Industrial Inorganic Chemistry
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Lecture – 30
Bromine and Bromine Compounds

Hello everybody. Welcome back to this class once again where we are talking about some compounds where you can have the chlorine oxygen bonds and how we can utilise those chlorine oxygen bonds for useful purpose.

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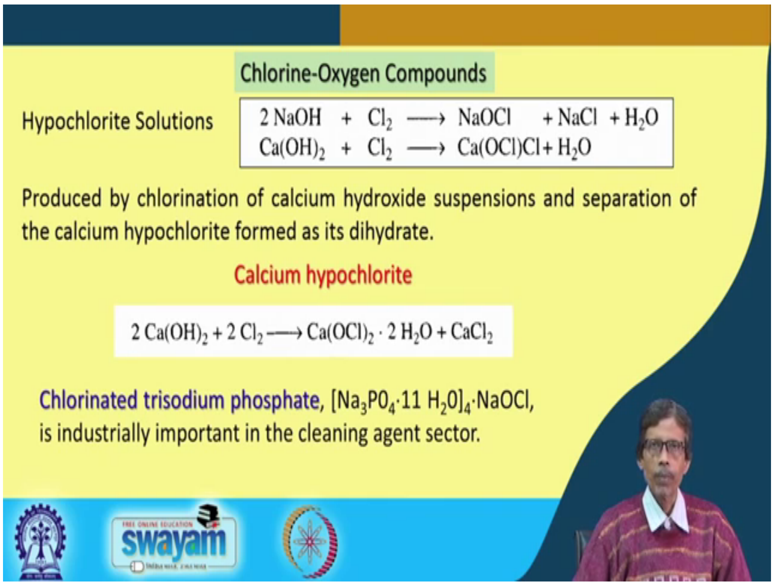

So, synthesis of hypochlorite, so which can be produced in large scale or the industrial scale by simple chlorination of calcium hydroxide suspensions. You do not need to have the calcium chlorite solutions, only calcium suspensions are enough because the suspended particles on the water surface you can have in between also because in the lower part also you can have the calcium hydroxide material, so which can be react with the chlorine gas if you purge chlorine gas in it.

So, the hydroxide suspension can give you the separation of calcium hydrochloride as its dihydrate. So, when we produce it this particular one as your calcium hypochlorite. So, this calcium hypochlorite; that means, a that is the once hypochlorite means one OCl and another Cl, you have the water produced also but which can be crystallized nicely as the dihydrate. So, you get the solid product which is only available the crystalline material is only available as that dihydrate.

So, that hypochlorite of calcium; that means, if we are able to substitute the second chloride ion of the chlorine, of the calcium centre by hypochlorite ion we have to use it for the reaction which having some excess amount of your Cl 2. So, Cl 2 concentration is increasing as well as your calcium hydroxide is reacting with two molecules giving you Ca OCl whole to dihydrate. So, that is the different type of is not the bleaching powder bleaching powder was your Ca OCl Cl. So, this is the calcium hypochlorite. So, that is the calcium hypochlorite is having 2 OCl groups attached to the calcium like your sodium, where one group is attached and is the separated as directly from the medium as you dihydrate as well as some amount is form also your calcium chloride.

So, from that reaction we will be getting the calcium chloride as your by product we should always be take care of this particular by product because calcium chloride also in a fused form which is a very good desiccant and which is also industrially very useful. So, if we can take care of this particular solid material of calcium chloride its cake and its fused form will be utilising for some other purpose. Then we do something that we see that the water of hydration, water of salvation, all these things are very important during crystallization. And during that particular crystallization process the solvent molecule the acid molecule the water molecule can be co-crystallized with the parent material or the parent crystals.

So, if we are able to crystallize it; that means, the sodium hypochlorite whether you can that salt basically it is a basically sodium chloride like salt whether we can trap this salt when we can make some co-crystallization of some bigger amount of bigger salt that huge amount of that other salt other part of the salt, so we get some double salt. We consider these as the double salt; that means, you can have a solid crystalline material having two different salts.

