Industrial Inorganic Chemistry
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Lecture –11
Phosphorus and its Components

Hello, good morning to everybody and welcome back to this class of Industrial Inorganic Chemistry, where we are basically talking about the chemical aspect or the chemistry aspect or the other inorganic chemistry aspect for some useful industrial compounds. So, it is not a typical course of some inorganic compounds which are producing directly from the industry. So, basically we are focusing our attention on the corresponding chemistry part of all these compounds, which are very useful. So, so far we have seen that how we can utilize the natural resources like water, like oxygen and like dinitrogen gas which is available in the atmosphere.

So, if we consider that all these natural resources we can utilize nicely for the conversion or some value added compounds, like that of your making ammonia or urea what we have seen our last 4-5 classes that, how nitrogen can be utilized for making some useful nitrogen compounds like urea or ammonia. So, today will go slowly for going to other compounds like that of our phosphorus. So, if we consider how we can get the Phosphorus Compounds, so only phosphorus as well as its compounds.

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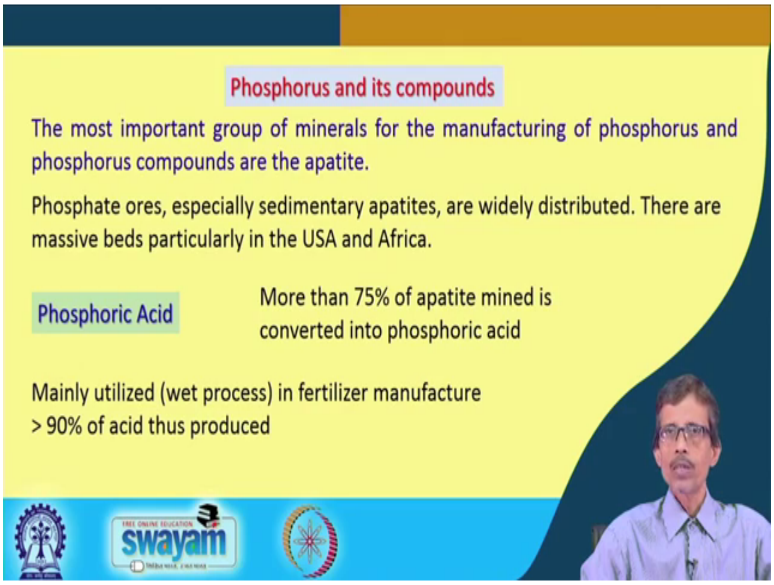

So, as we all know that like that of nitrogen, nitrogen is present in atmosphere as N2 and phosphorus can have some mineral sources also and these mineral sources from the earth surface or the earth crust we get it.

And how, we can extract out that phosphorus as the elemental phosphorus which has a molecular formula of p 4. So, utilization of that thing; that means, from the geochemical point of view or a geologists point of view, that how we can get from some rock material that particular phosphorus element and that phosphorus element can be isolated in the pure form; such that, we can utilize that particular phosphorus as our sources. As we all know that phosphorus can have the different varieties like white phosphorus red phosphorus, as well as the black phosphorus.

So, this particular p 4 compound how we can utilize for making some useful compounds because, the phosphorus chemistry is very rich and particularly when we talk in terms of typical inorganic chemistry class we talk in terms of all the large number of phosphorus compounds and which are academically important as well as industrially, but in this particular class we will focus our attention on those compounds which can be produced in a large amount not by our country, but many other countries advanced countries like US, the European countries and the china they have these natural resources and they get all these from the nature and if they are having a huge source of all these natural compounds like that of a natural material like that of your phosphate based rocks.

So, these phosphate based rocks are very interesting area of study and so we should know we are not able to talk about the different structures, the solid state structures of all these phosphate rocks. And if we can have only the supply of these phosphate rocks for industrial purpose or industrials sake, we can utilize the earth particular phosphate rock for isolating the phosphorus as the elemental phosphorus.

