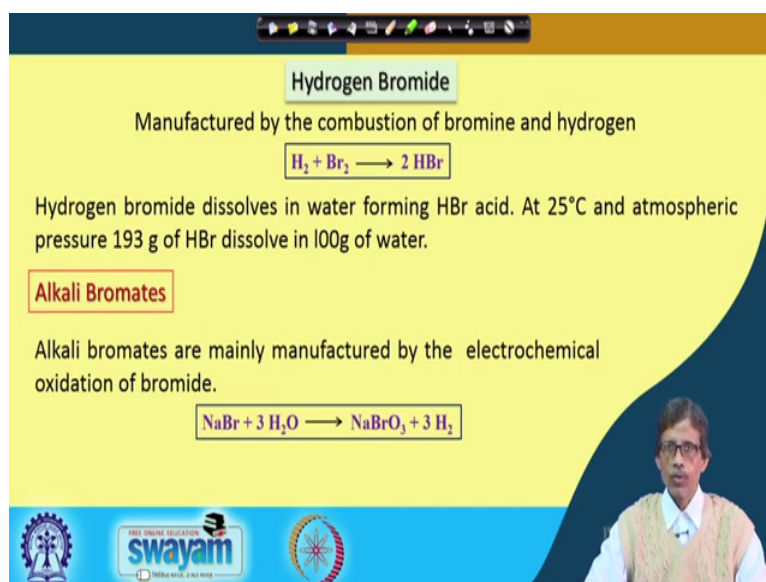


**Industrial Inorganic Chemistry**  
**Prof. Debashis Ray**  
**Department of Chemistry**  
**Indian Institute of Technology Kharagpur**

**Lecture - 31**  
**Hydrogen Bromide and Alkali Bromates**

Hello and good evening everybody, so we were discussing in this class about the different halogen compounds and how they are useful for industrial purposes. So, after fluorine we were now with bromine. So, the elemental bromine production we have seen that how this can be utilized for different purposes, now today we will just go for it is other compounds such as your hydrogen bromide.

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**Hydrogen Bromide**

Manufactured by the combustion of bromine and hydrogen

$$\text{H}_2 + \text{Br}_2 \longrightarrow 2 \text{HBr}$$

Hydrogen bromide dissolves in water forming HBr acid. At 25°C and atmospheric pressure 193 g of HBr dissolve in 100g of water.

**Alkali Bromates**

Alkali bromates are mainly manufactured by the electrochemical oxidation of bromide.

$$\text{NaBr} + 3 \text{H}_2\text{O} \longrightarrow \text{NaBrO}_3 + 3 \text{H}_2$$

The slide also features a video inset of Prof. Debashis Ray in the bottom right corner and logos for IIT Kharagpur and Swamyam at the bottom.

So, HBr we all know is a very useful compound like that of our HF and HCl and HCl as the typical mineral acid is largely used in different sectors of the industry. But HBr is not that much useful as an acid, but it can be useful as a brominating agent sometime. So, when we consider that how we get HBr from elemental bromine also.

So, from the natural sources we have seen that the sea water was useful to give you the bromine and that particular bromine if you in your hand we can convert it nicely to HBr. So, the direct combination this manufacturing process or the process utilized for the industrial scale production of HBr is dependent on the combination of bromine and hydrogen that means Br<sub>2</sub> and H<sub>2</sub>.

So, that combination in a straight way can give you 2 molecules of HBr. So, those HBr we can handle and those HBr can be utilized for different purposes. So, as this HBr what we have in the form that what we get this HBr that HBr dissolves in water forming HBr acid. So, HBr when it is dissolving in water we get it as like your HCl; HCl we know that the gaseous thing HCl which is being solubilized in water giving you the hydrochloric acid in aqueous medium. Similarly, this particular one is also soluble water so at 25 degree centigrade HBr dissolves to certain extent which is 193 gram and which is dissolving it 100 gram of water.