So, which is nothing but your trisodium phosphate that Na 3 PO 4 if we have. The Na 3 PO 4 if we can crystallize it in presence of sodium hypochlorite solution, we get chlorinated trisodium phosphate. So, industrially it is known as a chlorinated but is not a typical chlorine or anything but it has the hypochlorite sodium hypochlorite as its crystallized form with that of your Na 3 PO 4 with 11 water molecules of crystallization.

So, how this NaOCl is being trapped? So, you have huge amount of water of crystallizations for the sodium phosphate is simple sodium phosphate but is the another variety of sodium phosphate, where 11 molecules of water of crystallization are present stabilizing this in a particular crystalline form. And during this particular process we know that when you have large number of hydrogen centres from the water molecules are in hydrogen bonding environment. So, it is basically all are forming the intra molecular hydrogen bonding interaction between individual hydrogen centres of the water molecules, so which also utilised for trapping this particular sodium hypochlorite salt also.

So, the OCl part and the Na part is also being trapped inside this network of 11 water molecules. So, that is why we have only one NaOCl per this huge next the network of sodium phosphate as well as 11 water molecule and is also a very useful industrial agent industrially important agent. In the cleaning agent sector where people are producing only the clean, not bleaching or anything but only for the cleaning purpose this is a very useful material or salt which can be produced industrially.

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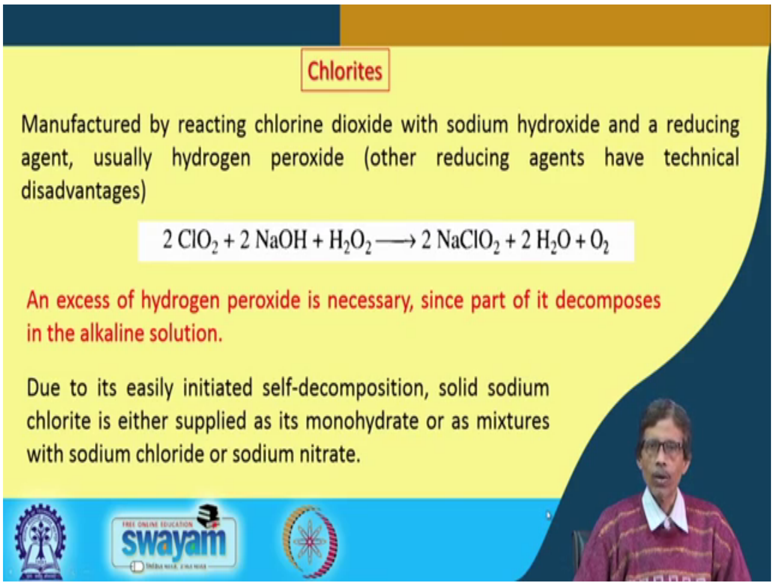

Then we moved to the chlorites. So, chlorites having more number of oxygen centres attached to this chlorine. So, is manufactured basically by reacting chlorine oxide; that means, Cl 2 O with sodium hydroxide and a reducing agent, usually hydrogen peroxide. Other reducing agents can have other disadvantages, so we do not use or we do not prefer to use, other reducing agent. So, the very selective one is your hydrogen peroxide. And that hydrogen peroxide, we all know that it can give you the corresponding supply of hydroxide groups as well as the oxide functions if it can go for the different type of reactions.

So, it react basically directly with chlorine oxide ClO 2 in alkaline medium with hydrogen peroxide and that hydrogen peroxide is basically giving us NaClO 2, that ClO 2 itself was there. So, that is our chlorine oxide dioxide we consider and ClO 2 we are converting it to ClO 2 minus; that means, it is getting reduced. So, that reduction is being done by alkaline hydrogen peroxide. So, this is a very simple reaction of reduction but the agent is very much specific. People do identify that particular reagent for the reduction of chlorine dioxide.

So, the chlorite when it is in the anionic form we get like your hypochlorite another chlorite salt which is ClO 2 minus is simple and very efficient one if we are able to transfer one electron to that particular neutral molecule of ClO 2 by making ClO 2 to ClO 2 minus and now alkaline hydrogen peroxide is the specific one. And hydrogen peroxide itself is getting oxidised we all know O 2 as O 2 minus, when it is getting oxidised by transferring 2 electrons from each and individual peroxide molecule; that means, O 2 2 minus the 2 electrons will go to utilise the reduction reaction of two molecules of ClO 2. As a result your CO that O 2 2 minus and hydrogen peroxide will be converted to O 2.