So, isolation of elemental phosphorus as well as its conversion to the compounds will be our today’s discussion. So, if we consider that those are coming from a mineral source, as we have seen that what are those minerals and ores we know. So, this can also be an important group of minerals for the manufacturing of phosphorus as well as phosphorus compounds.

So, the source is apatite and if time permits will also talk about this particular thing that is also very important nowadays, as the materials which are useful for our biological world our body itself. So, biomaterials and some of these biomaterials can also be useful for medicinal purpose. So, as nature give us this particular thing; that means, the appetite, so large number of appetites are available and these appetites, how we can utilize those appetites for the conversion of phosphorus that will see; that means, extracting out of that phosphorus from that appetite source will be a useful understanding for this particular course.

So, all these appetites are therefore, are the phosphate based ores. So, what is that? That means, we can have the typical inorganic anion what we all know that, the phosphate which is po PO 43 minus is the usual form of that corresponding phosphate anion. And we all know that the corresponding acid is your phosphoric acid, the syrupy phosphoric acid or we call it as the orthophosphoric acid which is nothing, but your H 3 PO 4. So, if we can get that phosphate ores, particularly from the apatite source and that apatite source where from we are getting, is particular terminology we use from the geological knowledge, that is the sedimentary rock we call or the sedimentary apatites will be the source.

So, the appetites are there which the nature of those appetites are the sedimentary nature. So, sedimentary appetites are there, so which is widely distributed throughout the earth crust or some below the earth crust also and there are massive beds because the source is particularly concentrated in the USA and Africa. So, there are massive beds particularly in USA and Africa, which can get out this all these phosphate ores or the phosphate rock.

So, interconnecting these things that how we get phosphorous from the phosphate rock and how the particular mineralization process for the apatite is also a very important understanding, because this material what we have as the bone material or the teeth material which are calling we are calling as the biomaterials. So, these biomaterials will also be useful in understanding if we want to know that how the material is aggregating and how the crystallization is taking place, within the biological environment for the formation of the typical compound which will have also the another cationic metal ion which is calcium.

So, these 2, the cation is the calcium and the anionic part is the phosphate, but it is not a simple calcium phosphate type of molecule. So, which is a complex one and its solid state structure is also completely different. So, that solid state structure and how we can utilize these as material or as some small molecules for some other purposes, that we will see So, if we directly go from there; that means, if we just take the ore which is a sedimentary apatite ore or rock we consider, then if the supply of this phosphate material is more, we can consider it as also a supply for your ore. How we can get it as the phosphoric acid. So, basic idea behind this is that, that you have the phosphate ore and in a complex structure we have the typical phosphate anions present in it.

So, if we can protonate those phosphate anions and we can leach out all those phosphate anions in a pure form, what will be getting; that means, PO43 minus is the phosphate anion which will be protonated and that protonated form will give you the corresponding phosphoric acid, which I just now told you that it is your H_3PO_4. So, that H_3PO_4 formation is a important form from those phosphate ores.

So, making this phosphoric acid from phosphate ore or appetites, so how we can make that. So, more than 75 percent of this apatite, what we mined basically for direct use for all other purposes, so 75 percent of that what we get out of from the mining process or them from the mining industry. So, so that 75 percent of will be converted into this particular useful form; that means, the phosphoric acid.

So, like your nitric acid what we discussed earlier, this phosphoric acid can also be a useful mineral acid inorganic mineral acid and that will be useful for some all different purposes, where we can use this particular acid as well as its different acid salts also.

But where we use this, why we produce those much phosphoric acids? So, you see that our mineral apatite is giving some amount of phosphorous and those phosphorus if we can convert to that some phosphate ore and that phosphate ore is giving you the phosphoric acid. So, the ready supply of phosphoric acid what we can have in our hand can be converted to some other phosphate salts or the phosphate, corresponding a phosphate material, where we can have that for a as a micronutrient because we all know that phosphorus can be a micronutrient for the our soil, that it can be a good component for your fertilizer.

