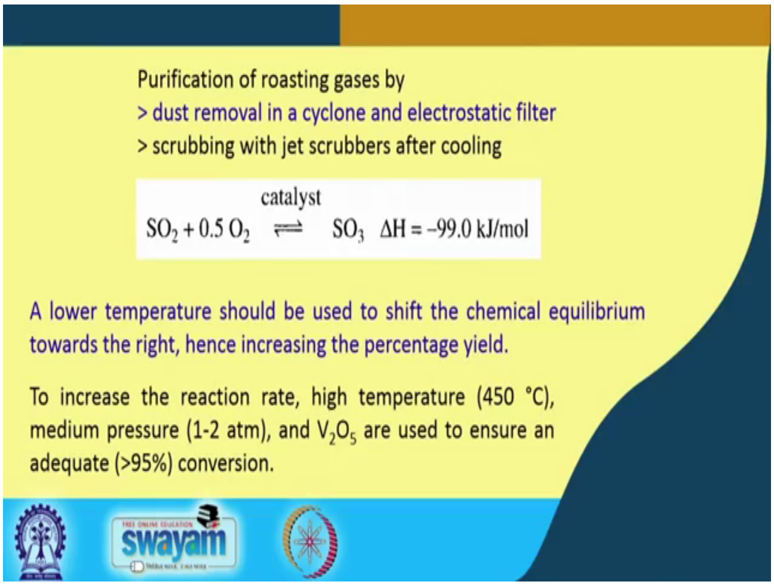
Industrial Inorganic Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 18
Sulfuric Acid, Catalyst and S2CL2, Applications

(Refer Slide Time: 00:26)

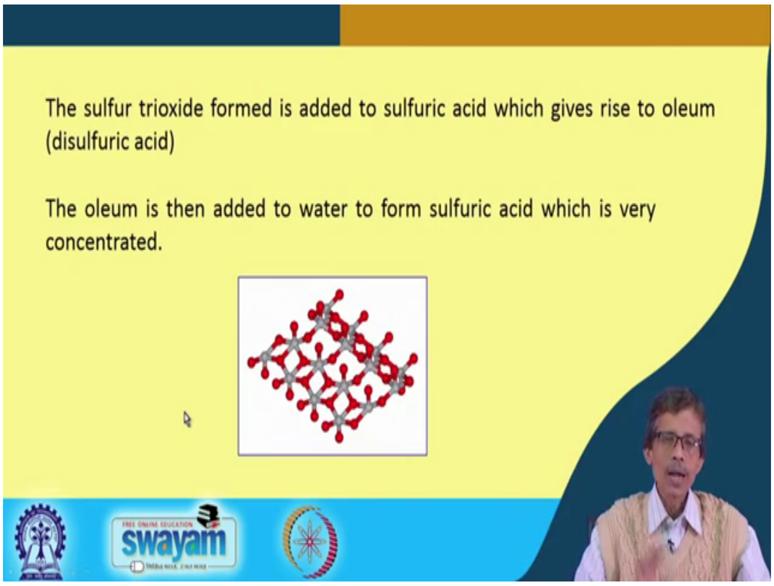


Welcome back to the place where we are talking about the conversion of sulphur dioxide to sulphur trioxide and there we have seen that we require a Catalyst. So, catalyst is required and we should go for a low temperature reaction to increase the conversion amount; that means the percentage yield of the reaction for SO 3. And now if we try to increase the reaction rate; that means, if we try to decrease the activation barrier for this reaction a high temperature we cannot go down to a very low temperature because the rate of the reaction should be sacrificed in that case.

So, the optimized conditions we should know only because its very easy to remember the optimized condition then we can vary the all these thing. And a medium pressure not much is only 1 to t atmospheric pressure 1 to 2 atmospheric pressure of your O 2 is sufficient to go for this particular conversion and the catalyst is V 2 O 5. So, is well known is a common text book catalyst still we are using this 1 and is cheaply available also because this can also be considered as the vanadium O type of thing because this is a oxidic material of vanadium. So, vanadium pent oxide is your catalyst for your conversion which is 95 percent overall.

