Industrial Inorganic Chemistry
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Lecture – 17
Sulfur Compounds and Sulfur from H2S and SO2

Good evening everybody, welcome to the class of Industrial Inorganic Chemistry once again where, we are talking about how we can get the sulfur as well as the different sulfur compounds. And definitely, we will talk about at first the production of huge amount of sulfuric acid, what is industrially very much required for all the different purposes.

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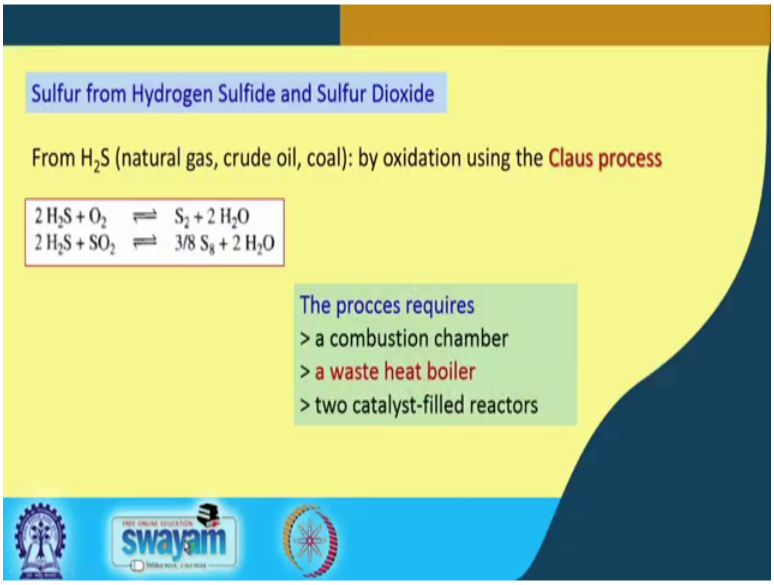

So, in terms of the production of sulphur, what we know now that the earth crust or below the earth crust, we have a huge deposit of sulfur in many places. So, sulfur we can get it from your, it is pure elemental form as S 8 and we can process it for it is purification or it is regular utilization.

Next we now see that how we can get from hydrogen sulphide; that means, our H 2 S as well as sulfur dioxide. So, these are the two very industrially pollutant gases, what we produce as a side product in some different reactions or manipulation of reactions, where we are handling sulphides as well as other sulfur compounds.

So, if we can have a huge source of hydrogen sulphide; that means, H 2 S as well as sulfur dioxide how we can get the elemental sulfur out of this. So, one of the good source of H 2 S is our natural gas as we all now know that the CNG and the crude oil or the coal. So, during the production of the natural gases or the compressed natural gases; that means, the CNG or during the production of the crude oil, some amount of sulfur as well as the sulfur based compounds are eliminated as H 2 S.

So, how we can get elemental sulfur; that means, S or S 2 or S 8 from your hydrogen sulphide gas; that means, H 2 S. So, the best technique is simply the oxidation process; that means, sulfur is present in H 2 S as H 2 minus; that means, the sulphide ions or the sulphide anions, which is w negative. So, w negatively charged. So, this S 2 minus has to be oxidized to S 0. So, one such procedure is the typical process is Claus process. So, the Claus process is the industrially known process, where we basically utilize the oxidation of hydrogen sulphide H 2 S by O 2; the oxygen from the air or any other source in pure form.

So, what happens basically from the chemical reaction point of view or the stoichiometric reaction of H 2 S with O 2, we see from the first reaction where 2 molecules of H 2 S is reacting with one molecule of O 2 giving us S 2 plus 2 molecules of water. So, it is possible to oxidize your sulphide ion by O 2 giving us the elemental sulphide as S 2 form for your chemical balance and balancing the chemical equation, we write it in the form of S 2, but in all these cases it is basically forming as the S 8.

So, S 8 species we will get here as well as the O 2, which will be a reduced back that this O 2 in the 0 oxidation state will be reduced back to your water molecules. So, we get that in a nicer way that simple oxidation by O 2 of the H 2 S, we produce S 2 which is your elemental sulfur. So, if our environment the atmosphere is also contaminated with S 2 and if we are can able to detect the source of that H 2 S; that means, some industry is eliminating H 2 S to the environment, what we can do? You can do the some simple thing, that whether we will be able to pass that particular H 2 S in some reaction chamber, where it will be oxidized by simply air or the O 2 present in air.

