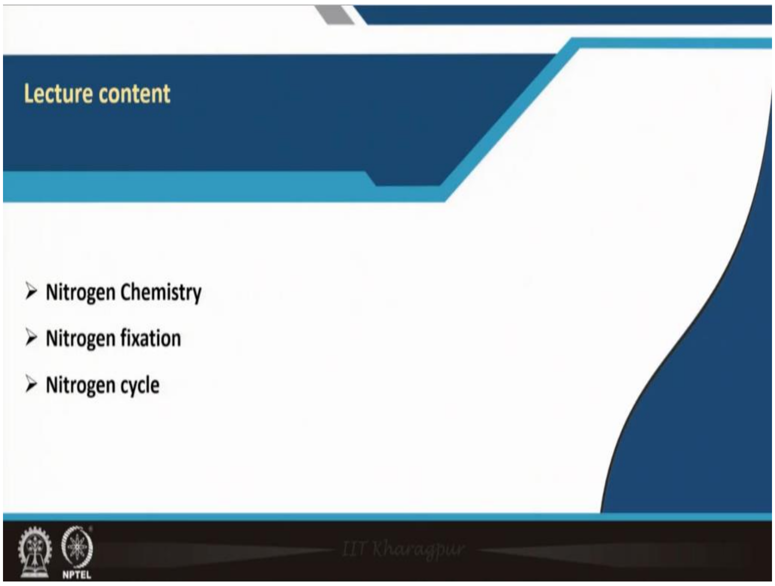
Environmental Chemistry and Microbiology

Dr. Anjali Pal
Dr. Sudha Goel
Department of Civil Engineering
Indian Institute of Technology - Kharagpur

Module - 5
Lecture - 21
Nitrogen Chemistry (Part A)

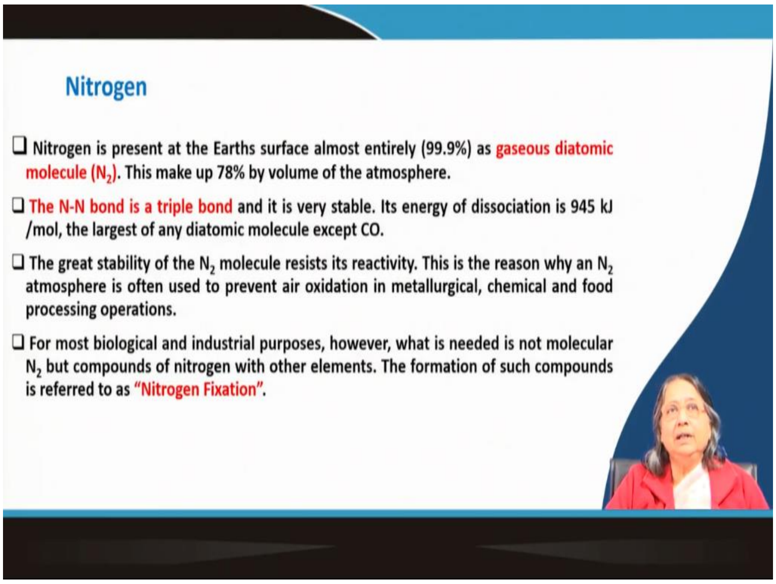
Welcome everyone to our online NPTEL course of Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We both are from Civil Engineering Department, IIT Kharagpur. We have divided this course into two parts. The first part is Environmental Chemistry. It will be covered by myself. The second part is Environmental Microbiology and it will be taught by Professor Sudha Goel. In my first module, I have discussed about the acids, bases and salts. In my second module, I explained the chemical equilibrium. In the third module, I discussed about the chemical kinetics. In the fourth module, I have discussed the catalysts. And this is my fifth module. In this module, I will discuss about the nitrogen chemistry and the chlorine chemistry. This is my lecture number 21, where I will talk about nitrogen. This is the part A of this lecture.

