

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

**Lecture – 07**  
**Inorganic Peroxide Compounds**

Hello and welcome to this class of Industrial Inorganic Chemistry, where we are talking about the different peroxy compounds starting from your hydrogen peroxide. And as we have seen that these are very reactive oxygen species. In our biological world also, when we have O<sub>2</sub> only; and if it gets one electron transferred to that O<sub>2</sub> molecule, we get superoxide followed by another electron transfer also gives you the peroxide system.

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**Alkali Peroxodisulfate**

Diammonium peroxodisulfate produced electrochemically from solutions of sulfuric acid and ammonium sulfate on platinum electrodes

$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2$$

The voltage used is between 5 and 7 V (theor.: 2.1 V) and the current density between 0.5 and 1 A/cm<sup>2</sup>.

Graphite or lead cathodes and platinum anodes are used.

So, industrially preparations of these peroxides are also very important. And today we just finish that particular part by knowing how we can synthesize alkali peroxodisulfate. So, this peroxodisulfate so is a very simple one compared to that of your hydrogen peroxide and sodium peroxide or any other peroxide species like barium peroxide, this can also be electrochemically produced. Earlier we have seen the different techniques for making hydrogen peroxide, and also they are corresponding different salts like sodium peroxide or potassium peroxide. So, in this particular case, how we do that we simply go for electrochemical oxidation from solutions of sulfuric acid and ammonium sulfate on platinum electrodes.

So, electrochemical production of these basically giving rise to the reaction of ammonium sulfate, one is to one reaction between ammonium sulfate and  $H_2SO_4$ , giving you diammonium persulfate or diammonium peroxodisulfate formation that means, we are basically introducing the peroxy linkage between the two similar fragments of  $SO_3$  that we will see afterwards also that how we can have these. So, one hand you can have the  $SO_3$  unit and other hand you can have another  $SO_3$  unit, and in between you have the O linkage so that basically gives us the production of ammonium peroxodisulfate or ammonium persulfate.

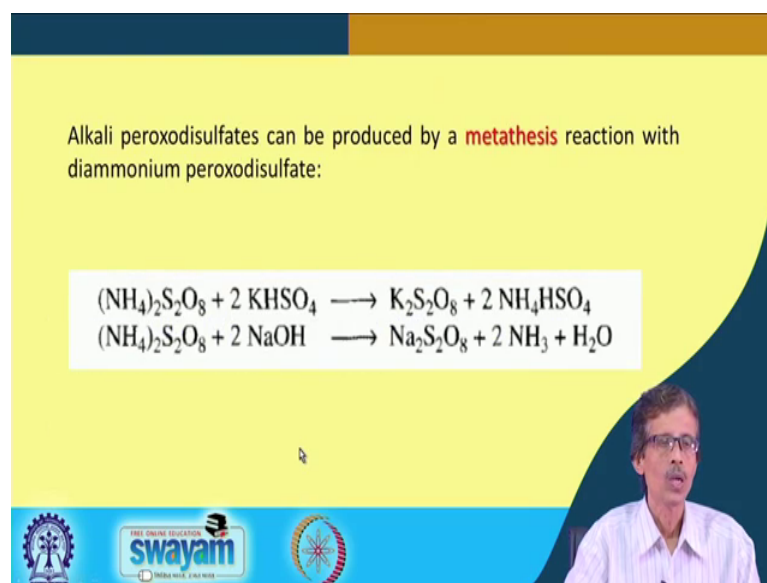
And for this particular case also, the voltage window for this is 5 to 7 volt, because theoretically we can use it to 2.1 volt; but for over voltage we have to cross that particular limit, and we can go up to 5 to 7 volt. And with the current density between 0.5 to 1 ampere per centimeter square is useful for this production. So, based on these electrochemical parameters for say certain type of electrochemical transformation, that we know, simply for different types of oxidation or reduction reactions by using a constant potential coulometric oxidation or coulometric reduction.

Here also we fix the potential, and corresponding amount of current which will be passed through the reaction medium or the electrochemical cell also can be controlled. So, this basically gives us some idea that how quickly we can get the production of that alkali peroxodisulfate, because this is a very neat and clean reaction; because only product we can have, because hydrogen is also produced there. And what are the types of electrodes we can use for this particular purpose. So, graphite or lead cathodes we can use for reduction and platinum for the oxidation.

