Industrial Inorganic Chemistry
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Lecture – 16
Sulfur and Copper [1] Phosphide

Well, welcome back. So, we were talking about some phosphorus based compounds which will be useful industrially. And now the last part of this particular phosphorus compounds which are interested in important will be talked about the phosphide.

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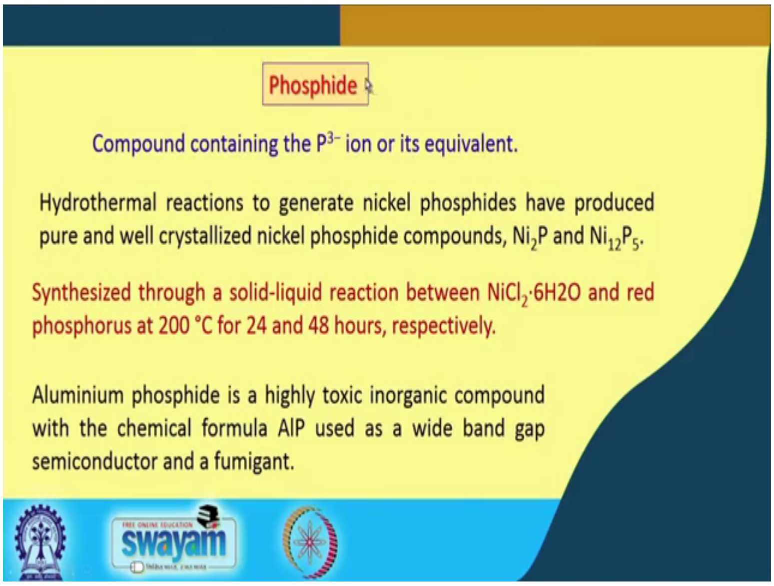

So, what we will see that, this particular phosphide is not your typical phosphorus molecule or not the corresponding phosphoric acid or the phosphorus oxides or phosphorous sulfides. But these are some compounds which are very useful containing P 3 minus ion or its equivalent, because sometimes if you have can oxygen or if you can have hydrogen attached to the P 3 minus ion which is nothing, but the corresponding anionic part of your well known pH 3.

If we consider what is that particular phosphide because it has huge solid state applications because those phosphide materials like that of your oxide or your carbide, we know calcium carbide very useful molecule and how we get that also we know. So, when we talk in terms of the carbon compounds and the carbides will come back definitely for that carbide, but right now since we are talking in terms of the phosphorus based compound.

So, if we can have the corresponding anionic part or the anionic congener of trif phosphine pH 3 like ammonia NH 3. So, we can get it as the corresponding PN 3 since its typical phosphide ion like that of your oxide ion, we can get the corresponding metal ion based phosphides.

So, first example if we consider that what we can have for nickel based, which are nickel phosphides. So, is a typical reaction because it is a very something these reactions are little bit complicated because simple mixing in a test tube or some reaction vessel like that of your round bottom flux or any other container we may not get this particular one.

So, specially designed reaction chamber we can have and we can go for a water medium or any other solvent medium reaction at high temperature and high pressure, because industrially whatever we have seen starting from making your ammonia to production of sulfur dioxide we always we know that balancing these two parameter; that means, the pressure and temperature is always important.

So, we can go for a very high temperature reaction or a high pressure reaction for these. So, these hydrothermal reactions are well suited also if we can make some compound which we have to produce in a very small amount. So, the inorganic compounds which are useful in electronic industry like semiconductor industry so those we are not making in a huge quantity like that of your production of sulfuric acid or production of phosphoric acid or any other thing in some metric ton amount, but only in some gram scale.

So, that particular reaction we can do simply whatever we do in a laboratory reaction. So, hydrothermal reactions are those reactions where we will be using water; that means, the hydrous form the hydrated form. So, water will be there so H2O will be the medium and thermal is your temperature which is very much similar to that of your conversion what we get below the earth crust so geothermal reactions.