So, which is basically utilized to ensure an adequate conversion definitely the adequate conversion for an industrial point of view and if we can optimize this that at a temperature of 450 degree centigrade and a pressure of 1 to 2 atmosphere and the catalyst we are happy to get that particular conversion.

(Refer Slide Time: 02:11)



So, the sulfur trioxide formed over there now is added to water and if we add to water that particular sulfur trioxide we get sulfuric acid, but if we add that particular 1 to the formed H 2 S O 4; that means, H 2 S O 4 plus SO 3.

So, H S O 4 plus S O 3 is giving us that particular one as H S O 7. So, that H S O 7 is known as disulfuric acid this is simply add up you have H S O 4 which is the concentrated one and that concentrated H S O 4, we are adding more amount of sulfur trioxide. That means, it is super saturated and you do not have any excess water molecule available for its conversion of that S O 3 which is available over there to produce more and more H S O 4, but it will be trapped inside.

So, the sulfuric acid the concentrated sulfuric acid containing excess amount of S O 3 and if we write directly that formula of that particular species which is being formed over there will be H 2 S 2 O 7.

So, that is known as oleum we all know that what is oleum because, in different organic chemistry reactions the pharmaceutical industry or some medicinal conversions, medicinal chemistry conversions, we use this particular oleum. Basically it is a reaction on sulfuric acid where sulfur tracks that is basically reacting very quickly what is available from that particular oleum and commercially it is known as your disulfuric acid.

Then at a highly concentrated version of this the oleum is then added to water to form sulfuric acid and which is therefore, highly concentrated. Because, in that particular case that particular oleum is again another version of your anhydride because sulfur trioxide is nothing, but our anhydride of sulfuric acid which is hydrated when hydrated it gives you sulfuric acid and that produced sulfuric acid can trap further your S O 3 and that SO 3 giving you the oleum.

So, that oleum can take further water molecule to giving you again a super saturated highly concentrated sulfuric acid. And the catalyst this is the solid state or 3 dimensional structure of your V 2 O 5 and we all know that when you write a V 2 O 5 will not be able to write that particular formula in a species like that if you have vanadium centers. And this vanadium centers can have 5 oxygen centers, which are oxide irons O 2 minus and we can get a discrete dimeric form of your vanadium, but the molecular formula of it is such that you have the repeating unit of that one; that means, V 2 O 5 whole n.

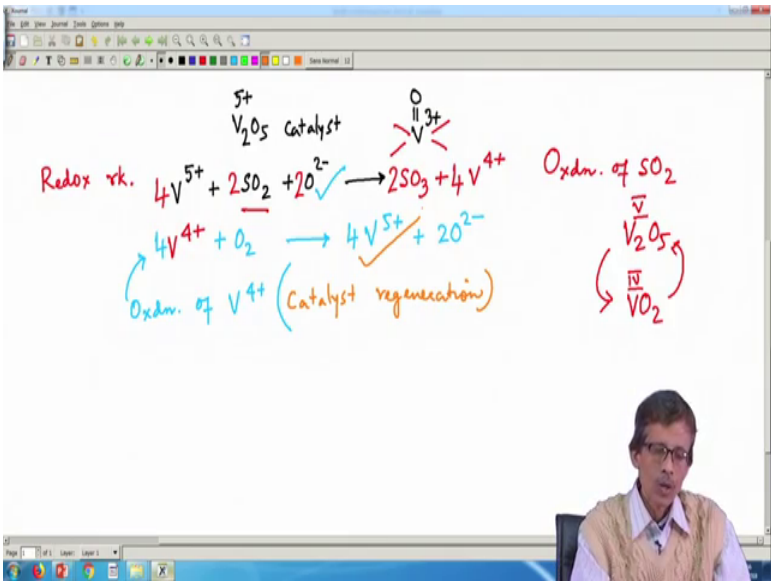
So, that gives us the typical solid state structure because when we produce that from any vanadium salt or any other vanadium ore we basically get that particular as the solid material. And that solid material is basically in our hand and that solid material is utilized for its catalytic function. And if we look at nicely over here what we find if we focus our attention on this particular part or the next part or the next part what you see that the three consecutive part because only thing is that the orientations are different from there.

