textiles.

Also used as a bleaching agent in the textile and paper industries.

So, we are talking with sodium dithionite is N-a-2-S-2-O-4 which is the reduced version of your sulfur dioxide molecule. So, if we have sulfur dioxide as we know that we can produce huge amount of sulfur dioxide by simple burning. Your elemental sulfur what we get from the earth crust or some in from some sedimentary level or the sedimentary rock level. So, when we have sufficient amount of sulfur dioxide in our hand. The next thing is that what we are doing we try to reduce it. And we have seen that your sodium amalgam was also useful, sodium formate was also useful for that particular reduction.

And today we take another example, where the typical reducing agent what to use in the laboratory, the sodium tetrahydroborate thing. That is N-a-B-H-4; that means, the hydride ions will be used. That means, it is the hydride reduction process where sulfur dioxide in strongly alkaline aqueous medium is treated with sufficient amount of that sodium borohydrite. So, what you have in your hand? Therefore, that our plan is to reduce your sulfur dioxide and that sulfur dioxide in strong alkaline medium. Because this particular want the reactivity of these thing is dependent on the BH of the medium. Industrially also it is very useful to consider the corresponding ph medium or the range of the ph where, the reaction is taking place, because this sodium borohydride is the hydride species.

Because you have large amount of H as H minus and these H minus can very quickly react with your water molecules. Here we see we have not written anything on the left hand side as your water molecule. But we are producing 6 molecules of water on the right hand side. So, in alkaline aqueous medium definitely, we should also have water on the left hand side, but that water is not solely reacting with borohydride species, destroying it as for the production of hydrogen H 2. Because your borohydrate can also be utilized for the production of hydrogen gas and that hydrogen gas may or may not reduce your sulfur dioxide. But we should also be careful, for this reaction condition.

So, when N-a-B-H-4 is reacting with 8 molecules of N-a-O-H and 8 molecules of sulfur dioxide it is giving 4 molecules of N-a-2-S-2-O-4 that is our desired product. Where we are looking for a typical reduction of your sulfur dioxide giving you sulfur-sulfur bond for the formation of S-2-O-4 and sodium borate is also forming, and 6 molecules of water. If it is not effective, in reducing this particular one sodium borohydride through some side reaction can be destroyed, through its reaction with water molecules producing sodium borate.

So, we should be careful about knowing all this composition of this reaction. And this dithionite this N-a-2-S-2-O-4 has huge applications and we should know because we are all the time what we are looking for is, the production how industrially in a big scale. We can produce this particular one and what are the areas where this particular material can be useful. So, from application wise, it is important reducing agent in the dyeing and printing of textiles.

So, where we all the time, we require some reducing agent for colouring the textile material or the printing material. So, the reduced form, because sometimes we find that a dye you have. And the dye is not coloured in its original form that means, in the oxidized form you can reduce it to its reduced form and the reduced form is coloured.

So, fixing the dye to the printing material the paper material or the textile material can be followed, through the treatment of your sodium dithionite which is a useful reducing agent. So, dye can also be reduced and giving you the coloration. And also sometimes it is used in the bleaching agent in the textile and paper industry. Sometimes we want to destroy some these dye molecules or some other material which can be reduced very easily, by the treatment of your dithionite and can be washed away from this textile and paper material. So, is also useful as a bleaching agent. As we all know that the typical sulfur dioxide, the sulfur dioxide gas itself or sodium bisulphite N-a-H-S-O-3.

These are also very good bleaching agent in terms of their capability of reduction. Since they are very useful reducing agent, they can reduce this and it can show some kind of bleaching action through that particular reduction. So, production of this useful reducing agent in the industrial scale is also a very important area of study.