As we have seen earlier that while making, the nitrogen based fertilizer we can have the ammonia, we can have the urea, as well as we can have saw the other converted nitrogen salts like that of your ammonium nitrate. Similarly here also the phosphorus based salts basically; that means, the corresponding other salts of phosphoric acids, so we have to produce phosphorus not only phosphorus, we have to convert that phosphorus to phosphoric acid and from that phosphoric acid will be making your corresponding salts. So, if those salts are available for increasing the corresponding health of the soil or it can serve as a very good micronutrient for our soil, it can be considered as a component of our fertilizer.

So, we know that we have nitrogen in the fertilizer, we have phosphorus in the fertilizer and also we know that we can consider some fertilizer as NPK fertilizer. What is that NPK? So, N is for nitrogen, P is for the phosphorous and K is for the potassium. So, potassium can come as the corresponding salts as the potassium ions, but before that whatever we have seen earlier is that nitrogen, now today we will be talking about the corresponding amount from the phosphorus.

So, making fertilizer, we always use phosphoric acid and one such particular process is known as the wet process. So, this wet process basically for making this fertilizer, so how much phosphoric acid we basically use, so industrially throughout the world the data is in our hand.

So, that particular statistics tells us that we can consume up to 90 percent of the acid what we can produce in industry as making for the corresponding fertilizers. So, the industry which is devoted in making phosphoric acid is therefore, a huge industry, only thing is that, you can have some cheap and regular supply of all these phosphates and how cheaply we can make that particular phosphoric acid from the phosphate ore that is also important.

So, wet process as we all know that simply, it is a wet chemical process; that means, in the wet method we will be utilizing that particular mineral which may or may not be soluble in water or in aqueous medium or in some wet condition.

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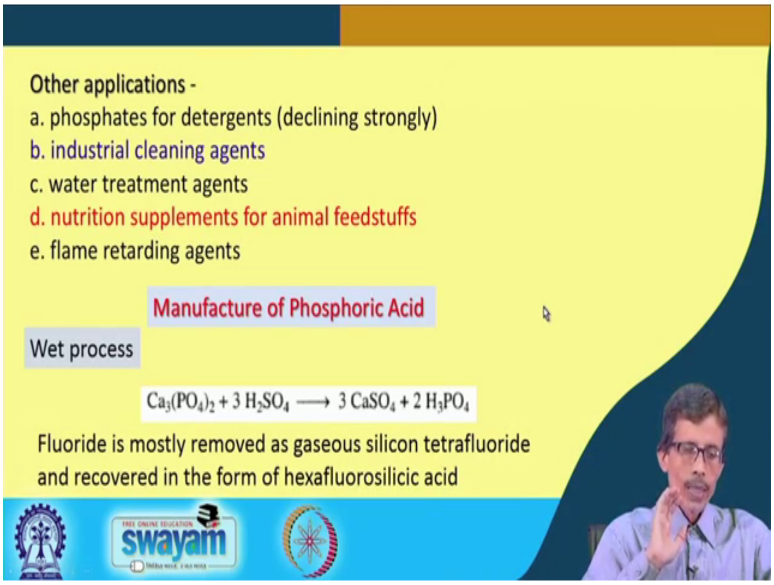

So, that basically gives us some idea that how we get these as the corresponding form. So, first of that is therefore, our use or application of these making of these important compounds.

So, one such is you are making fertilizer and apart from that basically phosphates are also utilized for making several detergents. Nowadays we know and everybody should know now that, what is the difference between soap and detergents. So, is a special type of thing that what can take out your dirt from our clothes and all other things. So, these particular detergents, which we are making in solution and that solution is useful is taking out that dot basically. So, that particular one is basically based on the phosphates.