What we see that the reds balls are these are basically considered as from the three dimensional X ray structure we considered it as the ball and stick model. And in that particular ball and stick model what we see that the red balls are basically or the red spheres are the oxygen spheres. So, you have this particular grey sphere which is the vanadium center.

So, vanadium center is at the center forming 5 bonds attached to it and sometimes it can be considered because when a particular center having 5 bonds to it we can have regular geometries one can be square pyramidal you have a square base and one pyramidal one or you have a trigonal base and is by pyramidal one above and one below. But in this particular case you have this particular vanadium center as a square pyramidal one and you have these vanadium so, these vanadium center is in the networking of the oxides.

So, different oxides so, it can be mu type or mu 3 type oxide ions and you can have for each and every vanadium centers you have one vanadium oxygen double bond; that means, you have the terminal oxygen attached to that particular vanadium. So, this particular vanadium center now, we will see that how this one basically is utilized for its conversion.

(Refer Slide Time: 07:28)



So, you have your V 2 O 5 catalyst and everywhere we have this V O is there; that means, V O if we consider the charge. So, this vanadium is in the 5 plus oxidation state. So, this is V O 3 plus. So, we take this as V 5 plus for this catalytic reaction with sulfur dioxide.

So, we have the sulfur dioxide and this vanadium with many number of oxidic ions; that means, O 2 minus. So, this is the typical reaction what we can have in our hand. So, vanadium in oxide environment that we have seen that, you can have the square pyramidal geometry of the vanadium so, that square pyramidal geometry is being utilized, but since these particular reaction is a redox reaction. Where we are talking about something where we can consider is that will be oxidizing this because we are converting this V O 2 to V O sorry S O 2 to S O 3.

So, it is oxidation of S O 2 molecules. So, this will be converted to S O 3 plus vanadium will be reduced to tetravalent vanadium. So, this is pentavalent then the vanadium in plus 5 oxidation state and this is vanadium in plus 4 oxidation state. So, if we can have a catalyst as V 2 O 5 and even in the solid state structure it will lose some amount of your O 2 minus because, this vanadium if it is in the plus 5 oxidation state. And if we say that this will be converted to vanadium 4 like this V 4 plus it will be converted to vanadium O 2 and will again converted back to your V 2 O 5 because we are talking in terms of your corresponding catalytic cycle.

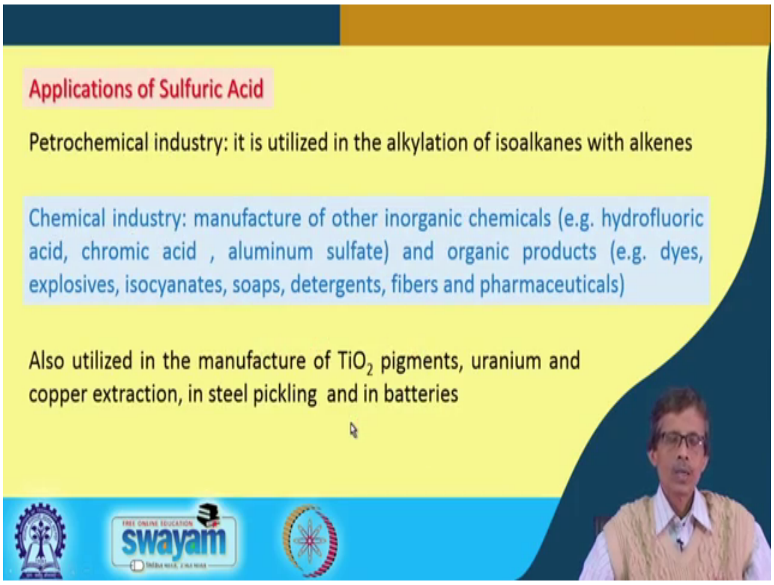
So, that particular catalyst will be regenerated. So, the vanadium preset in vanadium pentoxide as V 5 plus is reduced to vanadium as a tetravalent center as V 4 plus. So, we have of this S O 2 and 4 of this V 4 5 plus for your electron balance that number (Refer Time: 10:14) electron balance will give you twice of S O 3 and 4 of your V 4 plus. So, this oxygen basically, what you have? So, this oxygen from your air S O 2 or oxygen from your vanadium center is being utilized for your formation of S O 3.