So, it will be converted to this water molecule that water molecule is being formed and that water molecule is available over there and the sodium hydroxide is basically responsible for giving you the corresponding production of 2 molecules of H 2 O.

In this particular case, we have to use some excess amount of hydrogen peroxide. So, this is the limitation of this particular reaction because hydrogen peroxide use is a costly affair, we should minimize the use of sodium the corresponding hydrogen peroxide for this particular reaction. Why we use? Because the strength of the hydrogen peroxide is not well known all the time because it has self decomposition pathways and a part when we use basically decomposes in this particular alkaline medium itself between O 2 and H 2 O. So, we should use a higher concentration of hydrogen peroxide for converting this ClO 2 to the chlorite ions.

So, you have a very easily available form of the self decomposition. So, solid sodium chlorite is either supplied as it monohydrate, so it should be crystallized as its the monohydrate taking the water molecule what is being produced from the reaction medium as its water of hydrate or mixture of sodium chlorite or sodium nitrate. Because sodium nitrate can be utilised for stabilizing the sodium chlorite itself. The sodium chlorite like your sodium hydrogen peroxide is also can undergoes self decomposition reaction.

So, these are basically functioning as a stabilizing effect. One is your crystallization as the monohydrate that means, the crystals are not that much susceptible for decomposition and another way of getting this is or avoiding this for decomposition avoidance of that self decomposition is the use of sodium chlorite either or sodium nitrate as the stabilizer or the stabilizing agent for NaClO 2.

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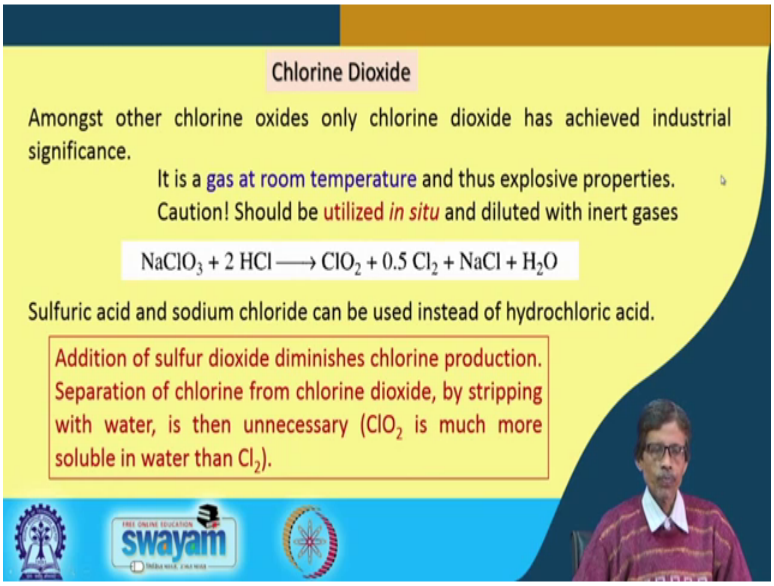

So, how we get it the making of silver dioxide? So, how we get it? How we make this particular chlorine dioxide? So, that chlorine dioxide preparation basically is now we will see where from we get it. So, different types of chlorine oxides are available but here we will just use talk about the chlorine dioxide; that means, the ClO 2; just now what we have utilised for the chlorite preparation because after hypochlorite we are talking about the chlorite now we will go back to the starting material preparation; that means, the ClO 2 preparation.

So, in this particular case which is a gas at room temperature and can thus have some explosive properties because it is a very to other things because it is a basically the chlorine is present and oxygen is also present. So, this is the mixture of these two because it is not a mixture of chlorine and oxygen, but is a different molecule itself.

So, it should be utilised, it should be produced also in situ because the reaction what we are utilising now for the production can do in the laboratory or industrially such that we can produce chlorine dioxide when we require that particular molecule to be used. And sometimes it can also be diluted with inert gases. Mixing with inert gases basically reduced the concentration of your corresponding ClO 2 what is being produced as a result the explosive nature of that particular gas molecule is being reduced.