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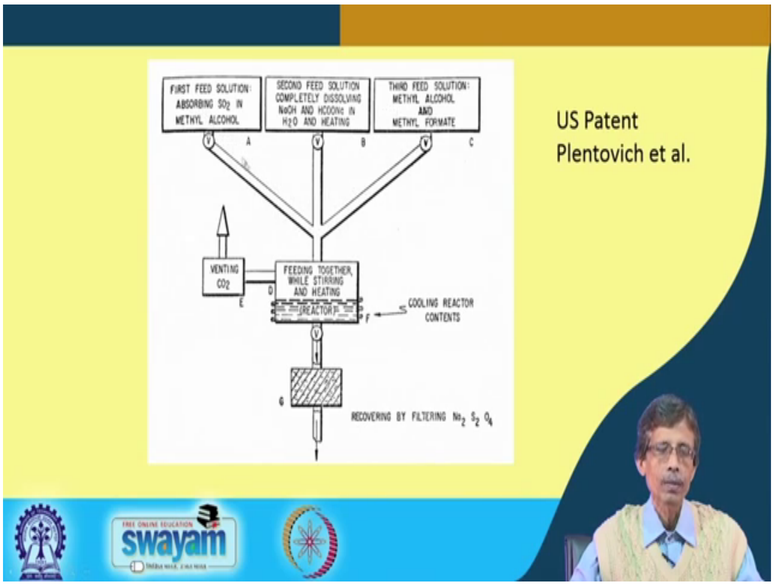

US Patent
Plentovich et al.

If we consider that, what we are doing for this particular production. And if we consider that, in the previous case what we have seen that we can use some amount of format. So, or the some methyl format is the methyl ester of formic acid in methyl alcohol, can be utilized for the reduction of S-O-2 to produce your N-a-2-S-2-O-4. So, what we have in the reactor basically? So, how you feed the reactor? The reactor is being feeded, from a solution which we consider as the first solution- first feed solution which is nothing but a saturated methyl alcohol solution, saturated by the sulfur dioxide gas. Then the second one is again a feeder solution dissolving N-a-O-H and sodium formate in water and in heating condition.

That means, you heat the system; that means, you have sulfur dioxide for A- the first feed. Then, the corresponding reducing agent as the B- that means, sodium formate is basically and also some solvent medium the medium is in terms of your methyl alcohol and methyl formate. So, three of them we together mix up and the feeding together while stirring and hitting the reactor; so, this is the reactor. And initially for the reaction we heat it and then, your methyl formate is reduction equivalent is being transferred for the reduction of your sulfur dioxide molecules, is also producing carbon dioxide. So, you have to remove that carbon dioxide. So, a path is there from the reactor which is nothing, but your venting path for C-O-2 and when the reaction is over, you cool the reactor contents.

So, some cooling arrangements should also be there or you can transfer it to some other chamber. Where the material can be cooled and then it is passed for recovering through filtration. So, a saturated solution of your sodium dithionite can be in your hand and that particular one can be evaporated in open basin or some other technique for crystallization. So, crystallization of that particular saturated solution will give you a good quality of your sodium dithionite or good crystals of your sodium dithionite, because it has a very good crystalline nature in the solid state.

So, this particular procedure what people can adopt and is mostly all these industrial processes are dependent on the company what they are producing, but is protected through some patent. So, it is the patent of Plentovich who has done or implemented this for a simple reduction by sodium formate. So, if we consider any other reducing agent. So, you should have the mechanism, a different mechanism for treating this B to the mixture of this sulfur dioxide in some solvent or in some aqueous medium.

