Industrial Inorganic Chemistry
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Lecture - 26
Electrochemical Fluorination, Sulfonyl Fluorides

Welcome back to this class where we are talking about the important fluorine base compounds. So, now we can move to another area where we can use the organic compounds.

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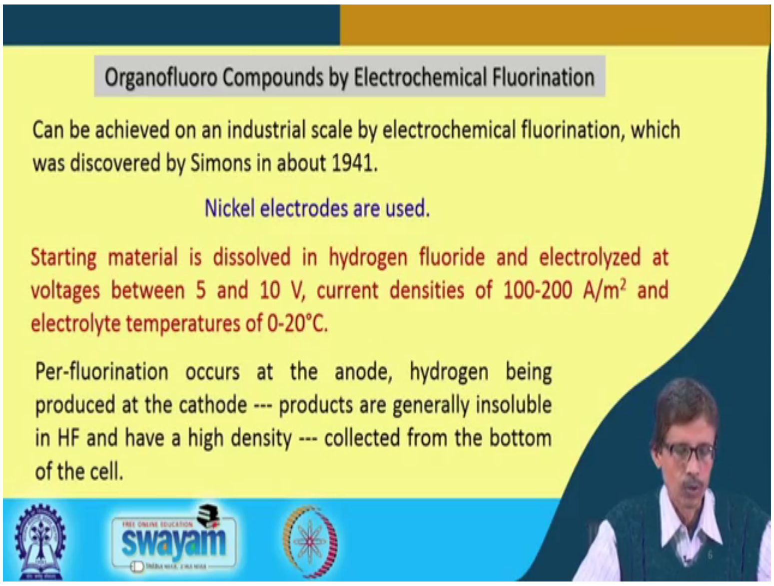

Organofluoro Compounds by Electrochemical Fluorination

Can be achieved on an industrial scale by electrochemical fluorination, which was discovered by Simons in about 1941.

Nickel electrodes are used.

Starting material is dissolved in hydrogen fluoride and electrolyzed at voltages between 5 and 10 V, current densities of 100-200 A/m^2 and electrolyte temperatures of 0-20°C.

Per-fluorination occurs at the anode, hydrogen being produced at the cathode --- products are generally insoluble in HF and have a high density --- collected from the bottom of the cell.

So, organofluoro compounds how we can get it? As we have seen that you can substitute the hydrogen atoms on the organic backbone. So, starting from your polymer to typical pharmaceutical compound where you can have the CH function and those CH functions, if you substitute by fluorine centre its property will change drastically from electronic property. That means, the fluorine is highly electronegative from the electronic property to all other properties will change. If you can go for its corresponding fluorine derivative and also physically it is also different.

As we know that typical polyethylene versus the corresponding material which we know as the Teflon. So, Teflon is the corresponding polyethylene type of molecule where you do not have any CH functionality in the polymeric backbone. So, what we find basically that this particular material will be useful for different industrial purposes. So, we can get some examples of making this organ of fluorine compound by electro chemical fluorination. So, you can take the help of electrolysis where the organic molecule will be fluorinated electrochemically. So, we get this industrial scale also for electrochemical fluorination is a typical technique basically and Simon and Simon et al first introduced in during 1941 also.

And it is still very much popular for making useful organofluorine compound through this particular process, where we use nickel electrodes. What are the type of electrodes you see? The nickel is a transition metal and is not so costly also. So, we can use a cheap nickel as the nickel electrode like that of your nickel crucibles we can have the nickel metal use as making of nickel crucible also. Similarly nickel can be utilised for making the nickel electrodes. When we will consider the industrial utilisation production of all these metals will again consider this particular aspect that how we can get.

Because very small amount of nickel will be utilized for making these electrodes, but these electrodes are useful for this particular electrochemical process. So, when you have the starting materials, what is the starting material? The starting material is nothing, but your substrate what you are taking for fluorination. That means, organic molecule where we try to do or intend to substitute some of the CH functions by CF functions so is dissolved in the original hydrofluoric acid is you should have to have to some medium because in that medium you can go for the electrolysis.