(Refer Slide Time: 01:56)



The lecture content is the nitrogen chemistry, nitrogen fixation and nitrogen cycle.

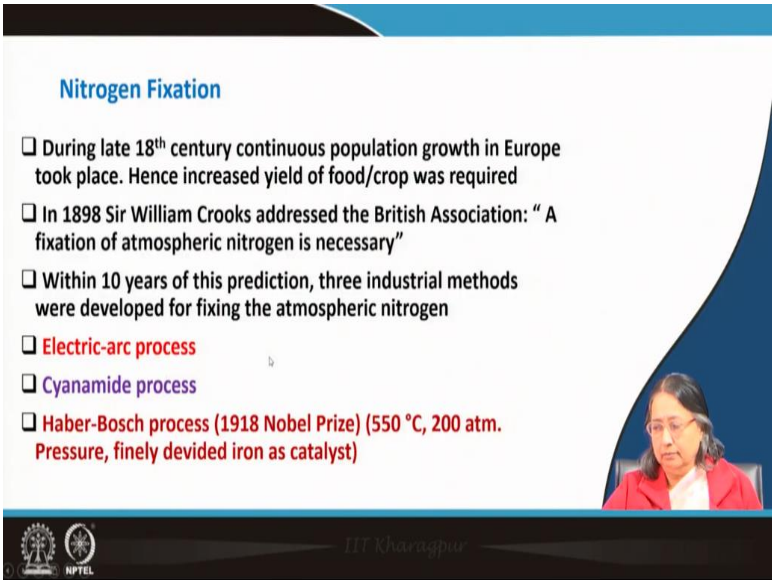
(Refer Slide Time: 02:07)



We all know nitrogen is present at the earth surface, almost entirely as gaseous diatomic molecule. We know that nitrogen is a very inert gas. Now the question is that, whether the nitrogen and nitrogen bond is single bond, double bond or triple bond? Actually, the nitrogen nitrogen bond is a triple bond and many people call nitrogen as just nitrogen. But most appropriately this should be called as dinitrogen. We all know that it is a very stable molecule. And the energy of dissociation is very high, 945 kJ/mol. It is the largest of any diatomic molecule except carbon monoxide. That means it is a very stable molecule and inert molecule. Due to this inertness, it does not react very easily. We sometimes use nitrogen in many reactions to keep the atmosphere very inert. And sometimes we mix nitrogen; to dilute the oxygen, we mix the nitrogen in the gas cylinder, oxygen cylinder which is used by the diverse. And we know that; usually when I asked to the students that, can you tell me that whether a nitrogen is more soluble in water or oxygen is more soluble in water. In 99% cases, I get the answer that oxygen is more soluble. But actually, nitrogen is more soluble than oxygen in water. We know that with temperature the solubility varies. So, we know that oxygen at 0° C, the solubility is around 14 mg/l. But if we see the solubility of nitrogen at that temperature, we will see it is around 20 to 23 mg/l. So, it is quite high compared to oxygen. But most important thing is that we do not need the molecular nitrogen, but we need the compounds of nitrogen.