So, geothermal reactions we all know that the material is converting for several years so, 1000 years or 100 years of these something is converted and we can have something which we considered as the hydrothermal vents also, through that hydrothermal vents some reaction chamber is forming over there. So, is very much similar to that of geological conversions, these hydrothermal reactions. So, for getting your nickel phosphide we can take the same procedure. So, only thing is that your reaction vessel is different. So, is the autoclave type of thing. So, autoclave reaction chamber is there and you have that a corresponding acid medium, also if it is required then the metal and salt and the phosphorous source.

So, pure and well crystallized nickel phosphide compounds. So, two of these examples they cause large number of compounds we can have. So, Ni 2 P and Ni 12 P 5 can be formed depending upon its condition reaction, condition and how you slowly cool the reaction vessel. So, if we heat the particular reaction the way we are talking here also we will be talking at temperature not very much is only 200 degree centigrade what we are considering.

So, a 200 degree centigrade, which we rise slowly from room temperature say 25 to 28 degree centigrade we go up to 200 degree centigrade in a stepwise manner. So, that the regulated temperature nowadays is all these hydrothermal reaction chambers are available, in our college or university laboratories we are having now all these hydrothermal chambers reaction chambers. So, is well monitored so temperature rise is also well monitored. So, through off a times such as here we are exam giving the example of 200 degree centigrade rise in a timeframe of 24 to 48 hours.

So, we will be reaching to 200 degree centigrade in a time span of in one case it is 24 hour in another case it is 48 hours. So, the rate of increase in temperature in that way we have to monitor it. So, during that process the reactants are reacting and when you reach the final temperature; that means, 200 degree centigrade you keep that particular temperature for some while.

So, that is the reaction conditions how you set the reaction condition that means, you can keep that particular temperature for 1 hour or 2 hour or 5 hours or 6 hours or more. Then we can go for slow cooling of that particular temperature it again from room temperature 200 degree centigrade as you moved, you can go down from 200 degree centigrade to the room temperature again in an incremental fashion such that you go down to the room temperature in a different steps. Not that the way you reach there you can have a different monitoring, you can different programming for that particular temperature drop from 200 degree to room temperature temporary room temperature.

So, during that process what you get ultimately you are reaching after sometimes if 10 hours or 5 hours will be reaching to the room temperature condition for the reaction vessel. During that process what is happening? The reaction is taking place, reaction is there in some water medium or which is something like that of your molten condition and the molten condition is allowed to reach again; that means, you are going for a standardized cooling process.

So, during that cooling process you can have some good quality crystals so; that means, it is also assisting or helping the formation of the crystals. Sometimes the crystallization process is so good that you are able to get single crystals, because those single crystals are useful for molecular structure determinations by single crystal X-ray diffraction techniques. So, if we are lucky enough we will be able to get single crystals out of these for those molecules which are intended for and we can determine the structure for those molecules which has been prepared hydrothermally.

So, this preparation process is typically different, is not a simple solution technique at room temperature or typical mixing of 2 components in solution at some higher temperature, where we get it by refluxing in a round bottom flask putting it in any flux condenser. But is a different one, but the major advantage of this particular process is that we are going for making some phosphide; that means, P 3 minus ion will be having something with that of your metal ion. So, if we get Ni 2 P type of thing; that means, the nickel phosphide because do not bother about the corresponding oxidation states of all these because you may ask that is their corresponding one is not matching; that means, in the solid state you can have some fractional oxidation states for that.

So, this hydrothermal technique is utilized and synthesized through solid liquid reactions, what is that? So, sometimes we consider that some reactions we consider it is a sol gel reactions, probably you have heard the name. So, gel reaction but this time we are going for a solid liquid reaction which is under hydrothermal condition between nickel chloride, nickel chloride 6 water molecule 6 H2O and red phosphorus. So, if your nickel chloride is taken in solution so that is the liquid part. So, it is always we know that the nickel chloride is highly soluble in water.

So, a saturated solution or sometimes a little bit diluted one from that saturated solution of nickel chloride can be taken and red phosphorus is being utilized. But you see that the advantage of this particular process is that red phosphorus is a solid material and there is no need to take that particular red phosphorus in is solution medium, we will see that how we can have some solvent for this phosphorus.