So, simple oxidation chamber through which your H 2 S can pass. So, that oxidation chamber will convert your entire H 2 S to elemental sulfur. So, there is no need to worry about the H 2 S, what we are producing industrially such that, we are eliminating and we are discharging it into the air. So, we are not discharging it, if we can take proper precaution for managing that particular H 2 S and the second process is basically directly related to the two thing that what we are writing at the title that sulfur from both; that means, sulfur from hydrogen sulphide as well as sulfur dioxide.

So, there also instead of using O 2, we can use S O 2 as your oxidizing agent. So, this S O 2 now can disproportionate the reaction is that or the reverse of the disproportionate reaction, what we can say is the comproportionation reaction. That means, S 2 minus is with reacting with S in the tetrahydral state; that means, S O 2 the sulfur oxidation state is plus 4. So, the comproportionation reaction between H 2 S and S O 2 will give us S 8 and once again your water molecule. So, we can have two things either you can have a good supply of O 2 in your hand to take out your H 2 S or sulfur dioxide in your hand such that, you can destroy the amount of H 2 S, what we are eliminating or removing or discharging into the atmosphere.

So, as a result what we get we are getting something that we can produce sulfur the elemental sulfur production from H 2 S or S O 2 and the procces is basically the procces the procces is not p r o c e s s. So, the procces basically requires a combustion chamber where you can burn the thing; that means, it will have a high temperature reaction a waste heat boiler; that means, some amount of heat is being wasted. So, we will have some wasted boiler attached to it and the reaction is kinetic one.

So, 2 catalyst field reactor; so, we have the reactors even for your reactions between the 2 components in case of H 2 S O 2 both of them are gases in case of H 2 S and S O 2 both of them once again, they are also gases. So, this will be filled with 2 catalyst filled reactors. So, the catalysts are available and those catalyst filled reactors will be utilized for these simple reactions.

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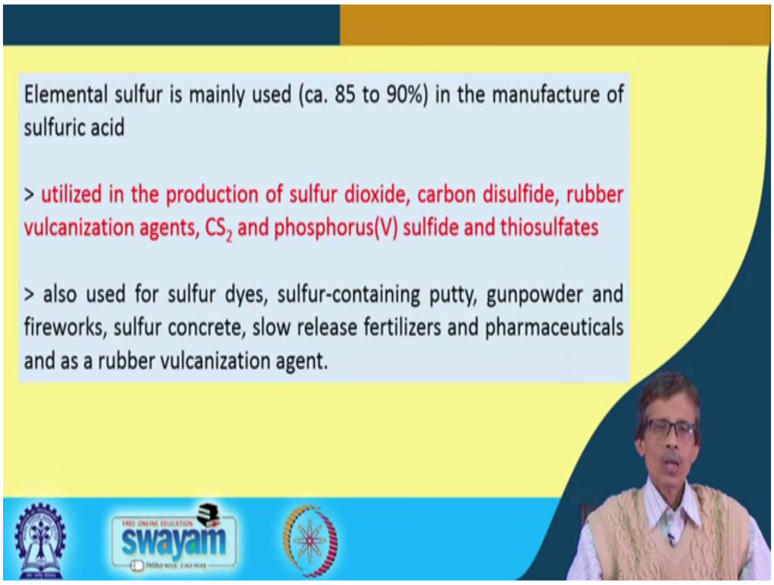

So, the produced elemental sulphur, what we are producing in a huge amount or we are isolating those from the natural sources from the earth crust or some volcanic eruption out of that amount of sulphur, what we are producing basically, we can consider it as a industrial thing that one particular industry is basically, devoted for the production of sulfur or the consumption of sulfur. Because, our main goal of knowing all these things. The discussion is focusing on the conversion of those sulfur; that means, the elemental sulfur to some useful sulfur based compounds.

So, about 85 to 90 percent of the sulphur, what we are producing is basically meant for the production of sulfuric acid because, this is the main thing because, this particular one like that of our nitric acid, this sulfuric acid has a huge demand in the industry and large amount of sulfuric acid, we have to produce for different purposes. So, sulfur is given to you the elemental sulfur is given to you should know, how we can convert it to sulfuric acid and what should be the corresponding industrial process. That means, the industrial procedure that will tell us the underlying principle behind the inorganic chemistry dealing in industry because, this particular one. That means, this elemental sulfur main amount; that means, up to 90 percent is consumed for sulfuric acid production.