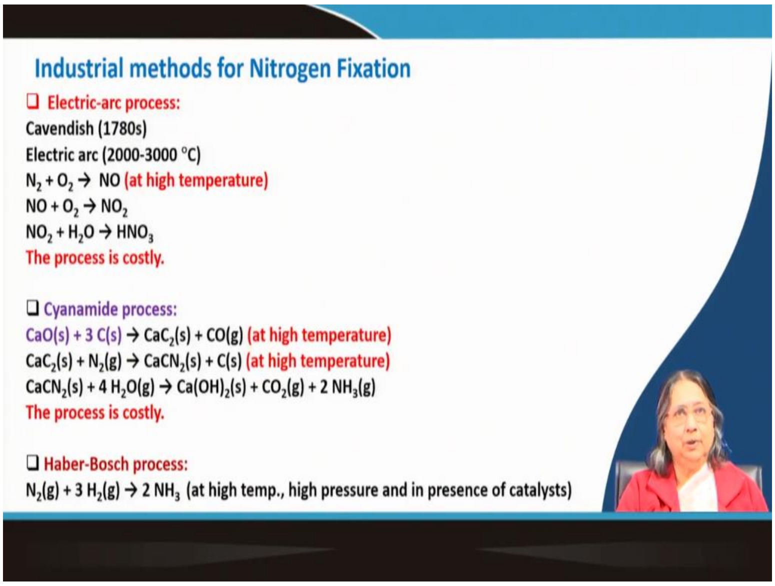
Plants take up nitrogen. We need nitrogen for our biological systems. In amino acids, proteins, DNAs, urea, nitrogen is present. But if we see in what form nitrogen is present, then we will see that nitrogen is present in combined state. It is not present as just elemental nitrogen (0 state). It is present in combined forms and the formation of such compounds is referred to nitrogen fixation. We know oxygen fixation. Those who are from environmental engineering background or environmental chemistry background, we all know that when we determine the dissolved oxygen (DO), then we use the Winkler method and we have to fix the oxygen by doing some reaction. Here also, when we want to use the nitrogen, then we have to fix the nitrogen.

(Refer Slide Time: 06:44)



From long time back, we see that the nitrate or ammonia is required for plant growth. We have seen that the ammonia fertilizers are often used. So, for the plants to grow, we need some combined form of nitrogen. Before the eighteenth century, we were mainly dependent on the animal waste and many minerals (say for example Chile saltpetre, nitrate). But during the late eighteenth century when the continuous population growth occurred in Europe; then increased yield of food or crop was required. So, the source of nitrogen that was previously used was not sufficient. At that time, it was a crying need. So, at that time in 1898, Sir William Crooks addressed the British Association that a fixation of atmospheric nitrogen is necessary. We have enough nitrogen in the atmosphere, but that is in 0 state and that is not of much use to the plants. So, we need to have some methods by which we can fix the nitrogen for growing the plants and to make the food for the crops. When something is so much important, then lot of scientists start research on it to make it a success to produce and in this case, it was nitrogen fixation. Within 10 years of this prediction, 3 industrial methods were developed for fixing the atmospheric nitrogen. These 3 methods are electric-arc process, cyanamide process, Haber-Bosch process. I told in my earlier lectures that what is Haber-Bosch process. It is a very good example of nitrogen fixation and still it is in use to make the fertilizers. I will show you how we can fix the nitrogen by using these methods.

(Refer Slide Time: 09:41)



Cavendish first observed that when nitrogen and oxygen are mixed together and electric-arc is passed through that, then the temperature generated is very high. Then nitrogen and oxygen will combine to form NO. So, electric-arc method was suggested by Cavendish in 1780s. Now, after so many years, that method was utilised to form some combined state of nitrogen i.e., nitric acid. Nitrogen and oxygen at high temperature through this process combine to form the nitric oxide. Then nitric oxide, in presence of oxygen, forms the nitrogen dioxide. Nitrogen dioxide, is actually anhydride of some acids of nitrogen. I have not written the complete equation (in the last slide), but briefly NO_2 upon reaction with water forms the nitric acid. But this is a very costly process to generate such a high temperature by electric-arc. The second process is the cyanamide process: You can see (1) that calcium oxide (solid) and carbon at high temperature react to form the calcium carbide and carbon monoxide. Then this calcium carbide when reacts with nitrogen (0 state) to form nitrate (2). So, it is a type of fixation. Nitrogen when reacts with calcium carbide, it forms the calcium cyanamide. Then this calcium cyanamide when reacts with water; calcium hydroxide, carbon dioxide and ammonia is produced. So, you can see that nitrogen is converted to ammonia. So, this is also a process by which nitrogen is fixed. This method is also costly, because here also high temperature is required.

