Biological Inorganic Chemistry
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Lecture 52
Nitrogen and Silicon

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Hello students, so, good morning everybody. So, let us see where we have reached. So, we have reached to lecture number 52, under Module 11. And today, after carbon, hydrogen and oxygen we will see a little bit about the nitrogen and silicon. How we can correlate these two elements and their corresponding species for biological activities.

So, let us see from the very beginning, the very basic thing what we can understand from our school days the nitrogen bearing anions. We know many nitrogen bearing anions like agile is simple nitrogen bearing anions is all nitrogen bearing anion is in N3 minus, but whether that augite it can have something to play with in biological world is not. So, we will have the nitrate, nitrite like of thing, and how we can correlate to the elemental nitrogen, which is your N2, like elemental or gaseous nitrogen, we know that we have the dioxygen also. So, it is dinitrogen.

So, we will talk about have to talk about the biological nitrogen transformations, the nitrogen fixation and the nitrogen cycle. Today, we will be only talk about only few examples the whole cycle I will try to present it in today's half an hour class. So, is the associated engine basically, you should know very well that how the nitrogen bearing announced are important and what are the associated enzymes are there and what particular transformation it can do.

Whether it can have a corresponding role of your anions and the different nuclear species. As I told you, you have the nitrate NO3 minus and the dinitrogen is your neutrals species. So, how we can correlate and what sort of chemical reaction or enzymatic transformation you can think about for these transformations? And how we can see about if you have the electron acceptors?

What are the species that means the substrate? And lastly, the neglected silicon, we do not cover these neglected silicon much about our biological words from the plant kingdom to the animal kingdom, but we will see something about the silicon and we get some good information based on that silicon also.

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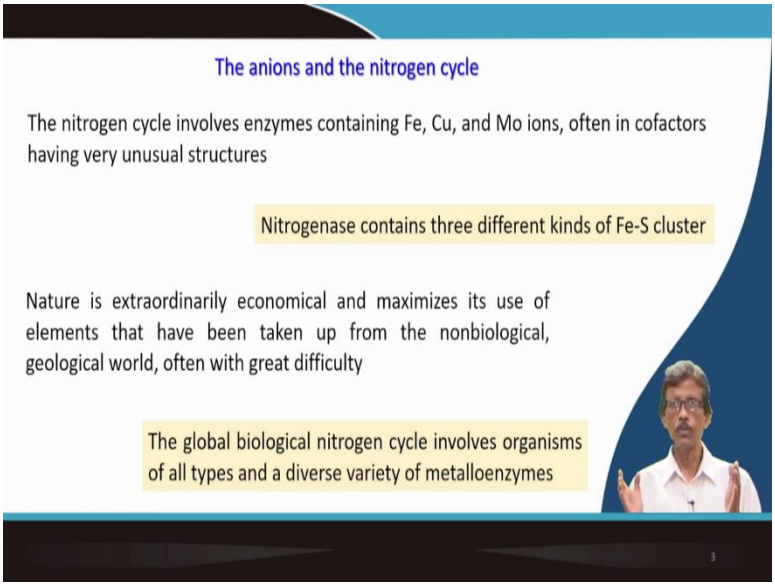

So, we have the nitrogen cycle. How we can identify these anions? Because again, from our school life, we know when you go to a chemistry laboratory, that you are asked to identify the presence of chloride anion, which is very important, already we have seen in our body also. You are not asked to identify chloride anion in a cell, that means, the biological cell not in the test tube.

Similarly, if we have the nitrates and nitrites, NO3 minus and NO2 minus, how it is related and how we can get it through the nitrogen cycles, the whole nitrogen cyclic process. So, we will have many enzymes, we are not talking all these things, but already we have discussed many about the corresponding properties of these metalloenzymes bearing iron ions or copper ions.

So, whether we can able to take quickly, the look on the molybdenum ions, which is different one and what oxidation states are involved if we think about or talk about the electron transfer behavior. So, when these three metal ions are present, they basically go for the cofactor behavior that means they are assisting the enzymatic activity, but they have very unusual structure.

So, if the structures are different, we try to find out something where we can find out that whether you have the iron center present or the molybdenum center present in the metalloenzyme, and then what structure is important because of your structure function relationship is important. So, we can have the different types of nitrogenases those are molybdenum bearing, three different kinds of iron sulphur cluster we can have.

So, when nature is doing some useful function an extra ordinarynically, ordinary economical and maximizes its use of elements, so how we can use both the nitrogen atoms of the dinitrogen to get something? From the non-biological, geological world, often with great difficulty. Because if we consider that we are going to reduce the dinitrogen molecule to two molecules of NH3, that means, your ammonia.

What sort of reaction you can think of even the simple chemical reaction then what is the corresponding, physical chemistry part of it, that means, the corresponding energetics whether it is thermodynamically feasible or not? And if it is a typical reduction reaction at what particular potential you can expect it? Even we simply see in the laboratory.

So, the biological nitrogen cycle. So, if all these enzymes and the biological world is involved so, we can talk about the biological nitrogen cycle that is why it is very much pertinent to our today's class where we are talking about the nitrogen as the element, silicon as the element, but we can connect it to the biological world. So, organisms of different times and diverse variety of metalloenzymes will be involved. To tackle all the different species, we can have the dinitrogen, we can have the ammonia, and we can have also the NH4 plus ion that means the ammonium ion.