It is also utilized for the production of some other things; that means, when we require sulfur dioxide also. Just now we have seen that, how sulfur dioxide can be consumed for the production of sulphur. Now the reverse reaction, if we require sulfur dioxide and we have only the stock of elemental sulphur, we should know that how it can be converted to sulfur dioxide for ready use of that sulfur dioxide then one most important liquid basically, this is liquid carbon disulfide C S 2 is a very useful one. And, that carbon disulfide, if time permits in afterwards, we will see that it has lots of applications starting from your laboratory detection of alcohols.

As we all know that, alcohols are R O H and that alcohol in presence of this particular compound; that means, carbon disulphide C S 2 in basic medium or alkaline medium. In terms of ammonium hydroxide, sodium hydroxide or potassium hydroxide that can be converted to; that means, the alcohol can be converted to xanthate and those xanthate are of the corresponding salts depending upon the base, what you are xanthate, if we use ethyl alcohol for the conversion of that particular process will get potassium salt of ethyl xanthate. Similarly if we have the sodium hydroxide or potassium hydroxide as basis will get they are corresponding sodium salts or potassium salts as the corresponding xanthate.

Because, this has very good application industrially also; that means, for the production of the different types of cellulose materials, the cellulose acetates or the cellulose xanthates basically for their final production and all these things this particular reaction is taken place over there through the conversion of alcohol to xanthate then direct sulfur; that means, we know that the sulfur is very much utilized for sulphur sulfur cross linking from our protein molecules to the rubber molecules. So, sulfur sulfur cross linking between a chain of a polymeric unit, whether it is a protein; that means, the biomolecule or it is the synthetically prepared protein that polymer chain, we can go for the vulcanization.

So, elemental sulfur is utilized for vulcanization of those materials also then as we have seen that the C H 2 and for the phosphorous pentasulfide production as well as thiosulfate production. So, these also we have seen earlier that how P4S10 can be formed or P 4S10 can be produced from elemental phosphorus as well as elemental sulfur. So, earlier we have discussed all about, how we produce phosphorus from mineral source or the ore source.

So, elemental phosphorus was in our hand. So, we should have the corresponding supply of sulfur now and at a high temperature reaction, it basically converted to phosphorus pentasulfide, whose molecular formula is basically the dimer of that pentasulfide, which will be P4S10. And, some amount of thiosulphate can also be dependent on the availability of elemental sulfur for it is reaction that we will also see that bisulfides or the sulfides is S O 3 only it S O 3 2 minus, when it is directly reacting with sulfur.

So, that sulfur attachment to the sulphite ion S O 3 minus will give you H 2 O 32 minus which is your thiosulfate anion. So, it can also be utilized for different sulfur dyes sulfur containing putty for their building material gunpowder and fireworks because, the sulfur is the main constituent of the different fireworks. We know the sulfur is being burned as sulfur dioxide then sulfur bearing concrete material slow release fertilizers are also there because, some amount of sulfur is utilized. And, when sulfur is converted to sulfur dioxide this particular fertilizer can be taken away as a slow release fertilizer and definitely for the pharmaceuticals because, the incorporation of sulfur as different sulfur drugs or the sulfur present in the beta lactam ring.

So, that sulfur present in the big organic molecule can also come from elemental sulfur. So, the sulfur is also utilized for making the different pharmaceuticals and definitely what already we told you that is for rubber vulcanising agent.