So, in all these cases whatever amount of these; that means, we can have the  $H_2$  plus  $Br_2$  was a liquid red liquid in your hand and direct combustion. So, you must have a combustion chamber in that combustion chamber we produce HBr and the produced HBr we have to take away and by dissolution in water you can get the corresponding aqua solution of HBr for the different purposes.

So, along with this HBr if we consider what are the different other bromate source it is not that suddenly we are jumping from some alkali bromides, but it has some relationship because that we have seen earlier that these two things; that means, the bromine can disproportionate between the 2 oxidation states of Br centre it is Br minus and Br O 3 minus.

So, the bromate 1 which is the oxidizing agent and it is alkali salts; that means, the corresponding sodium salt or the potassium salt or sometimes the ammonium salt are very useful for industrial purposes. So, these bromates if we get how we are getting these particular bromates.

So, again it is manufactured from the starting material of  $Br_2$ , that means the bromine we can have like that of our HBr formation. So, HBr formation you have and that HBr when react with some amount of bases, that means sodium hydroxide potassium hydroxide or lithium hydroxide give you corresponding alkali bromide salts. Similarly if we are able to make the bromide salt which is Br O 3 minus the typical anionic part of these bromide salts are Br O 3 minus.

So, these Br O 3 minus are electro chemically produced, that means the electrochemical oxidation of bromine as  $Br_2$  bromine oxidation state is 0. So, that elemental bromine can be oxidized electrochemically to get the corresponding bromates. So, in a typical fashion

what we see that the reaction of these in an electrochemical fashion that means, sodium bromide we get it from HBr; HBr on reaction with other things. That means, starting from your sodium hydroxide to sodium bicarbonate to sodium carbonate it gives you the sodium bromide as the typical salts.

So, the alkali bromide salt when it is dissolved in water again like that of your HBr is soluble is highly soluble in water and that aqua solution we just try to go for electrolysis. So, the electrolysis of this particular one and what we see that the entire amount of bromine as  $\text{Br}^-$  or the bromide ion. So, the bromide ion can be converted to  $\text{NaBrO}_3$  that means, this particular one is a very neat one that means electrochemical oxidation is very feasible for the oxidation of the bromide ion to give you  $\text{Br}^-$  to  $\text{BrO}_3^-$  and at the same time we always know that some component if we try to oxidize it we get the other component as the reduced form.

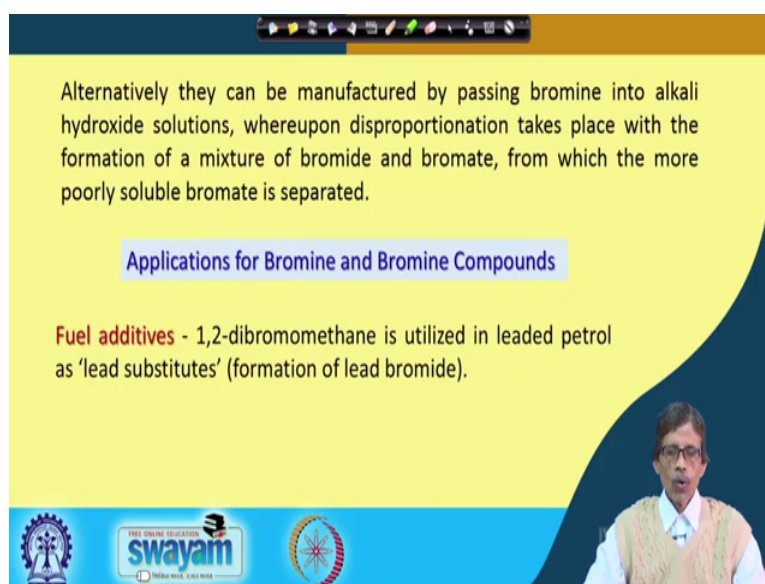
So, from the water medium if we have the proton; that means,  $\text{H}^+$  available. So, those  $\text{H}^+$  will take up those electrons during oxidation of the bromine will be reduced to the hydrogen, so hydrogen gas is again a by product for this particular reaction. So, from this reaction if we consider that now we have simply the bromine that  $\text{Br}_2$  and if we want to get that particular  $\text{Br}_2$  from  $\text{Br}_2$  that sodium bromide as well as sodium bromate what we consider that one is the reduced form  $\text{NaBr}$  is the reduced form from the bromine centre or the bromine or the elemental bromine.

