

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

Lecture – 06
Hydrogen

Hello welcome back to this class, where we are talking about Hydrogen. So, how we can utilize the corresponding production of hydrogen that we have seen. And we have seen that the electrolysis is the most important and the most viable technique, where electrolysis of water can give rise to the production of large amount of hydrogen. And this hydrogen can be utilized for different purposes and how we can categorize the application of this hydrogen that we now see.

(Refer Slide Time: 00:51)

Hydrogen Applications

1. ammonia production
2. methanol reforming
3. refinery processes
4. food (fats and oils)
5. metal refining
6. electronics industry
7. miscellaneous

Hydrogen is marketed as a gas or a liquid

H₂-transport:
as a gas in gas cylinders or pipelines
as a liquid in pressurized cryogenic containers
as a solid in the form of hydrides

So, the application of these different things is that, as I told you that it can be utilized for ammonia production. How as we have seen that if we can have a good source of CNG or source of methane. So, we can break that methane molecule or we can oxidize that methane molecule for the production of hydrogen, because the amount of nitrogen available from nature; that means, from atmosphere is plenty.

We can have huge amount of nitrogen in our hand, but we cannot convert it nicely for the production of ammonia as well as production of urea or any other ammonium based fertilizers such as ammonium nitrate.

Because we all know that bacteria through their hydrogenases can fix nitrogen directly into the corresponding leguminous plants and those bacteria had some nitrogenases, where that nitrogen can be reduced very easily through some other different reactions.

So, this reduction of nitrogen is a difficult task because the reduction of nitrogen; that means, N_2 molecule as we all know; that N_2 molecule is basically the triple bonded. Nitrogen is triple bonded to the second nitrogen and during the production of ammonia we get 2 molecules of ammonia from 1 molecule of nitrogen. Through the addition of 6 hydrogen and 6 electron; that means, 6 protons and 6 electron.

So, nitrogen is basically go for multiple number of electron transfer to the nitrogen molecule along with the corresponding transfer of H plus ions; that means, the protons. So, in essence what we can give if we can supply 6 number of electrons and 6 protons to the nitrogen molecule. Basically we are supplying 3 hydrogen molecules.

So, nitrogen when react with 3 hydrogen molecule give us the corresponding production of ammonia. So, industrially important technique; that means, we all know that the other process that we will discuss once again when we talk about the corresponding nitrogen based industrially important inorganic compounds.

We see again how we can use the corresponding techniques for the production of ammonia through the production of hydrogen. So, if we can have the electrolysis process or the coke or coal bonding process when we produce hydrogen.

So, production of hydrogen as gas is also directly related to the industry important other compound which is your ammonia. Then we can have hydrogen application for methanol reforming reaction, then refinery processes then one important aspect is food; that means, the food technology.

So, dairy technology and all other cases if we can have fats and oils as we all know; that there are large number of unsaturations. So, unsaturations if we can go for saturation; that means, the hydrogenation. As we all know that the vegetable oil which is the oil.

So, that particular oil if we can go for hydrogenation, which we call as the vanaspati. So, or is a trade name was there earlier we know as the it as a dalda. So, vanaspati we get through hydrogenation of those corresponding vegetable oils.

So, if your oil is edible oil and if we can go for hydrogenation, so this particular hydrogenation always require a high purity hydrogen that is why we require high purity hydrogen for our food material conversion starting from all these hydrogenated product; that means, making dalda making margarine. Nowadays we are using very much amount of that margarine.

So, margarine is also useful for going for hydrogenation utilizing a catalytic hydrogenation process using some catalysts. Then fats are also produced through hydrogenation. So, for this purpose we require good amount of hydrogen, which is of high purity. So, starting from our hydrogen as well we can utilize them as for food material. Then metal refining how it is utilized for metal refining, the name itself tells us that hydrogen can be useful for metal refining in terms of it is reduction.

So, not only this particular one for your metal refining process, but also sometimes we can use it for the different hydrides production that calcium hydride products, and the titanium hydride products, and the sodium hydride production.