So, phosphorus elemental phosphorus like sulfur is soluble in some other solvents some organic solvents like carbon disulfide or anything. So, here we are directly introduced phosphorus as the powder material so that phosphorus as the powder material is introduced over there as a solid material. So, is a basically a solid liquid reaction, try to remember it nicely that is a solid liquid reaction under hydro thermal condition at elevated temperature which is 200 degree centigrade and is maintained for a timeframe of 24 to 48 hours. So, this will give you not only the formation of your nickel phosphide, but also it is in its crystallized form.

Similarly, aluminum phosphide where you do not have any problem regarding the formula is simply right that is at AlP that aluminum is trivalent. So, AlP plus and phosphorus is present as phosphide ion as P 3 minus. So, is one is to one composition for that solid material would be 1 is to 1 for presence of your aluminum and phosphide ion, but we can have some special purpose of this, but is highly toxic inorganic compound. So, always remember it that whenever some compound is labeled which is environmentally banned or restricted item, we should be careful in handling that and we should not make in a huge amount. Only for some special purpose when it is needed we will make it for that particular purpose.

So, why where it is used basically is, basically the wide band gap semiconductor, as I told you for electronic industry we can have this particular aluminum phosphide where you can have the band gap is a very huge one so is the wide band gap semiconductor materials. So, semiconducting material is there and also it is a fumigant; fumigant means when it is react with water it will give something which will destroy the bad environment, the polluted environment or some environment, which is contaminated with some bacteria or fungus or any other thing. So, we want to destroy those things, even for destruction of all those things from the soil, from the air or from the water also.

So, when this is slowly reacting with water. So, aluminum phosphide if it slowly react with water what happens? Like calcium carbide as we all know when calcium carbide is slowly reacting with water because this is a solid material, this reaction is not very fast and most of these reactions are exothermic in nature, that it slowly release the acetylene gas. Similarly reaction of AlP with H2O will slowly release phosphine gas and phosphine gas is not a very good gas for all these things so it is a deadly one. So, is basically a fumigant based on the phosphine gas. So, is a pH 3 based fumigant, which will clean some bad thing clean from the some bad thing by the production or slow release of phosphine from the reaction.

So, if we put that aluminum phosphide in soil and the soil has the moisture from the environment or the or the moisture from the soil itself. So, slowly it will react with that. So, amount of moisture will control the amount of phosphine production like that of your hydrogen sulfide production, as I told you in my previous class that the way you make it in a keep separators. Slow the slow release phosphine basically will be useful for destruction of all these bad materials or bad elements from the soil material. So, phosphide will therefore, be very much useful.

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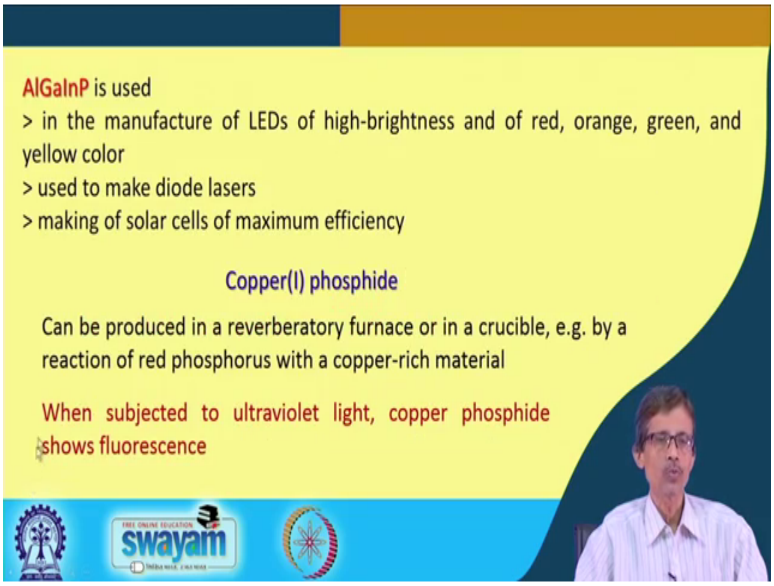

So, not only the simple phosphide, but something which is a very complicated one say not one metal ion like your aluminum phosphide, but some other phosphide also we can have, like aluminum, gallium, indium it is basically a alloy type of phosphide. So, whenever we have 2 metal centers not the metal ions, but metal centers metal in the 0 condition, 0 state. If we get aluminum gallium we can have some allowing condition we can consider it as aluminium gallium alloy. Similarly if you can have the gallium indium also and also we know that from our school days knowledge that you can have the brass, you can have the bronze where more than 2 elements or the metals are present.