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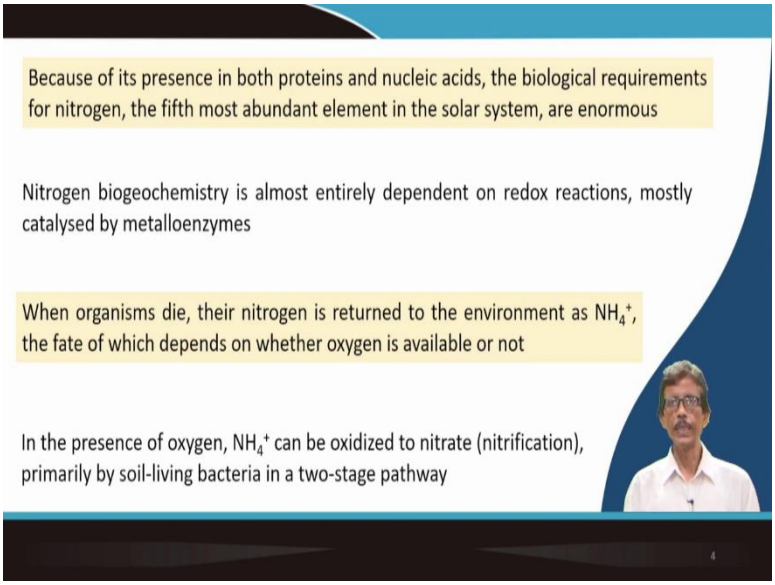

So, since this is there, so, you know the cycle. Why we require that cycle? Why that is so, important? Because you have to get that nitrogen, whether you fixed it in some useful molecule or any organic molecule like simple amino acid. We know the nitrogen is there as amine function.

Because of that, your nitrogen chemistry your nitrogen biological chemistry is important, because you can see that you can incorporate that in the polypeptides or the protein molecule where your building blocks are amine acids. So, already we have considered that your amino acid will have the immune function.

So, your proteins will always have the amine function. And when it gives you the metalloenzyme definitely you have all the nitrogens. Then the nucleic acids, for the DNAs and the RNAs as we know the nitrogen is there. So, how these heterocycles are forming? How the macrocycle porphyrin is forming, which we know that the indispensable part of our blood for hemoglobin and myoglobin we again need nitrogen along with carbon, hydrogen and oxygen.

So, the biological requirement is massive is a huge thing. So, it is basically a fifth most abundant element in the solar system are enormous, having anonymous activity. So, if we consider apart from silicone, carbon, oxygen and hydrogen, you can get it that you can have the corresponding nitrogen.

So, your biological nitrogen fixation you can consider it to the life where you can have the corresponding microbes, your soil, your lightning all these things are related basically. So,

whether the fixation of this nitrogen in the soil material, you do not have to add urea from outside you do not have to add ammonium chloride from outside because the plant material, the plants and other vegetation will require nitrogen because they are also producing many useful molecules like your nitrogen bearing proteins and polypeptides.

So, they are basically dependent on the redox reactions, which are catalyzed by the metalloenzymes. And when you see that when we have the dead bodies of these organisms from the virus from the bacteria to the animal kingdom, basically, whatever nitrogen is there in that body and the degradation process is basically leading us to the production of many useful nitrogen-based molecules like that is the incorporation as the ammonium ion.

Therefore, the fate of which depends on whether oxygen is available or not that means, you are talking about some environment where oxygen is present and in some other environment where oxygen was not present, because we know the pre-historic ages oxygen was not there before the discovery of your photosynthesis.

So, when you have the oxygen NH_4^+ can be oxidized to nitrate, is very simple thing. The way a chemist can see, okay, I have nitrogen and dinitrogen is nothing but you had the triple-bonded two nitrogen atoms. So, you have the triple bonds. Nitrogen, triple bond nitrogen is very inured, is very difficult to open up those huge fixed type of thing compared to your dioxygen where you have that double bond corrector.

But this particular thing it required that is why very high temperature, high pressure, catalyst and all these things to break these nitrogen-nitrogen bond to get at least the nitrogen-nitrogen single bond. So, the soil living bacteria can go for this transformation which is known as your nitrification.

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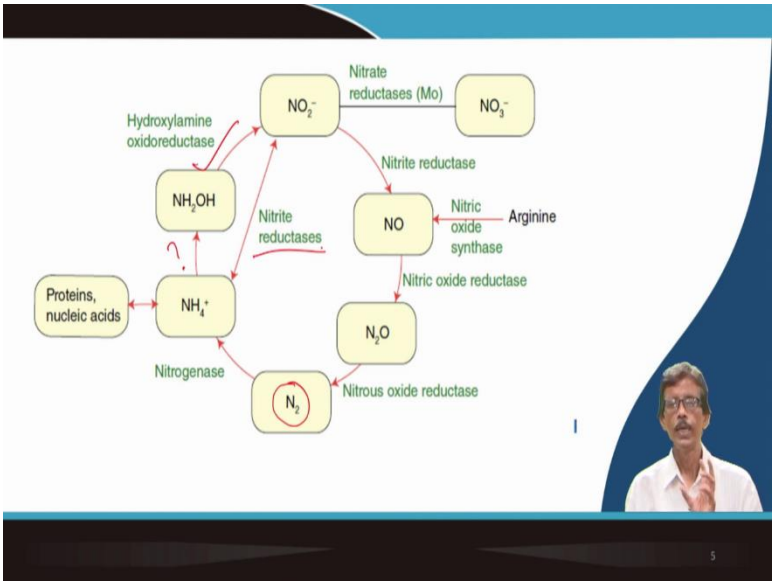