So, not only metal refining as well as the corresponding metal hydride production is also dependent on the hydrogen. Then different electronics industry because the different electronics industries also utilizing hydrogen; that hydrogen for removal of some of these surfaces or for getting the clean surfaces and different miscellaneous techniques can be utilized for hydrogen applications.

So, when we can have hydrogen in the market as a gas or a liquid what we can get it as a corresponding hydrogen in cylinder or a direct supply of hydrogen from the source, where hydrogen is getting produced as a gas. So, either it is liquefied or as gas we can directly use if we can use say, for the hydrogenation reaction sometimes this hydrogenation reactions are taking place at some partial pressure of hydrogen at higher partial pressure compared to our atmospheric pressure of hydrogen in presence of some catalyst say Raney nickel.

Finally divided nickel particles known as Raney nickel are very much useful for the production of some hydrogenated material. Simple hydrogenation reactions laboratory important hydrogenation reactions or conversion of nitro group to the amine function can also be utilized for the use of our hydrogen gas.

So, if we can have hydrogen in gas or as liquid. So, transport of hydrogen would be a difficult task so as a gas it can be transported by cylinders or in pipelines or as a liquid in pressurized cryogenic cylinders, because at cryogenic means at a low temperature we have to go for pressurized liquefaction of these or as a solid in the form of hydrides. Just now as we have seen that it can go for the corresponding hydrides, the different metal hydrides which are sometimes not of stoichiometric type.

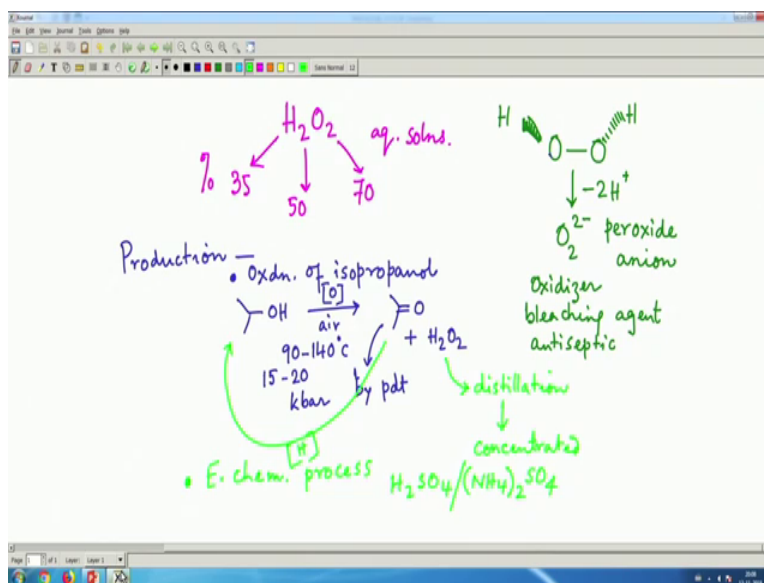
So, you can have some extra hydrogen over there and those hydrides can be utilized for getting hydrogen directly from those materials. Similarly, nowadays people are talking about some solid materials the metal oxides or some metal ox frameworks or metal organic frameworks the mofs we call. So, those mofs are also utilized for gas absorption and people are also working on it different laboratories are also working on it how good those mofs are in storing hydrogen gases.

Because if the solid material the mofs the metal organic frameworks because you can have the extended ligand framework which are coordinated to the metal ions. So, those big structures indefinite structures sometimes or the metal ion polymers coordination polymers we call, they can have some void spaces in between and those void spaces are utilized for storing hydrogen gas. And storing of that particular hydrogen gas is important because at low temperature or at room temperature it can store hydrogen, but at elevated temperature it can leave those hydrogen which is stored.

So, these solid material can be transported nicely instead of carrying those gas cylinders or the liquid cylinders in the compressed form. We can take those solid materials for getting those hydrogen for some useful purposes.

So, next we will go for some of these important compounds where we can see that how this particular material can be utilized for other cases. Now we talked about the corresponding important compound after water and after water and hydrogen.