So, similarly this is something like that, but is have a corresponding anion also present; that means, the phosphide and so is a very complex phosphide molecule which is aluminium, gallium, indium, phosphide. Why we are making this complicated phosphide unlike your aluminum phosphide the simplest possible phosphide, but is application for this use for the industrial purpose for any other good purpose is limited, but if we get for this for electronic industry, it will be the application is very huge one. So, this particular material is useful for the manufacture of light emitting diodes.

So, for making your LEDs of high brightness of special type of LEDs, not all LEDs are of this particular material making of this particular material, but there are some cheap material available where form you can get the LEDs. But if you use some high brightness and brightness and of red, orange, green and yellow color so some specific colors are also given. So, for those color ranges from red to yellow you can have this high brightness LEDs made of off aluminum gallium indium phosphide.

So, you know how phosphides are making, we are making like your nickel phosphide preparation so some special techniques can be useful, by not only supplying because that was a hydrothermal technique for nickel phosphide preparation. But here is basically not a hydrothermal preparation you can go for a simple solid state synthesis in oven or in muffle furnace, by utilization of a typical phosphorus source as the elemental phosphorus or the white phosphorus along with that aluminum powder gallium as well as the indium as in the corresponding metallic state.

It also very much useful for making diode lasers, because we have to make in a very small amount, but making these for diode lasers will also be useful so, the phosphide compounds are useful. So, these are the typical applications and lastly the application for making solar cells with maximum efficiency. Because whenever you have the different material for making solar cells, we always keep in our mind that how good that particular solar cell is that, how much solar radiation or the solar H nu or solar power is falling on that particular plates. So, solar collector, the solar radiation collector and is converted to corresponding electricity, that conversion basically is known as its corresponding efficiency of that particular material for a useful material for making solar cells.

So, but in this particular case, it can be achieved up to 40 percent. So, 40 percent efficiency can be achieved with this aluminum gallium indium phosphide for making your solar cell. But definitely, since we are handling indium which is a very costly metal metal then gallium also aluminium is definitely a cheaper one, but introduction of this gallium in indium making this material a costly one. So, you should also consider the cost effectiveness not only in your efficiency for your conversion of the solar radiation.

And one more example is your copper phosphide. So, copper phosphide and it is in the cuprous form because the P 3 minus ion having a huge charge which will be highly reducing one. So, it is not possible to stabilize the corresponding counterpart, the cationic counterpart in its highest oxidation state or the higher oxidation state like that of your cupric state.

But it would be easy to preserve that particular one in the reduced form; that means, the cuprous form which is your cuprous or the copper one phosphide, how we can produce it can be produced in a furnace and that is a reverberatory furnace or in a crucible; that means, what we see that sometimes we can be have some crucible the porcelain crucible or the nickel crucible or any other vitreosil crucible or any other material crucible.

So, crucible is there because the crucible can withstand a very high temperature reaction. So, here instead of taking white phosphorous for making copper phosphide because always we change from one material to the other we change the starting material from white phosphorous to red phosphorus why? Because one thing is that how good we are getting this particular compound that way conversion should be very easy, and the purity of the compound and the excess of that phosphorous material what should be there which can be burnt away or which can be removed away or which can be reached least away.

So, in case of making nickel phosphide we have used white phosphorus, now we are taking the red phosphorous and the cost wise these two elemental phosphorus materials are also different white phosphorous and the red phosphorous and with a copper rich material; that means, copper rich material is a very useful term what we are using over here. That means, is not a copper salt or a copper metals or a copper powder or a copper wire, but it is only a copper rich material what we define, how we define the ore and minerals the ore and minerals when we go for a typical enrichment.

That means, whatever we get from the earth crust is something, then we purify it some process, then we go for the enrichment; enrichment in terms of your copper content. So, the enriched material; that means, the enriched ore or enriched mineral, mineral what is in your hand can be supplied for making your copper metallic copper when the copper industry which is making your copper metal or some copper alloys or some copper added things.