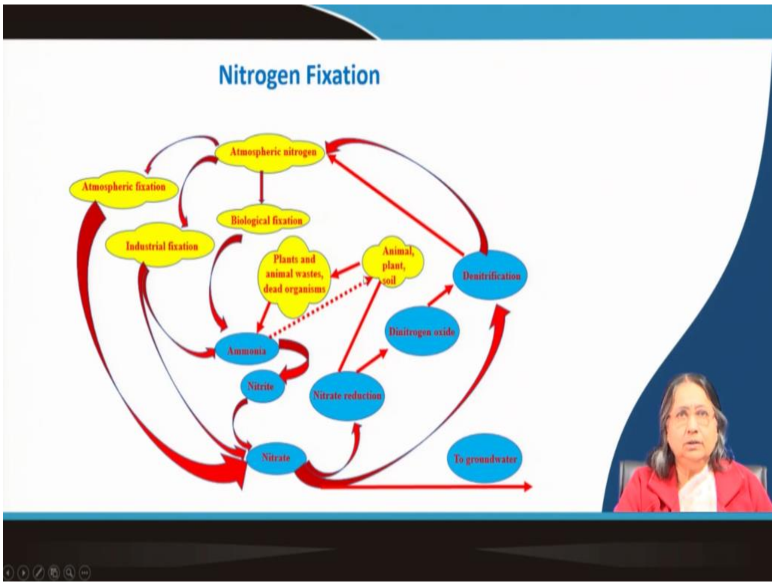
$CaO(s)+3C(s)\rightarrow CaC_2(s)+CO(g)$……………………….(1)

$CaC_2(s)+N_2(g)\rightarrow CaCN_2(s)+C(s)$……………………………..(2)

$CaCN_2(s)+4H_2O(g)\rightarrow Ca(OH)_2(s)+CO_2(g)+2NH_3(g)$………………….(3)

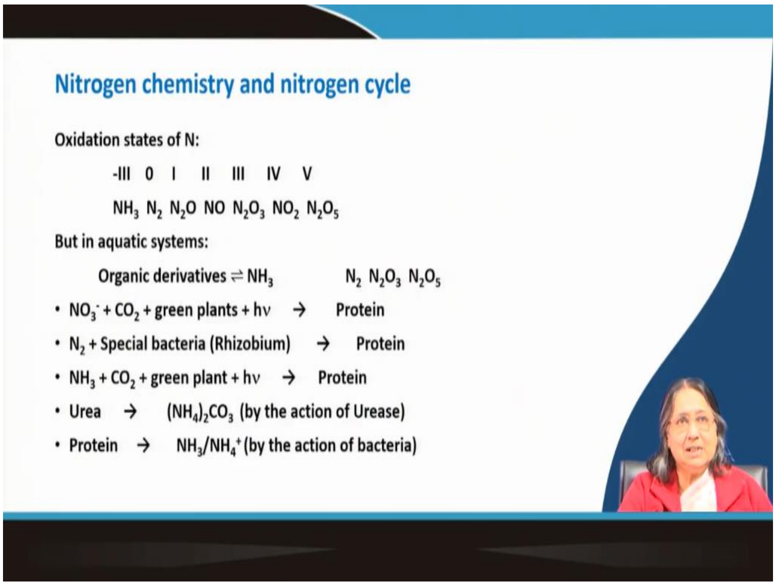
I have already explained Haber-Bosch process. You have seen that it is done at very high pressure (200 atmosphere pressure), 550° C and in presence of catalyst (finely divided iron as catalyst). Sometime molybdenum is used as a promoter. This process is also not energy efficient process. But this process was so much useful and so much important at that time that Haber got the Nobel Prize. I also discussed about that. The yield is also very low and there are lot of processes have been tried to increase the yield.

