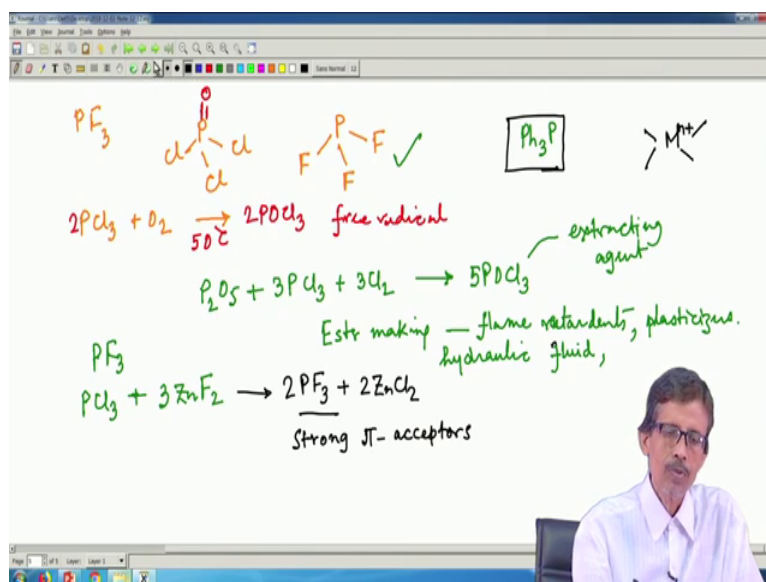


**Industrial Inorganic Chemistry**  
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**Indian Institute of Technology, Kharagpur**

**Lecture – 14**  
**Hydroxy Apatite**

Welcome back to this class again, where we are considering the hell generated person of the different phosphorous species. So, we are talking about the phosphorus pent chloride, phosphorus trichloride and PF<sub>3</sub>. So, along with this PCl<sub>3</sub>, we can have the PF<sub>3</sub> also.

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So, that particular PF<sub>3</sub>, what we get like that of our phosphorus here it is is basically these 2. So, we can have the different types of this bond distances and bond angles.

So, this particular one will be soldered, the angle will also be solder for these compounds, so when you get this tri phenyl phosphine and all these things, so we can utilize this as for oxidation also. So, if we get this PCl<sub>3</sub>, its reaction with O<sub>2</sub>. So, another interesting compound we will get from there and which is our twice of these plus O<sub>2</sub>, when we do the reaction at 50 degree centigrade, we get basically twice of POCl<sub>3</sub>.

So, that twice of  $\text{POCl}_3$  is basically a free radical mechanism and which can be purified by fractional distillation. So, this mechanism of this reaction is through free radical. So, that particular free radical reaction we get for this particular production.

So, here you see that if you have this; that means, you can have this particular  $\text{POCl}_3$  formation. So, through that lone pair of electrons you get some oxygen over there and those compounds are very useful by one of this particular process. Another one process we can get it from  $\text{P}_2\text{O}_5$  and that  $\text{P}_2\text{O}_5$  we use it and its reaction with thrice of  $\text{PCl}_3$  and some extra chlorine, that gives us 5 of this  $\text{POCl}_3$ , so phosphorus oxychloride.

So, these are very useful because, it can also give you for this corresponding supply of chlorine and we get this as the corresponding compound for making that esters. So, it they are useful in Ester making and also it is useful for flame, flame retardants. Then it is useful as plasticizers, useful as hydraulic fluid and also sometime, it can be very useful as good extracts and agent. So, it is extracting, good extracting agent.

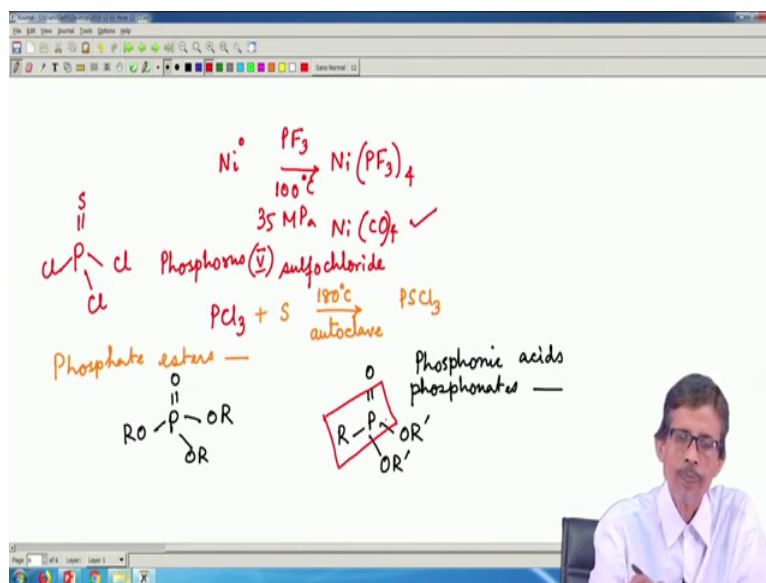
So, making this  $\text{POCl}_3$  will therefore be very useful process when you have amended as demand for all these cases; that means, starting from flame retardants to making these hydraulic fluids. So, next we see that how we can make this  $\text{PF}_3$  compounds. So,  $\text{PF}_3$  compound like that of our other types of compound like already we have seen that we can have that useful ligand is 3 phenyl rings attached to the phosphorous center.

