Environmental Chemistry and Microbiology
Dr. Anjali Pal and Dr Sudha Goel
Department of Civil Engineering
Indian Institute of Technology, Kharagpur

Lecture -07
Chemical Equilibrium-II

Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Professor Anjali Pal. We are both from Civil Engineering Department, IIT Kharagpur. We have divided this course into two parts: the first part is Environmental Chemistry which will be covered by me and the second part is Environmental Microbiology, that will be taught by Professor Sudha Goel.

In the lecture number 7 (i.e., under module 2), I will explain some aspects of chemical equilibrium. I have already told about chemical equilibrium and how to setup the expressions for chemical equilibrium.

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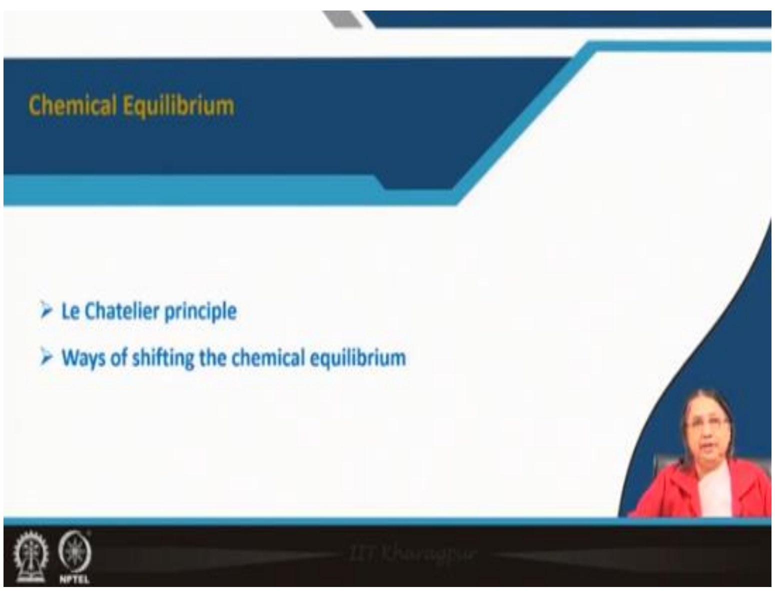

Now in this lecture, I will talk about the Le Chatelier principle which is very important in chemical equilibrium concept and I will also tell you that how we can drive a chemical reaction towards the forward reaction or backward reaction (that means how we can shift the chemical equilibrium).

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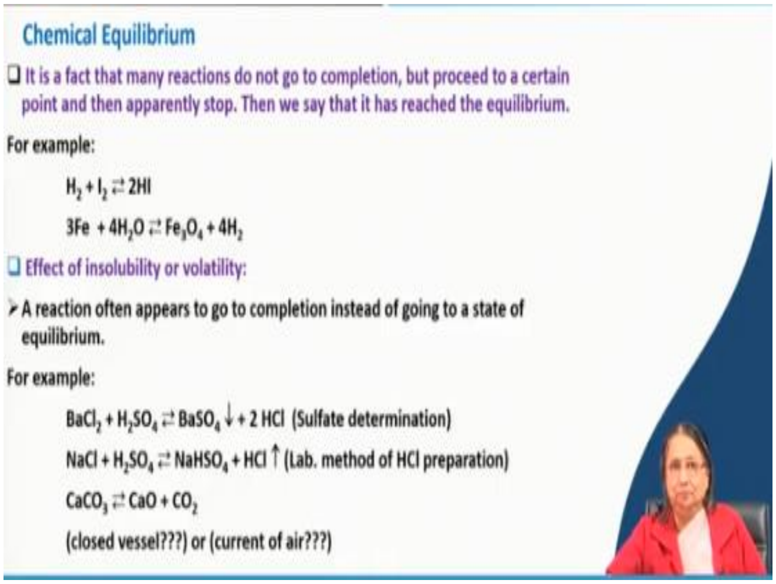

It is a fact that many reactions, you know, they do not go to completion. But they proceed to a certain extent and then they apparently stop. Then we say that the chemical equilibrium is reached. For example, hydrogen gas reacts with iodine in vapour form to form the hydroiodic acid. The reaction is shown here:

$H_2+I_2 \leftrightharpoons 2HI$..........(1)

Hydrogen and iodine are in vapour form and they produce the hydroiodic acid (HI) which is also gas. So, all are in gas phase. So, this is actually you have seen that here "$\leftrightharpoons$" is the sign where we tell that it is in equilibrium. Actually, this reaction reaches to equilibrium after some time. It depends on the temperature and the presence or absence of catalyst, but finally it gives some composition where all three will be there (hydroiodic acid, iodine and hydrogen) and what is the composition that depends on the condition. Now at that point when the equilibrium is reached then we can till that the forward reaction and the backward reaction, they are the same. That means the rate of forward reaction and rate of backward reaction is the same and then we can tell that no more reaction goes on. Actually, reaction is going on but the amount that is produced (the amount of HI that is produced from hydrogen and iodine) is equal to the amount of HI that will be decomposed to form the reactant.

The same we can explain here for the next reaction that is iron when reacts with steam then it will produce the hydrogen gas and the iron oxide (Fe_3O_4).

$3Fe+4H_2O \leftrightharpoons Fe_3O_4+4H_2$..................(2)

This is the equilibrium reaction (2). This reaction is reversible reaction and here we think that it has gone to equilibrium stage. In some cases, we need to achieve 100% completion of reactions for various analytical purposes and other purposes. The main question is that how we can do that. Below given are some of the examples of such reactions:

$BaCl_2+H_2SO_4 \leftrightharpoons BaSO_4\downarrow+2HCl$ (sulfate determination) ....(3)

$NaCl+H_2SO_4 \leftrightharpoons NaHSO_4+HCl\uparrow$ (lab method of preparation of HCl) .....(4)

$CaCO_3 \leftrightharpoons CaO+CO_2$...........................(5)

In reaction (3) barium chloride reacts with sulphuric acid to produce barium sulphate. "↓" is the sign of precipitate. That means in this reaction barium chloride when reacts with sulphuric acid it gives barium sulphate which is precipitated and also it produces HCl. Now when some product is going out of the phase then the reaction goes towards the forward reaction. Why? It is so because you know from the equilibrium expression that when the product is removed, then more and more reaction will go on to produce more product. That is why the reaction goes towards the forward direction and this type of reaction we use for sulfate determination. You know that for any analytical method of determining or quantifying something, reaction should be complete otherwise if it is not complete then our analytical method will be wrong. So, this method (reaction (3)) is used for sulphate determination and this reaction should be complete when we use it for sulphate determination. Now the next reaction (reaction (4)) represents laboratory method of HCl preparation. In this method we take solid sodium chloride and then we drop concentrate H_2SO_4 on to it, then we see that HCl gas is produced which is taken out. That means it goes away as a gas from the reaction mixture and then more and more reaction goes towards the forward reaction. It is precipitate in case of reaction (4), so it is going out of the phase and in case of reaction (3) it is gas, so it is going out of the phase. Basically, the principle is same when some product goes out of the phase then more and more products are produced from the reaction. That means ultimately it goes to 100% conversion. Now one interesting example is shown here in reaction (5). You know that when calcium carbonate is heated at a high temperature then it forms calcium oxide and carbon dioxide. But if you take calcium carbonate in a closed vessel and heat it at high temperature, then what will happen? And when you take calcium carbonate and you heat at same temperature, but under the current of air then what will happen? This is the question. When you heat the calcium carbonate taken in a closed vessel then you will see that equilibrium is reached and some calcium carbonate will still remain in the vessel at the bottom of the vessel and some calcium oxide is produced with some carbon dioxide. All remain together in that closed vessel. But when you heat calcium carbonate in a current of air (that means in an open vessel at the same temperature) then carbon dioxide will go out as a gas. So, then what will happen? More and more calcium carbonate will be converted to calcium oxide and carbon dioxide. And if you give sufficient time then you will only will be left with calcium oxide and carbon dioxide will go out. So, no more calcium carbonate will be there. It means that in one case in a closed vessel when you are heating (at the same temperature) you are reaching the equilibrium and when you are heating in a current of air in an open vessel then you are going to the completion. So, these are the case two different behaviors of same thing under two different conditions.