(Refer Slide Time: 13:14)



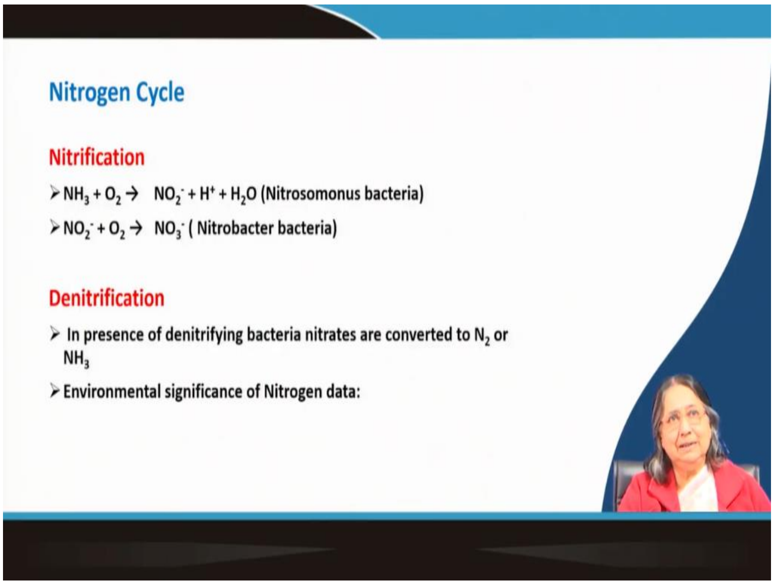
You can see in the last slide, that there are many methods for nitrogen fixation. Actually, combination of nitrogen and oxygen to form the nitric oxide (electric-arc process) is happening in the atmosphere. When there is thunderstorm, there is lightning. In the atmosphere there is always nitrogen and oxygen. So, they combine automatically to form the NO. Then NO in presence of oxygen forms NO_2. When the rain comes, then water is coming and NO_2 is dissolved. Then it forms the nitrate. So, you can see in the last slide that nitrate can go in the soil or ultimately it can go to the groundwater or it can go to any river water, pond water as a runoff. So, in the natural process this is atmospheric fixation. It is going on all the time. There is also industrial fixation. Electric-arc process, Haber process etc. are industrial fixation. Now there is another way i.e., biological fixation: What is biological fixation? You know that there are many plants where, say for example peas. If you notice in the nodule of pea, some microorganisms grow. When these microorganisms grow the specialty of the microorganisms is that they can fix the nitrogen from the atmosphere. It is called symbiosis. That means give and taken policy. It is converting the nitrogen to some combined form and that combined form of nitrogen is taken up by the plant who has given the microorganism shelter in their roots. So, this is biological fixation. I already told you that nitrogen is a very stable molecule. So, breaking the nitrogen nitrogen triple bond is very difficult. But you can see here that in nature it is going on so smoothly. The microorganisms can do it in very mild way. Then you can see that plant and animal wastes are converted ammonia. Then ammonia it can be oxidised to nitrite or it can further oxidised to nitrate. These are also carried out by some microorganisms (e.g., nitrosomonas, nitrobacter group of microorganisms). Then nitrate reduction can also take place. Nitrate are also taken up by plants from the soil. From the plants it is transferred to animals when they eat plants. From plants and animals, it again may come to the soil in form of waste products. Say for example, the protein molecules can be degraded to ammonia. So, this is some type of cycle. Even sometimes the nitrate upon reduction, forms some oxides it can produce. Then it can undergo denitrification and then it can go to the atmosphere as atmospheric nitrogen and it form the cycle. So, these are the different processes going on in the nature.

(Refer Slide Time: 17:46)



Now, why nitrogen is so much interesting? You know from the periodic table that nitrogen belongs to group 5. Then the highest oxidation state is 5. You can easily calculate that nitrogen in ammonia, is in -3 oxidation state. In elemental nitrogen, it is 0. It has many oxidation states ranging from -3 to +5 as shown in the last slide. So, it is a very interesting chemistry. But in the aquatic system, you know that organic derivatives are also decomposed; say for example, protein molecules, they can decompose to produce ammonia. I told you that nitrogen can be dissolved in water. So, it is in 0 state. And then nitrite, nitrate also can be formed and they are present in aquatic systems. Some other forms like +2 state or +4 state are not very common. Nitrate in presence of carbon dioxide, green plants and the light can form protein. Then this is the rhizobium group of bacteria (I told you just now) can fix the nitrogen directly to form protein. Ammonia also can be converted to protein. Urea comes as the waste product of animals. Then by the action of urease, it can form that ammonium carbonate. Protein is a very complex molecule. So, it can be degraded by microorganisms to form the ammonia or ammonium ion by the action of bacteria. So, these are the different things that are going on in the nature with nitrogen compounds.