So, platinum anodes and graphite and lead cathodes are very much useful for the production of a very important, industrially important material based on peroxides, because we will see also the production of these important peroxide compounds are very useful and we will also see what are the areas, where we can use those material for our other purpose.

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Alkali peroxodisulfates can be produced by a **metathesis** reaction with diammonium peroxodisulfate:

$$\begin{aligned}(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2 \text{KHSO}_4 &\longrightarrow \text{K}_2\text{S}_2\text{O}_8 + 2 \text{NH}_4\text{HSO}_4 \\(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2 \text{NaOH} &\longrightarrow \text{Na}_2\text{S}_2\text{O}_8 + 2 \text{NH}_3 + \text{H}_2\text{O}\end{aligned}$$
The slide features a yellow background with a dark blue header and footer. The text explains that alkali peroxodisulfates are produced via a metathesis reaction with diammonium peroxodisulfate. Two chemical equations are shown in a white box. The first equation shows the reaction of diammonium peroxodisulfate with potassium bisulfate to produce potassium peroxodisulfate and ammonium bisulfate. The second equation shows the reaction of diammonium peroxodisulfate with sodium hydroxide to produce sodium peroxodisulfate, ammonia, and water. The Swayam logo and other institutional icons are visible at the bottom.

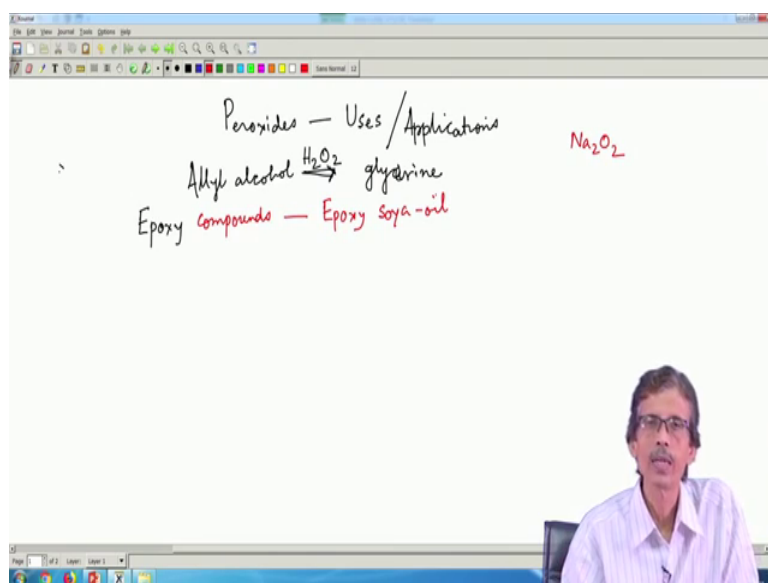
So, from that ammonium perdisulfate or ammonium peroxodisulfate; if we want to make the corresponding potassium and sodium salt, how we can do that because by making these from electrochemical oxidation we have to go for the corresponding substitution of this ammonium ions by potassium, ions and ammonium ions; again by sodium ions for the production of that particular potassium perdisulfate and sodium perdisulfate.

So, for these particular reactions we simply go for wet chemical synthesis, and that particular reaction is known as the metathesis reaction. So, in that particular metathesis reaction, what we can use is that, that same diammonium peroxodisulfate is used and which can be substituted that means, the cation metathetic reaction or cation metathesis can be achieved by use of instead of giving one other potassium salt, like potassium chloride or potassium nitrate. We have to use something, which is common having some common anion to the potassium ion that means, the potassium bisulfate salts.

So, potassium bisulfate salt producing your  $\text{K}_2\text{S}_2\text{O}_8$  and the corresponding other part will be ammonium bisulfate formation. Similarly, in case of this particular part of a sodium perdisulfate preparation; industrially important sodium salt, because sometimes we can see we cannot use the corresponding potassium salt, we have to use the corresponding sodium salt; because of your some other reactivity pattern or solubility pattern as well as some other into a introduction of the corresponding ions.