So, hydrogen fluoride medium that means the hydrogen fluoride acid medium is electrolysed at a voltage. This voltage window is also very big is only 5 to 10 volt. So, you see that we can have some battery operated thing also is not very much. So, at 5 to 10 volt and with the current density is also not much is 100 to 200 ampere per metre square an electrolyte temperature at room to less room to 0 degree centigrade, so, 0 to 20 degree centigrade. So, you see the conditions for the electrolysis or the electrochemical production of that particular organofluorine compound is very friendly one.

We are not having very adverse medium or very high voltage, very high current density or very high temperature, all are very reasonable. So, we can use it. So, that is why it has been popularized. It is also cost effective and people are using this particular process for fluorination reaction and the per fluorination that you can go for substitution of one hydrogen on the carbon centre by the fluorine and sometimes we consider that we can have a per fluoro compound that mean and all the CH functions have been substituted by fluorine centres.

So, it occurs at the anode basically and hydrogen being produced at the cathode. So, hydrogen is also a by-product for this particular electrolysis reaction because you are using hydro fluoric acid. So, hydro fluoric acid basically it gives you something you are not doing corresponding reaction of HF for the production of fluorine as well as hydrogen. But this particular electrolysis technique you see is very interesting and very helpful also in producing the organofluorine compound that instead of getting fluorine gas. So, in situ we can do that means we are not going for the production of fluorine gas.

Storing that fluorine gas in the cylinders and utilisation of that fluorine for the fluorination reaction of this organic molecule, but in situ this electro chemical techniques are very useful. That is why because this is the electron driven either you put electron or take out electron in the cathode or the anode. That will be useful for immediate or the direct fluorination of the organic compound as well as the corresponding reduction of the proton or the hydrogen ions from the hydro fluoric acid medium, for the production of useful hydrogen because hydrogen is also a value added material what you can produce simultaneously during this fluorination reaction.

So, what you get the products what is formed most of the time if we can consider this that is also very useful to consider also that you are starting material soluble in hydro fluorine acid or HF, but your product is insoluble in nature. So, that is very useful criteria for doing this particular electrolysis reaction that you check that your starting material. That means, the reagent what you are using for fluorination is soluble in HF, but your product the p if you considered as the product is your p which should be in soluble in HF and have a high density that means is a heavier one.

So, it is a heavier one and its fluorinated molecules are heavier than the starting material. So, it is collected from the bottom of the cell. So, it will be precipitated out in that particular medium. One condition is that it is insoluble in HF. So, it will try to separate out from the HF medium and since it is heavier it will only be settled down at the bottom of the electrolysis cells. So, you can have some exit pathway from the bottom of the electrolysis cell which we also consider that is corresponding tank basically like your water tank.

So, that tank has some outlet at the bottom and that outlet can give you the product very quickly and very easily and you can go for further purification of that particular material.

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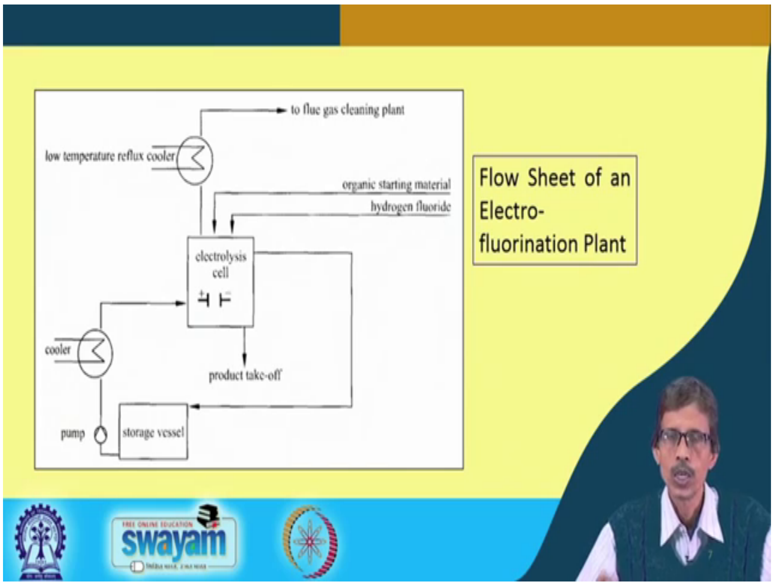

Flow Sheet of an Electro-fluorination Plant

So, we get that fluorinated compound very easily and basically what you get therefore that means, you can have the electrolysis cell in your hand. So, you have the electrolysis cell and you can have the anode and the cathode and basically some arrangement is there. That means, the electrolysis cell is the thermo stated as I told you that you can have a temperature range of 0 to 20 degree.