So, is a very simple one as your corresponding organo phosphorous compound, where you can have the phosphorous center attached to the 3 phenyl ring and will also be a very useful ligand system like your ammonia. So, this particular one that  $\text{PF}_3$ , so making this  $\text{PF}_3$ , how we get that, so in this particular case starting from your  $\text{PCl}_3$ , so we will have  $\text{PCl}_3$  plus thrice of  $\text{ZnF}_2$ .

So, we will have this compound, if we react this phosphorus trichloride with zinc fluoride. So, reaction of these will basically give us 2 molecules of  $\text{PF}_3$  plus twice off now the zinc fluoride will be converted to zinc chloride. And this particular one if we compare, this is also a ligand to us the triphenylphosphine and if we can have a typical metal ion center  $\text{Mn}^{n+}$  plus as we all know and it can have several coordination sites and some of these coordination sites can be occupied by triphenyl phosphene, some will be coordinated by the chloride ion sometimes we get as this got funding one as the rhodium center or the palladium center we get some useful catalytic site.

Similarly, we can compare this with that of our PF<sub>3</sub> thing with that of our triphenylphosphine. So, it can also be a very good ligand because, it is a strong pi acceptor, it is a sigma donor and it is a strong pi acceptor because you have electron withdrawing fluorine centres are there. So, that is why they are strong pi acceptors. And these strong pi acceptors will be useful for making some different types of compounds in our hand.

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So, what are those compound basically if we want to make a compound like this, say a nickel compound of 4 trifluoro phosphine ligand attached to it, how we make it. So, this will be very much similar to the compound what we know through the Mond's process; that means, nickel tetra carbonyl compound this is also a tetrahedral one.

So, like that of nickel tetracarbonyl we can make it from there with the supply of PF<sub>3</sub> at a high temperature because, this is formed at room temperature and some elevated pressure of the carbon monoxide here the pressure required for this tri fluoro phosphine is 35 MPa. So, that basically gives us the corresponding production of this particular compound. So, the ligand production, because these ligands are very much useful compound for catalytic industry, so we can make this and we make this a phosphorous based ligand and that phosphorous based ligand will be spool in giving you all these compounds.

So, phosphorous can also be useful for making a corresponding compound which is P double bond S, like that of our P double bond O; whether we will be able to make this

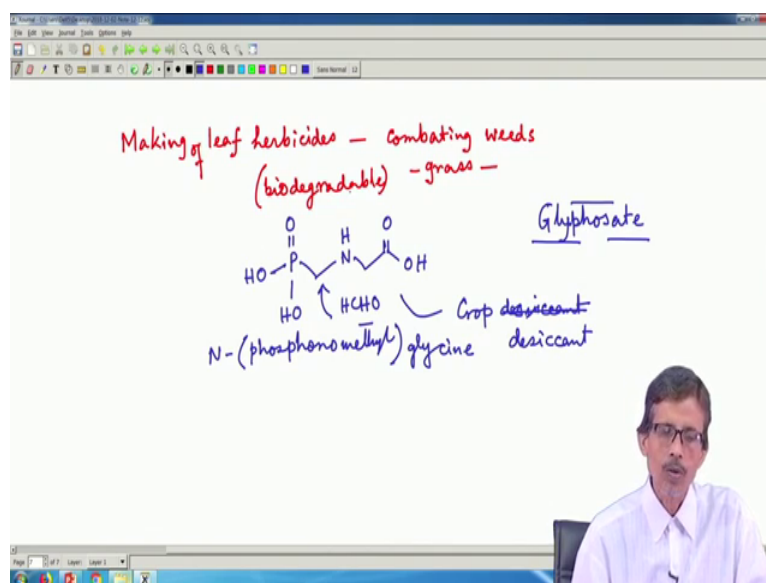
compound phosphorus sulfo chloride. So, this will be therefore, your P double bond is Cl and Cl. So, which is phosphorus in 5 oxidation state plus 5 oxidation state so, Phosphorus 5 sulfo chloride. These basically again simply by doing this reaction with  $\text{PCl}_3$  plus sulphur at a temperature of 180 degree centigrade in an autoclave, we get  $\text{PSCl}_3$ . So, all these compounds are basically useful for some purpose or other and the phosphate esters therefore, how we see the different phosphate esters as I told you that we can get these Phosphate esters from the corresponding phosphoric acid.