So, chlorate we have seen similarly we can also make some other procedure or electrochemically we can make also the sodium the chlorite also. So, that the sodium chlorite (Refer Time: 12:17), hypochlorite chlorite and then sodium chlorite NaClO 3, one more oxygen you have. So, this chlorite molecule can be reacting with the hydrochloric acid or HCl giving you ClO 2, then chlorine as well as NaCl plus water you see. A little bit of complicated reaction giving you 4 different products one of them is your ClO 2 the chlorine oxide, along with that you have the chlorine, you have the NaCl and you have H 2 O.

Then addition of the sulfur dioxide, if you put some amount of sulfur dioxide which is a reducing agent along with your HCl, so addition of these basically take care of the excess amount of your chlorine production. And when chlorine is present, we can go for the separation of chlorine from chlorine dioxide we have to separate it, otherwise we cannot get pure chlorine oxide by stripping with water. So, chlorine can be stripped off can be taken out through the reaction or some absorption tower or the stripping tower of water.

That can be avoided if we use sulfur dioxide. So, that entrapment all the stripping of chlorine dioxide by use of water is unnecessary because the ClO 2 is much more soluble in water. So, when we go for this chlorine dioxide stripping with water is much more soluble in water than ClO 2, ClO 2 if we use water the ClO 2 will go with that water. So, we have to remove that particular process of use of water for separation and purification of this chlorine gas as the Cl not chlorine dioxide gas as your ClO 2.

So, sulfuric acid and sodium chloride can also be used in place of your HCl for this particular type of reaction for production of ClO 2.

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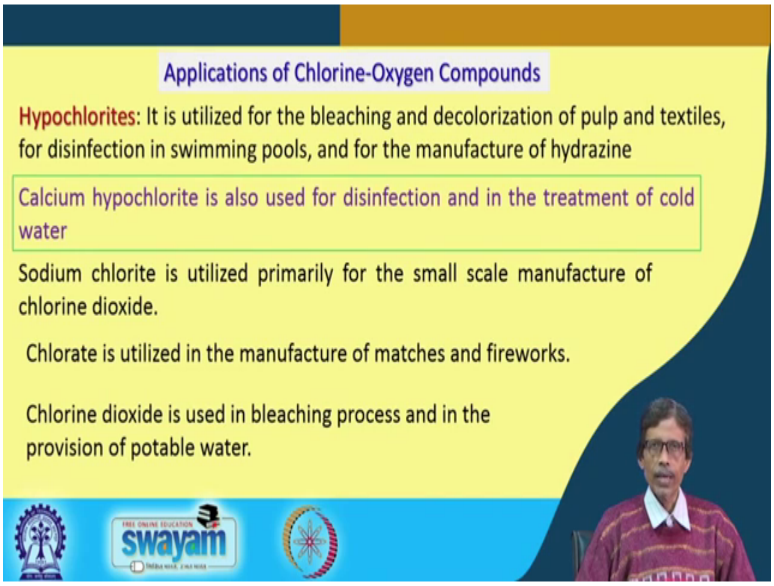

Then we see how we can have the different areas of application where we can use the produced ClO 2. The chlorine dioxide what we have produced, which can be used for the different or useful purposes. So, first of all you have the hypochlorites what we have seen earlier that is a very good bleaching agent. So, it can be useful for bleaching and the decolorization of the material what is used for the paper industry, the pulp. The pulp which is always red to brown to very dark solution if your coloring matters are still present.

So, if we want to remove those coloring matter from the pulp material or the pulp bulk mixture we use hypochlorite to decolorize those things such that you have the colourless solution. Similarly, for the textile industry always we try to have these the bulk material or the bulk thing; what we have from the textiles should be colourless. And for the disinfection of swimming pools we know the bacterial growth the fungal growth and all these things should be destroyed if we use chlorine gas itself or the hypochlorites to disinfect the water why the water present in the swimming pools and the corresponding areas the surfaces or the bottom of the corresponding pools for this particular purpose.