It can directly be used for making copper one phosphides because these are also some other application like that of your other complex phosphide what we have seen just now. This particular copper phosphide the copper one phosphide can have some relationship with the fluorescence.

So, is a UV light activated fluorescent material. So, we can use this as a standard material for checking fluorescence or if we can have something where we can utilize the fluorescence and which can be activated by UV light. So, not only it is giving our some useful application of handling ultra violet light. So, if you light handling and we can measure the corresponding fluorescence once so is a very important thing with the correlation of UV light to that of our fluorescence which is of a different wavelength using your copper phosphides.

So, copper phosphide can be checked with that UV light of particular wavelength for getting the fluorescence for this so large amount of materials. So, materials chemistry is can also be enriched by this particular technique and we can use for making this copper phosphide and the different types of crystals that saves the morphology. And it can so happen that it can also give you some interesting idea for its catalytic activity, if it is a highly reducing material so for the reduction reactions we can use it nicely for some stoichiometric reaction or some catalytic reactions ok.

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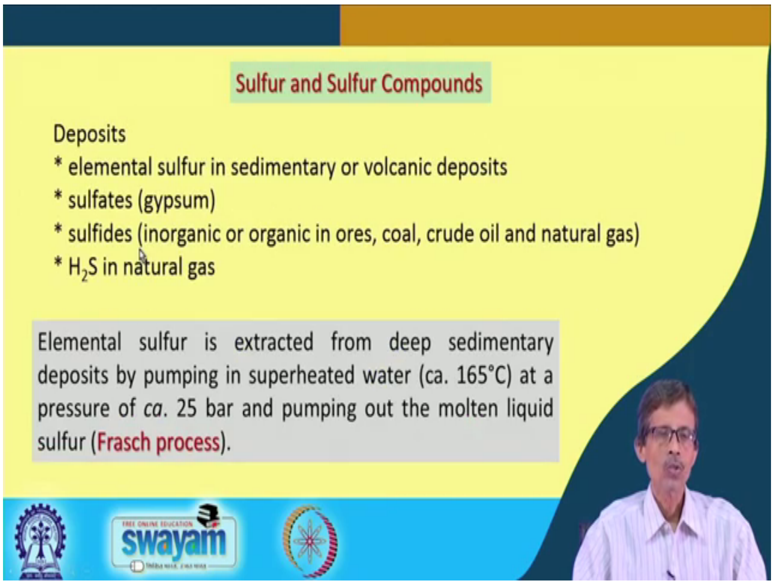

So, next we move from this; that means, the story of phosphorus compounds and the phosphorus industrial applications and some useful convergence is over now. Now we quickly move to sulfur and sulfur based compounds. So, again we will take the help of nature and the natural resources and the material, what we can have with us with that of your typical sulfur sources. Because we started our journey from oxygen then we have seen that nitrogen, then we have seen the corresponding phosphorous now we have reached to sulfur, but still we are dependent on the corresponding natural sources.

Because we can have huge deposits the natural deposits the geologists can help in this regard to us. So, the chemical industry can only be built up with the help of the all different types of people starting from a geologist to an engineer, in between the chemists are there particularly the inorganic chemists will be there such that you know that where you can get the cheap supply or the cheap resource of the sulfur, if you are trying to get this sulfur as a regular supply for the industry.

So, there are different deposits. So, one such deposit is the elemental sulfur, if your country or any other country have something of this sort of deposits where these are these are in some sedimentary rocks or some sedimentary deposits people call or some volcanic deposits out of the volcanic eruptions.

So, if we go from India to Japan we just get some volcanic sources. So, volcanic deposits are there. So, we may get the good sulfur source from here, but in this country will have very poor source of sulfur if we do not have any volcanic eruption or volcanic deposits, but we can have the sedimentary deposits from the sedimentation. So, these deposits we should carefully check out that whether we can have a huge amount of sulfur deposits, such that we can go to the laboratories purpose also using sulfur compounds for making some useful sulfur compounds.