So, that second step is basically this is form. So, we have to convert it; that means, that V in the tetravalent state the vanadium in the tetravalent state. So, V 4 plus will be oxidized to V 5 plus and now your O 2 is coming into the picture because we have plenty of that dioxygen molecule in our hand.

So, that dioxygen molecule should be utilized for giving us that particular conversion which is 4 or V 4 plus 4 or V 5 plus plus degeneration of twice O 2 minus. So, this will be also regenerated. So, from all the solid state reactions this is happening so, we get that particular one is the oxidation. So, is basically that oxidation of V 4 plus and which should be known as your corresponding one as the catalyst regeneration. So, it is catalyst regeneration because, we are regenerating the vanadium in plus 5 oxidation state. So, the pentavalent vanadium is being formed again and again.

So, we are not consuming the material that is why it is known as the catalyst for this particular reaction. So, what we will see now is that, that when we have this as the catalyst and its corresponding reaction for its reduction and oxidation.

(Refer Slide Time: 12:30)



Then how we can use the produced sulfuric acid huge amount of sulfuric acid the industry is producing that huge amount of sulfuric acid and where we basically use that particular sulfuric acid. So, the most important industry we know that a very good industry for handling the petro chemicals because, we have the petroleum products in our hand. So, petro chemical industry is basically utilizing it for alkylation of isoalkenes with alkenes isoalkenes with alkenes.

So, concentrated sulfuric acid so, if we have the corresponding condensation reaction because the concentrated sulfuric acid is a very good dehydrating agent and the corresponding isoalkanes are there. So, that can be considered as the one of the isoalkane that in isopropane type of thing. So, ISO function is there. So, that ISO function can be converted with respect to your different alkenes for the typical alkyl product. So, is known as the alkylation.

Then after petro chemical industry we can have the utilization in chemical industry. So, different chemical industries like making of useful inorganic chemicals why we are talking all these in terms of your industrial inorganic chemistry because, we are only looking for what basic information what primary chemical industry knowledge is required for production of your inorganic chemicals.

So, what other inorganic chemicals we can produce with the help of your sulfuric acid that we have produced already. So, other inorganic chemicals such as hydrofluoric acid, chromic acid or the aluminium sulfate. So, you see by knowing the name only the three examples are given over here as the H F the CR2 O 3 and the aluminium sulfate, how you get this one and what is the role basically for your sulfuric acid?

So, hydrofluoric acid is very simple that if you have some supply of fluorine based minerals or ores or the fluoride ions F minus you have to supply H plus. So, that H plus can come from your sulfuric acid producing hydrofluoric acid. Similarly chromic acid which is basically CR2 O 3 as a oxide basically.

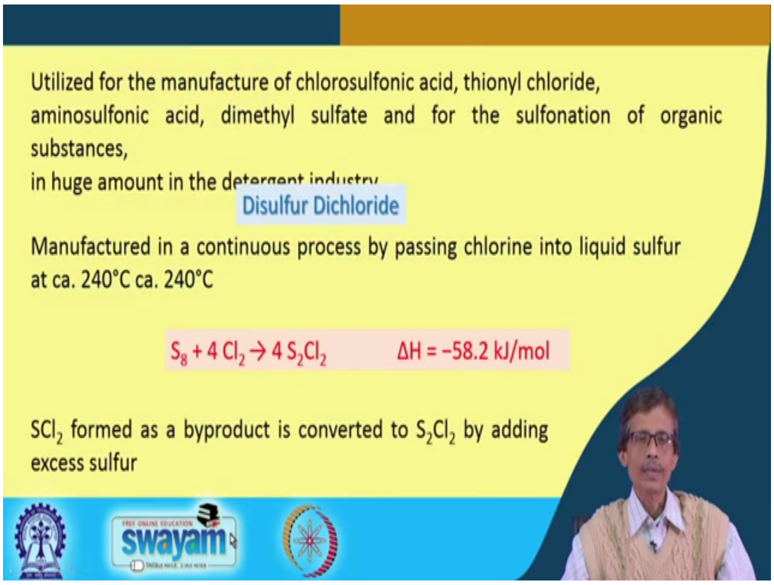
So, that oxide basically we can get it when we dissolve the corresponding chromate or dichromate in concentrated sulfuric acid. So, potassium dichromate or sodium dichromate or potassium chromate or sodium dichromate when you go for its dissolution in sulfuric acid, we get the corresponding very useful color also that very orange red color of your chromic acid. So, you get that particular utilization of sulfuric acid then aluminium sulfate; that means, simply from aluminium powder aluminium ore as bauxite or any other scrap aluminium.