Similarly, the bromate the  $\text{BrO}_3^-$  is the oxidized form. So, if we allow some amount of this proportion a chain reaction between sodium between this bromine centre. So, one of the bromine centre can be reduced to  $\text{Br}^-$  and another can be oxidized to bromate centre. This was the original principle what people considered earlier that if we have both the availability of bromide salt as well as the bromate salt in sulfuric acid media if you go for  $\text{H}_2\text{SO}_4$  medium, these two can combine together to give you the production of elemental bromine.

So, that is the another way of getting your bromine that means the preparation of the bromine what we have seen through oxidation of the seawater by chlorine. So, if these two are plenty in availability that means if both bromide as well as the bromate salts are available in nature or some other industrial sources we can combine them together in sulphuric acid medium to production of your bromine.

So, the disproportionation reaction in that way, that means the electron transfer reaction is very much feasible for this bromine elemental bromine for giving you this particular bromate salt and when we use this for your direct combination of hydrogen we get the HBr and it is corresponding alkali bromide salt.

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Alternatively they can be manufactured by passing bromine into alkali hydroxide solutions, whereupon disproportionation takes place with the formation of a mixture of bromide and bromate, from which the more poorly soluble bromate is separated.

**Applications for Bromine and Bromine Compounds**

**Fuel additives** - 1,2-dibromomethane is utilized in leaded petrol as 'lead substitutes' (formation of lead bromide).

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So, after getting this particular bromate salt, what we use that alternatively it can be manufactured also by passing simply the chemical reaction, utilization of the chemical reaction that means the elemental bromine  $\text{Br}_2$  in alkaline hydroxide solution.

So, alkali hydroxide solutions like that of your sodium hydroxide or potassium hydroxide again allow you for getting a disproportionation reaction. So, that particular disproportionation reaction from  $\text{Br}_2$  giving you  $\text{Br}^-$  as well as  $\text{BrO}_3^-$ . So, you get a mixture of bromate as well as the bromide, from which how we separate it out your bromate salt is less soluble that means it is poorly soluble, so it will be separated first then we get the sodium bromide.

So, sodium bromide will be highly soluble so it will in the solution when most of the bromate or the entire bromate can be separated as sodium bromate. But remember if both of them are the corresponding sodium salt, but depending upon the anionic part one is the  $\text{Br}^-$  and another is the  $\text{BrO}_3^-$  the bromide bromate thing.

So, they can basically separate it differentially. So, you must have a typical combination of these two. So, if we allow in alkaline medium only, so if you have this typical alkaline medium that alkaline medium can go for this particular disproportionation reaction. And if we try to get the reverse one, that means the combination of bromide and bromate mixture to produce the elemental bromine we have to go for an acidic medium. That means, in that particular case the  $H_2SO_4$  medium is sufficient to combine bromide and bromate to produce  $Br_2$  and the alkaline medium is sufficient to give you the corresponding disproportionation between the bromide and the bromate mixture.

So, whatever raw materials is in your hand judiciously you have to think of the corresponding procedure and your demand for all these elemental things, that means the bromine as well as the bromine compounds and we are not taking much more examples we are concentrating our attention on  $Br_2$  and two of these bromine compounds the bromide compounds or the bromate compounds is the  $NaBr$  and  $NaBrO_3$ . So, what are those applications where we can use this particular one that means where we can use these compounds.