So, it should be thermo stated one depending upon its corresponding production of heat generated during the reaction. So, you can have this in this particular one. So, some storage vessels will be there and the product take off since I told you that you can have the corresponding path way from the bottom of the electrolysis cell. So, you put the organic starting material as I told you that you can put the organic stating material as and you get the product out of that.

So, product is p is going out from the path. So, from the top basically you add the starting material as well as hydrogen fluoride from that particular pathway. So, if you can have two channels on this electrolysis cell, electrolysis chamber or electrolysis reactor basically when you talk in terms of your industrial scale, it is basically the corresponding reactor is a huge one. The size is also increasing, increasing, increasing from your laboratory trail. So, this particular size is there.

So, you can get it. So, and during this process basically that you can have the corresponding cooler as well as sometime you can have the low temperature reflux cooler is also used because you have the flue gas cleaning plant, because you get the corresponding hydrogen and hydrogen is also some amount of HF can also be escaped out from the reaction medium or the corresponding electrolysis cell.

So, the product H2 also H2 along with your HF can be taken away from in the top of the electrolysis cell which is your gas because gas will be at the top of the electrolysis cell, but you are in a safer side to get the product p from the bottom of the electrolysis cell and basically therefore, is basically is a flow sheet diagram for the electro fluorination plant and the basic flow basically.

Basic how the reaction is taking place and what are the basically pathways and what are the ingredients we are using for that particular electrolysis step is basically the corresponding flow sheet. Try to remember it little bit because otherwise it is very difficult to understand what reaction is happening over there and if something is given to you which is drastically wrong in it, that means you can have a wrong flow diagram can be given to you and you should be able to identify which one is wrong and which one is correct for this particular plant.

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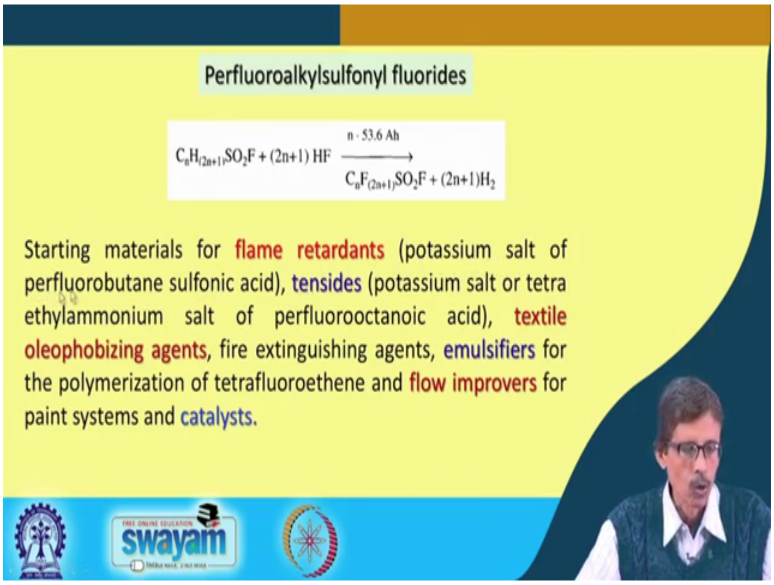

Perfluoroalkylsulfonyl fluorides

$$C_nH_{(2n+1)}SO_2F + (2n+1)\ HF \xrightarrow{n \cdot 53.6\ Ah} C_nF_{(2n+1)}SO_2F + (2n+1)H_2$$

Starting materials for flame retardants (potassium salt of perfluorobutane sulfonic acid), tensides (potassium salt or tetra ethylammonium salt of perfluorooctanoic acid), textile oleophobizing agents, fire extinguishing agents, emulsifiers for the polymerization of tetrafluoroethene and flow improvers for paint systems and catalysts.