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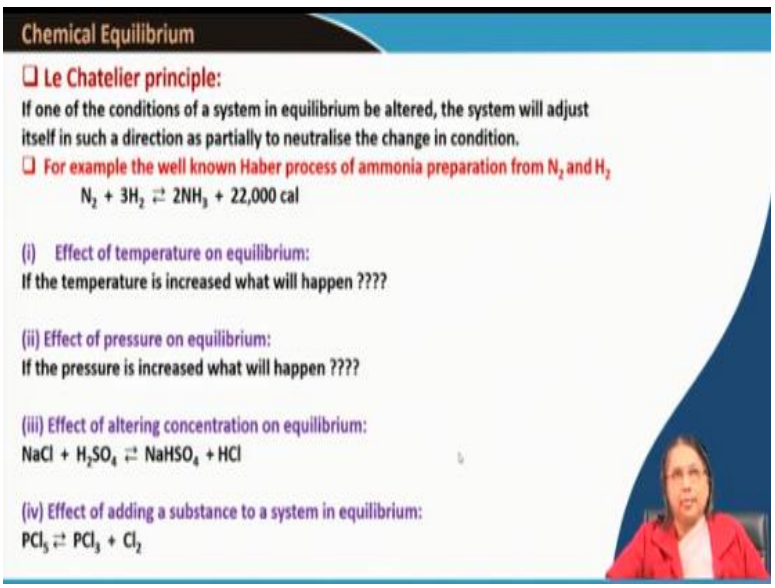

Now what is Le Chatelier principle? This is very important in chemical equilibrium. It is said that if one of the conditions of a system in equilibrium be altered then it will adjust itself in such a direction as partially to neutralize the change. You are producing some disturbance on a system which in equilibrium. So, what it will do? It will try to nullify the disturbance. It is shown by using the following example:

$N_2+3H_2 \leftrightharpoons 2NH_3+22000$ cal.......................(6)

This represents the ammonia production by Haber's process. In this method we take nitrogen and hydrogen, then we give high pressure (200 atmospheric pressure) and we use the temperature

550^0C, then ammonia is produced and it is an exothermic reaction. So, some heat is general. This process was developed by Haber and Bosch process, where he obtained ammonia production he obtained from the nitrogen and hydrogen. This is also one type of nitrogen fixation. I will discuss nitrogen fixation later in my other lectures. But here just remember that high pressure is to be given (200 atmospheric pressure) and also temperature 550^0C in presence of some catalyst. Here, finely divided iron is the catalyst.

Now, we have to explain the effects of temperature and pressure on equilibrium. Say for example we increase the temperature. If the temperature is increased then what will happen? So according to Le Chatelier principle if we disturb the condition then it will try to nullify that disturbance. That means if we increase the temperature it will act in such a way that temperature is decreased. How it will be done? Because it is an exothermic process so it will go in the reverse direction. So, it will go to the reverse direction to nullify the increase of temperature. Now if we increase the pressure what will happen? If we look into the number of moles, we know that at a constant volume number of moles it is related to pressure. So, you can see that on right side of equation (6) side there are 2 moles and on left side there are 4 moles. So, if we increase the pressure then what will happen? It will try to go in that direction where the number of moles is reduced, that means when the number of moles is more, then the pressure is also higher. So, it will act in such a direction that number of moles is reduced. That means it will go towards the forward direction. So, effect of temperature and effect of pressure have been explained.

Now consider another reaction which is also in equilibrium.

$NaCl+H_2SO_4 \leftrightharpoons NaHSO_4+HCl$............................(4)

Say for example, $NaCl$ and H_2SO_4 is producing $NaHSO_4$ and HCl in a closed vessel. That is why it is equilibrium but if we do it in open vessel HCl will go out. So, one product's concentration is becoming less. So, it will become it will go towards the forward direction. Now if we add NaCl then again, it will go towards the forward direction. Because this concentration increase means it will always try to decrease this concentration and how it will decrease? It will do such by going towards the forward direction. So, this is the effect of altering concentration on equilibrium. Now here, you consider another equilibrium reaction:

$PCl_5 \leftrightharpoons PCl_3+Cl_2$............................(7)

So, this is a reaction ((7)) which is in equilibrium. From outside you put some amount of chlorine gas inside this vessel then, what will happen? It will try to reduce the Cl_2 gas. How it will do it? It will do such by going towards the backward reaction. If you increase the PCl_5 concentration, it will go to the forward reaction to decrease it. So, effect of adding a substance to a system in equilibrium is involved here.