So, one of the industrially important compound is the additives what we use in the fuel, as we all know that the tetra ethyl lead was earlier we use as the anti knocking reagent to increase the performance of the fuel while it is burning in the internal combustion engines. So, another organic compound which is the bromo di bromo derivative basically 1,2-dibromomethane; we know that if you have the corresponding methane, methane is  $CH_4$ . So, two of the hydrogen atoms of from the methane centre can be replaced by the bigger bromine centres we will get it is dibromomethane.

So, that particular one is utilized for your leaded petrol as lead substitute. So, it is the particular fuel additives when the lead can be removed through the formation of lead bromide. So, lead was present as tetraethyl lead, so tetraethyl lead can react with your that dibromomethane to produce your lead bromide itself and the corresponding methane which can be burned inside the corresponding fuel.

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**Brominated Fire-Retardants** - brominated diphenyl ethers, currently account for the largest number of bromine chemicals.

The ease with which the C-Br bond can be broken lead the organo-bromide compounds very useful materials as flame retardants.

**Tetrabromobisphenol A (TBBPA)**

It is mainly used as a reactive component of polymers, by incorporating into the polymer backbone.

A lower grade of TBBPA is used to prepare epoxy resins, used in printed circuit boards

Use of it is controversial because they are persistent pollutants.

BrC1=CC=C(C=C1)C(C2=CC(=C(C=C2)Br)O)C(C)C3=CC(=C(C=C3)Br)O

Then we can see that the some of the important brominated compound as the fire reducing agents or fire retardants. So, what are those compounds because, the substitution of these thing on the organic entire organic molecule can give you something that where the fire is there and fire is trying to burn all the available material around.

That means, if you have only the hydrocarbon part that means any fuel or simple methane or ethane or any other hydrocarbon it will burn very quickly, such that you can have the corresponding burning for your destruction of your CH bonds or CC bonds giving you the production of the corresponding water molecules from this hydrogen of the hydrocarbons and the carbon monoxide initially and finally carbon dioxide for the production of all the carbon oxides. But if you use some brominated diphenyl ether what is that is a very simple you have the diphenyl ether we all know ethers are ROR.

When you have two of the phenyl rings attached that means, PH O PH is the diphenyl ether. So, is a bulky one and which should not be very fire friendly, that means it is not very easy to burn it very quickly. So, the brominated form of these that means it is further brominated also and this particular compound it has a huge industrial demand also as a fire retardant agent, currently account the largest number of bromine chemicals what industry produced for us ok.

So, why this particular one is very useful is that the ease with which the CR bond can be broken which basically produce the organo bromide compounds which are very useful

material as the flame retardant. So, if you break the C Br bond of the diphenyl ethers which is brominated. So, the intermediate compound what we get basically after the removal of the bromine, so that organo bromine compounds basically can destroy the supply of the corresponding fuel and can reduce the corresponding flame or the fire.

Another example of this phenol based compounds because, these are all very much important and industrially those are very important and they are basically value added compound in terms of the bromine addition to the organic molecule or the organic chemicals, one such is further bromination is the tetrabromobisphenol A.

So, it is the typical variety of that so is a bisphenol compound and that bisphenol compound we all know that what is phenol and you can have two of these bisphenol compound and which is basically substituted in 4 different positions for your bromine incorporation.

So, it is basically coupled together with this particular centre, where is the carbon centre you have that means it is not CH<sub>2</sub> but dimethyl C. So, dimethyl carbon is there so it is 2 methyl function as the carbon. So, dimethyl carbon attached phenol unit from the para positions and further it is substituted for it is 4 positions of C H CH C H C H by C Br C Br C Br C Br. So, this compound is mainly used for as a reactive component or the starting material or the component for polymer formation. So, it is a reactive component of polymers by incorporating into the polymer backbone.