So, the alkaline medium, so medium is highly alkaline with respect to sodium hydroxide and with respect to that sodium hydroxide what we can use that the same ammonium perdisulfate metathetically, now produce  $\text{Na}_2\text{S}_2\text{O}_8$  with the liberation of ammonia now and water, basically what we are having in the medium is the corresponding ammonium hydroxide. So, these particular thing that means, the preparation from your any sodium or potassium salt of peroxide, like that of your hydrogen peroxide also and perdisulfate. Now, we will see what are their uses basically, in terms of their application. So, these applications what we will see now is that different peroxides.

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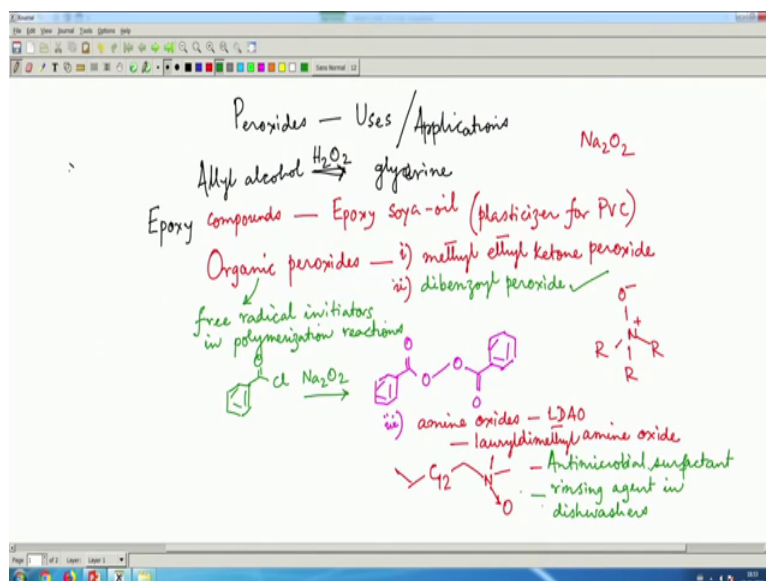


So, we have peroxides in our hand and uses as well as applications, what we can see for them. So, what we can get that if we have any substrate like allyl alcohol, and if we go for the corresponding oxidation of these by simple hydrogen peroxide. So, hydrogen peroxide can oxidize these two the production of glycerin. So, the glycerin production will be dependent on your this particular thing that where you can have this formation of this glycerin.

So, this allyl alcohol can be oxidized by hydrogen peroxide, similarly if we can have some reaction, where the epoxy compounds, we know that the epoxy resins are there. So, epoxy compounds can be prepared very easily with the use of this reaction from your sodium peroxide or hydrogen peroxide.

So, another alternative chemical which can be industrially prepared in a large amount is their sodium peroxide. So, making this epoxide compound is one of them is your epoxy soya-oil, which is epoxy soya-oil that oil instead of hydrogenated; you can go for the corresponding epoxide formation. So, this epoxides soya-oil is useful for plasticizer for making polyvinyl chloride.

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So, one of the important thing is that we can use these for a plasticizing material for PVC production, then we can use this particular one; that means, whether we can have this  $H_2O_2$  or  $Na_2O_2$ , we get these for so we can have the epoxidation of the typical soya-oil for making some plasticizers. So, if we can have these organic peroxides, so organic peroxides what we can get that organic peroxides; we can make it such as examples are plenty, one such is methyl ethyl ketone peroxide, methyl ethyl ketone peroxide or we can have the second one as the dibenzoyl peroxide, because these are very important compound from industrial point of view as well as for the laboratory purpose.

We can use these as very good free radical initiators in polymerization. So, both these organic peroxides are very useful for our free radical generation, which can initiate some polymerization reactions. So, free radical initiators in polymerization reactions. So, in all these cases, what we can have that if we just use to get this reaction on benzyl chloride, this benzyl chloride when reacts with sodium peroxide  $Na_2O_2$ , we get basically this dibenzoyl peroxide.

So, this dibenzoyl peroxide formation from there is also very useful which gives us O O O O. So, this peroxy linkage can be introduced within this molecule such that which can be a typical organic derivative of your hydrogen peroxide or sodium peroxide. In a similar fashion, we can also use these examples the third example.