And for the manufacture of the hydrogen we have seen that from ammonia NH 3, we can use sodium hypochlorite for the manufacture of hydrazine what we have discussed earlier when we are talking about the production of hydrazine the rocket fuel and the different types of hydrazine based compounds. So, along with sodium hypochlorite, the calcium hypochlorite is also useful for disinfection and in the treatment of low temperature water; water which is in the low temperature, not at high temperature.

So, low temperature water can have excess amount of dissolved oxygen. So, that oxygen can be a very good material for the growth of the bacteria, the growth of the fungus or any unwanted material. So, the fungal growth can be very good where your oxygen content of the water is more. So, in place of your sodium hypochlorite we can use calcium hypochlorite for treating water at low temperature. Then, the other one the sodium chlorite the sodium chlorite can also be utilised for small scale manufacture of chlorine dioxide that we have just now seen. So, utilisation for one material or one chemical for the production of the other chemical as and when required.

So, we if we need chlorine dioxide preparation or manufacturing we use we can have a store house of sodium chloride for that particular purpose for this. Then we have the sodium chlorite NaClO 3 or potassium chlorite or ammonium chlorite at any other metathesis salts what we can use for this purpose is also utilised. Because it is a very useful material for making the different matches the safety matches as well as the different fireworks, the material what we use in the different fireworks the chlorite is also supplying huge amount of oxygen for the burning process of this fireworks mechanism or burning of the matchstick in the matchboxes.

Then utilisation of chlorine dioxide; so, chlorine dioxide is used again for the bleaching process and in the provision of the portable water. So, if we are able to destroy or if we can able to kill the corresponding bacterial growth or the fungal growth or any other contamination from other material that the die material or any other small organic molecules which are present in the water molecule we can destroy all of them by safe use of chlorine dioxide. Instead of using direct chlorine gas in presence of some medium whether it can be acidic little bit or a basic, but that particular use of this gas ClO 2 is a safer one. So, we can use chlorine dioxide for that particular purpose.

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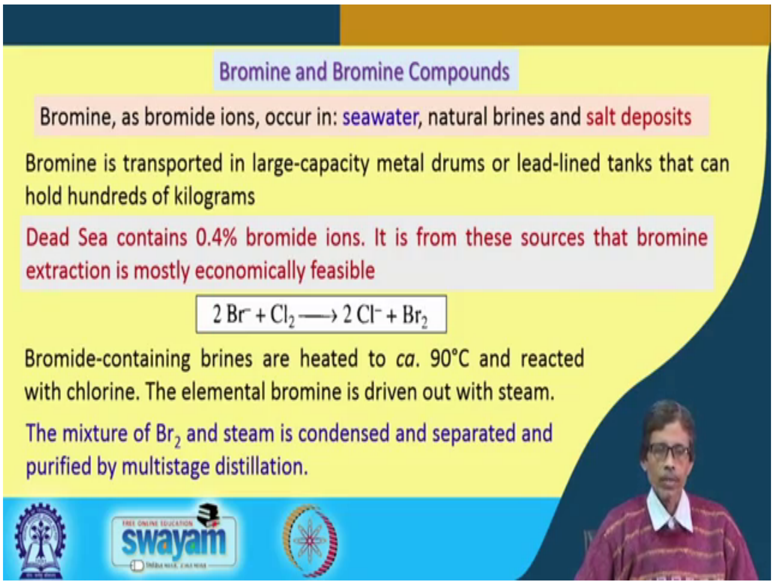

So, after chlorine and the chlorine oxygen based compounds we can move to the corresponding bromine and bromine based compounds, because bromine is also a very useful material or halogen compound industrially. So, the bromine is also a very good source from the sea water and when you have the sea water the bromine in sea water is present as the bromide salts like sodium bromide itself. So, that bromide salt which is present in sea water can be acidified and you can adjust that particular material for a pH of say around 3.5 and we try to produce or try to oxidise those salt as the bromide salt for the production of free or elemental bromine as Br 2.

So, this bromine the equivalent amount of bromine what we are considering the amount of bromine what is present in sea water or any other water, we have to control the corresponding pH and that bromine as free bromine is considered as the presence of the other bromide ions, is present in sea water, it is also present in natural brines and in some cases it is also present as the salt deposits; that means, the sodium bromide.