So, bisphenol polymer we know and if we try to improve the property of that particular polymer we incorporate a proportionate of this bromine derivative of bisphenol. So, this bromine derivative of bisphenol along with the original one which is not bromine derivative of bisphenol compound through polymerization give you a variety or a new type of polymeric compound.

So, the lower grade of this TBBPA, so this TBBPA which is not highly pure basically, but the cost of production of that particular TBBPA is less which can be very useful in preparing the epoxy resins. So, it is not a simple type of polymer, but making of epoxy resin is useful and in the electronics industry it is basically used in the PCB is the Printed Circuit Boards.

So, you see the we know how because it is basically in the domain of polymer industry but we are not talking all these things, but it is utilization how you use the brominated compounds because, we are talking in terms of the consumption of bromine the production of bromine and the bromine derivative of these thing. So, if you have elemental bromine and you know the procedure how your methane can be brominated only the techniques you should know, how methane can be brominated how your bisphenol biphenol can be brominated or bisphenol can be brominated.

So, the bromination technique will give you the starting material where the bromine can be consumed to a large extent for making these new compounds for very useful industrially important materials. So, but is use it is controversial because, these are persistent pollutants.

So, not only your bisphenol compound or the bisphenol a compound because we always try to restrict our use of this polymeric compound because, it will not be destroyed in the environment it will remain in this environment for many many years. So, the brominated variety is also because once the compound or the polymer is available we throw away the compound after use or after rejection, it the burden of the environment. So, basically it is the controversy, but if we take a proper precaution bromine can also be utilized very nicely for making all these useful compounds.

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**Fumigants and biocides**

Ethylene bromide, obtained by addition of  $\text{Br}_2$  to ethylene, was once of commercial significance as a component of leaded gasoline.

It was also a popular fumigant in agriculture, displacing 1,2-dibromo-3-chloropropane ('DBCB').

**Dyes**

Brc1ccc2c(c1)c(=O)c3c2c(=O)c4ccc(Br)cc43

6,6'-dibromoindigo

The slide features a yellow background with a dark blue curved border on the right. At the bottom, there are logos for Swamyam (Free Online Education) and other educational institutions, along with a small video inset of a man in a white shirt and glasses.



Then they are also useful in another area which are known as your fumigants or biocides, biocides you know that is how you destroy the biologically available different dangerous things; that means, the corresponding one the half's which we do not require. For that purpose we have to make through bromine ethylene bromide and that ethylene bromide obtained by the addition of simple bromine addition to your ethylene molecule.

So, the direct addition so it is a typical addition reaction of bromine throughout the carbon double bond. So, is also a commercially important procedure as a component of leaded gasoline. So, ethylene bromide again like that of your di-bromomethane we add it as the corresponding leaded gasoline component for your improvement. It was also a popular fumigant as agriculture so not only your addition to the gasoline material, but ethylene bromide is also a fumigant in agriculture because, in agriculture we sometimes we spray all these things displacing the original one original one is 1,3-dibromo-3-chloropropane.

So, it has a over burden of not only 2 bromine centres it is a dibromo plus 3-chloropropane molecule. So, is less harmful compared to this compound DBCB that we use simple ethylene bromide which is only bromine based. Then we can move to making some dyes; dyes we all know that which is a very useful colour absorbing material and dyeing industry span from textile to you are paper industry to cloth industry and everywhere we can have the dyes.

So, the dyes which are nothing but your brominated dyes. So, indigo we know that indigo earlier it was naturally we reproduce indigo from agricultural sector, but during this particular knowledge that we make this indigo dye in the laboratory.

So, that is useful we know for our textile industry that blue colour of the indigo we put on the jeans the jeans material, then to improve that material for it is life or for it is utilization for it is industrial processing which is useful for your textile material, we can go for it is bromination.

So, what we should know we should know a little bit that what is indigo and how indigo can be brominated and that indigo bromination can improve the quality of that particular dye. So, that particular step we are only considering or focusing our attention that how bromine the bromine industry can help in making this 6,6-prime dibromo indigo molecule for a useful dye molecule.