So, these phosphate esters can be very useful like that of our different organ of phosphorous compounds. So, if we have the corresponding phosphorous center like this P double bonded O and we can have this RO, OR, OR. So, these are the corresponding phosphorus centers and those phosphorus centers can be useful for making these phosphate esters.

Then we can have the Phosphinic acids or Phosphonic acids and different phosphonates. So, in this particular case only that since we do not have any phosphorus carbon bond over here in these phosphate esters, but this particular phosphonic acid and phosphonates, we will have a typical r function on it and that R function is basically attached to the phosphorus center with OR that R can be different, so it can be OR prime.

So, these basically giving you and much more complex compound which is can be further corresponding phosphoric acid and definitely what we can have over there is our corresponding this function; that means, phosphorus carbon bond over there. So, one such compound if we can make is therefore, very useful as making herbicides.

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So, how we get some industrially important leaf, the plant leaf herbicide making off leaf herbicides, which is also very interesting to know from the environmental point of view, these are bio degradable. So, we have these biodegradable herbicides which are basically based on the phosphorus and they are useful for removing the weeds. So, they are useful for combating weeds, sometime it can reduce also the unwanted grasses in the field.

So, they are very useful in the agricultural industry. So, one such compound if we can think of is a very simple one because since, we are talking all in terms of getting this as the phosphorus oxygen bond and 2 other bonds are that OH OH bonds one other bond; that means, the 4th bond what we can have already in the typical phosphoric acid is your another POH bond, but instead of that if we can now have a carbon over here.

So, that will be a typical different compound and we can classify them as the typical organophosphorus compound which is industrially very important and making these as you know also in a very low scale also useful, because these are very good herbicides. So, if we take this and is also a very useful compound known as Gly faucet, which is Gly then, phos phos then ate. So, it is basically a glycine based gly is coming from glycine.

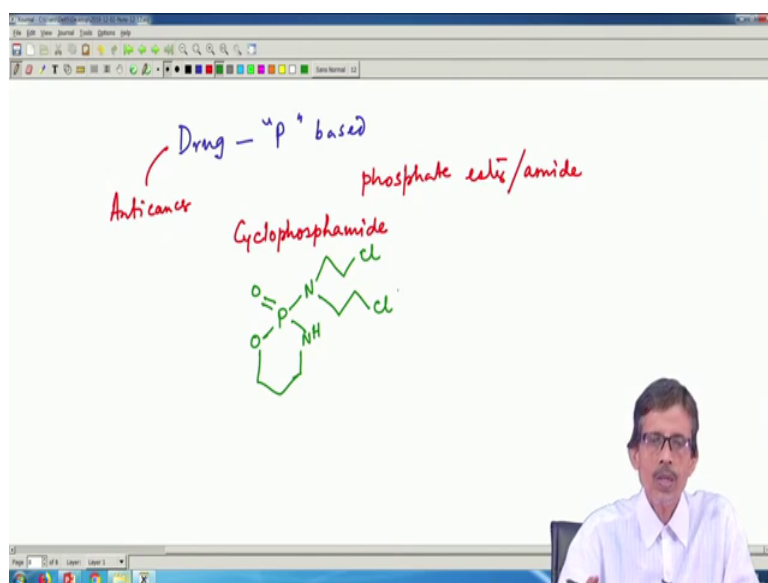
So, and this phosphate esters thing will be the other part. So, is a glycine based phosphate ester therefore, we get these as the corresponding nitrogen of the glycine through this carbon. So, it is attached to the nitrogen of that particular center through this particular carbon and the remaining part is your glycine part. So, is a not only is the

herbicide, is a which combats the weed also, it is also a crop desiccant, as a crop one establish, so crop desiccant, the crop desiccant.