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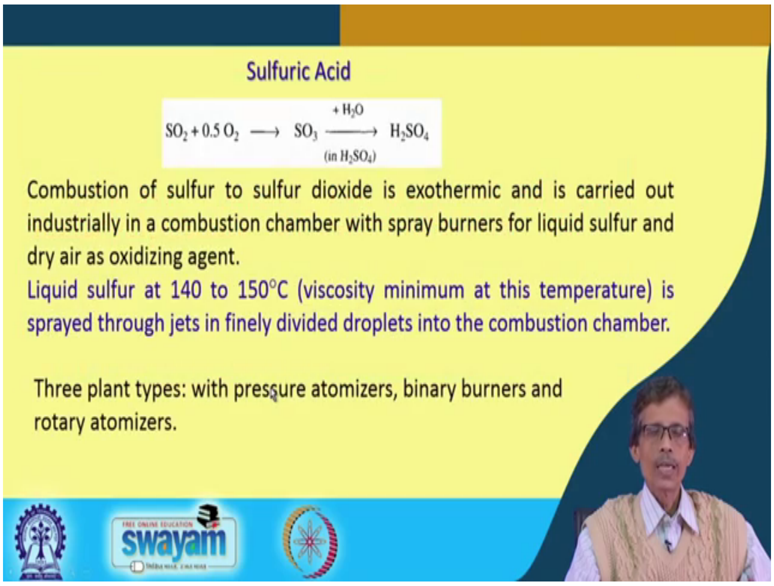

So, these are the main uses of elemental sulphur, what we can use, but the major utilization of elemental sulfur is the production of sulfuric acid as I told you that 85 to 90 percent of it will be utilized for sulfur bearing oxides and then conversion of that particular oxide to the highest possible oxide; that means, sulfur dioxide to sulfur trioxide and then to H 2 SO 4.

So, how we go for that? So, the direct reaction their chemical reaction, if we see which is SO 2 plus half of the O 2 will giving you SO 3. So, towards the left basically, what we are doing? We are doing nothing, but elemental sulfur is in your hand and you burn it in plenty of air huge amount of air. So, sufficient air is available. So, air will be available for oxidation of your sulfur to sulfur dioxide and that sulfur dioxide has to be converted to sulfur trioxide.

So, this is a different step of pure chemical reaction and always try to remember, that when we burn in excess air and whatever amount of other thing, we add there we will not get sulfur trioxide directly from elemental sulphur. It has to go through sulfur dioxide formation so that sulfur dioxide formation is basically giving us some idea that in a double step reaction SO 2 is being converted to SO 3 and then through the absorption of your water molecule; that means, we can have some mechanism, where water can be absorbed by the gas molecules, which are SO 3.

So, when SO 3 is being absorbed by water molecules. So, direct incorporation of that particular one in SO 3 producing H 2 SO 4 and with the variation in different concentration as we all know that hydrochloric acid, which is available in water medium, but the HCL, what we produce is basically a gas. So, the dissolution of that HCL; that means, the hydrochloric acid gas, we if we consider; so, that HCL when it is absorbed in air we basically get as your hydrochloric acid, but here the direct reaction of that H 2 O with SO 3 is giving us a straight support. So, water will be one of the constituent of that H 2 SO 4.

So, in a highest possible concentration of that H 2 SO 4 we have the maximum amount of sulfur trioxide in it and sometimes we can see also we know that this produced H 2 SO 4 in the first step can further absorb some amount of SO 3. So, H 2 SO 4 plus SO 3 can give us something, which you all know that this is basically the oleum, when you have excess amount of sulfur trioxide present in the produced sulfuric acid this is giving us a highly concentrated sulfuric acid version, which is basically some portion is the anhydride of sulfuric acid. So, step wise what we gave, we can go from combustion getting sulfur dioxide and the reaction is exothermic; that means, it is producing some amount of heat and is carried out industrially in a combustion chamber and with spray burners for liquid sulfur. So, liquid sulfur basically.

So, the solid sulfur is not the powder we are spraying, but spraying the liquid sulfur. So, the molten sulfur and dry air is utilized for the oxidation of that sulfur to sulfur dioxide and that liquid sulfur not at a very high temperature, but at a temperature of 140 to 150 degree centigrade, because at that particular temperature it reaches a minimum viscosity value is spread through jets, where is fine orifice of that particular one. So, the supply line will have some small jets and the jet is finally, divided into droplets into the combustion chamber. So, the liquid sulfur is basically getting injected into the combustion chamber, where it is being burned to form your corresponding sulfur dioxide. So, if we get the droplets the contact of that particular liquid sulfur with oxygen; that means, O 2 will be the highest one.