So, now coolly you see this cycle what we are talking about. So, if you have the nitrogen, which is at the bottom, so that nitrogen basically when we can have so that nitrogen what we get, so, here you are. So, you have the triple-bonded nitrogen, nitrogen-nitrogen triple bond. So, what we can do?

So, the nitrogen is in enzyme scamming, so it is from the plant origin also we know the plant root nodules can have the nitrogenous enzymes which we cannot reproduce in the laboratory or in the industry that is why still we follow the Haber Bosch process for the nitrogen fixation, which is a very high temperature, high pressure condition and the catalyst also. For the ammonia production as well as finally the area production to get the soil the corresponding fertilizers.

So, once you have the nitrogen is in hand you just immediately go for the redox and reactions that we know and the ammonia mindset there those are very useful thing the entity is NH3. And what we can to take from there that is the typical source of your ammonia or ammonium ion or ammonium chloride salt.

So, if the organic material or organic molecule can be we go for the introduction of the amine function the NH2 function, we get the amino acid, we get the protein chain or the polypeptides and also the nucleic acid, then some other enzyme will come and try to convert the ammonia or the ammonium ion to hydroxylamine, so there will be something so, we are not talking about all these things, but it was remember that you have something over here for that particular conversion.

Because one of the hydrogen-attached to the three hydrogens on the nitrogen will be converted to OH. So, then, if you go for that, so, that is basically a path. If you go through that particular path, you can have the corresponding hydroxylamine oxidoreductases. So, once you have the hydroxylamine oxidoreductase in this particular step, it can go for your corresponding conversion of the nitrite, not nitrate.

So, remember it, that is important, but the reversible conversion between NH3 and nitrite is your nitrite reductase, which is a direct conversion not via ammonium hydroxide. Then once you have the nitrite formation the nitrate reductase, which is the molybdenum-based thing can put one more extra oxygen on the NO2 minus.

It is a very important and very interesting anion. So, that is why we are talking about these anions in the biological world. You have nitrogen and you have two bonds NOO and you have the chart, but that nitrogen is very reactive and sometimes can give you very useful reactions.

When you go for the corresponding nitrate reductase that means you can go for the corresponding oxidation. So, that oxidation gives you putting one more oxygen atom transfer, so that we will see, how the molybdenum of this metal ion present is the molybdenum and how the molybdenum is important to go for that particular attachment of the oxygen on the nitrogen which are having only two oxygens.

So, basically you can immediately go for that particular reaction that the nitrogen having lone pair of electrons. We know in organic chemistry also if you have the pyridine, we can go for pyridinium oxide, if you have the amine, we can go for the amine oxide because the nitrogen lone pair, the pair of electron can be useful to form the bond quickly to any oxygen center which can be available from other reagent.

Then we can have the redaction process and other enzymes are required, and how NO is formed, but we are not talking all these things because we have considered that we will be talking about only the anions. So, these are the two anions, the nitrite what is initially forming and the nitrate. How we can manage these two things in this particular catalytic cycle of your nitrogen fixation.

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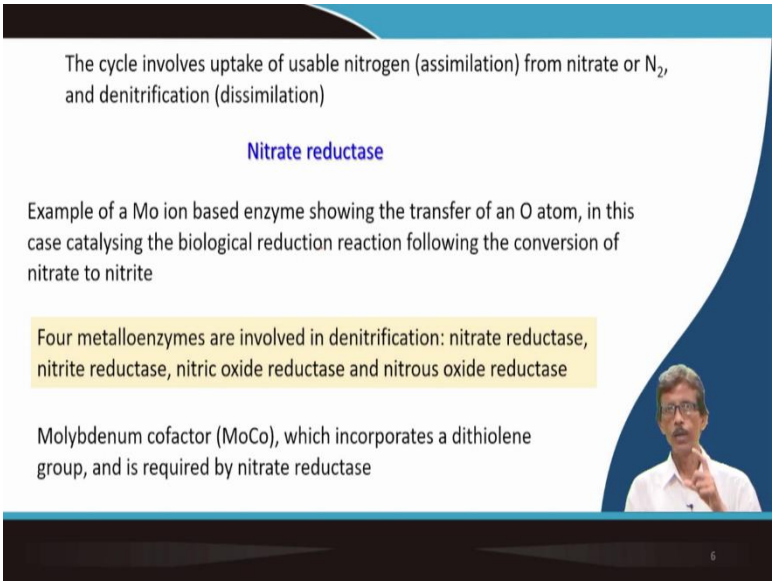

So, here basically we can go for the uptake of usable nitrogen when we take out this nitrogen and we can go for the assimilation from nitrate to dinite or dinitrogen also we can go all these because these are all reversible in nature. And as well as denitrification which is dissimilation that we will see, which is your assimilation and which is your dissimulation.