So, the compound is basically what we have the N substituted; N substituted this phosphate unit in phosphono methyl glycine. So, if we know the typical reactions for all these things because, we can have the elaborate preparation procedure, we can have so many steps over there, so we can use this as the compound source from basically we utilize formaldehyde for introduction of these on glycine.

So, if one hand you can have some other phosphorus based compounds starting from your phosphoric acid then formaldehyde or a other glycine part we can have, we can make this particular very important compound. So, next we will see another example where we get some drug molecule.

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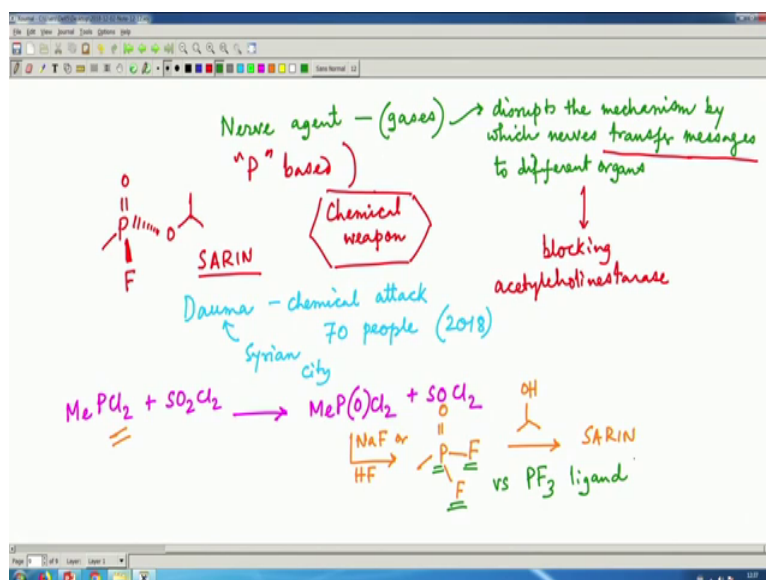
Very few of these drug molecules are known, which are phosphorus based. So, what are those phosphorus based drug molecules we can have, based on the information or the knowledge whatever we have gathered so far; that means, it should be a typical phosphate ester, phosphate ester or some part can be also an amide part. So, phosphate ester part or the amide part in a very typical configuration which is a typical anti cancer drug, which is a cyclic one, so cyclophosphamide. How we get that particular cyclophosphamide?

So, already we have seen in case of the glyphosate preparation or glyphosate molecule itself that is a long chain 1 at 1 end we have the carboxy end and another end you have the phosphorous based acid part again. So, these 2 ends are basically the 2 acid ends, we cannot go for the typical cyclization reaction for that.

So, we go for some other particular type of reactivity or the reaction for making this, but here only we will see that what is that particular compound? What we can get over here? So, the tetrahedral phosphorous we can have and the cyclophosphamide part we get. So, basically the cyclophosphamide or we can also the one part as the eastern and the other another part is the corresponding NH function and making this as the typical 6 member tree.

So, this is the cyclic part cyclic phosphamide and basically when we get this as this one we can have for the nitrogen over here and CH<sub>2</sub> CH<sub>2</sub> Cl<sub>1</sub> and another CH<sub>2</sub> CH<sub>2</sub> Cl over here. So, these complex molecules we can get from all the different types of phosphorous based compounds taking into idea that we go for the preparation of different esters or the different amide because the phosphoric acid is the typical inorganic acid which can give rise to the different reactions based on making these esters or the amides.

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So, next we see that what we get for a typical molecule, which is deadly, also is known as a typical nerve agent. So, what is that particular nerve agent? Basically nerve agent is

nothing, but the gas, which is the deadly gas these gases, these gases are very deadly and they basically disturb the mechanism of the nerves.

So, they basically disrupts the mechanism by which our nerves transfer messages to different organs. So, basically is the idea that we just basically block this transfer of messages of the different knobs that is why it is known as a nerve agent. So, very quickly basically within 10 seconds or 20 seconds time we can kill people if they in hell these gases.

So, basically when we disrupt this, basically they go like blocking the or one particular molecule which is acetylcholine. So, the block basically, blocking acetyl acetylcholine esterase because, acetyl choline is your neurotransmitter, which basically transfers the corresponding nerve signals, transferring the messages to the different organs how your different organ can function and all these things.