So, different types of phosphates are utilized is not that long chain carboxylic acids what we know, that sodium stearate, sodium palmitate like of long chain fatty acids are known as your soaps. So, these are different from all these soap materials. So, these are little bit of the surfactant type molecules, but typical phosphates bearing molecules and those phosphate bearing molecules are useful for making detergents.

So, if you have a industry and if we are trying to plan to get some industry which will be devoted in getting phosphorus not only phosphorus, but phosphoric acid, the corresponding salts also then also we can think of how these can be utilized very easily for making detergents, because we are not looking for a huge amount of detergent compared to the amount of phosphate rocks what we can have in our hand as apatite.

So, making a small amount of detergent, we can use those phosphoric acids. So, these detergents will be very much costlier compared to the cost of your appetite. So, the value added thing, what we call as the value addition to the chemicals, so the inorganic chemicals, which has been converted through that which the value is added; that means, the price is more compared to your original crude appetites, such that we can convert it to the corresponding detergents.

Then some industrial cleaning agents as we know that now that detergents are phosphate based detergents. So, phosphate groups will be utilized for making or removing the dirts or the dust particles from the clothes and all other things. Similarly different industrial cleaning agents or different soap reagents nowadays available the detergent based soapy agents or the cleaning agents will also use these difficult phosphoric acid; either phosphoric acid or the corresponding salts.

Then some water treatment agents also we use those phosphates, then some nutrition supplements for animal feed stuffs like that, as we told you as I told you right now that, it can be a micronutrient for the soil; that means, it is useful for the health of the corresponding that plants. So, agriculture growth is also dependent on the amount of phosphorus or the right amount not the any amount.

So, right amount of phosphorus in the soil as a micronutrient. Similarly some of the animal feed stop can also be utilizing some phosphates as they are enhancer, so their nutritional value enhancer for all those feedstuff. Then some material which is very useful chemical material can be made from those phosphate based molecules is the flame retarding agents.

So, is the flame retarding clothes also we can have some clothes which cannot take fire very quickly or cannot catch fire very quickly. So, it can retard the physically the flame; that means, the burning process for burning the cellulose or all other things is not so easy in presence of those flame retarding agents. So, these are the 5 different applications of phosphates apart from its application as fertilizer. So, how we make the simplest one which is your phosphoric acid?

So, the simplest possible one is your phosphoric acid and manufacture of phosphoric acid is therefore, is important knowledge to us. So, as I told you that we can go for a typical weight process; that means, a typical solution based process can be utilized for making this was from the corresponding. Apatite based rock sample which is nothing, but our calcium phosphate. So, if you have in your hand the Ca3PO4 whole 2; that means, the calcium phosphate is in your hand.

So, apatite is hydroxy apatite, so you will find that there are something complicated once a formula is different because you can have some more hydroxy based compound. So, when you consider some 3 dimensional solid state structure of these form of compounds like apatite or calcium phosphate, what we can see that the solid state structures will be completely different, what we get as your corresponding minerals as the apatite.

Because compared to these if, we consider this simple calcium phosphate which is nothing, but a corresponding salt of phosphoric acid, calcium salt of phosphoric acid where we can have calcium present as the corresponding cation and phosphates presents as the corresponding anions. And if it is a typical salt like sodium chloride, what we can get? We can dissolve it in water; such that, it can dissociate completely depending upon its nature and as we all know that these are typically the corresponding ionic compounds.

So, these ionic compounds will be dissociated fully in water medium, giving you calcium ions and the phosphate ions separately. So, the presence of those calcium ions and phosphate ions can be detected nicely in terms of its chemical test. So, qualitative chemical test of that solution can give rise to the corresponding test for calcium ion, as well as the phosphate ions.

But if we take this particular apatite in some across medium it may or may not be soluble in water, if the solubility of that particular material is less we cannot get this as a simple calcium phosphate materials. So, what we are now using here is the sulfuric acids. So, treatment of calcium phosphate which has been derived from apatite is being treated with sulfuric acid.