So, the availability of these as the sodium bromide or any other bromide salt corresponding calcium bromide it can be or the potassium bromide in sea water natural brine or the salt deposits like sodium chloride we have to take out of this. And sodium bromide itself is a very good material for industry is also a costlier one compared to sodium chloride because the availability of bromide as the bromide salt in seawater or in salt deposits compare to sodium chlorite is very very less. So, the availability of less amount of all these things as the market demand tells you that the chemical economics is also tell you that the price of that particular bromine will go up. So, definitely the bromine price the free bromine price itself the Br 2 price will be higher than that of your Cl 2 price or the chlorine price.

Then when we have the bromine is can be transported in large capacity metal drums or lead lined tanks that can hold 100s of kilograms of this material. So, this bromine which is a very corrosive liquid, red coloured corrosive liquid which can be stored and which can be transported from one side to the other. So, if we can have the different sources of all this where you can have not very much of this bromide is present in our sea water which is our surroundings like Indian ocean or any other thing.

If we moved to dead sea because the country which are closed to dead sea, they are rich enough with that source and dead sea contains about 0.4 percent of bromide ion because the bromide concentration is very high in the dead sea. And as we all know that the water of the dead sea the density of the dead sea is also very high and it is from these sources the bromine extraction is mostly economically feasible, like that of your starting from seawater to the water which is available from dead sea. And what reaction we should follow? Because we are talking about the production of bromine from the bromide salts itself; that means, the bromide as present as Br minus.

And if we know the corresponding redox potential, the reduction potentials of chlorine as well as bromine we can compare that simple chlorine is sufficient enough to produce the free bromine from the bromide salts through the utilization of chlorine gas itself as the corresponding oxidizing agent. So, chlorine gas will function as a oxidising agents as we have seen just now or in our previous class that we have to produce chlorine gas industrially also. So, that industry is also very much helpful to produce bromine for us industrially, if we have a regular supply of the sea water or natural brines or the salt deposits for this reactions.

So, 2 Br minus is reacting to Cl 2 giving you 2 Cl minus plus Br 2. And thus the different types of bromide ion bearing brines, we heat it we take that thing. We adjust the ph and then we heat it to about 90 degree centigrade and then chlorine gas is being purged or allow it to react with rather chlorine. The elemental bromine is driven out with steam because if we heat it at 90 degree you are also producing sufficient amount of steam.

So, when you take out that particular steam, steam will not only leave the reactor alone it will also take out the volatile metal because is a red liquid and have an high volatility. So, it will come out with the steam and it can go to the other chamber where it can be cooled and it can be stored it is very much similar to that of the process what we know laboratory wise or industry wise is a very useful technique is the steam distillation.

That means, you have some material you put or you purge steam not any other gas not any other thing you purge steam and steam will go out through this outlet and while going out or leaving that particular chamber the steam will take out some other material. It can so happen that sometime some solid material also can be purified through steam distillation.

So, this is not a process of isolation but it is also a process of purification, where we find that this particular material which is going out along with the steam at a very high temperature because steam is always we are producing at around 90 degree centigrade, so which is being condensed. So, through that particular condensation reaction what we see, that your steam is also condensed, so is a low temperature arrangement you have and that low temperature arrangement steam is settling down as well as your bromine is settling down over there.

So, is a volatility is such that a steam can take out over there but when you condense it at a low temperature both these two liquids will be there and you have two different liquids and depending upon its density the bromine is definitely a higher heavier one, so it will be at the bottom of the container or the corresponding reaction chamber of the reactor where water is at the top. So, you must have some outlet take out bromine from that chamber the way we do in the laboratory by using your separating funnel.

So, separating funnel, separates the liquids in terms of their density differences in 2 layers or 3 layers and we take out from the bottom the heavier liquid first then the other lighter ones. So, it is driven out from the steam and the mixture of bromine and steam therefore, is condensed and separated and purified by multistage distillation. I am talking about only the example of steam distillation; only one example which is also very much similar to that of our laboratory knowledge, in laboratory what we do, how we do the steam distillation for purification of different types of organic compounds also.