What is your nitrification and what is your denitrification? So, these are basically the nomenclature you should be able to understand when you talk about the conversion of one molecule or form to the other. So, if we consider that we have the nitrate reductase the enzyme is known as your nitrate reductase.

So, first thing what we try to understand is what metal ion you can have. It is not that any other 3D metal ions, even the chromium is not helpful because the chromium we know that the chromium gives you the chromate and the dichromate which are pretty oxidizing in nature.

So, you require the 40 congeners of chromium which is your molybdenum, and again, something more softer in terms of your oxidizing capability is your tungsten that is why some enzymes we can have also tungsten can have also with the molybdenum, but very few only one or two examples will be based on chromium, but not for the animal system not for the human system.

So, which can transfer the oxygen atom. So, that was our goal we have discussed so, far that how you put the oxygen on the nitrite anion to convert it to nitrate anion or you can take out one of the oxygen from the NO3 minus to convert it to no to miners. So, it is basically

catalyzing the biological reaction, so addition of oxygen or removal of hydrogen we consider all these nomenclatures following conversion of nitrate to nitrite. So, you just convert, you take out that you will get this particular conversion.

So, there are basically four metalloenzymes are involved in the denitrification process. That means, you are adding oxygen, oxygen, oxygen. So, you have the nitrate reductase, nitride deduct is nitric oxide reductase and nitrous oxide reductase. So, you try to remember it what are the substrate basically we are talking about. When you have four such species two of them are enhanced and two are neutral molecules. The neutral molecules are nitrogen oxide gases which is NO the nitric oxide and nitrous oxide which is N2O. But again, we will retain our discussion within that to anions.

So, you bring molybdenum, you have identified the molybdenum is there in your hand and that molybdenum will basically work to give you this reactivity. Then once you identify molybdenum you will be interested to know the oxidation state of the molybdenum and your coordination environment. So, is basically functioning as a cofactor again for that enzyme. So, if you have a huge metal enzyme the supply for that particular part for the substrate binding, oxygen transfer and the redox process is basically governed on the manganese sorry molybdenum center.

What do you can have now, because we all know we have seen also that your molybdenum center is not so, oxidizing, that means, your E0 value is not very high compared to your chromium. Then you put something subdonal ligands dithiolane, thiol, we immediately know what is thio, basically is the Sulphur-bearing bidentate ligand like and so, two Sulphur groups not only one you put two sulfur groups on the molybdenum center and which is basically required for your nitrate reductase activity.

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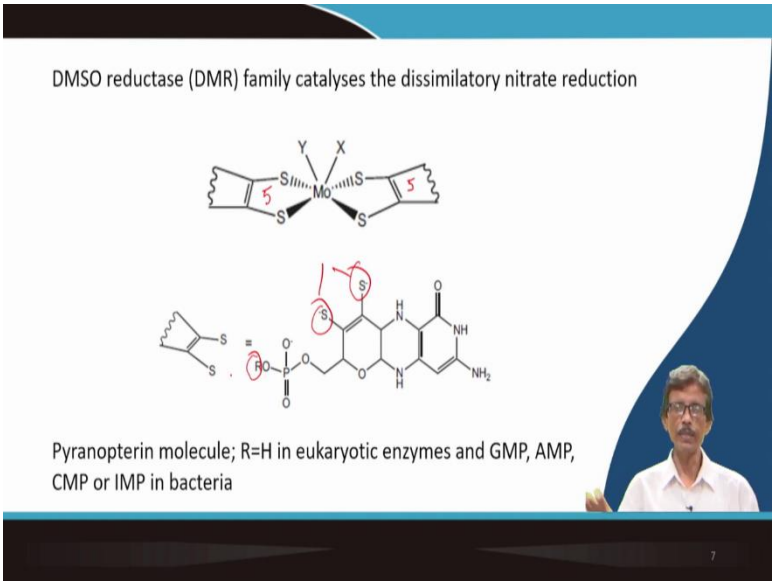

Another very closely related thing is your DMSO reductase dimethyl sulfoxide. So, you have sulfur two methyl groups and then what you can have the sulfoxide sulphone, all these then a Sulphur center can be oxidized that means you can transfer the oxygen on the Sulphur center like that what we are talking about the transfer of the oxygen center on nitrogen. So, they basically catalyzes the dissimilatory nitrate reduction.

So, you have the corresponding nitrate interactions. And if we now think of, okay, I can have the molybdenum center and how many of these bidentate. So, legend is identified how many of these ligands we will be bringing. So, you bidentate ligand SS type of dithiolane type of thing. That means, you have a corresponding clatter formation which is five member is not six members.

So very sort because you are satisfied with two Sulphur centers. The Sulphur centers are big that is why this particular clattering what you can have, which is five members, this is also five members, you are happy to accommodate a molybdenum center which is a little bit bigger compared to your chromium center.

And if it is little bit much bigger, you can have coordination number beyond 6 but it is not that, you can have the coordination from these two centers and how it is forming that you can think of what particular geometry you can expect there. Because the way we have drawn here sometimes we draw it also to confuse you people that you try to apply your brain that we know the isomerism and we know all these things so two bidentate ligand and two monodontid ligand giving you octahedral geometry around the molybdenum center.

