Environmental Chemistry and Microbiology

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Lecture -10

Chemical Equilibrium-V

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 department of Civil Engineering, IIT Kharagpur. We have divided this course into two parts. The first part, Environmental Chemistry will be covered by me and the second part Environmental Microbiology will be taught by Professor Sudha Goel. Now, this is the module two and this is my tenth lecture on chemical equilibrium.

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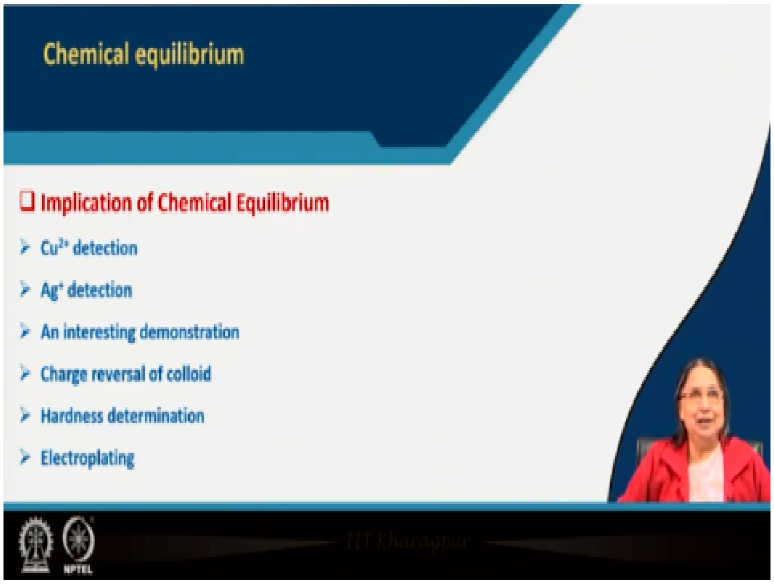

Chemical equilibrium

☐ Implication of Chemical Equilibrium
- Cu^{2+} detection
- Ag^{+} detection
- An interesting demonstration
- Charge reversal of colloid
- Hardness determination
- Electroplating

The topics here I have covered are different problems as well as observations that I wanted to combine here and all are on the chemical equilibrium concept. So, I hope you will like it.

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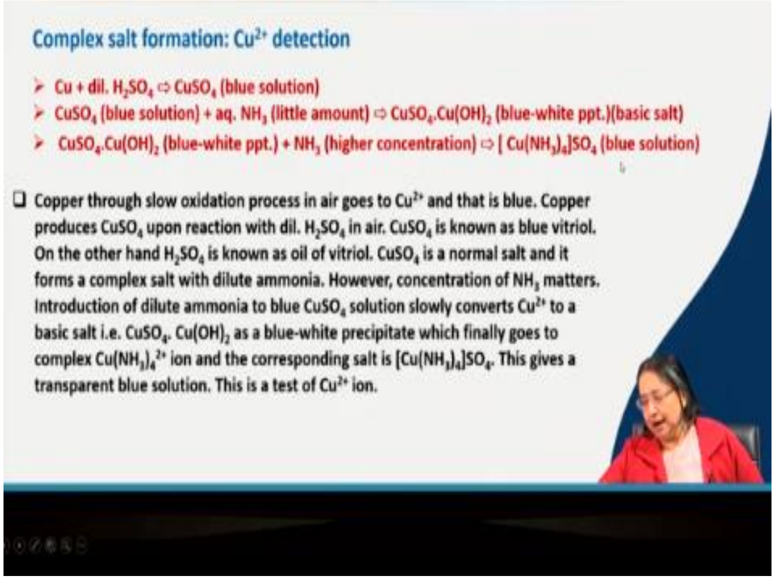

Complex salt formation: Cu^{2+} detection

- Cu + dil. $H_2SO_4 \Rightarrow CuSO_4$ (blue solution)
- $CuSO_4$ (blue solution) + aq. NH_3 (little amount) $\Rightarrow CuSO_4.Cu(OH)_2$ (blue-white ppt.)(basic salt)
- $CuSO_4.Cu(OH)_2$ (blue-white ppt.) + NH_3 (higher concentration) $\Rightarrow [Cu(NH_3)_4]SO_4$ (blue solution)

☐ Copper through slow oxidation process in air goes to Cu^{2+} and that is blue. Copper produces $CuSO_4$ upon reaction with dil. H_2SO_4 in air. $CuSO_4$ is known as blue vitriol. On the other hand H_2SO_4 is known as oil of vitriol. $CuSO_4$ is a normal salt and it forms a complex salt with dilute ammonia. However, concentration of NH_3 matters. Introduction of dilute ammonia to blue $CuSO_4$ solution slowly converts Cu^{2+} to a basic salt i.e. $CuSO_4$. $Cu(OH)_2$ as a blue-white precipitate which finally goes to complex $Cu(NH_3)_4{}^{2+}$ ion and the corresponding salt is $[Cu(NH_3)_4]SO_4$. This gives a transparent blue solution. This is a test of Cu^{2+} ion.