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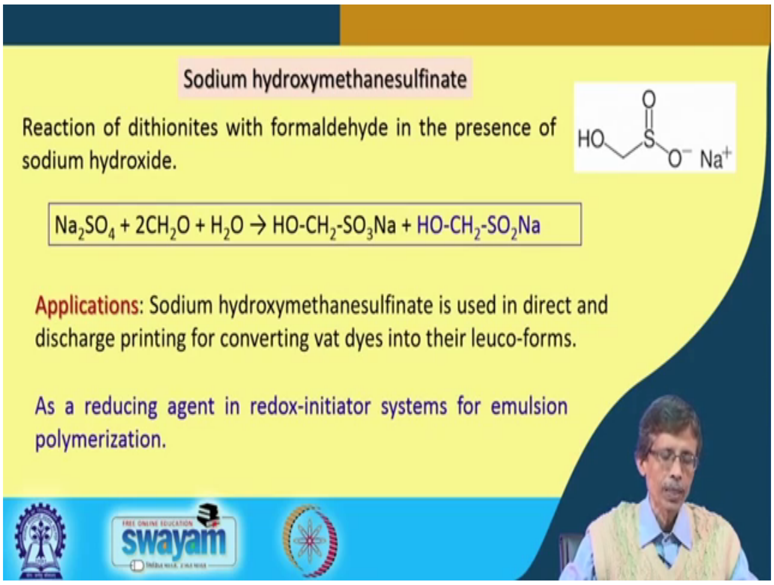

Sodium hydroxymethanesulfinate

Reaction of dithionites with formaldehyde in the presence of sodium hydroxide.

$Na_2SO_4 + 2CH_2O + H_2O \rightarrow HO\text{-}CH_2\text{-}SO_3Na + HO\text{-}CH_2\text{-}SO_2Na$

Applications: Sodium hydroxymethanesulfinate is used in direct and discharge printing for converting vat dyes into their leuco-forms.

As a reducing agent in redox-initiator systems for emulsion polymerization.

So, next we go for some typical molecule. Sometimes if we consider that we are doing something, but we are not in that particular domain where we can consider about the bulk quantity of organic molecule. Because in this particular class we are focusing only on some molecules which are of inorganic interest, so, in organic chemistry. So, this is-this is because the class is devoted to industrial in organic chemistry.

But some useful organic molecule can give you the very good example that how quickly we can make some useful molecule out of that particular knowledge which is here as the example of sodium hydroxymethanesulfinate. Try to read the whole molecule as a name, is not even your IUPAC recommended nomenclature, is a simple standard nomenclature because, it is a sodium salt.

Some hydroxy function is there which has been derivatized on the methane backbone. So, you have the methane backbone and then the sulfinate function at the end. So, is a very simple molecule therefore, so, you have the sodium salt is basically a typical salt. You can consider as a organic salt and at one end you have this hydroxy methane part. That means, it is C-H-2-O-H which can be derived from your methanol.

So, methanol is C-H-3-O-H, but it is C-H-2-O-H. So, one of the hydrogen is replaced by your S-O-2 minus function. Is not S-O-3 remember that, is not S-O-3 not even a S-O-4, because we have seen that for making the detergent material the S D S molecule the sodium dodecyl sulphate, we have introduced is as a sulphate. That means, oxygen of the alcohol molecule is converted to a sulphate species through the attachment of S-O-3 group on O.

But this is something different where you can have a carbon sulfur bond and not only carbon sulfur bond, but the functional group which is attached to that other part is S-O-2 minus is not a S-O-3 minus or S-O-4 minus is a S-O-2 minus that is why the name is all his name as sulfinate. Which I we get basically from our previous molecules what we are discussing so far is your dithionite the N-a-2-S-2-O-4. So, dithionite is basically giving you this particular reaction. In a very simple way, is a very simple technique you should know only what are the reagents you will be using for the production of this particular molecule. We take formaldehyde only, C-H-2-O, you know that is H-C-H-O is formaldehyde single carbon aldehyde is the simplest possible organic molecule and aldehyde family like your methanol or water molecule, we should all know the one carbon bearing aldehyde.

So, that basically the C-H-2-O function. So, that C-H-2-O function is being attacked by your dithionate in strong or medium alkaline medium of sodium hydroxide. So, you quickly look at the corresponding reaction. That is you have the corresponding reaction from this particular one, as your sodium is not sulphate is dithionite. Dthionite is formaldehyde plus water is a N-a-2-S-2-O-4 is not S is N-a-2-S-2-O-4 is a mistake there the N-a-2-S-2-O-4, is reacting with H-C-H-O, which is your formaldehyde then water. Giving two of these species; one is the corresponding sulfide function, that means, S-O-3 minus and another is S-O-2 minus. And this particular molecule which is the sulfinate molecule is the other one.