(Refer Slide Time: 10:41)



We will talk about H_2O_2 , the hydrogen peroxide; which is a very useful material what can be utilized and in different amount or different forms it is available in the market in terms of its percentage.

So, it is available as 35 percent variety or 50 percent variety or a 70 percent variety in aqueous solutions. So, these aqueous solutions of all these materials are useful for your thing for the molecule which is very important from the chemistry point of view, because it has a typical shape of this and it is basically utilized for this which can give rise to if we can take out $2H$ plus O_2^{2-} minus which is the peroxide anion.

So, we will see how this can be utilized because it has used very useful applications as oxidizer, as bleaching agent or as antiseptic. So, what do you see now that how we can use this particular production; that means, how we can go for production of hydrogen peroxide, because this particular molecule is different completely different from your water molecule or hydrogen molecule, because it has a typically book safe structure because this OO is in one plane.

And these OH bond is a different plane and the other OH bond is present also in a different plane.

So, one such process where we can get the production of hydrogen peroxide is the oxidation of isopropanol oxidation of isopropanol, where we can utilize the

corresponding oxidation of this so how we can oxidize this. So, we go for oxidation and it is the oxygen of the air, and that oxygen of the air can be utilized for the corresponding oxidation of isopropanol to acetone plus H_2O .

So, this particular thing can be formed along with this acetone as the corresponding by product, and this reaction is achieved at a higher temperature of 90 to 140 degree centigrade and a higher pressure also which is 5 to 20 kilo bar. And this hydrogen peroxide which is formed which can be utilized that can be taken away and if we can take out and the different amount of these; that means, 35 percent 50 percent and 70 percent, excuse me is formed.

So, in a very dilute solution it is produced there and this dilute form what we can get and this dilute form therefore, can be taken away through distillation. And once it is out through distillation we can go for concentration. So, it is therefore, concentrated to increase its concentration from say 20 percent to 70 percent which is available in the market.

So, concentrated hydrogen peroxide can be produced from isopropanol and this particular one; that means, the acetone which is obtained as by product can be recycled back to your isopropanol production through simple hydrogenation through reduction. Through hydrogenation or reduction, it can be produced back and then that cycle can be recycled.

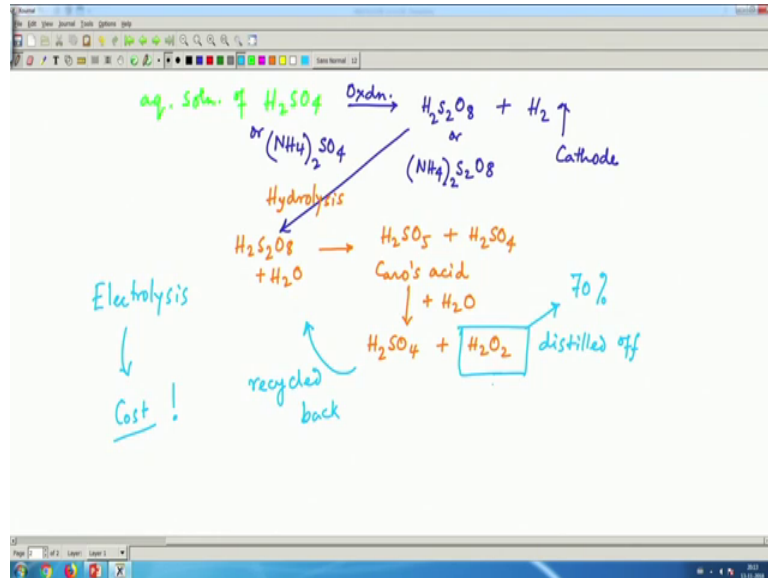
So, this particular recycling process will be there therefore, we can have the second process, and this particular second process what can be utilized like that of our production of hydrogen. What we have seen in our previous class that the corresponding oxidation and the reduction in 2 electrons of water molecule. Therefore, we can have the electrochemical process.

So, E chem process, that E chem process or electrochemical process can be utilized for the oxidation of say simple H_2SO_4 or its corresponding ammonium salt.