But what is that dithiolane ligand? So, dithiolane ligand is a pretty difficult one is a big organic molecule has been denied for some time because it is a biogenic ligand. You have to produce yourself in your body, you have the biological system have to produce it in within it. So, you see again, you have this particular part only the S minus and S minus part will be utilized for the molybdenum binding or molybdenum clipping.

Other parts is a big one. So, you have to put the big ligand around the molybdenum center, and two such ligands you are bringing around the molybdenum center and you have two other sides X and Y because these two sides are also important for your catalytic activity. So, is basically by pyranopterin.

So, pyranopterin molecule is a huge number of these examples you will find but the substitutions on the phosphate part, what is your art, sometimes is basically the free it is HOR is OH the enzymes can be originated from your eukaryotic domain, but for the bacteria and others you have the corresponding nucleobases attached to the phosphate because these a phosphate is added. So, AMP, CMP, IMP and GMP these are nucleobases attached to phosphate and other parts. So, these are basically important, but we are interested to know about the peripheral modification. Whether you have R is equal to H or r is equal to something that means you can have R is equal to some phosphate-related base of the nucleosides.

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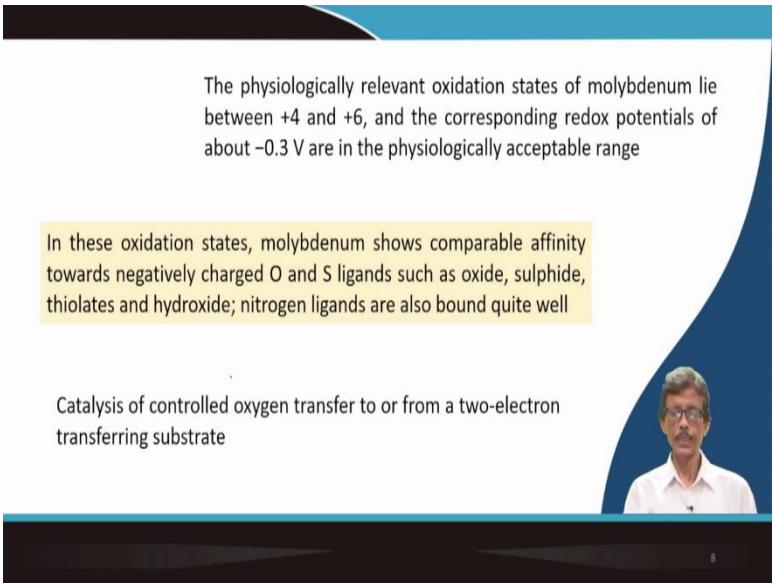

So, why this particular molybdenum center is important. Now, we will see, what type of reactivity it can show. In this particular case, it can go for two electrons type of reaction, that means, either it can go for two electron oxidation or two electron reduction. That means, you

can settle between the oxidation state of plus 4 and plus 6, you cannot have any other oxidation state in between, that means, you cannot have plus 5 oxidation state, which we require for single electron transfer, and the redox potential you see at the negative also minus 0.34.

That means, if you have air or if you have any other thing immediately we will be able to reach that hexavalent state of your molybdenum. It is not always so, easy to get the hexavalent state for the molybdenum center, but the synthetically prepared or the laboratory prepared molecules we know.

If you have a acetal acetone ligand we know the acetyl, acetone it a bidentate O ligand. So, when the acetyl acetone is binding to that particular molybdenum center you can have two Oxo centers the X is O and Y is also O. So, molybdenum also has some good affinity to stabilize its center to the higher oxidation state by attracting not only the Sulphur centers, but also the corresponding Oxo or the sulphide center, that means, double bond O, or M double bond S is also important to have.

And these oxidation states, that means, these two oxidation states can have the corresponding affinity for charged oxygen and Sulphur ligand that means sulphide and oxide ligands forming you M double bonded O and M double bonded Sulphur. You can have also thiolates, you can have also the extra hydroxide because it is sometimes through electron transfer, it is easy to convert that M double bonded O bond to MOH bond.

You can think of the electron transfer, you can think of the corresponding reactivity, but you put the electrode, we know that how the O bond can be converted to O2 minus and O22 minus. You are lengthening the bond because you are feeding the electron to the antibonding our O orbital similarly, here also you try to find out the corresponding molecular orbital picture of your MO, you go for the deduction of that particular hexavalent molybdenum how that is being reduced and how the MO bond will be stressed for MO single bond and your O can be charged and that O can also be protonated.

So, not only that, if you have some available nitrogen ligands also, those nitrogen ligands will also can come and bind to that particular active site or molybdenum. So, here only we will see that we have already seen earlier that how you use ferial iron center for your oxidase activity from the dioxygen molecule. Here we are we are not supplying say dioxygen, but you can have the nitrate, nitrite and all these things but finally, you can have dioxygen also. But

we will be talking about the reactions, which are the oxo-transfer reactions and two electron transferring system we have.