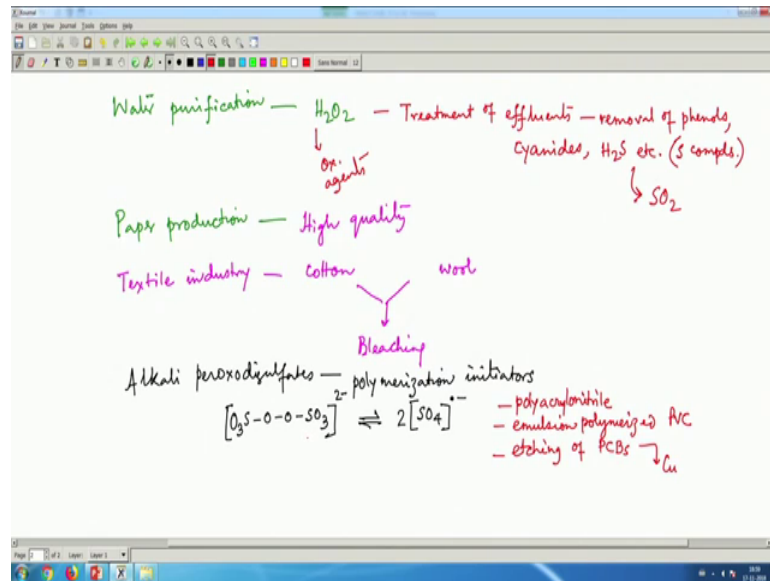
The third example is useful in terms of the production of corresponding amine oxides, because amine oxides are very useful. So, if we can have amine function, like R R R; if R is methyl or R is ethyl, we can have the tri-methyl or tri-ethyl amine and if we get these as oxide which can also be sometimes very much useful material.

So, the production of these amine oxides are also dependent on the availability of other peroxy compounds in large scale. So, one such example is the preparation of your L D A O o which is nothing but Lauryl Dimethyl Lauryl Dimethyl Amine Oxide. So, formation of these, which has a linear chain of C 12. So, this linear chain of C 12. So, it is a long chain. So, it is a lauryl group C 12 and which is attached to this particular nitrogen having two methyl groups attached to it.

So, dimethyl lauryl function and then this nitrogen like that of your N oxide formation or you have a charge separation, nitrogen having positive charge and oxygen as a negative charge. So, this has some very useful application for this preparation of making this amine oxide, because these are antimicrobial surfactants. So, antimicrobial surfactant where we use this, we use them in the typical dishwashers. So, where this particular one is the final rinsing agent is the final rinsing agent in our dishwashers.

Nowadays we use very much this dishwasher. So, the melting anti microbial surfactant which have some protection on ecoli or other bacteria, and which gives rise to some detergent type of activities is a special class of detergent making, which is also dependent on our use of this particular in oxide formation. So, what we get therefore, that in this particular case we get this as other applications like that of your paper production or water purification.

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In case of water purification as well as paper production, we use them very much, because the  $H_2O_2$  consumption will be dependent for purification of that particular water and we can have the corresponding water purification, because we can treat that also the effluent of the water. So, we can use them as for the treatment of effluents. So, what you can use the treatment problem, because this particular one that  $H_2O_2$  is the typical oxidizing agents, and which can oxidized all these things.

So, during this effluent treatment we can use the hydrogen peroxide for removal of phenols of that means, the oxidation of the phenols which can be achieved; further oxidation of the phenol which can be achieved with the use of hydrogen peroxides. Then removal of cyanides through cyanide formation, and the sulfur compounds like  $H_2S$ ,  $H_2S$  etcetera that means, all different types of sulfur compound.

And if they are converted to sulfur dioxide through this mechanism, so these contamination from  $H_2S$  or any other sulfur compounds can be removed and during the production of this paper. So, we can achieve this for making high quality papers production, also we can use them for textile industry in that case is the textile industry can have the cotton or wool they use; cotton or wool they use and those can be treated for bleaching. So, bleaching action of these peroxides can also be useful, when we use these in the textile industry.

Now, we will see how we can use the typical alkali peroxodisulfates. So, just now we have seen that the preparation of these alkali peroxodisulfates. So, alkali peroxodisulfates they are used in making all the different types of reactions, particularly they are using for polymerization initiators, polymerization initiators. How they can do? So, these alkali peroxodisulfate just now what we have seen that is  $S_2O_8^{2-}$  having two peroxy a one peroxy linkage, then  $SO_4^{2-}$  with a two negative charge, overall two negative charge on the species which can go for your typical sulfate based free radical production.