So, ammonium salt of this ammonium will correspond to ammonium salt of sulfuric acid ammonium sulfate. So, electrolysis or the electrochemical oxidation of sulfuric acid or ammonium sulfate can give rise to the production of hydrogen peroxide, how we get

this? So, we can have this; that means, we can have the aqua solution aqua solution of sulfuric acid or ammonium sulfate.

(Refer Slide Time: 17:21)



So, this aqua solution of sulfuric acid when we can go for it is oxidation. So, we can have oxidation or just now what we have seen that corresponding salt; that means, your ammonium sulfate can also be useful.

So, what we get therefore, that we can get the corresponding part sulfate production $H_2S_2O_8$ production plus hydrogen which is released at cathode. So, these or if we have this we get it the corresponding ammonium salt. So, ammonium part di sulfate so ammonium S_2O_8 ammonium part di sulfate. So, if we then go for hydrolysis of this. So, hydrolysis of this will give you the corresponding one; that means, your $H_2S_2O_8$ as we have seen hydrolysis means we have to trap water the lyses means the breaking down.

So, hydrolysis; that means, these utilizing water for breaking up of this material for H_2SO_5 plus H_2SO_4 back. So, this is known as Caro's acid per sulfuric acid, we call it as a part sulfuric acid so; that means, that part group has been introduced within the sulfuric acid framework. So, when this is utilized for the reaction with H_2O it is giving us back our H_2SO_4 plus H_2O_2 .

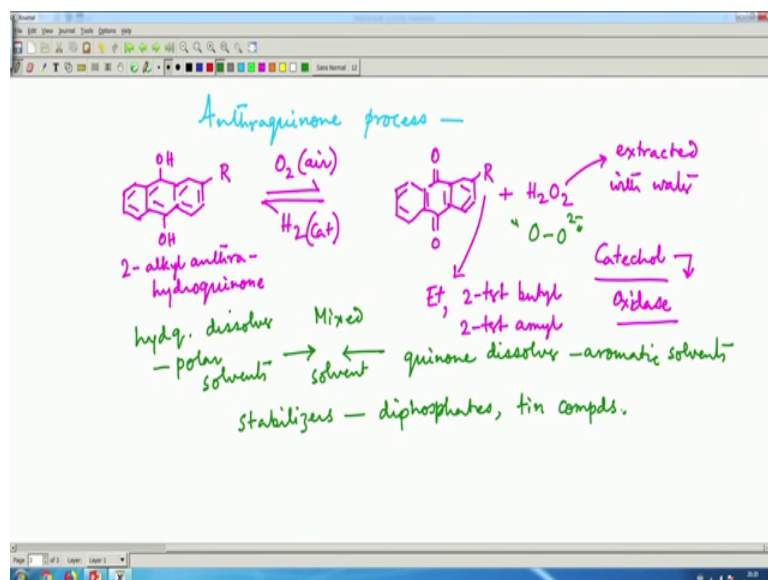
So, this particular one; that means, this H₂O₂ is utilized this H₂O₂ is being utilized. So, it can then be it is in the reaction medium it can be distilled off and the total yield can go up to 70 percent, it is a very useful technique where this can be utilized for the production of hydrogen peroxide.

And the sulfuric acid what is produced that can be consumed for some other purpose or it can be recycled back to this particular aqua solution of sulfuric acid what we have seen for this oxidation so it can be recycled back.

So, we go for electrolysis so electrolysis we can have and that electrolysis is definitely if the corresponding thing; that means, the cost. So, cost of the electricity is therefore, the guiding factor for us whether the produced hydrogen peroxide is cheaper to us or not that will be dictated by the corresponding cost of the electricity.

So, the countries where we can have very good availability of electricity and the electricity is also cheaper they can afford this particular technique for the production of hydrogen peroxide in this particular electrochemical technique. Then we just see that you can go for the corresponding one for the production in a different way; that means, the corresponding one is our Anthraquinone technique.