Then we will be to go to a little bit complicated molecule. Again your organic molecule organic part which is nothing, but your perfluoroalkylsulfonyl fluorides.

So, we all know that what are the sulfonic chlorides, we know the thionyl chlorides, sulfonyl chlorides. We have already discussed in terms of your only inorganic chemistry aspect or inorganic chemistry point of view. Now, you attach it to the organic molecule and organic compounds can have also the corresponding functions that means the sulfonyl functions. So, those sulfonyl functions the sulfonic acid group can be attached that is so 3 groups can be attached. So, 3 minus So 2n also be attached. So, if you can have a group like this and one of this is not your corresponding sulfonyl chloride, it is sulfonyl fluoride. So, sulfonyl fluorides are nothing, but you can have an organic backbone with a corresponding sulfonyl functional groups.

So, sulfonyl functional group which is nothing, but corresponding sulfonyl acid, that means it is not SO 2 H, H is not So 2 CL, but it is So 2 F. So, the idea is that the hydrogen present at the backbone of these molecule because these sulfonyl fluoride molecule, these sulfonyl compounds or sulfonates basically when you have the corresponding anionic compound, these sulfonates are very useful industrially. Only thing that you have to go for the fluorination of the entire amount of hydrogen present to the backbone Cn, n number of carbon is there you can have a long linear chain and for that linear chain you can have 2n plus 1 number of fluorine centres which can be obtained by replacing 2n plus 1 number of hydrogen centres from the backbone.

So, all hydrogen centres present in that particular backbone can be replaced by your fluorine centres from that part and on the other side also your sulfonyl group function can have the corresponding fluorine as the corresponding anion. So, this the right hand side. You have this already present over there from the starting material and at the same time you can also make 2n plus 1 number of hydrogen molecules through this particular production. So, why we are suddenly interested to make a particular type of compound?

Because as we know that we are moving from the bulk preparation from the overall, the mineral of the fluorine sources making HF making NF ammonium fluoride and all these things. So, these we can consider as the commodity material or the bulk material. So, the different types of acids which we make in a huge quantity which is your bulk chemicals or we can make it for as a commodity item also say it is the commodity item, but if you can go slowly down, down, down for making some speciality chemicals, so these speciality chemicals and sometime we can go for very fine chemicals also. So, the speciality chemicals fluorine based one example is the making of the Teflon also.

So, you can have this perfluoroalkylsulfonyl fluorides because the industry devoted to this can make huge amount of these molecules which can be your starting materials which can be starting materials for flame retardants. Because all this fluorine based compounds what we have seeing from your ammonium fluoride, the sodium fluoride and all this fluorine based compounds we are taking they have the direct relationship with either they are flame retardant or the flame extinguishing material. You cannot burn it because we know that a typical hydrocarbon what we are burning which is nothing, but your Cn H2 n plus 2 or something like that.

That means, your carbon is attached to your hydrogen when you burn in excess of oxygen where why your hydrocarbons are fuel because you are making carbon to carbon dioxide via carbon monoxide or hydrogen to water, but in this particular case this particular process or the burning process is not feasible because you are not able to oxidize the hydrogen available to the water because it has been substituted by fluorine centres.

So, that is why even if you have fire, it will not try to catch or burn the material as your hydrocarbons are burning. So, as a flame retardant which is red in colour they were just given this one, this one in line. This statement is given that is the flame retardant you have which is nothing, but your potassium salt of perfluorobutane sulfonic acid.

So, now this sulfonyl fluoride, but you have the sulfonic acid function which is SO3 H. It is instead of your fluoride salt, it is the corresponding sulfonic acid only, but is only for carbon centres are present which is the butane centres butane backbone, but all of them are substituted by fluorine. So, is the perfluorobutane sulfonic acid and the sulfonic acid then can be converted to its potassium salt. So, you have this instead of your this corresponding SO2F that means sulphur is attached to 2 oxygen and 1 fluorine.