So, inorganic industrial chemist can help you in this regard that how you convert this particular sulfur for giving you the corresponding compound which can reach to the laboratory, not only the inorganic or analytical chemistry laboratory, but it can go to organic chemistry laboratory also. Because that particular sulfur you can introduce in the corresponding organic molecules, the organic corresponding hetero cycles or the simple chain of this molecule sulfur can be introduced.

Similarly, you can go to the corresponding pharmaceutical industry who are producing drugs and medicines for us because we all know from our childhood days that we are consuming sulfur drugs. So, the name will tell you that you are using some compounds which are having sulfur ingredient in it. So, sulfonamides one of those group of compounds are sulfonamides as we the name tells you that you have sulfur in it and you have the amide part also in it.

So, if you have some part, which is sulfur based acids, which can react with some ammonia or amine giving you the corresponding amide; so you get the corresponding sulfonamides compound. So, you see how you connect a geologist at one hand who will be talking about the sedimentary deposit or the volcanic deposits to you regarding sulfur and other end you have the corresponding company who are making the corresponding molecules, the drug molecules or the medicines for us based on the sulfur compounds. Because these sulfur compounds or the sulfur in a complicated ring is also present in your beta lactam ring which are our penicillin.

So, introduction of these sulfur can start from the knowledge of knowing where from we get sulfur from the air or the earth's surface or some earth crust. Similarly the second level of deposit is for the sulfates, the sulfates what we can have is the simply the corresponding gypsum source if we can have not in the elemental form, but in the form of calcium sulfate. So, that gypsum we know from gypsum we make the Plaster Of Paris also, but all those sulfates can be handled for making sulfur also.

Then along with sulfates you can have sulfides in organic sulfides in ores roughly speaking then in the different coal material or the coal samples then crude oil or the natural gases, the CNG source. That can also give you the sulfides and those sulfides in most of the cases when you talk in terms of the CNG, what is that? That is nothing, but your H 2 S. So, H 2 S present in those CNGs can be trapped and can be removed and can be isolated and lastly the free H 2 S in natural gas. So, in the natural gas if we can separate out that H 2 S part you can have the corresponding good supply of sulfur as sulfides.

So, what we get therefore, in our next class we will be talking about the isolation of this sulfur, typically the elemental sulfur where you can have the sedimentary deposits how by pumping a superheated water; that means, the water sample you can have at a very high temperature of 165 degree centigrade at a pressure of 55 bar. So, we put that particular one so that water sample at a high temperature and high pressure is pushing back to that particular sedimentary deposit level, it can be below the earth crust.

But only thing that you have to detect where it is and the detection of that particular thing is useful that you can have the huge amount, that mean the maximum concentration of that sedimentary level or sedimentary a deposit level containing sulfur is there and we push that particular one through one bore basically. So, is a borehole technique.

So, through one particular hole you put that particular water. So, water is going there and will be reaching to that particular level and after reaching there is basically the high-temperature one. So, we get something is not that the all sulfur will be in the molten condition, but you get something a molten liquid sulfur. So, at a high pressure and high temperature, the idea is that you supply hot water at high pressure and you get that particular one as the molten sulfur.

So, from the deposit we take some advantage of melting of sulfur. So, which will be dependent on the melting point of sulfur, definitely that we should know. So, at a particular condition so you just say high pressure and high temperature you get the melt of that particular sulfur. So, in that particular level it is in the molten condition and water we are supplying we are generating some pressure also definitely and is also in high pressure. Before that what you should do? You should do some the corresponding orifice or corresponding exit pipeline or some other line that you can take out that thing at a high pressure also.

So, molten sulfur will come out from that particular hole, the other hole the exit hole. So, the entry hole will take the hot water at high pressure and the exit hole will take out that particular molten sulfur and we should have some reservoir, where you can store that particular sulfur and we can cool it down and definitely the pressure is not there and if possible we can crystallize it as the elemental sulfur. So, what we are doing? We are basically bringing the neat sulfur, definitely the sulfur concentration should be very high there and that on the surface.

So, basically this particular technique, which is known as the Frasch process. So, the Frasch process is basically useful for taking that particular sulfur from the below the earth crust to the surface of the earth crust. So, next day we will see how we can utilize this particular sulfur for making some useful sulfur compounds.

Thank you very much.