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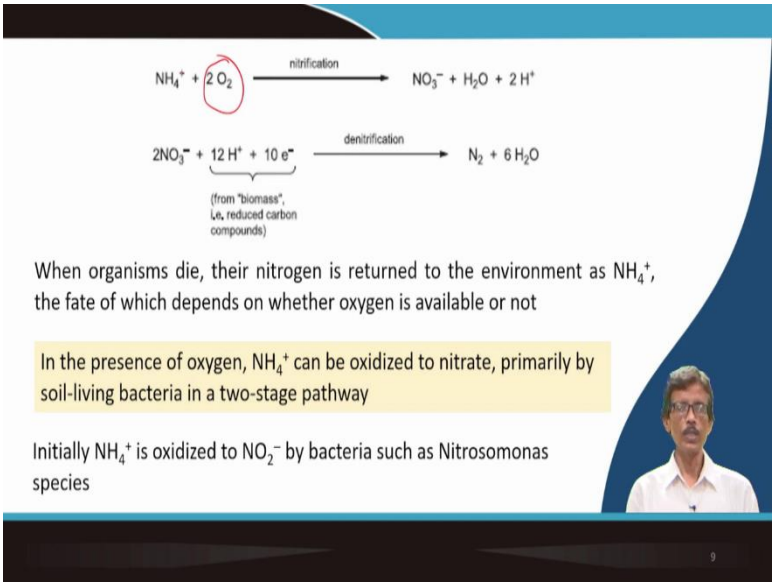

So, if we go for the nitrification that is why we have reached now the definition of nitrification and denitrification. Nitrification is the conversion of the ammonium ion to the nitrate and the denitrification is the corresponding conversion back to dinitrogen not ammonium ion. So, try to remember whenever you are reading any text, whenever you are reading a book, always try to remember this thing very nicely that you are talking something where we are not going back to the original condition of your ammonium ion.

So, ammonium ion is converting to your nitrate, but nitrate is being reduced the corresponding oxidized to your dinitrogen molecule. So, that is why we can have when organisms di, their dinitrogen basically is returned to the system giving you ammonium ion and the fate basically depends on whether your oxygen is available or not, because you are consuming the dioxygen molecule because you are producing water.

We all know, how many electron transfer can have if you have oxygen reduced to water molecule. So, the presence of oxygen everything will be converted to a nitrate is a two-stage pathway in the initial stage, ammonium ion is oxidized to nitrite by the nitrosomonas species and then nitrite will be converted to nitrate.

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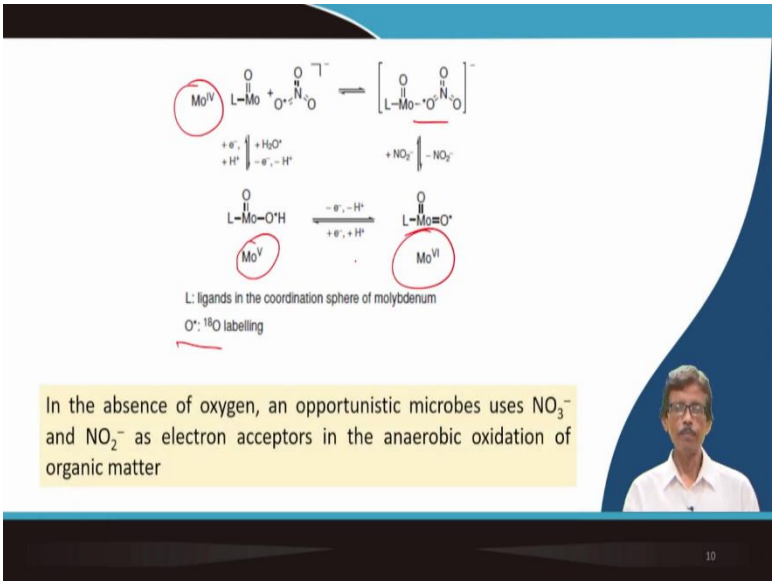

Now, if we consider that okay we have the molybdenum center and this molybdenum center bound to one L is shown, not that one L because you have to satisfy the coordinates and demand of that molybdenum center whether you are talking about a hexavalent molybdenum center or a tetravalent monitor center. But the nitrate, when nitrate is coming, you see, you are forming a molybdenum nitrate bond directly.

We all know, the nitrate is a very good species to keep outside the coordinates since as your anion typical anion, but this nitrate can interact nicely, you can go for the leveled experiment is O dot is not that free electron is the leveling experiment how you can identify these O dot. Bit dot is your leveled oxygen is of 17 or O18. So, that basically giving and basically molybdenum is taking up that thing molybdenum is taking up that oxygen, so is very much greedy about that particular oxidations of that particular oxygen.

So, molybdenum will be converted to molybdenum 6, and again one single electron transfer gave you hydroxide O bond form, so that is the intermediate basically but not the stable one, but the stable one is your molybdenum 4 and the molybdenum 6 will suttle will between these two and intermediate will be forming the molybdenum 5. But when you have no oxygen, we can have the microbes then microbes can also go for electron transport reaction in an aerobic condition and products will be different because you do not have dioxygen available to it, only the carbon is available as your organic matter.