But from outside you can introduce some inert gas also it will have also some type of effect. When you introduce some gas from outside then it will increase the pressure and it will always try to decrease the pressure. So, it will act in such a way that it will go towards either forward or backward direction to reduce the pressure. That example I have not shown here. But obviously we can get it if we understand this thing.

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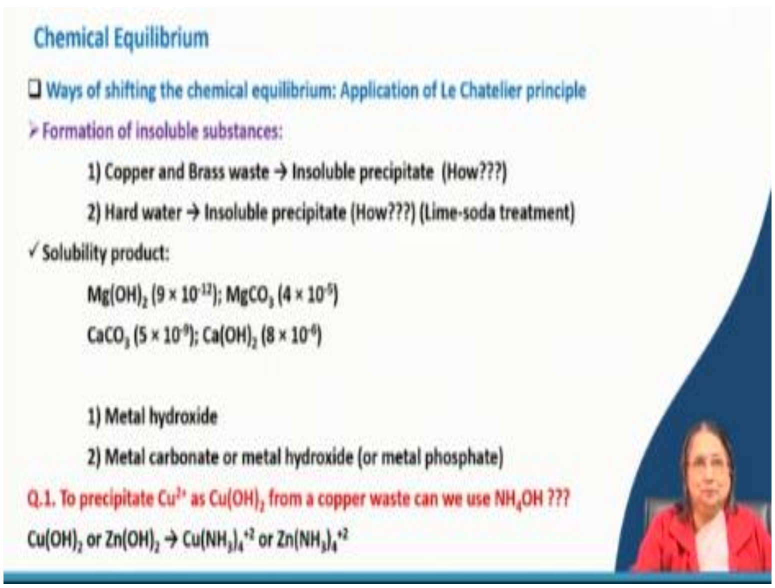

Now we will see, how we can shift the chemical equilibrium? Here we have to apply Le Chatelier principle. Now how you can do this? This has enormous application in environmental engineering. It should be properly understood so that we can apply it to solve different problems. Now here we will see first, the formation of insoluble substances. We have already encountered some examples. Here are many other examples I have shown which are practical problems actually.

1) Copper and brass waste →Insoluble precipitate (How??)

2) Hard water →Insoluble precipitate (How??) (Lime soda treatment)

3) Formation of metal hydroxide, metal carbonate or metal phosphate

In the first example copper and brass waste is written. Now, what is the composition of brass? First of all, in both brass and bronze copper is there. In bronze there is "z". So, zinc is absent and it is made up of copper and tin. On the other hand, in brass there is no "z". So, it is composed of copper and zinc. Now if we consider the copper waste or brass waste then in the waste water, there is some copper ion present or zinc ion may be present. Now how to remove them? If you look into the removal of metals in most cases, you will see that metals are removed by producing some hydroxide. Because most of the metal hydroxides are insoluble. So, in this case also we can remove copper as copper hydroxide. Copper hydroxide is insoluble. So, if we increase the pH then copper hydroxide will be precipitated and we can remove it. This way, we can treat the water which contains the copper ion. We can use NaOH, KOH for the purpose. But my question is that we can use ammonium hydroxide? We have already learnt that ammonium hydroxide is also base. Can you use any NH_4OH to precipitate copper as copper hydroxide? The answer is no. Why it is no? It is so because ammonia at the same time is a complexing agent. If you use ammonium hydroxide to precipitate copper hydroxide, then this copper hydroxide will not be formed but instead it will form the cuprammonium complex $[Cu(NH_3)_4{}^{2+}]$. Similarly, in case of zinc it will form zinc amine complex $[Zn(NH_3)_4{}^{2+}]$. These two complexes are soluble in water. So, it will not be precipitated. So, this is a very nice example.