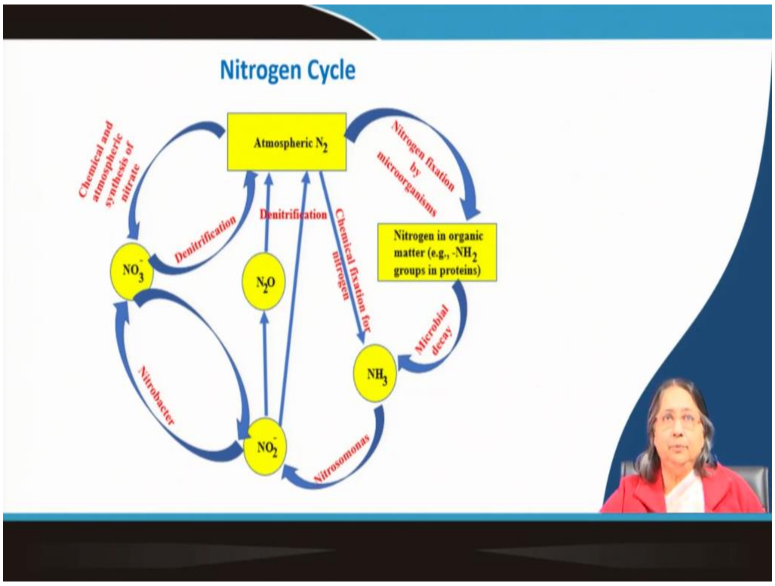
(Refer Slide Time: 20:30)



You know nitrification and denitrification. When ammonia in presence of oxygen forms nitrite it is called nitrification. This is by some special group of bacteria which is nitrosomonas bacteria. In the next step, the nitrites can be oxidised to form nitrates. This is nitrobacter group of bacteria. This process is called nitrification. You have seen, in the BOD determination, we always do the 5-day BOD. But why we do the 5-day BOD? Why don't we do 7-day or 10-day BOD? It is so because, after 5 days, the bacteria oxidise the nitrogenous compounds like ammonia. So, ammonia is oxidised by the oxygen and it is called NBOD. Up to 5 days, it is CBOD. So, it is the conversion of carbon that is present in the organic molecules to carbon dioxide. After that, the nitrogen containing compounds, they also take part in this type of reaction to form the nitrites and nitrates.

But what is denitrification? In presence of some type of bacteria nitrates are converted to nitrogen or ammonia. So, denitrification means reduction process and nitrification means oxidation process and under some special atmosphere it happens.

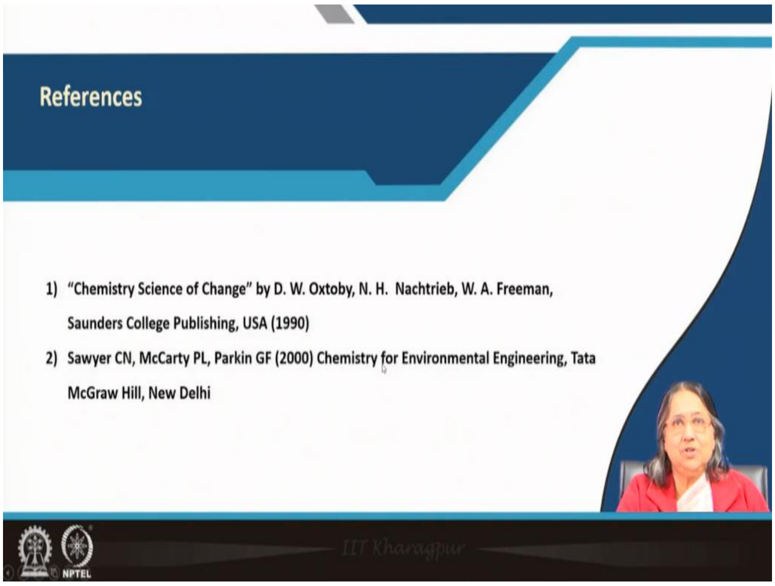
(Refer Slide Time: 24:04)