(Refer Slide Time: 21:53)



So, Anthraquinone process so this particular process can be utilized for the production of hydrogen peroxide, where substituted anthra hydroquinone which is this particular

molecule R is the substituted one. So, we can have so anthra hydroquinone 2 alkyl anthra hydroquinone which is oxidized by O₂ of air at 30 to 80 degree centigrade, and 5 bar pressure. So, this is the hydroquinone. So, what happens to it so it basically goes for it is corresponding quinone formation.

So, this is the corresponding quinone backbone and with the other part still there with R over here and this is also so this quinone is forming. So, 2 alkyl anthraquinone so this is also 2 alkyl anthraquinone is forming. So, that 2 alkyl anthraquinone when it is forming it is giving us also the production of hydrogen peroxide. So, this hydrogen peroxide is then extracted with water.

So, we get this so this particular one when we not only produce this one because it is a very useful technique and biochemical. It is also very useful one because we know that catechol is there everywhere from biological world to different other cases also. And this catechol is if it is getting oxidized we get this particular type of quinone.

If these 2 hydroxy groups are in ortho positions, we get ortho quinone. So, this particular one can undergo always with some oxidize reaction using oxidize. So, catechol oxidize is in biological world, these catechol oxidize is also available for the conversion of this particular catechol molecules to quinone molecules, even our skin color what we know that skin color is due to the formation of the melanin.

So, that particular melanin formation is also dependent on the activity of the catechol which is the catalyst. So, this particular reaction for the production of hydrogen peroxide if we can go for a catalytic one; that means, if it is hydrogenation is feasible; that means, the quinone can be hydrogenated back to the hydroquinone; it can be a very useful technique for the production of hydrogen peroxide from industrial point of view.

So, this R this R can be of some typical substitutions it can be ethyl it can be 2 tertiary butyl or 2 tertiary amyl. These are the most commonly used material which can be utilized for your production.

So, we can have the different solvent medium; that means, the quinone and hydroquinone can have different solubility. So, we can have at one end this particular one the quinone dissolver, quinone dissolver and other one we can have a hydroquinone dissolver.

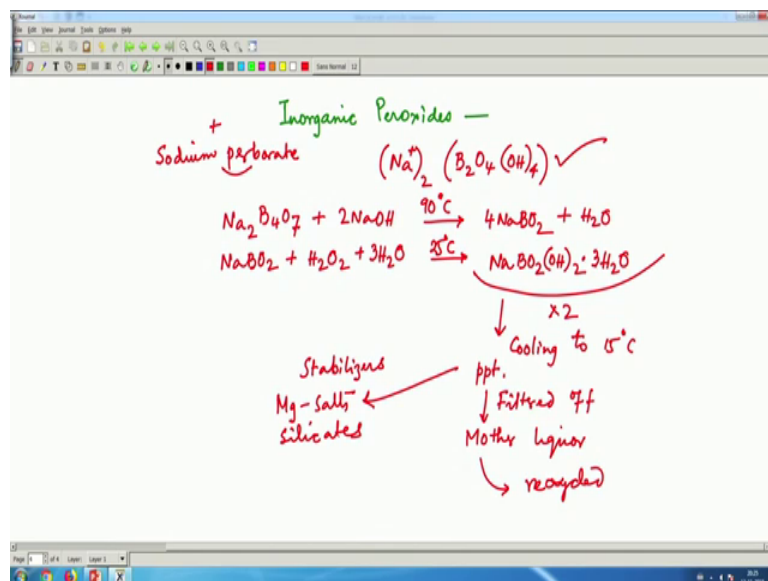
So, if there is a very difference in all these things because the hydroquinone dissolvers are basically the polar solvents and these are other aromatic solvents or sometime some mixture of aromatic solvents.

So, these can go for we can go for therefore, the mixture of these 2 to get a uniform solvent medium for the production of this hydrogen peroxide. So, this uniform solvent medium can be utilized for the production of this hydrogen peroxide can be known as your solvent mixture or the mixed solvent. So, in a mixed solvent medium we can have this, and lastly we can see that this particular hydrogen peroxide.