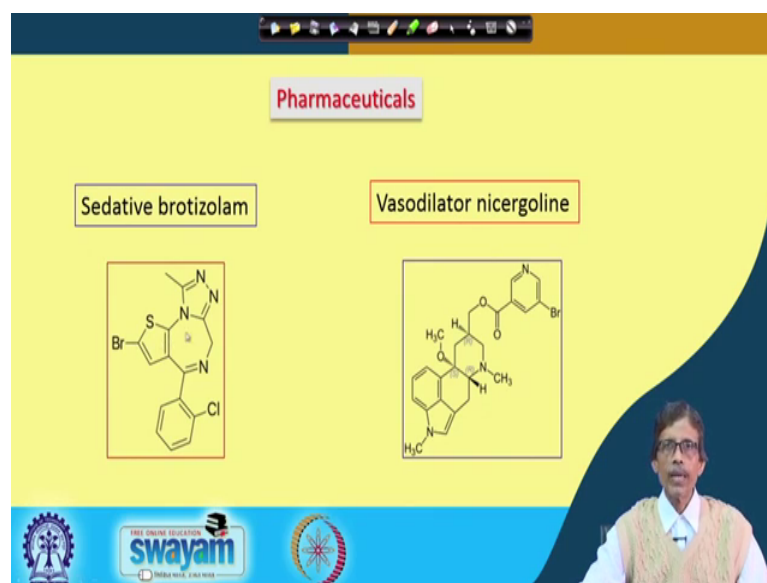
So, this particular one so we have these two selective positions; that means, most of the time it is like that of your bromination of the ethylene is a direct one we take indigo and we go for it is typical bromination, that means sometimes we simply add bromine. So, that particular thing can so good; that means, the reaction is so facile that immediately the bromination can take place through the direct aromatic substitution reaction.

Because you have the 2 phenyl rings and we have the phenyl C H bond over here and another phenyl C H bond is here. So, you get the corresponding aromatic substitutions, aromatic nucleophilic substitution by the bromine centres to give you the corresponding bromine derivative.

The way we get for a simple organic molecule such as that we know that for analytical reagents we have the oxygen molecule that 8 hydroxyquinoline and if we want to derivative that as the corresponding bromine derivative, it is simply through addition of elemental bromine drop by drop diluted solution of bromine addition to that particular organic molecule or sometime in C 2; that means, in within the reaction medium we produce bromine.

So, production of that bromine again we know just now we have seen that the combination of bromide bromate mixture can give you the liberation of bromine in a particular acidic medium. So, the acidic medium the slow release of that bromine through the production and then again the organic molecule if it is available will attack that organic molecule and produce it is brominated version. Similarly, some procedure we should have also for industrial or large scale production of this dibromo indigo molecule. So, this is also another important application of your bromine compound.

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And lastly we will see that how the pharmaceutical industry can also be benefited, because, the pharmaceutical molecules we all know that that can be used as a useful drug molecule or is a useful medicine for our purposes for our use. So, those molecules we know that is they are sometimes they are very big molecule they are mostly the organic molecules sometimes they are hetero cyclic having hetero cyclic structure. But new drug discovery or new drug molecule availability sometimes is dependent on a very simple reaction it is nothing but a simple bromination reaction.

Earlier we have seen that a particular type of molecule organic molecule which is a pharmaceutical molecule, that pharmaceutical industry can take the advantage of typical fluorination. Now we will see that the typical bromination can also change the corresponding structure.

So, do not worry about the complicated molecule what you have in your hand, but it is the molecule what you see that this particular molecule the entire part we knows you have to know. Just now what we have seen that the dye molecule can be brominated. So, similar type of bromination can be achieved on the pharmaceutical molecule where we see that this particular C Br bond.