So, why this sulfuric acid? Because sulfuric acid we all know there is a little bit corrosive acid like though from nitric acid is highly oxidizing also, but it is also a very strong mineral acid and that strong mineral acid can basically attack the mineral or ore samples. Why we consider it as the attack? Because it can break large number of solid state network structure, because it can go for protonation of the different groups and ionic groups.

So, what are those ionic groups as we all know when in their our introductory classes, when we have discussed about the formation of iron ores like hematite and magnetite, which are basically a three dimensional structure of iron bound by hydroxide groups and the oxide groups and which has been derived from typical ferric hydroxide.

So, when we dry the typical dry up the typical ferric hydroxide, which is slightly soluble in water, but is precipitated out from the alkaline medium as FEOH whole 3 is the simplest possible formula of that, but when we dry it up or if we put that in the oven and burn it is basically converted to some other form which are oxides, which is either can be FE2O3 or FE2O4.

So, getting these forms from the hydroxides or some other type of thing as carbonates, we get some networking of these oxides and hydroxide groups; such that one of the hydroxide or the oxide group can bind or can form bonds the covalent bond with 3 to 4 iron centers. Similarly these phosphate groups if they are having some interaction with the calcium in the solid state structure, so it can bridge between the different calcium ions and we all know that that phosphate group phosphorus is the central atom, which is covered by the 4 oxygen, which are in tetrahedral orientation.

So, if we can have the extended tetrahedral structure out of that phosphate groups will get the basically the phosphate rock. And that particular oxygens will have some affinity to bind to the calcium ions. So, we can have the corresponding 3 dimensional structure based on these phosphates.

And the typical apatite which can also have some hydroxy groups also, which are that is why known as hydroxyapatite. So, further to that of our phosphate anions we can have the hydroxide groups also. So, those hydroxide groups are also clipping or bridging those calcium ions. So, supplying protons from the sulfuric acid, what we are supplying from this sulfuric acid that we are trying to protonate these particular phosphate groups or the hydroxide group; such that when they are protonated because acid concentration is very high.

So, we are forcefully protonating the corresponding phosphate ions or the hydroxide ions such that will get the corresponding amount that whatever amount of phosphate you have with that of your calcium salt will be converted to your corresponding phosphoric acid. So, that phosphoric acid, once it is forming as a phosphoric acid that will not be present as a phosphate network within the metal ion centers. So, that will be the corresponding typical liquid the character what we know is the liquid.

So, that phosphoric acid will come out or leach out from the rock sample or the corresponding solid sample. Living behind in your hand is only the calcium sulfate. So, calcium sulfate will be precipitated out and in the liquid form, what we get is your phosphoric acid. So, that why it is known as the corresponding wet technical process or wet chemical process, the industry can also use that particular process; such that, we have to separate these 2 things, that means, you have to separate once they are produced, that calcium sulfate as well as the phosphoric acid, we have to separate out if their calcium sulphate is getting precipitated.

So, in the upper layer you will have the corresponding phosphoric acid, so phosphoric acid should be drained out and that phosphoric acid can be collected can be purified and can be utilized further for our other uses. So, then we are bringing or making life little bit complicated, it is respect to the rock sample or the mineral sample.

We are now saying that if we have the fluoride, so as we all know that the apatite is our material for our teeth or the bone. So, calcium phosphate is the material for our teeth or material for our bone, but sometime we all know that the small amount of fluoride what we get as the fluoride toothpaste, so making try toothpaste will also be another industrial aspect for getting that fluoride from this source and utilizing that and all these toothpaste making mechanism or the industrial process.

So, that particular one giving us something where the strength of the apatite is a solid state thing, what we are talking about is the corresponding strength. So, the hydroxy apatites will have the corresponding strength in terms of your corresponding introduction of the hydroxide function. Similarly the fluoride groups you can have and that fluoride groups basically can also bound to the calcium as we all know that typically calcium fluoride is a salt CF2 is a salt.