So, basically what we are getting that particular one, the reactivity of this S-2-O-4. Formaldehyde molecule is giving us, one of the oxygen. So, you have some extra oxygen. So, it is not disproportionating between 2-S-O-2 fragment. One will be S-O-3 fragment, and another will be the S-O-2 fragments. So, our desired material is the second one, which is having a corresponding carbon sulfur bond.

And carbon to sulfur bond is attached to a function which is S-O-2 minus. So, this particular molecule is also very useful one, because this sulfinate molecule is used in direct discharge printing for converting vat dyes. Because in the dyeing industry people know the container, the reaction medium where they do the reaction is a vat and in that vat the dyes are formed. And the vat dyes are utilized in to their leuco form; leuco form means they are colourless form.

So, you have to discharge the corresponding printing in such a way that either as i told you that, the coloured form is the reduced form and sometimes the leuco form; that means, the colourless form is also the reduced form. So, again in relation to your dye industry or the printing industry, you use not directly the N-a-2-S-2-O-4, but this methane sulfinate molecule for that particular purpose. It is also reducing agent. In redox initiated systems, for emulsion polymerization, so, in a typical polymerization step if we can go for a reducing agent. That means, sometimes we know that during polymerization we can have a oxidation or we can have a reduction. That means, electron transfer is taking place for a particular type of polymerization.

And if you have the corresponding material as emulsion, so, is known as emulsion polymerization. So, as a reducing agent in a redox-initiator, because sometimes we know that if it is a chain reaction type of things, some reaction which is initiated. So, electron transfer reaction can be initiated by addition of this particularly redox reducing agent. So, instead of your dithionite, you can have this methane sulfinate as a very good useful reducing agent for emulsion polymerization and the molecule can also be broken very quickly for its components.

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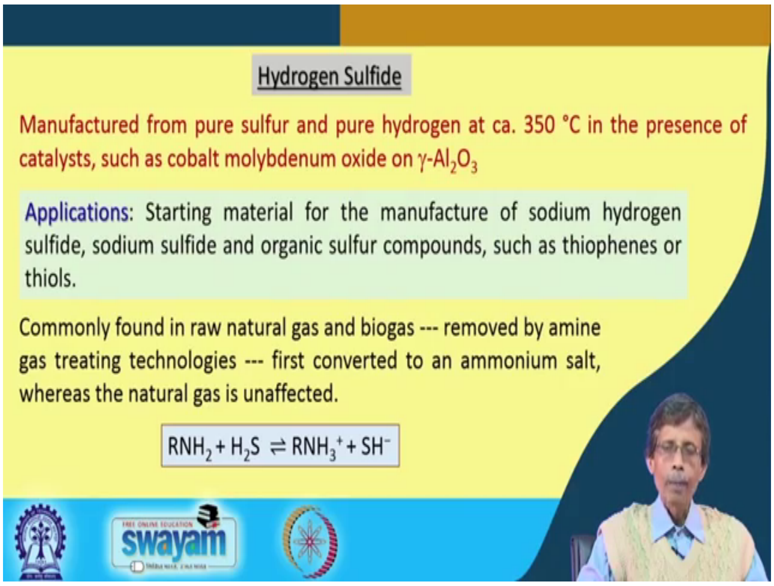

Hydrogen Sulfide

Manufactured from pure sulfur and pure hydrogen at ca. 350 °C in the presence of catalysts, such as cobalt molybdenum oxide on γ-Al_2O_3

Applications: Starting material for the manufacture of sodium hydrogen sulfide, sodium sulfide and organic sulfur compounds, such as thiophenes or thiols.