In case of hard water, you all know that hard water contains multivalent cations and mostly we see that magnesium or calcium ions or iron ion is there. But if we want to remove this hardness then what we do? We have to remove it by forming some precipitate. So, what is the precipitate that we should form? In case of zinc or copper we have seen that hydroxide you have formed. In this case of hard water, we have to form either at the carbonate as precipitate or hydroxide as the precipitate. Now here we have to see that which one is more insoluble. In case of magnesium removal if we consider magnesium hydroxide and magnesium carbonate then from solubility product values, we can easily see that magnesium hydroxide is more insoluble compared to magnesium carbonate. Solubility product of $Mg(OH)_2$ is $9x10^{-12}$ and that of $MgCO_3$ is $4x10^{-5}$. I will tell you about the solubility product in my next lecture. But from solubility product we can conclude that magnesium carbonate is to some extent soluble but magnesium hydroxide is more insoluble. So, it is always preferred to remove magnesium as magnesium hydroxide. But reverse is true for calcium. If you look into the solubility product values of calcium carbonate ($5x10^{-9}$)

and calcium hydroxide ($8x10^{-6}$), then you see that calcium carbonate is more insoluble compared to calcium hydroxide. Calcium hydroxide is to some extent it is soluble. In case of calcium removal, we have to think about calcium carbonate precipitate and in case of magnesium, we have to think about magnesium hydroxide as the precipitate for the removal of hardness. You know that to remove hardness we use the lime soda treatment. What is lime? Lime is calcium hydroxide and soda is sodium carbonate. So, lime soda treatment means we are supplying both hydroxide as well as carbonate ion to remove the magnesium or calcium ions in the appropriate way. So, for the environmental engineers all these problems come all the time and we have to solve it. So, if we know the equilibrium concept then we can easily solve the problems.

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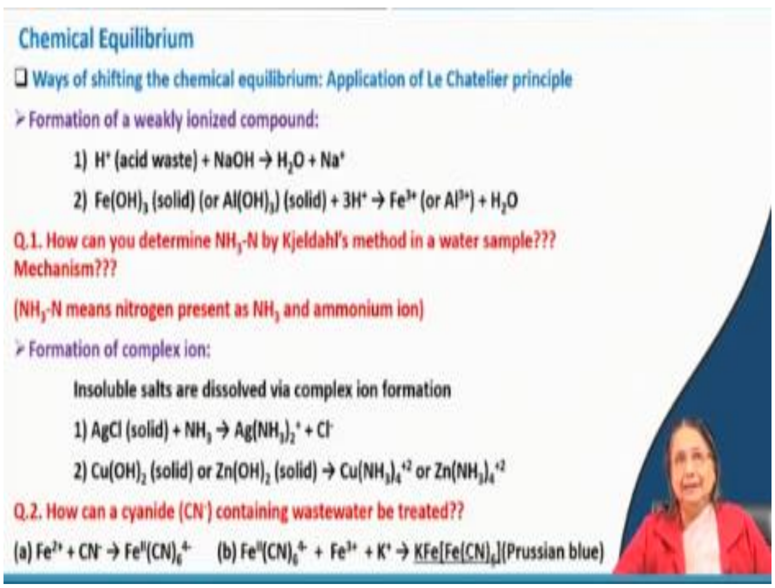

Now another way to shift the equilibrium is the formation of weakly ionized compound.

H^+(acid waste)+NaOH→H_2O+Na^+.........................(8)

Reaction (8) is a very simple example. It is the acid base titration. We know that we take some acid then we apply the alkali to it. It is some type of neutralization reaction. It involves the formation of water and salt. Now this water is very weakly ionizing, we have seen the equilibrium constant (K_w) value is 10^{-14}. It is very low value. Although it ionizes, we know but it is very weakly ionizing. So once the weakly ionizing compound is produced then the reaction goes towards the forward direction because to go to the opposite reaction water has to be strongly ionized. But it is not like that, that is why it goes and for the titration we always know that each should be complete. Otherwise, we cannot use for determining something. There is another example:

$Fe(OH)_3$ (solid) (or $Al(OH)_3$) (solid)+$3H^+ \rightarrow Fe^{3+}$ (or Al^{3+})+H_2O..................(9)

If you take ferric hydroxide (or aluminum hydroxide) it is very insoluble substance. If we add H^+ (say for example HCl) there, it will solubilize. Why it will be solubilize? Because with reaction of acid it forms the soluble ions and when the soluble ions are formed, that means it will go towards the forward direction. Another example is the Kjeldahl’s method of ammonia nitrogen determinations. We know that ammonia nitrogen means the nitrogen present in ammonia or ammonium ion. So, in that case, we make it alkaline and then we steam distillate. Then when we make it alkaline then 100% ammonium ion goes to ammonia and ammonia is highly volatile and it will be it will remove with the steam and then it will be collected and then it will be titrated. So here also it is the same principle is applied. Now, there are some formations of complex

$AgCl(solid)+NH_3 \rightarrow Ag(NH_3)_2^{+}+Cl^{-}$.............................(10)

$Cu(OH)_2$ (solid) or $Zn(OH)_2$ (solid)$\rightarrow Cu(NH_3)_4^{+2}$ or $Zn(NH_3)_4^{+2}$...................(11)

So, it is also by forming the complex salt which is soluble we can make the reaction complete. You can drive the reaction towards the forward direction. Now in case of cyanide some complex formation, for example $Fe(CN)_6^{4-}$ i.e., ferrocyanide, when you do this then this reaction will also go towards the forward direction and by this way, we can remove the cyanide from cyanide containing wastewater. We can remove the cyanide through formation of Prussian blue that is a complex which is precipitated.

$Fe^{II}(CN)_6^{4-}+Fe^{3+}+K^+ \rightarrow \underline{KFe[Fe(CN)_6]}$ (Prussian blue).............(12)

When we put this underline then we know it is a solid substance and it is precipitated.

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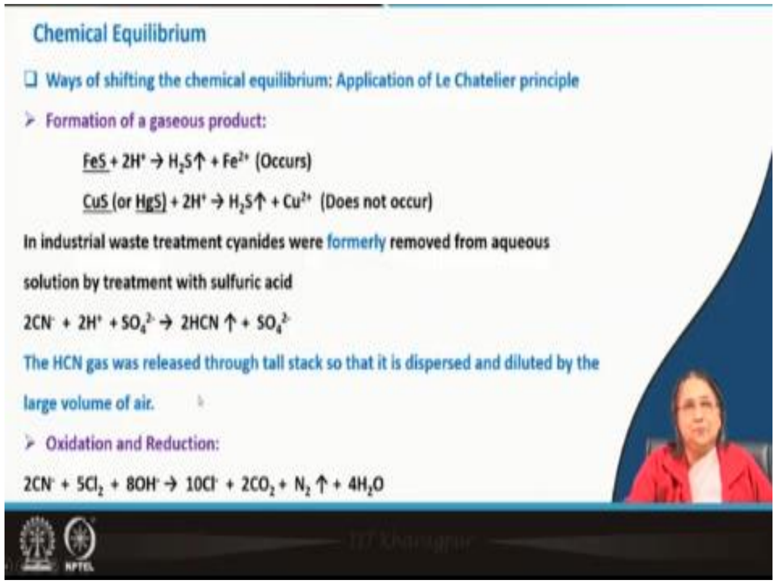

Now another way to shift equilibrium is the formation of gaseous product. Say for example, FeS is a solid. It is reacting with the H^+ to form the H_2S gas which is going out of the equilibrium then the reaction goes to the forward direction.

$FeS+2H^+ \rightarrow H_2S\uparrow+Fe^{2+}$...............(13)

But with copper sulphide and mercury sulphide this reaction does not occur. Why? It is so because it is so much insoluble that even small amount of H_2S is generated to drive the reaction towards the forward direction.