So, without that C Br bond the function of this is again they are so that the whole molecule is also a functionally active molecule and which is nothing but a nicergoline, so which is a vasodilator type this function is a vasodilating activity. So, it is a vasodilator

nicergoline so vasodilator nicergoline can be formed when you get a typical brominated derivative of the original organic compound. So, what do we have the whole molecule you can consider as R and you have this C H bond as RH like that of your methane or anything else.

So, which can be brominated to give you the corresponding big R molecule as you are the pharmaceutical molecule as well as you are the corresponding insertion of the bromine at a specific position. So, bromination at this particular point at this particular position can tell us that we can improve sometimes it is not always true, that we can improve the quality of the pharmaceutical through bromination.

So, if we are able to improve the quality or it is performance in terms of it is activity we can go for its bromination. So, one more example also we can have again it is a little bit complicated molecule, but forget about the complication in terms of it is pharmaceutical structure or the pharmaceutical molecule we are only focusing our attention for your brominating part.

Again if we consider that the whole molecule is your R and R is attached to your H. So, H is there. So, RH can be converted to convert that compound to RDR which is again a drug responsible for sedations. So, it is Sedative brotizolam Sedative brotizolam and that selective molecule is again obtained through bromination of the corresponding part which is the corresponding thiophene ring it is heterocyclic ring.

So, the thiophene ring here you have the pyridine ring at one end. So, at one end the pyridine ring at the meta position is getting brominated, here also the thiophene ring the ortho position of the sulphur of the thiophene ring is getting brominated to improve the nature of that particular pharmaceutical molecule.

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Tear gases contain bromoacetophenone and bromoacetone.

Inhalation anesthetics is 2-bromo-2-chloro-1,1,1-trifluoro-ethane.

Iodine and Iodine Compounds

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So, this also can give you some other example that where the bromine can be useful for this. So, tear gases are also useful we will see we will continue for your next class also, the tear gases what are the molecule we use for the tear gases. So, it should be pungent it is its pungently smelling also it can bring tears in your eyes, so people discovered this molecule that this a very simple molecule which are only simply bromo derivative it is not the bromo form it is not the other bromo derivative of any other small compound. But we know that acetophenone molecule; acetophenone molecule has not such effect or only acetone.

So, if we have in our hand the only acetophenone molecule and acetone molecule and if we are able to brominate them through the use of the elemental bromine we get the typical application of their as the tear gases. So, this is nothing but your tear gas smoke and the tear gas smoke is basically is available.

So, this is the cell when you break the cell it is basically the fumes people will simply move away from there to avoid that particular fumes. Then it is also useful for some inhalation anesthetics which is 2 bromo 2 chloro 111 trifluoro ethane.

So, is one basically is 1 1 1 trifluoro ethane, so fluorine is there, chlorine is there and bromine is there. So, it is a little bit complicated molecule and that molecule is therefore is a very important because what we see that in this particular case once you have an the halogens because, we are talking after fluorine the corresponding use of your

bromination. So, you have fluorination, you have chlorination and you have further at the end if possible the bromination.

So, this complicated molecule it is again possible to make and through inhalation anesthetic molecule. So, this anesthetic molecule again is possible to make through the introduction of your compound as its corresponding bromine derivative.

Next the next class will continue basically for the third (Refer Time: 29:27) molecules, that means the elemental thing the third elemental thing is your iodine and iodine compounds. So, when we talk in terms of the iodine and iodine compounds the iodine compounds are completely different if we have some little bit of experience of knowing that what iodine compound is. So, we have the fluorine as the corresponding gas molecule then bromine as the liquid, but iodine in its room temperature laboratory condition it is present in the solid form.

So, it is sometimes very easy to make it that particular iodine molecule easy to store it and sometimes we will find is also a very useful reaction in terms of it is reactivity with the different materials. So, the sector industrial sector which is producing large amount of iodine can make more and more new compounds which are also very much useful industrially.

Thank you very much.