Commonly found in raw natural gas and biogas --- removed by amine gas treating technologies --- first converted to an ammonium salt, whereas the natural gas is unaffected.

$RNH_2 + H_2S \rightleftharpoons RNH_3^+ + SH^-$

Then we just take the example of the very old and very well known molecule is the hydrogen sulfide gas H-2-S. We know the stock of our hand, which is your sulfur. And from the sulfur how we get sulfuric acid and all other sulfide bearing or the sulfur bearing compound. This particular one is a typical reduction process, so, we are moving in the opposite direction. For making sulfuric acid we have oxidized your sulfur to sulfur dioxide and then to trioxide. Now what will you do we just simply reduce the elemental sulfur or the pure sulfur what we have in our hand.

And that particular sulfur in hydrogen. So, solid sulfur yellow coloured solid powder material as the sulfur, with a gas discharge of hydrogen gas. So, hydrogen you can have a huge source of hydrogen in the different areas we all know that hydrogen can also be obtained from your natural gas sources or simply the methane source. If you not get the hydrogen from water or hydrogen from any other sources. So, that hydrogen, whether you are getting it through insitue generation or from the cylinders or from some any other source, so, that hydrogen at a temperature of 350 degree centigrade, in the presence of catalysts. So, you should require some catalyst, for that particular conversion that means, the reaction of your hydrogen gas with a elemental sulfur. What is that it is nothing, but cobalt molybdenum oxide.

So, is the two metal oxide system is not a cobalt oxide only or molybdenum oxide. But is a cobalt molybdenum oxide and that cobalt molybdenum oxide on a surface of gamma alumina. So, gamma alumina surface is used and on the surface you have the layering of that particular catalyst, on which you can have a mixture of this sulfur and which is being parts through your hydrogen gas. So, this hydrogen sulfide what you can have in your hand, can be very useful also because we will see also how we can make other sulfide salts.

The most important one is your sodium sulfide. How we get this sodium sulfide? Because sodium sulfide also have some huge applications. But for this H-2-S it can be a starting material for the manufacture of sodium hydrogen sulfide. N-a-H-S. So, you have two hydrogen centres or two hydrogen atoms attached to the sulfide center. And if we can replace one of the hydrogen by sodium you get N-a-H-S or N-a-2-S which is sodium sulfide or different types of organic sulfur compounds.

Large number of organic sulfur compounds we can have, we can make also such as thiophenes and different thiols. Even the biological molecules we have the sulfur bearing amino acids also we have. So, the sulfur assimilation in terms of the supply of inorganic sulfur; inorganic sulfur what we are getting from the naturally available sulfur source. And that sulfur source can be utilized for incorporation of sulfur in thiophene say. So, production of thiophene is therefore, dependent on the production of your sulfur and some other important molecule which are sulfur based, for the right introduction of sulfur in your organic backbone.

Where we get this? Because these as i told you that is the from the raw natural gas or biogases. Because both of them are the corresponding thing, what is present there is the methane. So, C-H-4 is the main constituent of this and it also has some amount of H-2-S. Because the sulfide or sulfur bearing molecule because the biomolecules also can have sulfur, because it has the protein origin, amino acid origin.

So, sulfur bearing amino acid, so any other sulfur source can be reduced to your hydrogen sulfide. So, when we take out your natural gas or for bottling your C N G the compressed natural gas or any other bio gas source. It can have the corresponding hydrogen sulfide in it and how you remove it? So, you should have a technological knowledge for that. That amine is utilized for gas treating technologies, is first converted to its ammonium salts. So, if you have H-2-S, if you directly use ammonia or any other amine, you get ammonium hydrogen sulfide or ammonium sulfide.

Whereas, the pure natural gas which is your methane is remain unaffected. So, the basic reaction what will be looking for, either you have a organic amine molecule and that organic amine molecule is nothing but your R-N-H-2 it can be your ammonia also when R is equal to H. Which is being treated with H-2-S any contamination or any other source, giving you the corresponding R-N-H-3-S-H salt.