So, direct sulphur fluorine bond in this particular sulfonyl fluoride, but here the sulfonic acid you have that means, SO3 minus you get and it can be converted to its potassium salt and some speciality molecules also known in industrially as the tensides and that tensides it is nothing, but your potassium salt of tetra ethyl tetra ethylammonium salt of perfluorooctanoic acid. So, is basically the typical octanoic acid and where you can have the corresponding tetrafluoro salt and that tetra pseudo salt is basically corresponding tetra pseudo salt giving you something where you get is as the corresponding octanoic compound.

That means, you have 8 carbon centers present in it, again it is a perfluro compound. That means, all the foreign centers has been substituted and those foreign groups are attached to the carbon centers with 8 carbon backbones and the salt is now not potassium salt, but it is a tetra ethyl ammonium salt. So, either potassium salt or tetra ethyl ammonium salt if you do not require potassium over there, then textile oleophobizing agents is something we call says the oleo chemicals. We know that olephobizing agents also that is not related to the weighting and all these things.

So, it is a very sophisticated compounds material people make in the textile industry for improving the texture of the surface of the textile material. As already told it is also not as retardant, but also can extinguish the fire also. So, that is why it can be used as a fire extinguishing agents. It is very good emulsifier in making paints and all other things and for the polymerization of tetrafluoroethane, what is the tetrafluoroethane? We had been discussing that is tetrafluoroethane is nothing, but the corresponding perfluorinated compound of ethylene and that ethylene through polymerization give polyethylene. So, this tetrafluoroethane will give you the Teflon.

So, polymerization of tetrafluoroethane which is nothing, but CF2 double bond CF2 and through polymerization it basically gives you the corresponding Teflon material which is very useful industrially and it basically can also be used as flow improves. That means, it can improve the flow rate of a particular material whether you are handling a fluid, a paint, material or any other thing which can give you a surface coverage. So, you have to increase the flowing capacity of that particular liquid or the corresponding heavy liquid also some time.

So, it can be used as improvement of that particular flow and in the paint material particularly in the paint system. So, it is basically improving the flow material such that you can have the effective coating or the spreading when you apply this as a paint or varnish and also this particular material because it is SO2F type of molecule. So, that functionality forget about the remaining backbone of it. It can function as a useful catalyst also because it is an organic fluorine derivative and that organic fluorine derivative can function as a very good material for catalysis.

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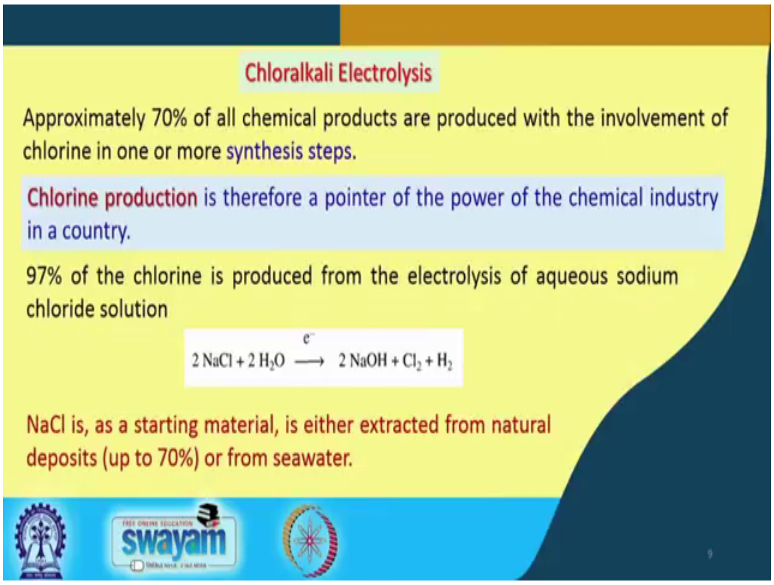

Chloralkali Electrolysis

Approximately 70% of all chemical products are produced with the involvement of chlorine in one or more synthesis steps.

Chlorine production is therefore a pointer of the power of the chemical industry in a country.