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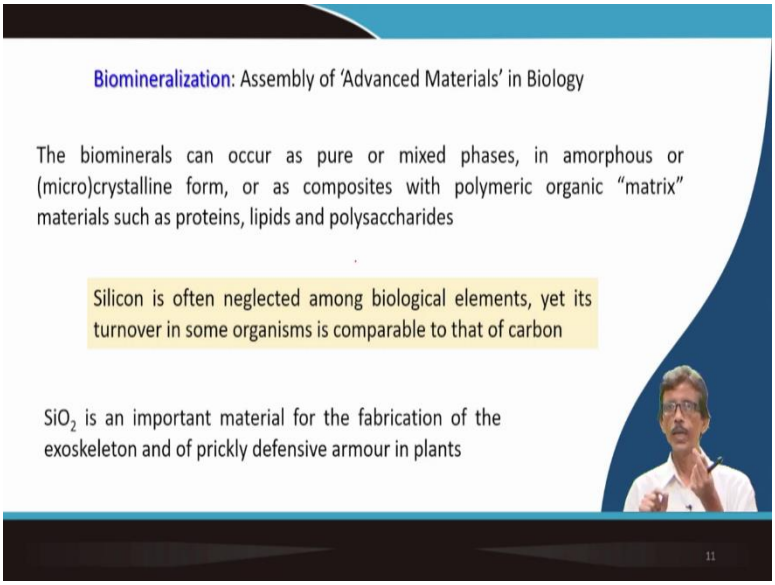

So, lastly, we will see about the biomineralization because people are very much encouraged with these things for the last 30 years or so, because the materials chemistry research or the materials physics research has got a boost to understand the biological thing what is obtained from there.

So, bioremediation process we are forming some microcrystalline form of these things. And if you have the organic metrics like protein, lipid polysaccharides and all these, so on that support basically you go for the deposition of something, the metallic deposition or the metallic oxide deposition like your silicon. If you consider that you have the silicon is I-only elemental silicon, which you do not consider much about its biological effects or biological function or the biological chemistry of silicon.

But with the advent of all these materials chemistry research people now can think of can talk about the silica, SIO2 the sand what do we get from the sand the silica. It is important material for the fabrication of the exoskeleton and prickly defensive armor in plants. Because the plant leaf you can have the silicon which can also prick your finger to take out your blood. So, that is why you have not only the carbon-based solid structure, but also you can have the silicon-based solid structures.

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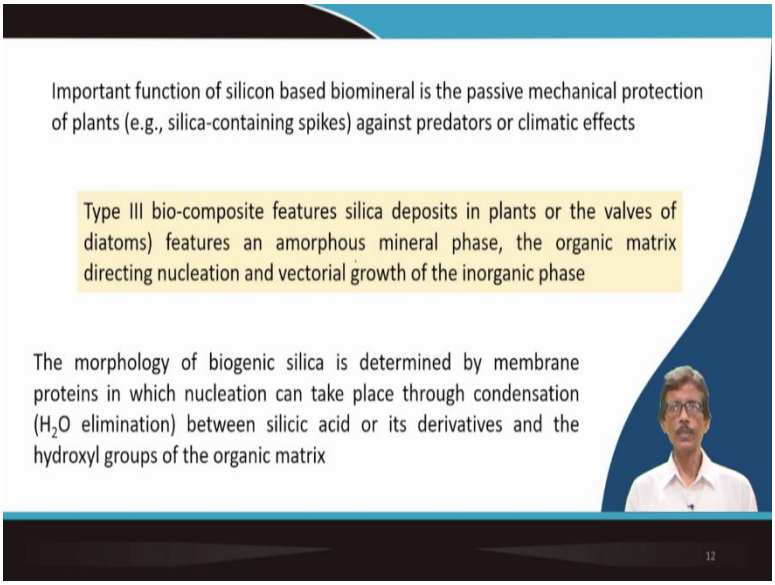

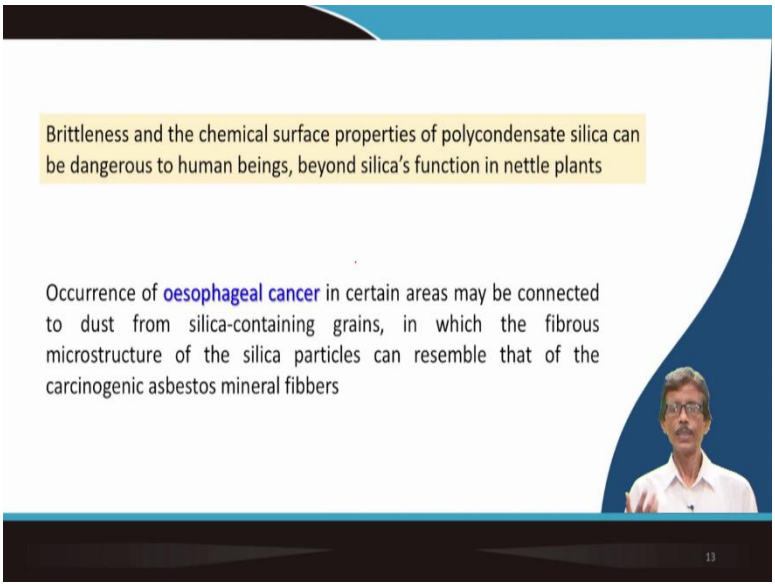

So, you can have many functions which are related to the silicon-based biomaterial for the mechanical protection of the plant silica containing spikes you can have, you can have the end of the leafs to protect themselves from the climate affairs from the other predators. So, type 3 composite we call them composite, because you can have the organic part and the nucleation and the vectorial growth of the inorganic phase that means silicone first and then silicon dioxide.