So, the conversion to SO 2 is also should be the highest one until and unless we talk in terms of the solid sulfur is burning in some medium in presence of oxygen at some temperature coming from some flame or some other thing. So, the plants we definitely require for that particular industrial production. So, the 3 plant types are known with pressurised atomizer; that means, we are forcing the liquid sulfur to spray inside then binary burners and rotary atomizers. So, atomizers are nothing, but very fine droplets the mists are forming from the liquid sulfur and which are being sprayed inside the way, we spray for the different atomizer. So, we know that the atomizers are required for different spectrometer such as your atomic absorption spectrometer, where the system is such a manner is form that we basically spray and we get the atoms of the corresponding elements or the metal ions.

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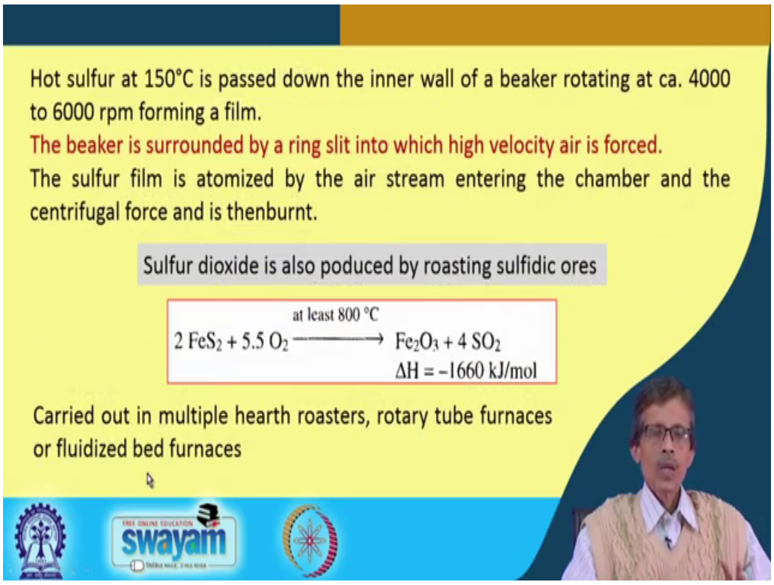

So, the we get the hot sulfur and that hot sulfur at 150 degree centigrade is passed down into the inner wall of a beaker basically, if we consider that you have a beaker and which is rotating at a very high speed from 4000 to 6000 rpm and it is forming a film of sulfur and now that particular beaker is surrounded by a ring slit into which high velocity air is introduced. So, we are bringing that particular sulfur as a film into the contact of the air such that we get the reaction directly from sulfur with oxygen giving you sulfur dioxide.

So, the sulfur film what is forming over there through that rotation is atomized by the air stream entering the chamber and the centrifugal force and the burnt out and then burnt; that means, it is then quickly burnt out and the burnt out process is basically giving us the corresponding sulfur dioxide and we have that SO 2 now in our hand. And, we will see next that how we can convert that a SO 2 to SO 3 before getting that sulfuric acid; that means, H 2 SO 4; so, one other source not the direct elemental sulfur.

So, any sulfide source it is also a good source of sulfide ions as we have seen earlier that if we use H2S, we can produce elemental sulphur. Similarly, the corresponding sulfidic ores like FeS to the pyrite ore. So, FeS to having polysulfides is not a pure S2 minus, but is a basically a poly sulfide type of thing; that means, S2 has the overall charge of 2 minus. So, that poly sulphide type of thing can also be oxidized in presence of air, but very high temperature of say 800 degree centigrade and that temperature is utilized for the production of sulfur dioxide.

So, sulfur dioxide is formed so, whatever amount of sulfide was present which is attached to that particular ore is taken away as sulfur dioxide living behind you that iron oxide; that means, the ferric oxide. So, this particular oxidation process is carried out in a multiple hearth roasters roasting, we all know that is basically a burning process that ore roasting is a very common procedure for making all these things and sometimes, we basically get for the corresponding value addition of all these things.

So, if your iron pyrite is not a very useful or mineral for the production of iron or steel making industry, what we can do we can go for it is conversion from $FeS2$ to $Fe2S3$. Because, we know as the hematite or magnetite these oxides like $Fe\ 2O\ 3$ or $Fe\ 3O\ 4$, they are very useful or for iron and for steel manufacturing, but at the same time we are also producing sulfur dioxide. But, now we are focusing our attention on the other part; that means, the production of $SO\ 2$ from these ores and that $SO\ 2$ will be utilized for sulfuric acid production. So, a particular industry which is focusing their attention for making iron and steel industry can have some by product of sulfur dioxide. And, if they are careful enough without dumping that $SO\ 2$ in the air or atmosphere, they can utilize that particular $SO\ 2$ formation from that reaction for the production of sulfuric acid.