If we are synthesizing nitrosobenzene in the laboratory it has to be purified by steam distillation only. So, the solid, it is a solid product, so, the solid product can also be purified by steam distillation. So, bromine is the most easiest example of purification, but for industrial thing is that like that of your repeated distillation. So, you have a multistage distillation such that your contamination can be reduced one after another stage. So, once you move from one step to another step your contamination or your purity is increasing step by step through this multistage distillation process.

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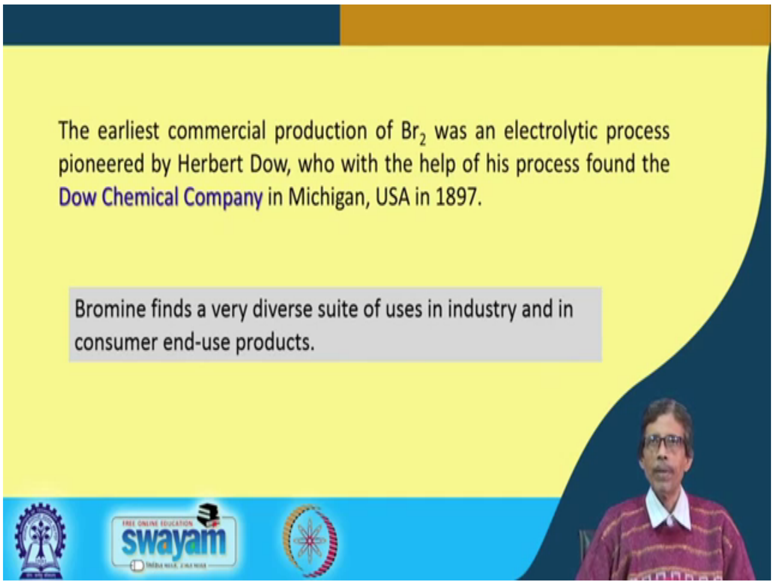

So, what you see that, what people have started basically long back say in this sort of activity what you have if you have huge amount of the corresponding bromide salt supply, whether you are importing from other country or where whether you have in your own country or you have the nearby supply or some industry is also producing the corresponding salts as your corresponding bromide salts you can take all these things for getting the pure amount of bromine. Because the bromine is a very useful material, we will see when we see in our next class the corresponding use of this bromine for the different purposes starting from making pharmaceutical the drug industries also.

So, the commercial production has begun in the year of say 1897 you see is more than 100 years back people were doing all these things. So, historically this particular information or knowledge is important to everybody to us also where people have used the electrolytic process; that means, the electrolysis, because the bromide to bromine conversion is nothing but oxidization.

Here we are using chlorine in large scale but electro chemically also because that time also nothing was known much about science about chemistry and all these thing. Even we do not know about the corresponding oxidizing activity or oxidation potential of the different material so but the electrochemical thing people have tried that anode and cathode thing and the oxidation and the reduction thing was known to that time.

So, it is that person who is Herbert Dow because we know the Dow Chemical Company, and the former the Bhopal disasters also the Dow chemicals were responsible for that we all know. But, who was that person we know; that it is a person who is the Herbert Dow who with the help of his process found the company the Dow Chemical Company in Michigan, US, where he first introduced the corresponding electrolytic process where that particular electrolytic process was useful for making that particular Br 2.

So, always you see the purity will be higher, and if we can selectively make this bromine through this electrochemical process because making bromine and the utilisation of bromine is very use very diverse in nature. And bromine find a very diverse suite of uses in industry and in the consumer end use products because the consumer products what we are using starting from all these materials what we use in our day to day life it can be brominated compound sometime also.

So, the industry, the pharmaceutical industry, the drug and medicine industry they are using the bromine as corresponding compound what we will see also afterwards. And it can also be a very useful material for the end used products where the bromine is present in all different useful molecules or polymers or the different types of materials ok.

So, these we will see how bromine can be a useful material, for all these cases that means, the application we will see and then we will move for the discussion of the iodine. It is the last halogen in this family, the halogen how industrially it is important and how we can use all this.

Thank you very much.