So, this phosphorus based nerve agents variants. So, these are phosphorus based like the drug molecules. So, these phosphorus based nerve agents basically go for blocking these particular neurotransmitters, which is your acetylcholine So, one such compound will take one example only and which is very useful as where we can use these nerve agents as the chemical weapon, we so, in the chemical war also when we use these chemical weapons for chemical war killing a mass destruction or mass killing of people of one country to the other we can use this particular one.

So, we have the P double bonded O attached to some methyl group; that means, you can establish the phosphorus carbon bond over there and like your PF 6, we get these as the corresponding fluorine compound because the corresponding covalent nature of the phosphorus fluorine bond is different. So, that is why instead of chlorine or oxygen or oh we have this fluorine bond and then we basically get is as the corresponding oxygen from the isopropyl function.

So, is they basically isopropyl function over there, so isopropyl ester we get it. So, this particular compound is known as SARIN, is well known. So, this SARIN basically is a chemical weapon for that and in the Syrian city Dauma recently the Syrian city Dauma people are suspecting that this has been attacked, this has been used for a chemical attack, is a very recent story killing 70 people, this year only 2018. So, is Dauma is a Syrian city in Syria. So, how we get this compound? So, what are the things we can



have? So, when we talk about the corresponding making of this compound, we should have the corresponding philosophical aspect that how we make it.

We know that the phosphorus we get it from the elemental phosphorus. So, how you can convert it to phosphorus trichloride or phosphorus trifluoride, even you know how the grignard reagent can be useful for establishing the corresponding methyl function on the phosphorus center. So, if we can take a corresponding compound like  $\text{PCl}_2$  which we can have, already we have the corresponding methyl phosphorous bond; that means, it is already an organo phosphorous compound and we react with  $\text{SO}_2 \text{Cl}_2$  to get is as  $\text{MeP}=\text{O} \text{Cl}_2$ .

So, this phosphoryl chloride in all other cases, in all other organic chemistry reactions we know that this  $\text{SO}_2 \text{Cl}_2$  can be useful for supplying chlorine to that particular other compound is the chlorinating agent also, but here you see is the typical reaction. So, this particular reaction it is supplying the oxygen to the phosphorus center.

So, this is giving you the starting material for making this serine molecule and we get  $\text{SOCl}_2$  from that. So, in the next step basically when we utilize this with the reaction for substituting this particular one; that means, we substitute now these 2 chlorine by 2 fluorine molecules so; that means, the corresponding fluorine salts we get. So, use of  $\text{NaF}$  or hydrofluoric acid, we will convert this molecule; that means, you get these 2, that means, the substitution on this  $\text{Cl}_2$  will be by these 2 fluorine unit.

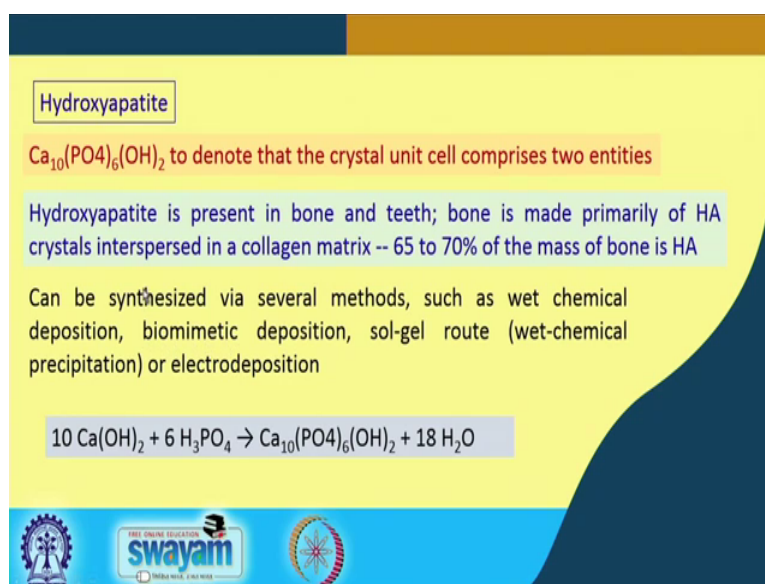
So, you have that P double bond O and these 2 R your F. Then reaction of these from this for alcohol part, so alcohol part is that your isopropyl alcohol, so we use this with that apart isopropyl alcohol and reaction of this isopropyl alcohol giving us this compound back; that means, you prepare this with that of our serine molecule.