So, not only that industry will be devoted for making iron or steel or any other material based on iron can also be able to produce sulfuric acid from a very straight cut reaction of getting sulfur dioxide converting it to sulfur trioxide and that sulfur dioxide through water absorption giving you $H\ 2\ SO\ 4$. So, these basically can be carried out in multiple hearth roasters rotary tube furnaces and sometimes the fluidized bed furnaces, there is a typical terminology for these that you have the fluids and you have the beds, where that contact of the corresponding reactions can be achieved and these are basically the furnaces; that means, a typical high temperature reaction.

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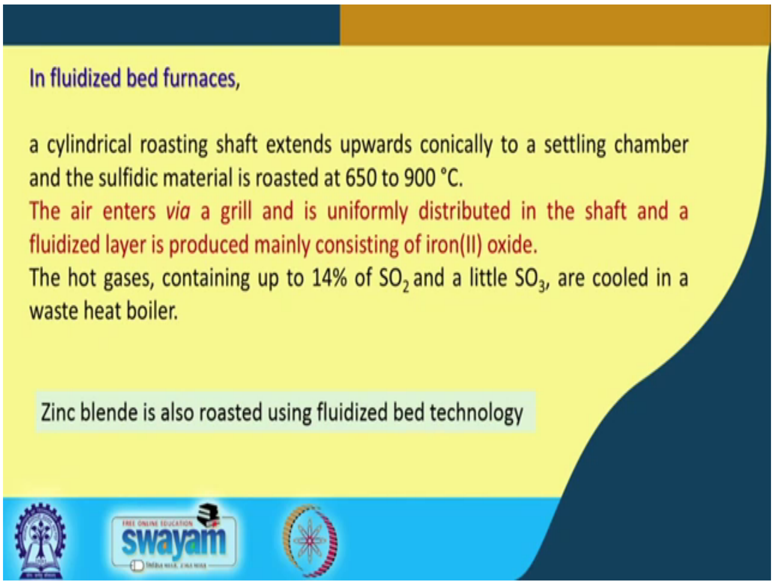

So, for this particular example that in fluidized bed furnaces what happens basically there a cylindrical roasting shaft is available that extends upward conically to a settling chamber. So, these are basically because these are the basic components, what we are talking in terms of only the components of this, if we try to avoid a detail drawing that the flow chart of all these thing, but we should know the basic component. Because, we are focusing our every attention for the product formation and how we can achieving all these through the reactions and what are the reaction chambers. Basically because, when you do some reactions of these sort of reactions in the laboratory, we all know that the wrong bottom flasks the beaker and all these small-small containers are available for your reaction, but when you go to industry you have all these huge furnaces or the chambers available for it is conversion.

So, you have a settling chamber and the sulfidic material; that means, the or material that FeS 2 material which can be dumped over there and which can be burnt in air for roasting and roasting is done at a very high temperature it is less than 800 or more than 800 from 650 to 900 degree centigrade and the air basically is allowed to pass through a grill. So that means, we are spreading the air such that you can have a huge or good contact over there and you have uniform distribution in the shaft and a fluidized layer is produced mainly consisting of iron 3 oxide.

So, during that oxidation process the all particles of FeS 2 will be oxidized and we get that thing; that means, we are only interested to get that particular material as your gas material. So, if your solid material remains intact and is only converting from FeS 2 to FeO 3, we are happy to have the corresponding oxygen for bonding process as your sulfur dioxide. So, air or O2 is entering into the chamber and S0 2 is going out from that particular chamber, converting your FeS 2 to Fe 3 S 3. So, the hot gases is basically a mixture containing up to 14 percent of sulfur dioxide and a very little of sulfur trioxide because, some amount of sulfur dioxide can also form and is cooled in a waste heat boiler.