I told you what is nitrogen fixation. Now see the nitrogen cycle (in the last slide). It is a similar thing shown in a different way. You can see chemical and atmospheric synthesis of nitrate from atmospheric nitrogen. By lightning nitrogen and oxygen combine forming the nitrites. Then it is forming the nitrate. Again some atmospheric nitrogen is produced through the denitrification. Now, you can see on the right side that nitrogen fixation by microorganisms (biological fixation). Sometimes in the villages in between two main crops, we grow the peas. Why? It is so because, you know that there are some nitrogen fixing bacteria present in the roots. So, when those plants die, they just automatically mixed in the soil and then the soil becomes richer in nitrogen. So, it is green manure type.

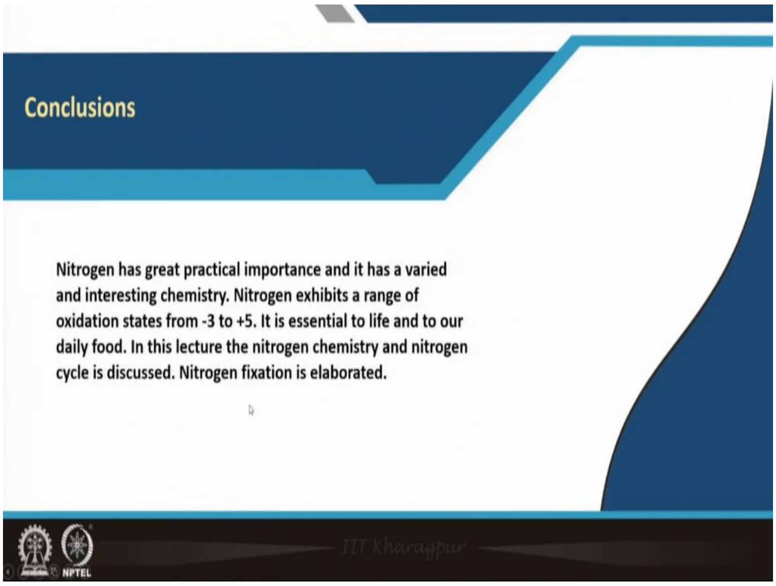
Nitrogen is also present in organic matter such as amines. When it is decayed by microorganisms, they form the ammonia or ammonium ion. Now, from ammonia or ammonium ion, it can form nitrites by nitrosomonas bacteria. Finally, by nitrobacter group of bacteria, it can form the nitrate. Again, from the nitrates or the nitrites, through denitrification it can go back to the atmospheric nitrogen. So, basically it is a cycle.

(Refer Slide Time: 27:17)



Now, regarding the references for this nitrogen cycle or nitrogen fixation; you can get from any books. But I can prescribe two books shown in the last slide. You already know the book Chemistry of Science of Change. I already referred for my previous lectures and the other one is by Sawyer and McCarty book. This also I referred in my earlier lectures. You can read from these 2 books.

(Refer Slide Time: 27:55)



So, in this lecture I have discussed about the nitrogen. Nitrogen, has great practical importance and it has a varied and interesting chemistry. Nitrogen exhibits a range of oxidation states from -3 to +5. It is essential for life and to our daily food. In this lecture, the nitrogen chemistry and nitrogen cycle are discussed and nitrogen fixation is elaborated. Thank you so much.