97% of the chlorine is produced from the electrolysis of aqueous sodium chloride solution

$$2\,NaCl + 2\,H_2O \xrightarrow{e^-} 2\,NaOH + Cl_2 + H_2$$

NaCl is, as a starting material, is either extracted from natural deposits (up to 70%) or from seawater.

Now, we just move to the other part; that means after fluorine we have the chlorine and what you should have in your knowledge or in your idea that what are the very important thing what we should study if we go from fluorine to the other member in the halogen family is your chlorine.

So, production of chlorine will again be a very useful component and from the inorganic chemistry point of view you know how to get the chlorinated derivative of the inorganic compounds, how to get the bleaching powder, how to get the corresponding other organic compound. Earlier we are using that hexachlorobenzene also and this sort of thing whether you substitute a organic backbone by chlorine or you get some derivative of inorganic compound like calcium hydroxide or any other thing to your bleaching powder which is calcium hypochlorite Ca OCl.

So, that particular material how you can go for a typical chlorination reaction like that of your fluorination reaction? So, in your hand industrially you should have a huge amount of chlorine stock or chlorine gas or in situ you are able to prepare chlorine gas in the laboratory. That is also a related question to you that how at a room temperature how will you prepare chlorine gas from the individual components or the reactant. You should know those reactants which will react together to give you a chlorine gas at room temperature only such that you can have a regular supply of chlorine gas from there.

Similarly, this particular process is devoted to again by electrolysis because most of the time industry is looking for this particular technique because it is a cheap one, easily available, easily doing also and is a chloralkali process. That means, you have to have something where the chlorine is present and you have the alkali part is there the alkali metal ions are present which is nothing, but when chlorine is present and alkali metal ion is sodium is nothing, but the electrolysis of sodium chloride. So, chloralkali process is very useful because it is the natural resource of sodium chloride we know is such a cheap material because till now our edible sodium chloride, the common table salt we get at a price of less than 20 rupee kilo.

So, you see that the process of making that sodium chloride the edible version of your table salt is so easy that you are getting that huge amount of sodium chloride. So, if you have a huge supply of sodium chloride do you think that you will be able to get chlorine also at a cheaper level or very low cost? If your technology is available or the industrial process is available in such a fashion that you can attack or you can degrade the sodium chloride giving you Na plus and Cl minus definitely. So, chloride is present as the chloride ion which is the anion. So, you have to go for oxidation of that chloride ion to give you the corresponding chlorine as the chlorine gas which is Cl 2 0.

Just now what I asked you that how will you make a chlorine gas in laboratory at room temperature is nothing, but your oxidation of your any chloride source even if you have the hydrochloric acid which is readily available in the laboratory. So, this hydrochloric acid can be oxidized to give you the chlorine gas. So, simple manganese dioxide which is also naturally available as pyrolusite the responding ore of manganese is a black powder and that black powder material you can have and if on a reaction vessel or a reaction gas chamber.

If you have the powder of that, that means manganese dioxide and drop by drop if you add hydrochloric acid not very concentrated one is 1 is to 1 hydrochloric acid, you can add drop by drop. So, immediately that reaction will give you the corresponding production of a chlorine gas and you can have some mechanism. That means, another exit through which you can take out the chlorine gas from there.

So, approximately in that way 70 percent of chemical products what do we have in the industry are produced with the involvement of chlorine. We have seen in previous 2-3 classes that how much your fluorine is important. Incorporation of fluorine or the fluorine based different compounds are so important that you can have a huge industry based on fluorine, so you can get that particular introduction of chlorine or the chlorine based typical inorganic compounds in one or more synthesis steps, you can you can go for further synthesis, then you can make new molecules which can be useful industrially also.

So, once you make it in the laboratory in a good skill, your yield is very high and conversion rate is also very high and is not so costly one. You can go for that for industrial production of that particular material, so you can have it number of synthetic steps involving for the production of the final product. So, a particular country or a particular industry large number of industries should be there which will be devoted for chlorine production and how quickly you can get that.

That means, you have to make chlorine out of what, out of what? Cheaply available material which is nothing, but your sea water is brine. Sea water has large amount of sodium chloride and from the sea water basically through evaporation technique we get the corresponding salt as the cake, table salt cakes are available from through evaporation only. So, natural evaporation, sunlight evaporation, sunrays evaporation is sufficient to get you sodium chloride.