When we store it in bottle and we supply for some other purposes it can supply with stabilizers. We stabilizes this peroxide bond because the peroxides all have this O bond O 2 minus basically so we have the O peroxide bond.

So, this peroxide bond is not so stable so it immediately breaks into water molecules and this particular one can be stabilized by addition of some stabilizers and those are some also again some inorganic compounds. So, that has also some potential market from industrial point of view that some di phosphates and several tin compounds are useful stabilizer for stabilizing these peroxides as the corresponding compound as only simple hydrogen peroxides.

(Refer Slide Time: 28:45)



So, this also we can see for the different peroxides so inorganic peroxides. So, since we are talking about industrial inorganic chemistry so it will be fascinating to know about the different inorganic compounds which are different peroxides so inorganic peroxides, so inorganic peroxides which can be utilized for the production of different organic peroxides also.

So, this can be utilized for different reactions. So, one such is known as sodium perborate commonly known as sodium perborate. So, when name tells us that we are talking about some per thing; that means, it has some per borate; that means, peroxide structure is there and peroxide compound, it is on borate base and sodium is basically present as a cation.

So, if we say that this is Na^+ and 2 such Na^+ is there for stabilized a compound which is $\text{B}_2\text{O}_4\text{O}^-\text{H}^-$ whole 4 , which is nothing but sodium perborate or sodium permetaborate.

So, it can be obtained from borax $\text{Na}_2\text{B}_4\text{O}_7$. When it reacts with sodium hydroxide at 90°C it gives sodium metaborate NaBO_2 plus H_2O and this sodium metaborate NaBO_2 , when reacts with hydrogen peroxide that is the way how we can introduce introduce that peroxide linkage to sodium metaborate.

This when reacts with 3 molecules of water at 25°C we get $\text{NaBO}_2\text{O}^-\text{H}^-$ whole 2 is half of this formula along with sometimes we write 3 water of (Refer Time 31.28) and actually we get double of it.

So, then we go for cooling to 15°C and that cooling to 15°C is basically responsible for precipitation, and that precipitate can be filtered off. So, we get the mother liquor back, which can be recycled.

So, if we get this. So, precipitate is basically giving us this compound which is that boron based peroxy compound or boron based inorganic peroxide. So, we have to add like that of our corresponding that hydrogen peroxide H_2O_2 , we have to add the stabilizer here also and these stabilizers are magnesium salts and some silicates.

So, this basically gives us some idea how we can have some inorganic peroxide which is very much important to understand and important to know also because this can have a very useful structure.

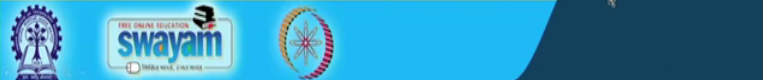
(Refer Slide Time: 33:09)

Sodium perborate (more correctly sodium peroxoborate)

$$\text{Na}_2 \left[\begin{array}{c} \text{HO} \quad \text{O} - \text{O} \quad \text{OH} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{B} \quad \quad \quad \text{B} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{HO} \quad \text{O} - \text{O} \quad \text{OH} \end{array} \right]$$

Sodium perborate production. **Step 1** : Formation of metaborate from borax and sodium hydroxide

Step 2: Reaction of metaborate with H_2O_2 forming perborate, which is then filtered off from the cooled solution and dried



Because sodium perborate can have a useful structure where we can have this particular peroxy linkage between these 2 boron centres, and the actual structure is like this very interesting structure of this compound and as we have seen just now from the reactions that the step one comprises of the formation of the meta borate from borax and sodium hydroxide.

So, this is the first step where we can utilize meta borate to get from borax is the starting material because basically a mineral type of thing from boron with sodium hydroxide and step 2 is the metabolite is reacting with hydrogen peroxide and we cool the solution and we then precipitate out and then dried the material.

So, it as a typical peroxy linkage, so boron base peroxy compound, so if we can utilize for the different peroxide formation organic peroxide formation on any other reactions, such as free radical initiators or the polymerization we can utilize this usefully for that purpose.

Thank you very much.