When they are together in solution they are separated away as cation, as the anion, but when you try to isolate it in from the salt like sodium chloride isolation. You get the corresponding ammonium bisulphate salt. So, ammonium bisulphate salt you can recover it as so, is some value added product, through that. So, recovery of that thing in terms of its corresponding salt is also achievable for the entrapment of your hydrogen sulfide in the natural gas. So, next we will see how we can go for your corresponding salt the typical hole salt is your sodium sulfide S.

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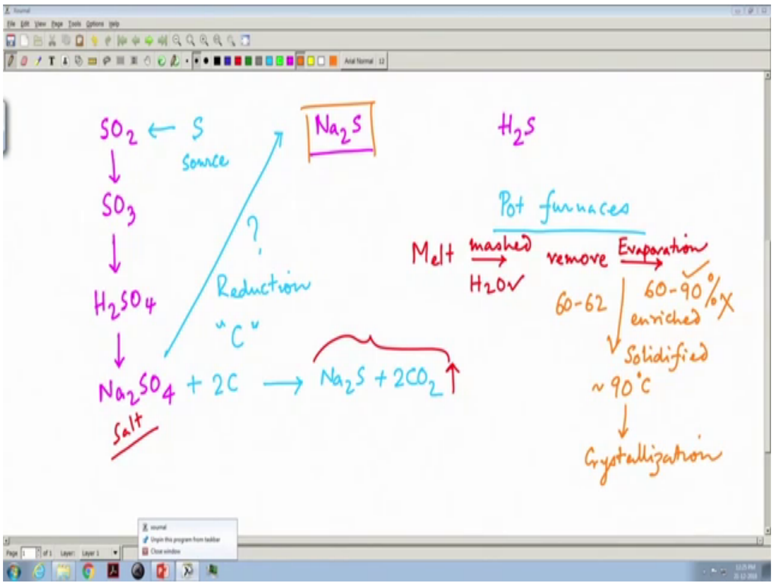

As we have seen that we are talking about H-2-S. So, you have N-a-2-S. So, you have to make this particular one, but if we try to produce it in some other source, because we know that we can have S-O-2 which is getting oxidized to S-O-3. Then we have H-2- S-O-4, then we can make its corresponding sodium sulphate salt. So, what you see here is that you can have this from your this. Because this we got from the sulfur, the natural sulfur source what you have. So, sulfur is getting converted up to this. Now, if i say that how will you make this?

Because it will be a very cheap source in your hand, large amount of sodium sulphate you can make from sulfur, the elemental sulfur, the ore sulfur or the mineral sulfur what you have as a resolve. So, what you do that your sulphate is the anion present and you convert it to sulfide, so, we should go for reduction. How? carbon is the simplest way is the carbon. That means, the charcoal reduction process. So, the charcoal reduction process for your N-a-2-M, S-4, with that of your twice of C is giving you N-a-2-S plus.

So, that is the most simplest way of making sodium sulfide to you. What we use? We use some Pot furnaces, your reaction chamber for this particular procedure. Where we use this and we get a melt, because this particular sodium sulphate is a salt. So, we have to make a paste and that particular melt is mashed with water, giving water you mashed it.

Then remove the water insoluble material, which is not going into water. So, what we try to get? We try to get the soluble part the water soluble part from here. So, we get that so, you have this, so, you get this, so, this is a kept away.

So, we have the sodium sulphate melt out of this. So, you removed and you go for evaporation. And through that evaporation, you get corresponding enrichment a concentration from 60 to 90 percent of these can be enriched. But roughly speaking it is remain and 60 to 62 percent basically achieved, because the high range is not is very easy to achieve, so, 60 to 62 percent is there. Then we go for crystallization or solidification. So, it is solidified at high temperature, say about 90 degree centigrade. That means, at 90 degree centigrade you get the corresponding saturated solution. And that saturated solution is allow for your crystallization. So, you will get good amount of your sodium sulphate crystals in your hand.