So, this chlorine production is basically an indicator or marker basically how good we are, how good our country is for industrial inorganic chemistry the subject what we are studying. So, for that particular subject, that means industrial inorganic chemistry how strong we are we should know through a particular index where we know that how much chlorine we are producing annually because we can compare the advanced countries different advanced countries chemically advanced. Obviously, some are there like us like Germany, like China, like Japan and all these things.

So, if we can able to compare it from that point of view that the chlorine production is therefore a pointer which points basically that how strong you are in terms of your chemicals. Pointer of the power of chemical industry in a particular country we have the huge country surrounded by seas and we have huge amount of sea water and sodium chloride. If we consider that is a useful value added marine chemicals which is naturally available. We are not thinking of the ore or minerals and all these things from which we have to dig out the corresponding useful material as ore or mineral; it is a very simple technique.

Still now we have the cheapest possible material which is available in the common market also is your sodium chloride. So, the index is that that you are not only producing huge amount of sodium chloride for your edible consumption, but you have to think of some useful compound where chlorine can be inserted or chlorine can be introduced for that particular purpose. So, chlorine production will be a useful thing for that particular sake.

And 97 percent of the chlorine is produced basically simply from that particular electrolysis of aqueous NaCl solution. So, that is the technique therefore is your chloralkali electrolysis. So, you go for electrolysis of sodium chloride which is chloralkali. So, is basically industrial term for so many years 2 to 300 years. People are using this that what is that chloralkali and then when electrolysis has started, people are trying to do that thing also that what we had doing. We are doing the electrolysis of your material which is your chloralkali. So, if we will look at reaction wise what reaction we should follow.

The reaction wise if we consider that we are having chloralkali which is nothing, but your NaCl and the aqueous solution of it and is also very important to know that we are not using anything. That means, not any other medium because previously we are seeing that you can have a medium of HF hydrofluoric acid medium and in that medium we are doing electrolysis.

Even for making aluminum for the electrolysis of the cryolite which is having a very complicated electrolytic medium compared to all these cases, your medium is very simple, is simple water based medium. So, what you can think of that you can take simple the sea water or the brine water supply. Only thing that you can purify little bit such that your sale is not contaminated, your efficiency, your production of all these materials will be higher. So, you go for your electrolysis of your sodium chloride.

So, what is happening in there therefore that we are looking for your oxidation of your chlorine that Cl minus oxidation giving you Cl 0 or Cl 2 0 the chlorine gas. So, is basically not a question or not a function of both the two item. That means, anode cathode and all these things obviously that will come automatically when you produce hydrogen along with this. So, if you bring together for only one interest of oxidation of the chloride sample or the chloride ion or the chloralkali as sodium chloride, chlorine will be produced through that oxidation and deduction of the hydrogen ionic from the water medium.

So, we are basically intended to make or the production of chlorine that we have told you that the chlorine production is a good marker or good indicator for a country's development in industrial inorganic chemistry. Industry devoted to make some useful compound is for the production of chlorine, but along with that when you produce Cl 2, you also produce Na OH. That means, not only that you are going for some value added material what you consider that if as I told you that your sodium chloride as table salt is cheaper, is very cheap one, but your sodium hydroxide is not so cheap. So if you make the equivalent amount of sodium hydroxide out of these electrolysis process, so your price of chlorine will go down definitely because it is a by-product of your chlorine production.

So, during the production of your chlorine you are also producing sodium hydroxide as well as another value added material is your hydrogen gas. So, you see 3 components you are able to make, you are able to produce out of this simple electrolysis reaction of sodium chloride. That is why it is industrially so important that when you go for the electrolysis of the aqueous solution of sodium chloride, you get two other compounds. So, we take sodium chloride as a starting material for this particular process and is either extracted or from natural deposits.

Next day we will see how we can go for the purification of these sodium chloride molecules or the sodium chloride material and we can go for purification up to 70 percent or from direct sea water what we can use for this particular electrolysis process, ok.

Thank you very much.