So, throw away aluminium material which can be utilized for its reaction with concentrated sulfuric acid or some dilute version of it can give you the corresponding useful aluminium salt as sulfate. So, we are supplying sulfate enhance to produce aluminium sulfate. So, any metal salts any kind of metal salt as sulfate salt can be produced with the help of sulfuric acid. Then some example of organic products; that means, different dyes we can make; that means, sulfate dyes or sulfonation.

If we can go for with the help of sulfuric acid different explosives can make isocyanates can be made soaps detergents fibers and different pharmaceuticals are all dependent on the availability of the sulfuric acid and the use of sulfuric acid. And further it is also used in material production also that T i O 2 the titanium dioxide which is basically a version of its ore we call it as rutile.

So from rutile we get the pigmented or the pigments T i O 2 titanium dioxide with the utilization of sulfuric acid, then for uranium and copper extraction we use sulfuric acid and in steel pickling and in batteries. So, battery industry will be using steel pickling and the steel industry is also using this particular one acid as your regular supplies. So, sulfuric acid is most essential for all these industries.

(Refer Slide Time: 17:07)



So, basically what we get here that utilized in the manufacture of also the chlorosulfonic acid is also utilized for making thionyl chloride. So, some more compounds right now we will see now that this sulfuric acid how we can utilize that sulfuric acid for making of chlorosulfonic acid which is one particular variety we can think of; that means, the function of this on chlorine is your sulfonic acid function.

Then thionyl chloride is also that asocial to; that means, which can already produced from sulfuric acid amino sulfonic acid dimethyl sulfate and for the sulfonation of different organic substance. In huge amount in the detergent industry; that means, we all know that the different detergents. Now a days, we call this as the different micelles Sodium Dodecyl Sulfate one such example is S D S we call.

So, sodium dodecyl sulfate that particular one which the name will tell you that is the organic sulfate molecule. So, sodium dodecyl alcohol which is known as lauryl alcohol also commercially or common name of that particular molecule is the lauryl alcohol. So, dodecyl; that means, decyl is 10 do means plus 2 so; that means, it is a carbon number 12 bearing alcohol long chain alcohol only. So, the O H can be converted to your corresponding sulfate; that means, you are adding on the oxygen of the alcohol another S O 3 group making it as a corresponding sulfate giving you the sodium dodecyl sulfate which is a useful micellar molecule.

So, in detergent industry large amount of all this micelle in the cosmetic industry and all other finer areas of this chemical industry is being utilized for the use of all these micelle materials. Then we just see another very useful compound; that means, the sulfur compound the elemental sulfur we have. So, far we are talking about the oxidation of that particular sulfur and making of this sulfuric acid now we can go for chlorination; basically very simple reaction like your organic chemistry reaction or any other reactions as we all know that the chlorination of the metals as ore or mineral we can convert it to the corresponding chloride salts of that particular metal as metal ions.

So, elemental nickel or elemental copper or elemental iron or elemental chrome and chromium if you have the chlorination of all these metal ions can give you the corresponding chlorides as their corresponding salts. So, similarly sulfur is your nonmetal component because, is the main group nonmetal species so this main group species sulfur. So, we call it as a nonmetallic species or the main go species which can also be chlorinated ; that means, we are able to make new sulfur chlorine bond and it has some useful application so, since it has a useful applications so, definitely it is one of other value added compound.