So, in all this solid state structure you can have some where the calcium bound to fluoride, if their fluoride is not a typical in the ionic form because in the huge structures, the giant structure giant solid state structures can have all these fluorides entrapped within that particular structure it is not that a typical anionic form what do we get in the typical solid samples as the corresponding calcium fluoride salt. So, if we have the fluoride which is also can be a component of your appetite so that, fluoride is can be removed during this particular process as gaseous silicon tetrafluoride.

So, SIF4 we get it. So, this particular one; that means, what we have; that means, if we just hit thing or hit the sample with some presence of your silicon. So, silicon should be added, so silicon tetrafluoride can be formed and in presence of more and more of this acid; that means, you have the plenty of acid; that means, the protons you can have. So, SIF4 can be further fluorinated as we all know giving you SIF6 2 minus because the silicon can have a coordination number of 6, it can accommodate 6 fluoride ions in a octahedral geometry around the particular center..

So, SIF62 minus can be isolated as the corresponding salt of this protonated form; that means, H2SIF6. So, can this can also be recovered from here in the form of hexafluorosilicic acid. So, now, we should be a little bit careful, that if your appetite has fluoride fluoride will give you silicon tetrafluoride and finally, it can be converted to hexafluorosilicic acid and this hexafluorosilicic acid it can be a liquid one also. So, you will be contaminating your put a product which is your phosphoric acid, so it has to be separated differently.

So, the separation of this silicic acid or the corresponding hexafluorosilicic acid will be different from your phosphoric acid preparation. So, contamination as well as purification of this particular phosphoric acid will be an important talks, while making this phosphoric acid.

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So, what we get the calcium sulfate is getting precipitated and the precipitates initially in the form of hydrates because calcium sulfate dot H2O as we all know this is a formula of the corresponding gypsum and subsequently recrystallize as its hemihydrate; that means, hop of the water molecules will be present.

So, crystallization of this calcium sulfate will be important; such that the crystallized form that calcium sulfate can be removed and for this particular reaction for running a modern plant basically what we are seeing now that you can have a typical plant, where industrial thing can happen and industrially what we can produce these operating the corresponding dihydrate process. So, calcium sulfate what is formed initially as the dihydrate.

So, it is typically a dihydrate process; such that, we what we can have that we can have the reaction temperature of about 80 degree and separate the feed of ore and sulfuric acid. So, just we are introducing sulfuric acid and the ore to that they are. So, separate the feed for ore and the sulphuric acid what we are adding. Then vacuum evaporation cooling to ensure a constant reaction temperature, because the reaction if it is exothermic always we should have a constant temperature for the reaction otherwise the temperature will rise.

So, what we see now that the exothermic reaction should be handled in a nicer way by controlling that particular reaction by a cooling mechanism. So, cooling mechanism should be there; such that we can specify the corresponding temperature rise in that particular reaction. And monitoring the production of sulfates what we are producing as the calcium sulfate or the monitoring the corresponding sulfuric acid it concentration what we are adding should be controlled in a nicer way; such that, the necessity for recycling the whole material or the recycling part of the dihydrate what we are getting as the calcium sulfate because the calcium sulfate will be our by product for that particular reaction at that should be isolated in a very simple way; such that, it can also be purified and it can also be sold in the market.

So, while making phosphoric acid we are also producing some good amount of calcium sulfate. So, that particular industry is basically can supply a good amount of calcium salt because the calcium sulphate is a very important compound inorganic compound industrially important compound, that will see further it can give you something which can be considered as the corresponding supplement for calcium.

Not only the phosphate, so we are separating out calcium as well as we are separating out the phosphate, one we are taking out as the calcium sulfate material and another we are taking out as the corresponding phosphoric acid material, what will be considering for the next step of application or use or the reaction where will be making the different phosphate salts. So, in our next class we will be seeing that what are the different phosphate salts we can use we can prepare and we can apply for some other purposes.

Thank you very much.