So,  $S_2O_8^{2-}$ . So, this can be useful for your polymerization initiators for the production of our polyacrylonitrile. So, they can be used for making polyacrylonitrile, is full for making polyacrylonitrile, Then emulsion polymerize PVC polymerized PVC and then lastly etching reaction, etching of printed circuit boards in electronic industry.

So, etching of PVC is in their printed circuit boards in electronic industry can be achieved, because we know that these printed circuit boards has copper, copper deposition the copper metallic deposition on it. So, etching of those copper in the printed circuit boards can be achieved through the use of these alkali peroxodisulfates. So, what we can see now is that, this particular one for the formation of these.

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**Nitrogen and Nitrogen Compounds**

**Ammonia**

It is an important primary inorganic material. 85% of the worldwide production is utilized in the manufacture of synthetic fertilizers.

There are numerous large-scale ammonia production plants worldwide, producing a total of 131 million tonnes of nitrogen (equivalent to 159 million tonnes of ammonia) in 2010.

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Now, we just move on to the other species that are our nitrogen and nitrogen based compounds. So, these nitrogen based compounds when we talk about is the first one what we will be talking, in this particular segment of the class is the typical ammonia;



what we all know that the production of ammonia is always a real challenging task to and inorganic chemists, because it is the most important primary inorganic compound 80 percent of the worldwide production is utilized in the manufacture of synthetic fertilizers.

So, inorganic chemical based fertilizer which can be produced based on the production of large amount of ammonia in the system. So, this ammonia production because the biochemically as we all know, it can be fixed from the air nitrogen from the air that we have seen our previous classes, we have discussed also little bit in our previous classes; but for making synthetic fertilizer while we are talking about the production of hydrogen,  $H_2$  formation or  $H_2$  production that  $H_2$  if we can utilize that particular  $H_2$  for the reaction with the  $N_2$  available in air, we get the corresponding formation of ammonia through Haber's process.

So, for making this for the synthetic fertilizers, what we can use that we have to use this particular nitrogen as well as hydrogen for making ammonia. And for industrial point of view we should have a large scale ammonia production plants in throughout the world. We know that there are numerous large scale such production plants producing a total of a data of around 2010, tells us that a total amount of 131 million tonnes of nitrogen can be consumed on can be utilized for the production of equivalent amount, which is equal to 159 million tonnes of ammonia, so that is the very good achievement that how we can utilize is the nitrogen.

So, nitrogen is required for your fertilizer, nitrogen is required for our protein molecules, and nitrogen is required for our food material also; but it is not so easy task for us to get those nitrogen molecules from air to be fixed in fertilizer or in food material or in some proteins. So, making these ammonia particularly useful tasks for this particular case, where we can have this industrial production.

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Modern ammonia-producing plant first converts natural gas (i.e., methane) or LPG (liquefied petroleum gases such as propane and butane) or petroleum naphtha into gaseous hydrogen.

$H_2$  is then combined with  $N_2$  to produce  $NH_3$  via the Haber-Bosch process.

At 150–250 atm and between 400–500 °C, the gases (nitrogen and hydrogen) are passed over four beds of catalyst, with cooling between each pass to maintain a reasonable equilibrium constant.

On each pass only about 15% conversion occurs, unreacted gases are then recycled, and eventually an overall conversion of 97% is achieved.

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So, the modern ammonia producing plant basically first converts the natural gas that is methane, we have seen that we can have the coal bed methane also. So, methane from that particular methane, we have to extract the corresponding amount of hydrogen, and that hydrogen can be utilized for its reaction with the nitrogen. So, natural gas LPG petroleum naphtha can be utilized for the production of large amount of hydrogen that we have seen also in case of hydrogen production.

So, this hydrogen then combined with nitrogen producing ammonia via the Haber-Bosch process. And is basically a reaction condition can be set up from optimizing so many parameters is that at 150 to 250 atmospheric pressure and between 400 to 500 degree centigrade the two gases, both of them are ideally inert one that combination of nitrogen and hydrogen.