The first one is the copper detection. You know that almost all metals are white in color. But the copper you see is brownish in color and gold you see is yellow in color. Now when you keep copper in air then it slowly goes to Cu^{2+}. You see some blackish tint on the surface of the copper metal. That is nothing but copper oxide. We all know that Cu^{2+} is blue in color. Now, copper produces copper sulphate upon reaction with dilute H_2SO_4 in air. This is slow conversion. So, if you put copper in dilute H_2SO_4 then under air, it will slowly produce the copper sulphate solution which is blue in color and which is known as blue vitriol. On the other hand, we call the sulphuric acid as the oil of vitriol.

Now we know that from the acid base chapter I told you that copper sulphate is a normal salt. It is neither an acid salt nor a basic salt. It is a normal salt and it forms a complex salt with dilute ammonia. So, if you take some copper ion (say, copper sulphate) and then you put the ammonia solution there then different reaction occurs depending on the concentration of ammonia. What is happening?

If you take in a test tube some copper sulphate solution and then if you add low amount or low concentration of ammonia solution there then what will happen? Then it will form a basic salt. This is nothing but copper sulphate copper hydroxide ($CuSO_4.Cu(OH)_2$) and it is a blue white precipitate.

Now if you increase the concentration of ammonia then what will happen? Finally, this precipitate goes to solution. But how will it occur? It will go into the solution due to the formation of copper amine complex ion $[Cu(NH_3)_4{}^{2+}]$ and the corresponding salt is $[Cu(NH_3)_4]SO_4$. This gives a transparent blue solution and this is the test of Cu^{2+} ion.

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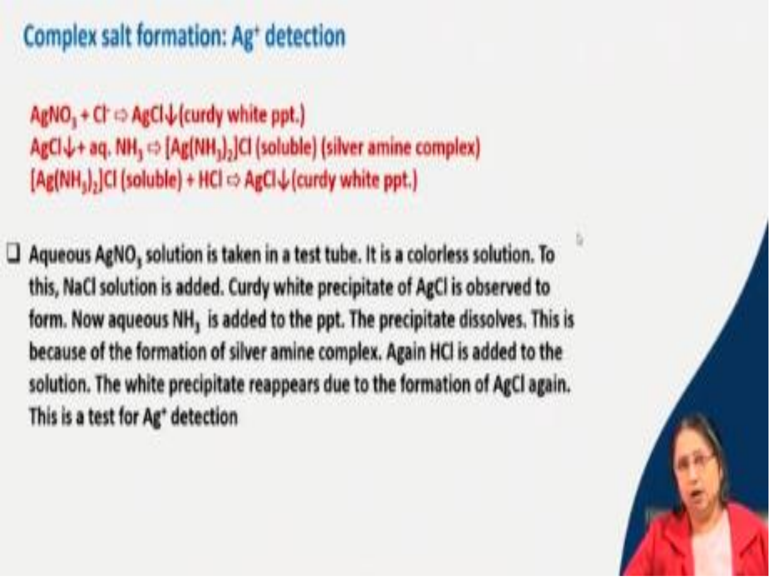

Complex salt formation: Ag^+ detection

$AgNO_3 + Cl^- \Rightarrow AgCl\downarrow$ (curdy white ppt.)

$AgCl\downarrow + aq.\ NH_3 \Rightarrow [Ag(NH_3)_2]Cl$ (soluble) (silver amine complex)

$[Ag(NH_3)_2]Cl$ (soluble) + $HCl \Rightarrow AgCl\downarrow$ (curdy white ppt.)

☐ Aqueous $AgNO_3$ solution is taken in a test tube. It is a colorless solution. To this, NaCl solution is added. Curdy white precipitate of AgCl is observed to form. Now aqueous NH_3 is added to the ppt. The precipitate dissolves. This is because of the formation of silver amine complex. Again HCl is added to the solution. The white precipitate reappears due to the formation of AgCl again. This is a test for Ag^+ detection

Now similar thing can happen for silver also and it is also a silver ion detection. What is happening? You take silver nitrate solution in a test tube. It is colorless. Now to this initial solution if you add NaCl solution then what will happen? As NaCl is a source of chloride so chloride will react with silver nitrate to form a white precipitate of AgCl. It is called curdy white because it is like a curd that we eat. Now if aqueous ammonia is added to the precipitate, then what will happen? Then the precipitate will dissolve. Why it will dissolve? It will dissolve because it will form some amine complex (silver amine complex that I already showed you). Now what will happen if you add again HCl what will happen? The white precipitate reappears due to the formation of silver chloride again. This I have already explained but you can do the experiment in the laboratory. As all chemicals that are used here is available in the laboratory so you can do it easily in that laboratory.