And the morphology of all these things for the biogenic silica because silica you are getting from the biological origin not from the seashore. So, you have the membrane proteins, and the membrane proteins are supporting all these things and you get the silicic acid and hydrolyzed silicic acid is giving you SIO2 for your structure.

And the brittleness, and the chemical surface properties of these polycondensed silica basically. Condensation will take place, we know ultimately, the formation of a SIO2, but sometimes we find that the asbestos which is also silicon-based material. Sometimes we considered that the silicon is important.

People studied the esophageal cancer connected to the dust the silica particle because it can go to your lung or esophagus and you can peer some points and can grow something can lead something, which can be cancerous also, because the asbestos miners the mining people who are going removing asbestos they are far going for something we call as the silicosis they can suffer from silicosis.

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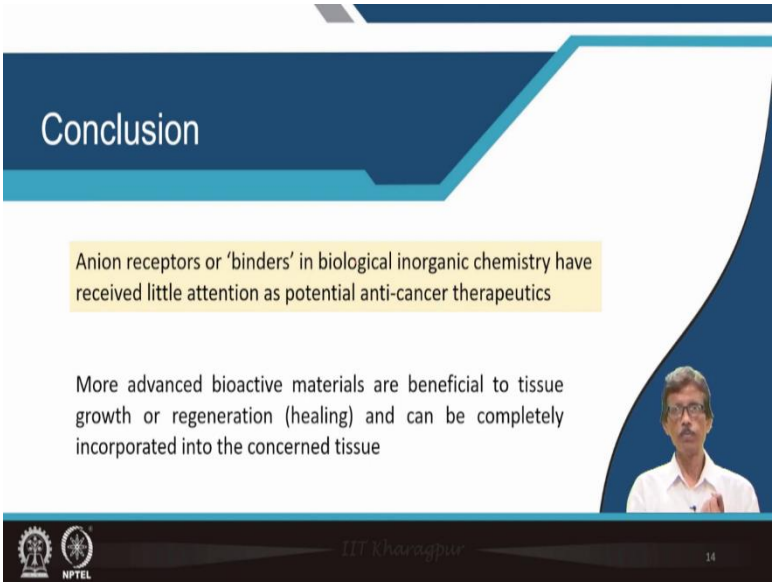

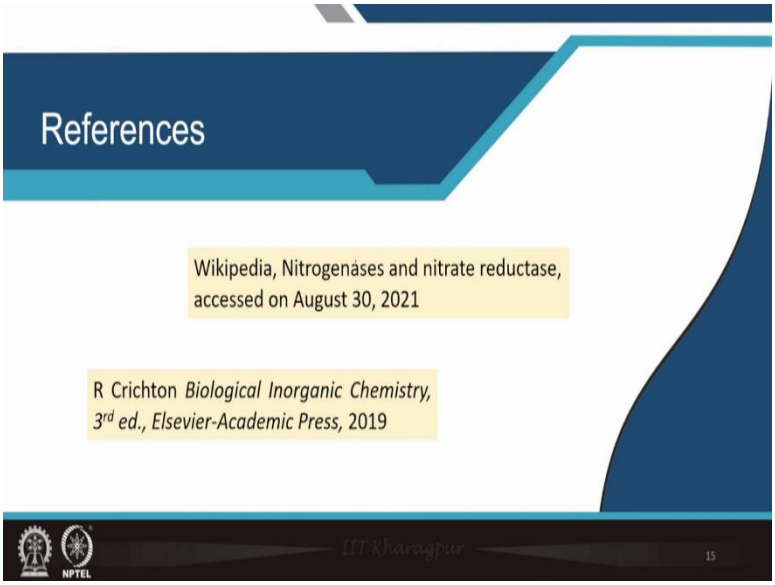

So, in conclusion, let us see, how what we have reached to this particular point because we are talking about the anions, not that, what we can think beyond is the future scope basically. Not only the conclusion what you have read, but you can, what you can you can think in the future, you can have the anion and anion like your other things that is the corresponding sodium and potassium already I told you can have the chloride receptors.

Similarly, for nitrate and nitrates, you can have the anime receptors or binders what we call receptors are nothing but binders, but it can differentiate from that of your ligand, because the ligands that are available to bind the metal ion. So, there are binders, binders your receptor, so, receptor send like a nomenclature you should know nicely. Basically, it is receiving the new day's attention to have something which can be considered as your anticancer therapeutics if we know the origin.

And the bioactive material because the materials chemistry research is also getting tremendous sell from this area which is beneficial for tissue engineering, we call for regeneration healing of all these things, something has been broken if we want to have make some new tissue which is biocompatible and we can put inside from outside world that means after making it in the laboratory, so it basically give some help for your tissue engineering.

So, you read the nitrogenous base from Wikipedia and nitrate reductase also from that page and we go for that book what every day we are giving you for your reference, and everything we are following from that particular book you read that book and nicely try to assimilate everything what has been told to you. Okay, thank you very much for your kind attention.