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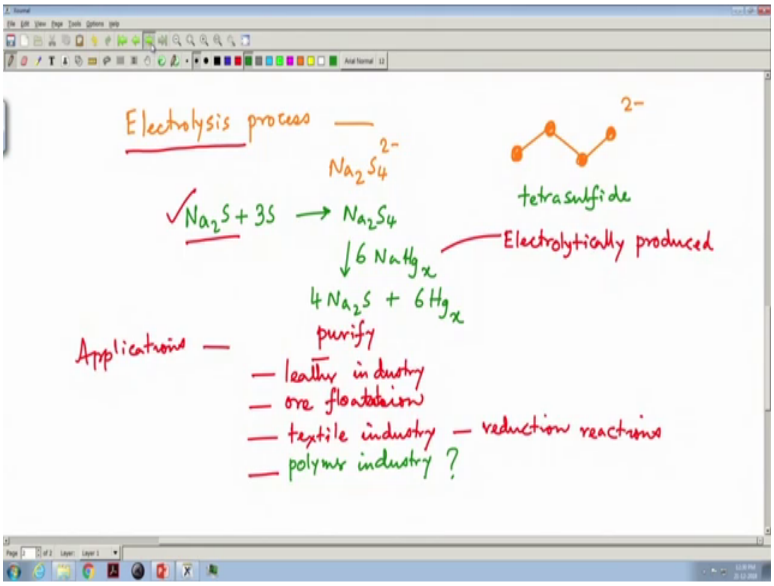

Electrolysis process —

$Na_2S_4^{2-}$

tetrasulfide $2-$

✓ $Na_2S + 3S \rightarrow Na_2S_4$

$\downarrow 6\,NaHg_x$ — Electrolytically produced

$4\,Na_2S + 6\,Hg_x$

purify

Applications —

- leather industry
- ore floatation
- textile industry — reduction reactions
- polymer industry ?

So, this is one particular technique what we can have. That one basically we get there, that one particular process also is known as your electrolysis process. In that particular process is electrolysis process, if we get if we make some new species like, N-a-2-S-4. What is this? We have seen that we can have an sodium sulfide, you can have sodium dithionite. Now we are talking something which is N-a-2-S-4. That means, it has a charge of 2 minus.

So, S-4-2 minus, so that means, is a species of this type. Having a charge of 2 minus, which is nothing but a species which is known as poly sulfide. So, this is your tetra sulfide, is very easy to make also in solution we get sometimes instead of simple sulfide you can have the poly sulfides also. So, this tetra sulfide which is S-4-2 minus and that we also produce from N-a-2-S itself with some amount of elemental sulfur, giving you N-a-2-S-4 and if we go for that is, reaction with sodium amalgam N-a-H-g-x.

With that giving 4 N-a-2-S plus 6 H-g-x mercury free, free mercury. So, is basically this sodium is coming from your sodium sulfide salt for production of the sodium sulfide. So, this is the one way. So, this is also in this particular process, it is electrolytically produced. So, we produce this particular one, so, you see that, we consume sodium sulfide.

Then we convert it to some poly sulfide, which is tetra sulfide over here. Then again we react with sodium amalgam to get back your sodium sulfide and mercury. So, this particular one can also be utilized to purify the material, if your sodium sulfide is a crude one. So, because this electrolytic technique or the electrolysis process is giving you high purity material; so, the high purity material can be obtained through this particular procedure. And then we see the different applications.

So, the different application first one is in leather industry. So, sulfur and sulfide one thing we know that the removal of the hair of the animal skin. So, is that in the leather industry if the sulfur bearing compounds for this particular reduction reactions is very useful. Then it can have for ore flotation t a t i o n -ore flotation, so, for floating the ore basically. So, this particular solution saturated solution of sodium sulfide can be useful and your this particular solution is also useful.