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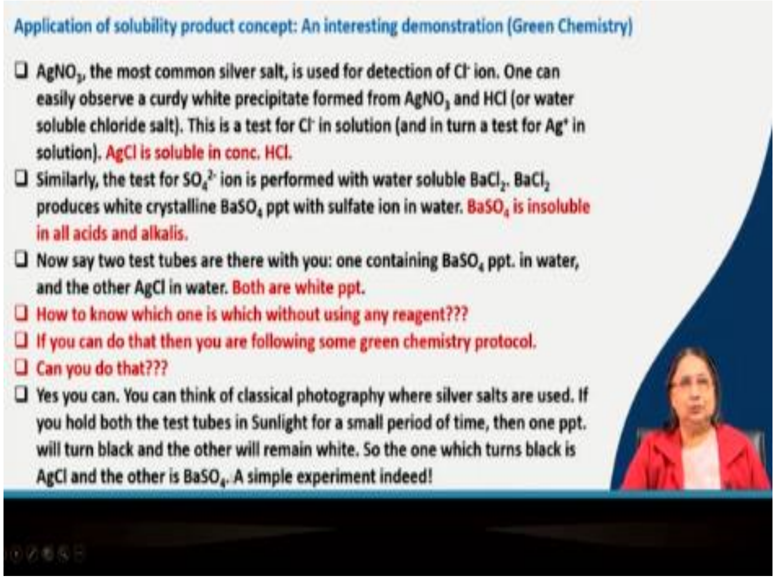

Application of solubility product concept: An interesting demonstration (Green Chemistry)

- ☐ $AgNO_3$, the most common silver salt, is used for detection of Cl^- ion. One can easily observe a curdy white precipitate formed from $AgNO_3$ and HCl (or water soluble chloride salt). This is a test for Cl^- in solution (and in turn a test for Ag^+ in solution). AgCl is soluble in conc. HCl.
- ☐ Similarly, the test for SO_4^{2-} ion is performed with water soluble $BaCl_2$. $BaCl_2$ produces white crystalline $BaSO_4$ ppt with sulfate ion in water. $BaSO_4$ is insoluble in all acids and alkalis.
- ☐ Now say two test tubes are there with you: one containing $BaSO_4$ ppt. in water, and the other AgCl in water. Both are white ppt.
- ☐ How to know which one is which without using any reagent???
- ☐ If you can do that then you are following some green chemistry protocol.
- ☐ Can you do that???
- ☐ Yes you can. You can think of classical photography where silver salts are used. If you hold both the test tubes in Sunlight for a small period of time, then one ppt. will turn black and the other will remain white. So the one which turns black is AgCl and the other is $BaSO_4$. A simple experiment indeed!

Now, let us see very interesting demonstration of green chemistry. I will ask you some questions here. So, please follow carefully. Say for example, silver nitrate which you know, that it is a very most common silver salt and it is used for chloride ion detection. Then one can easily observe a curdy white precipitate formed when silver nitrate and HCl react that I have already told you and this is a test for chloride ion and we also use this reaction in the chloride ion determination.

Now the property of silver chloride is that it is soluble in concentrated HCl. Now we do another experiment. Take a test tube. This is a test for sulphate. The test for sulphate ion is performed with the water-soluble barium chloride. We all know barium chloride produces white crystalline barium sulphate precipitate with sulphate ion in water. Barium sulphate is insoluble in water.

You have already learned from the solubility product in the earlier lectures. But the property is different. Here both silver chloride and barium sulphate are white precipitates. But silver chloride is curdy white precipitate which sticks to the surface of the test tube but barium sulphate is crystalline precipitate which you can see it. Now barium sulphate is insoluble in all acids and alkalis. So, see the difference in the properties. So, if I ask you that how can you say which one is a silver chloride and which one is barium sulphate? Then you can easily tell that in one precipitate if I add HCl it will dissolve and in another it will not dissolve. So, which one dissolves is AgCl and which does not dissolve is barium sulphate. This is a test by adding some chemicals. This is not green. You know that in Green chemistry approach, we have to do it without using some reagent or without using too many things. So, my question is coming now. Now say two test tubes are given: In one case it is having the silver chloride and in another test tube it is having it is having barium sulphate. Both are white precipitate. You are not given any HCl to test. So how you can taste without putting any reagent? This if you can do that then it is a green chemistry approach. Can you do that? Yes, you can.