So, that value added compound of sulfur is your sulfur dichloride or disulphur dichloride we call S 2C l 2. So, is again is manufactured not at very very high tempers, but it is manufacture at a low temperature of 240 degree centigrade. So, 240 degree centigrade temperature is fine for manufacture of these in a continuous process by passing again another gaseous material; that means chlorine gas. Already we have seen that how we can have liquids sulfur in our hand so, production and use of that liquid sulfur we have seen now the same liquid sulfur you can use to attract the reaction with the chlorine as a gas.

So, reaction of this is not a very hazardous one also because the temperature is not very high it is only 240 degree centigrade. So, that particular temperature is useful for converting directly the S 8 molecule. Now in the chemical reaction we are writing S 8 plus 4 C l 2 giving you 4 molecules of S 2 C l 2 again your delta H value you should know which is minus 58.2 kilo joule per mole. So, this S 2 C l 2 and whenever we have some compound definitely we are only talking in terms of your industrial production its value addition its usefulness and consumption.

But as a typical inorganic chemist so, we should know what sort of molecule it is; that means, the structural form the way we are discussing little bit about the corresponding catalyst structure the V 2 O 5 structure similarly how your S 2 C l 2 molecule looks like because S 8 molecule we all know because is the zigzag type of thing all sulfurs are connected which is a crown type of molecule.

So, all sulfur are connected through a crown type of molecule where 8 of these sulfurs in a particular unit like your p 4 unit in phosphorus the t 4 which is a tetrahedral molecule where all 4 phosphorus centers are connected through phosphorus; phosphorus bonds. Similarly in S 8 all sulfur are connected through sulfur, sulfur bonds and which is a crown type of structure and that is being cleaved basically.

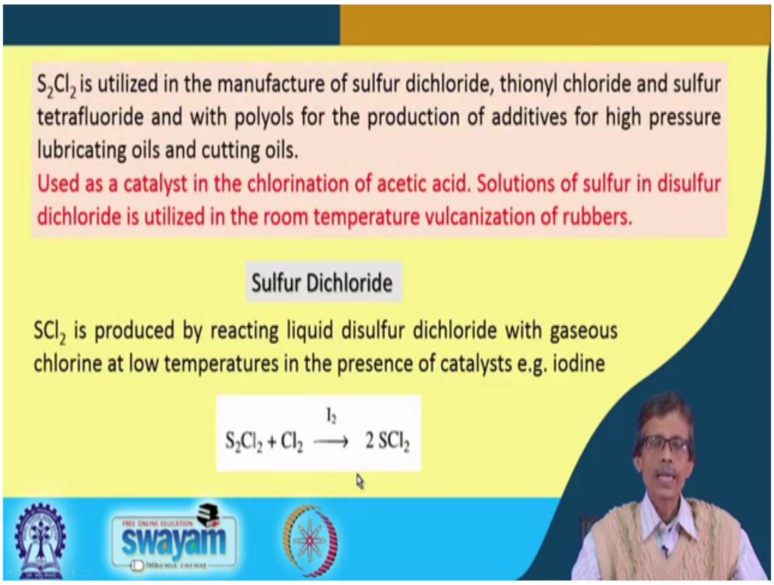
So, the molecular form of this particular species is S2 C l2; that means, when we are breaking this particular unit as S 8 into 4 units of that; that means, 4 S units are forming. So, you will have the still intact sulfur sulfur bonds only the other thing what we are doing we are doing nothing we are just adding chloride ions from the sides of that S unit. So, you have C l S S C l which is the molecular structure of that particular molecule.

And if we can have some intuition or imagination related to this sort of molecule we can consider it as the corresponding structure of hydrogen peroxide H 2 O 2 you all know that in H 2 O 2 we have the O O bond and ends we have hydrogen atoms attached to this oxygen, but is not in a linear fashion not in an angular one, but is only a open book type of structure in that open book type of structure what you can have the book what we are having. So, the connection over there is there to oxygen centers similarly you can have sulfur centers and one hand you have the sulfur chlorine bond and the other and you have the other page. In one page of the book you have the sulfur chlorine bond and in another page you have the sulfur chlorine bond on the other side.