Then in textile industry, again for the different types of reduction reactions, you can use. So, those reduction reactions can be useful for your decolourization or the change in the colour or sometimes for achieving this particular colour and in the polymer industry also in polymer industry. So, if you simply think that, we can have your sodium tetra sulfide in your hand a solution or sodium sulfide in ore and how you can help a particular material in polymer industry? That we will see for your thing that how this is there; that means, you have to incorporate sulfur.

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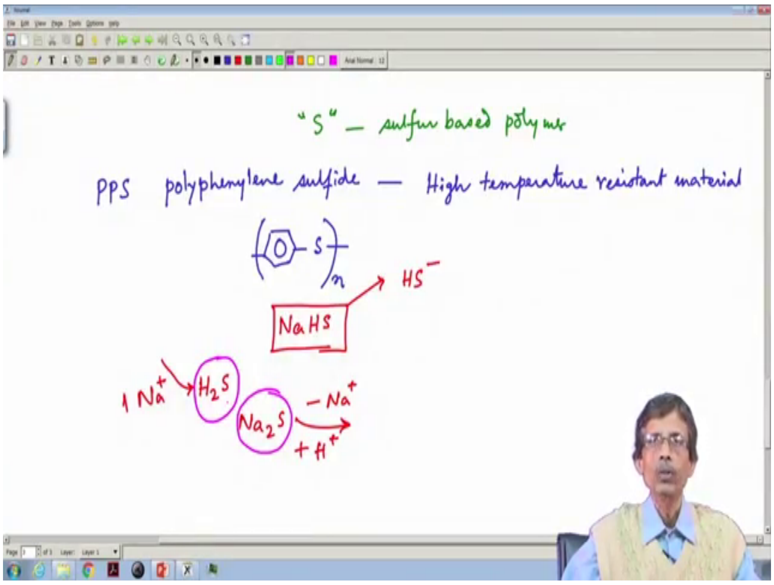

"S" — sulfur based polymer

PPS polyphenylene sulfide — High temperature resistant material

So, it will be a sulfur based polymer, you have to incorporate sulfur in it. That is why your sodium sulfide or sodium polysulfide can be useful in polymer industry. So, one very useful one, useful this polymeric material is known as P P S polyphenylene sulfide which is nothing but Poly Phenylene Sulfide. Because this is industrially useful is a high temperature; high temperature resistant material.

So, if you want to make a high temperature resistant polymer. We can go for some sulfur backbone in it and that sulfur backbone can be introduced from sodium sulfide only. So, you have this, so, you have therefore, the phenyl ring backbone the sulfur and this. So, these two positions basically is basically getting polymerized.

So, you have this poly phenylene sulfide. So, you have this phenol sulfer; phenol sulfur; phenol sulfur is a long backbone of these things. So, then coiling up all these things and all other things can be obtain from these. So, if we make some useful industrial polymer then, again we take the help of simple molecule like sodium sulfide. So, you should know what particular inorganic compound which can be produced in a huge quantity, is be useful for making a polymer bearing sulfur, that means, sulfur in it.

So, after the sodium sulfide, the other one, that means, if we can get the bisulfide which is also useful that how you make the sodium bisulfide species. Now, you have seen that how you can make hydrogen sulfide? And that hydrogen sulfide because these two hydrogen you can replace from this particular sulfur.

So, now, one of them can be used and you have in your hand. This is your basically H-S minus the bisulfide ion. Because these bisulfide ions are again very much useful for different purposes that we will see and what are the reactions basically we will see in our next class. That whether we can use directly your H-2-S or whether we can use sodium sulfide, so, two things you can have either you can incorporate or make it a mono sodium salt, one of the sodium ion can be replaced or you remove one of the sodium from here to get the corresponding one with the introduction of a proton.

So, these two things will see that you can have plenty of sodium hydrogen sulfide in your hand and plenty of sodium sulfide in your hand. How these two things can be separately tackled to make your sodium hydrogen sulfide that we will see in our next class ok.

Thank you very much.