Now another example is that industrial ways to treatment cyanide:

$2CN^-+2H^++SO_4^{2-} \rightarrow 2HCN\uparrow+SO_4^{2-}$...............(14)

This an example of formation of gaseous products, while cyanide is reacting with H_2SO_4 and then HCN gas is produced which is volatile which goes out to drive the reaction towards the forward direction. Another process is that oxidation and reduction:

$2CN^-+5Cl_2+8OH^- \rightarrow 10Cl^-+2CO_2+N_2\uparrow+4H_2O$.................(15)

You know that another process of removing cyanide is reaction with a very strong oxidation agent chlorine. Then it produces the nitrogen gas and carbon dioxide gas. Both are volatile. Both goes out and then the reaction is driven towards the forward direction.

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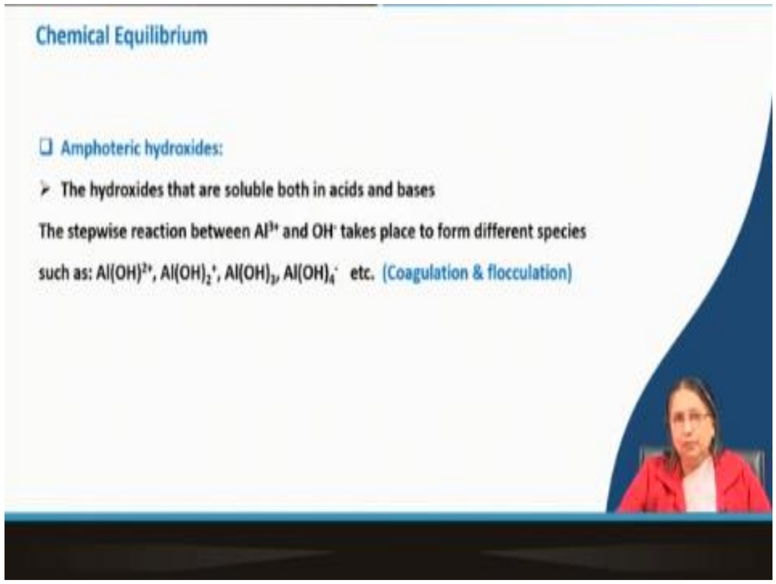

This way, we can drive the reaction towards the completion and these are very important. Amphoteric hydroxide like aluminum hydroxide or iron hydroxide which depending on pH they can form different complexes aqua complexes or hydroxide complexes. This has been used in coagulation and flocculation. We use alum and then these are in equilibrium and depending on pH they are present in different concentrations.

This is also applicable for removing the turbidity. So, this is also example of chemical equilibrium.

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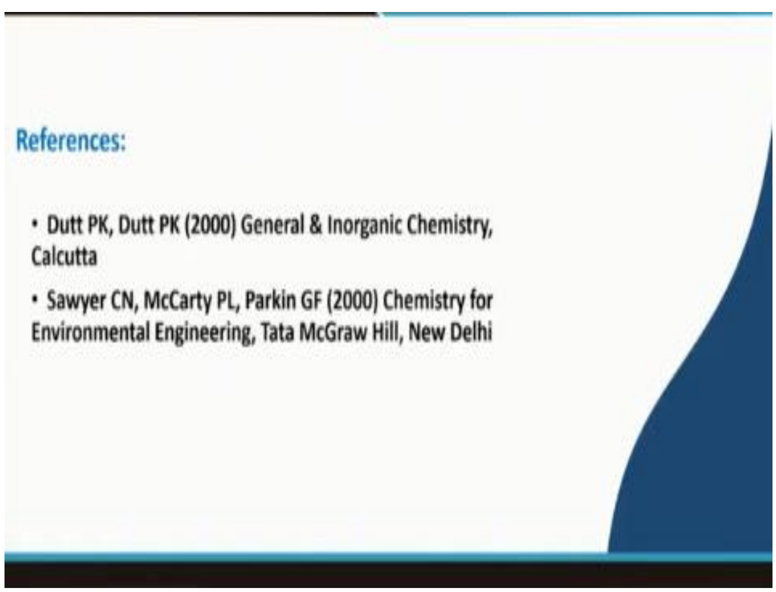

Now, the references are the same: PK Dutt and Sawyer McCarty. You can read to understand these more clearly and also other textbooks you can use to understand this. Thank you very much.