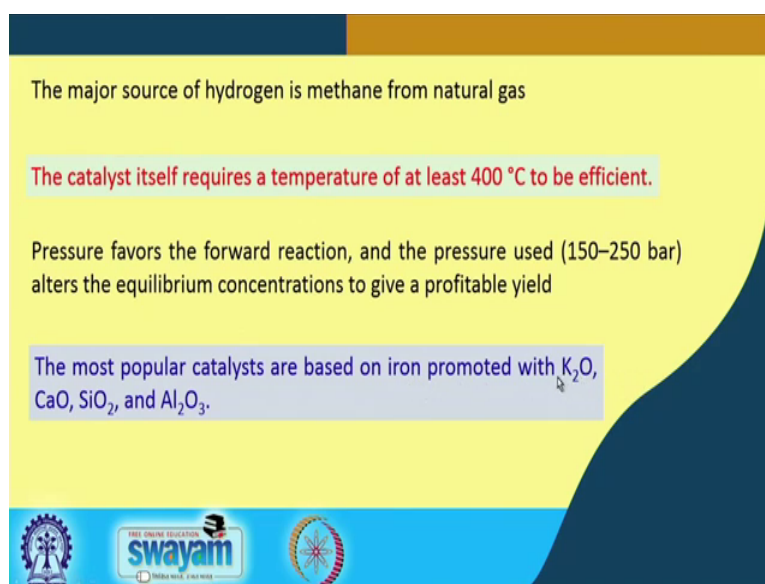
How we can utilize this particular reaction which is not so easily achieved; where biochemically the nitrogenases can do that particular one very easily at room temperature or at atmospheric temperature atmospheric pressure; but here we use the more drastic condition for achieve that particular conversion, where we can have four beds of catalysts.

So, catalysts are very useful for this particular case for conversion of these particular gaseous reactions, with cooling between each pass to maintain a reasonable equilibrium constant such that equilibrium constants should be favourable such that large amount of

ammonia can be produced and the conversion rate is also should be very high, but in some cases in each pass only about 15 percent conversion can be achieved.

And what we can have the unreacted gases, the two gases the unreacted nitrogen and the hydrogen gases can be recycled. So, the mechanism for recycling process should also be there for the industrial production of ammonia. And if we go for the stepwise this business, for the four beds of catalyst utilization of four beds of catalyst as well as the recycling process and that particular recycling process will be very useful such that in a stepwise manner ultimately a very high conversion rate can be achieved, which we can see from here.

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The major source of hydrogen is methane from natural gas

The catalyst itself requires a temperature of at least 400 °C to be efficient.

Pressure favors the forward reaction, and the pressure used (150–250 bar) alters the equilibrium concentrations to give a profitable yield

The most popular catalysts are based on iron promoted with  $K_2O$ ,  $CaO$ ,  $SiO_2$ , and  $Al_2O_3$ .

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Now, from our transparency that is 97 percent of that particular conversion can be achieved, but thing is that the major source of hydrogen what we are achieving it is from the natural gas, and catalyst itself requires a temperature of at least 400 degree centigrade, because below this particular temperature the reaction is not very much favorable.

And the high pressure of these two gases, also favors the forward reaction that is why we are utilizing a pressure of 150 to 250 bar, which basically alters the equilibrium towards the right hand side towards the product side which can give a profitable yield, because the energy consumption the prices of those gases, the catalyst and all other manpower, and all these things should be favorable such that we can get something which is very

much cost effective, because cost always playing to very important role, when we talk in terms of the industrial production of some material or some compound like ammonia.

Because these chemical basically play a significant role to the economics of a particular country and we can see, because we are not studying much about the thing what we can study as the corresponding chemical economics. So, the little bit of economics and the profitability of the production, and the high yield of that particular conversion is always the major guiding factors for using this thing and a very high rate of conversion towards the product side.

So, what are those catalyst, is the most popular one and most ah used one is the catalyst which are basically some iron. So, based on iron that we will see in our next class that how these iron catalyst can be prepared, and these iron promoted that means, irons can be supported on simple potassium oxide, calcium oxides, so several oxides. Several oxides like these  $K_2O$ ,  $CaO$ , silicon dioxide or alumina. These are basically supports, which are enhancing and which are increasing the corresponding surface area of the catalyst such that gas can come and adsorbed on those surfaces.

And it is contact for those things will be increased. So, by increasing the surface area that means, we required a supported catalyst for the reaction of all these conversion reaction between these two gases like that of your hydrogen and nitrogen for the production of your ammonia. So, next class we will see how we utilize these particular catalyst for the production of our ammonia and other useful nitrogen compounds.

Thank you very much.