So, that particular structure is very important to know sometime because is a confusion can come over here for the next product what is your sulfur dichloride. So, from this reaction if the reaction is not a direct one and a stoichiometric one; that means, the chlorination of elemental sulfur; we can ask is a very simple question to be asked to anybody who are going through this particular one that how you produce it and how you go for chlorination of sulfur.

So, you get S 2 C l 2 so, along with that you can have S C l 2 also that sulfur dichloride which is a byproduct and one some amount of a S C l 2 is formed as a byproduct you can convert it back to S 2 C l 2; that means, this original compound how you do that? You do the simple thing because the stoichiometry of sulfur; that means, the sulfur content of sulfur the mono sulfur dichloride or sulfur dichloride the corresponding amount of sulfur present in is less compared to your S 2 C l 2. So, you have to add more amount of sulfur so, if you add more amount of sulfur to it you get S 2 C l 2 back.

(Refer Slide Time: 25:37).



So, that basically tells us that S 2 C l 2 formation and its utilization in the manufacture of sulfur dichloride; that means, you get this as corresponding sulfur dichloride. So, that we will see in our next class possibly in detail because today just will briefly see that S 2 C l 2 we are producing it from S 8 and that S 2 C l 2 can be utilized for the production of S C l 2, not only S C l 2 sulfur dichloride, but it can also be consumed for thionyl chloride sulfur tetrafluoride S F 4 and with polyols and for the production of additives for high pressure lubricating oils and cutting oils.

So, these are all industrially important oils basically because the oil sector for some value added oils basically these are sometimes additive because for to increase the self light the longevity and the life of that particular oil for is useful purpose can be increased by some addition of all this material. And it can also be utilized as a catalyst in the chlorination of acetic acid you see the very simple reaction what we are now talking at as a reagent.

So, when we produce something from their sulfur source we are producing something as your corresponding sulfur disulfur dichloride S 2 C l 2 and in that particular case is we are utilizing it because if you can use these for some good purpose that one is that chlorination of acetic acid; that means, chlorination of acetic acid you can have points of chlorination whether you get the acetyl chloride or chloroacetic acid that we have to find out, but the same thing what we are talking is the simple chlorination.

So, the elemental chloride chlorine; that means, in the gaseous form is not utilized is avoided instead of that we can use S 2 C l 2 for that particular purpose. So, solutions of sulfur in disulfur dichloride is utilized also in the room temperature vulcanization of rubber earlier we have seen that elemental sulfur is being utilized now solution of sulfur in disulphur dichloride. So, disulphur dichloride if it is utilized as a solvent.

So, more sulfur of it will be solubilized and that can be utilized for your vulcanization. So, mono sulphur dichloride or S C l 2 can be produced from S 2 C l 2 that we will see in our next class in detail also and something here again we are adding and showing over the arrow is your catalyst; that means, this iodine is your catalyst. Now further chlorination of your disulphur dichloride will give you S C l 2.

So, it is produced by reacting liquid disulfur dichloride in which is in your hand with the passage of gas or passing of the chlorine gas. So, chlorine gas is passed over that particular liquid at low temperature in the presence of the different types of catalyst one most useful catalyst is your iodine elemental iodine solid elemental iodine. So, you have the liquid in your hand, you have the gas which should be passed over that liquid and you have the catalyst bed as the solid. So, how industrially we can produce you can think of you can imagine it that, you have the solid beds so, pulverized are in powder which is a black powder.

So, you can grind it which is shiny black material. So, you can make it a powder and that particular powder if it is there and your disulfur dichloride is there and that disulfur dichloride should bring in contact with the chlorine gas such that you can go for further chlorination. That means, you take out that S 2 C l 2 part one part of S C l and another part of S C l so, sulfur sulfur bond will be broken and that sulfur which is being broken from that side will be attached with again chlorine. So, it is basically like that of your S C l 2 directly that one sulfur is there like your H 2 S.

So, one sulphur having sulfur chlorine bonds in it and you get that S C l 2 molecule in your hand. So, we will continue this discussion in our next class whether we can have some more useful sulfur compounds because it is easy to make also once, you make sulfur from your regular source and sulfuric acid in your hand we can make different types of all these compounds which are very useful industrially.

Thank you very much.