So, making this particular molecule gives us all the ideas that how we get these as the corresponding formation of these and introduction of PCl bond, hydrolyzing ability of that particular bond and also converting that particular one through a deadly poisonous gas molecule and that gas molecules are very useful. So, it definitely is a very lethal and deadly also to ask.

So, handling this phosphorous compound because all these very deadly things we are handling we are not only handling the phosphorus, we are handling the sulfur center

from this particular molecule. But at one end we have seen that simple PH 3 molecule, the simple; that means, if we try to compare this with that of PF3 molecule, which is a very good ligand giving you us this corresponding metal ion complexes or metal complexes in the 0 oxidation state such that or that of our nickel 0.

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The slide features a yellow background with a dark blue and orange header. It contains text about Hydroxyapatite, its chemical formula, its presence in bone and teeth, synthesis methods, and a chemical reaction. At the bottom, there are logos for Swamyam and other educational institutions.

**Hydroxyapatite**

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  to denote that the crystal unit cell comprises two entities

Hydroxyapatite is present in bone and teeth; bone is made primarily of HA crystals interspersed in a collagen matrix -- 65 to 70% of the mass of bone is HA

Can be synthesized via several methods, such as wet chemical deposition, biomimetic deposition, sol-gel route (wet-chemical precipitation) or electrodeposition

$10 \text{Ca}(\text{OH})_2 + 6 \text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 18 \text{H}_2\text{O}$

Logos at the bottom include Swamyam (Free Online Education) and other educational institutions.

So, with these basically we have this particular situation, where we get and where we see for making this diphosphonates calcium phosphonates to up to the serine molecules and lastly with this particular slide we will try to understand how we get the different types of hydroxyapatites. In our previous class, we I told you that you can get these as a typical bone material or teeth material where, instead of the simple phosphate PO4 is the PO4, so Ca 10 PO4 whole 6 OH; that means, you can have the hydroxide groups and sometime those hydroxide groups can be substituted by fluorides known as the floor appetites.

So, hydroxyapatite or floor apatite they can have a typical type of crystal structure and when we write this as the formula which is double the amount of that which is really we write as the Ca5 molecule, but when you write as the Ca10 molecule; that means, it has a different composition; that means, it unit cell has 2 entities and is both of the these 2 things, that means, either a Ca5 molecule or the Ca10 molecule is present in our bone and teeth material.

And mostly our bone material is made up primarily by this with this hydroxyapatite and is 65 to 75 percent 70 percent of the bone mass is this particular one and which these crystals are spread over within our collagen matrix and the collagen is basically trapping for the growth of this biomaterial. So, it is the basically a very useful biomaterial which has a very similarity to it the naturally occurring apatite molecule. So, this week also consider as the bio mineralization in our body when we have the regular supply of not only the calcium ions, but also the phosphate anions.

So, the laboratory techniques or the laboratory processes those we can have also. So, how we can prepare in the laboratory; that means, if we just go for the synthetically prepared, the bone material or the synthetically prepared teeth material what we can have can be this can be synthesized by a different methods and one such method is our wet chemical deposition, but what we get that in both the 2 components in solution we add one component to the other, we get the precipitate and we ultimately it is settles down; that means, we get the corresponding deposition then biomimetic deposition.

That means if we have the collagen matrix on that matrix; that means, you have the matrix support like that of our simple filter paper support or some cloth material or some jute material if we can have that sub tickler support and on that support if we just go for the deposition of this material; that means, the crystallization of that material in a very slow and irregular manner, we get these as a corresponding filled matrix with that apatite material.

Then we can have the typical sol gel material is the wet chemical precipitation method; that means, formation of the corresponding salt form and which has been converted to the gel and then hitting that particular material will give you the corresponding hydroxyapatite material, which is basically a phosphorous based useful material biomaterial, what we can make in the laboratory also or sometimes we can get it as a typical electro deposition also.

So, the very basic reaction what we can have in our hand is that simple reaction of the calcium hydroxide what we get. So, this calcium hydroxide what we can take which can be immediately react with that of our phosphoric acid. So, 10 molecules of calcium hydroxide when reacted with 6 molecules of  $H_3PO_4$ , we get this particular compound as  $Ca_{10}(PO_4)_6(OH)_2$  with 18 molecules of water.

So, simple direct reaction between 2 components; one is a another is b, we get a compound which is your very basic compound which is your hydroxyapatite molecule and that hydroxyapatite molecule if it gets a solid support, it can be formed as a biomaterial which can be a corresponding biomagnetic for our bone and our teeth samples.

Thank you very much.