So, because the temperature is very high it is 650 to 900 degree centigrade. So, the gas what we are producing is also at a very high temperature and when we cool it at a low temperature is basically, we get some waste heat boiler; that means, heat is being removed from the medium. So, waste heat boiler is there; that means, some cooling tower is available and that particular tower is meant for cooling the SO 2 produced from that particular reaction. And, that particular production is basically giving us some elevated temperature of the air, if air is used for your cooling that particular boiler or water if water is used for cooling process. So, like FeS 2 we can have some other sulfidic ore, which is also your zinc sulfide ZNS, which is known as zinc blende, which can also be utilized for this particular purpose using the fluidized bed technology.

So, depending upon the availability of the ore whether we get FeS2 as a good supply or the regular supply or availability in the near vicinity of that particular industry, we can go for FeS2 for use, otherwise we can go for zinc sulfide for it is production of SO2.

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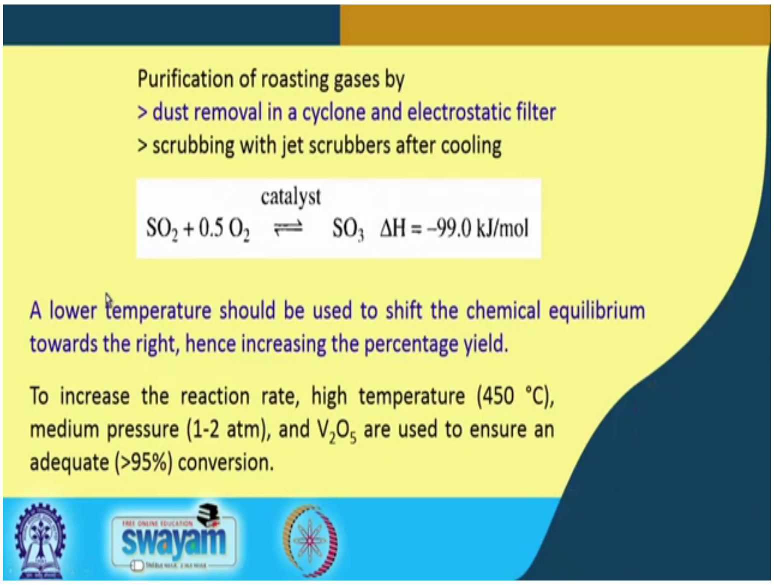

So this basically, we have in our hand; that means, we get it as your corresponding formation of SO 2 and the roasting gases; that means, if we use O 2 and that O 2 is giving you SO 2 and that SO 2 is basically the roasting gas; that means, the high temperature gas, what we are having and 14 percent of this is a SO 2 the remaining is your O 2. So, it will be purified by dust removal in a cyclone or electrostatic filter. So, electrostatic filter will be there, where the particles; that means, the dust particles will be removed or will be settled down at the bottom of the filter or is scrubbing with jet scrubbers after cooling. So, once you cooled it you can pass through a scrubber.

So basically, scrubber having very small pores basically and through those spores the gas is being passed and the particles will be retained by those scrubber and the jet scrubbers is being used for that particular removal of those particles. So, we have now reached to the position, where we can talk in terms of the conversion of SO 2 to SO 3. And how we can convert it now? So, we now write the chemical reaction is S0 2 plus 0.5 or half of O 2 giving you SO 3 and the head of the reaction the delta H is also little bit you should remember because, we are talking basically in terms of the temperature and the temperature what is being utilized for that particular conversion.

But the delta H values are sometimes a very good guidance, whether we get that particular conversion for a different types of catalyst; that means, the development of the catalyst, some people are also working on the development of the catalyst for this model reaction. We can consider this as a very simple model reaction; that means, how easily we can convert SO2 to SO3 by using a new type of catalyst. So, all these cases are all these processes, we are utilizing some amount of some model reaction.

So, this can also function as a model reaction for it is suitability of that particular catalyst, how good that catalyst is for this simple reaction. So, when we go for a low temperature conversion. So, a low temperature should be used to shift the chemical equilibrium towards the right; that means, the cooling process should be utilized for now this oxidation; that means, SO 2 to SO 3 oxidation and to shift the equilibrium towards the right hence, increasing the percentage of field. So, whether your reaction is exothermic and endothermic that basically guiding us that whether, you can change the yield of the reaction because, always we should be able to maximize the yield of a particular reaction.

So, we will just continue in our next class, what we are happening over here, what basically is happening for this particular conversion. And, we will see what sort of catalysts most used catalyst is utilized for it is conversion.

Thank you very much.