You can think of classical photography. Now everybody is using the digital camera. So now we are almost forgetting the classical photography where silver salts are used. If you hold both the taste tubes in sunlight then silver chloride will become black and the other will remain white.

It is so because with photon silver chloride form the silver and silver is black and barium sulphate will not react with the photon. So, it will remain the same. It is a very simple experiment to understand and this is a green chemistry protocol or green chemistry approach.

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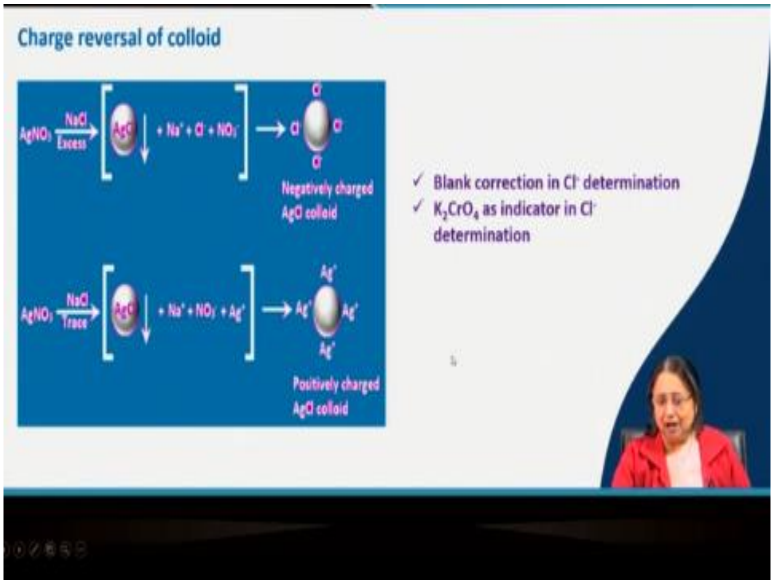

Charge reversal of colloid

- ✓ Blank correction in Cl^- determination
- ✓ K_2CrO_4 as indicator in Cl^- determination

Now I will tell you about another very simple experiment, that we use in chloride determination, where we use the potassium chromate as the indicator for chloride determination. Now the question is, can you reverse the charge of a colloid? We all know that colloids are stable particles. How they become stable? Mostly there are some ions are absorbed onto it.

They may be either positive or negative. But usually, negative ions are adsorbed onto it and they repel each other and they become stabilized. So, I will tell you about two experiments. The first one is a very common test. If you take silver nitrate solution and you add excess NaCl to it, some part of Ag^+ will form the silver chloride as a precipitate and it is a curdy white precipitate. It is so because when you added excess sodium chloride, chloride ion will be will be in excess. And in the solution, there are many ions. What is there? There are some sodium ions that is coming from NaCl, there is the chloride ion which comes from excess some chloride and there will be some nitrate ion which is coming from silver nitrate. Now who will get adsorbed onto the silver chloride. As I said that the colloids are always stabilized by charge, so it has choice different choice. Actually, you see that it will always prefer to have some ion which is a family member. What is that? Silver is there and chlorine is there. So, either silver ion or chloride ion will be deposited (adsorbed) onto it. There is no silver ion because you have taken less amount of silver nitrate compared to sodium chloride. So, all silver ion is precipitated as silver chloride. But you have excess chloride. So, neither NO_3^- will be adsorbed onto it nor Na^+. But chloride ion will be adsorbed because it is a family member of AgCl. So, it will be adsorbed and it will form a negatively charged colloid. Now, just do the reverse thing. You take silver nitrate in a solution and then you add sodium chloride in trace. You add a small amount of sodium chloride. Now here you will get the silver chloride as the precipitate. But here you have added NaCl in trace amount so silver nitrate will be remaining as excess. So, Ag^+ will be in excess. Nitrate will come from $AgNO_3$. You do not have any silver here. You do not have any chlorine ion here because sodium chloride has been added in trace amounts so all chloride will be converted to silver chloride. But you have choice between Ag^+ and Cl^-. So, who will get adsorbed on to it? Here you see that silver is the family members so Ag^+ will get adsorbed onto AgCl. Although it is a positive charge but still it will be adsorbed on to it. So now you get the positively charged colloid, positively charged same silver chloride in both cases. In the first case as chloride is excess so it will be stabilized by chloride ion. In the second case as silver is in excess so it will be stabilized by silver ion. Now once it is obtained then what will happen? If you remember the chloride ion determination then you remember that we used the potassium chromate as the indicator, which is yellow in color. But once positively charged AgCl colloid is formed, Ag^+ so it will immediately attract the chromate ion and then silver chromate will be formed and then you will see the brick red color at the end point. So, this is a very interesting observation, that you can easily perform in the laboratory.

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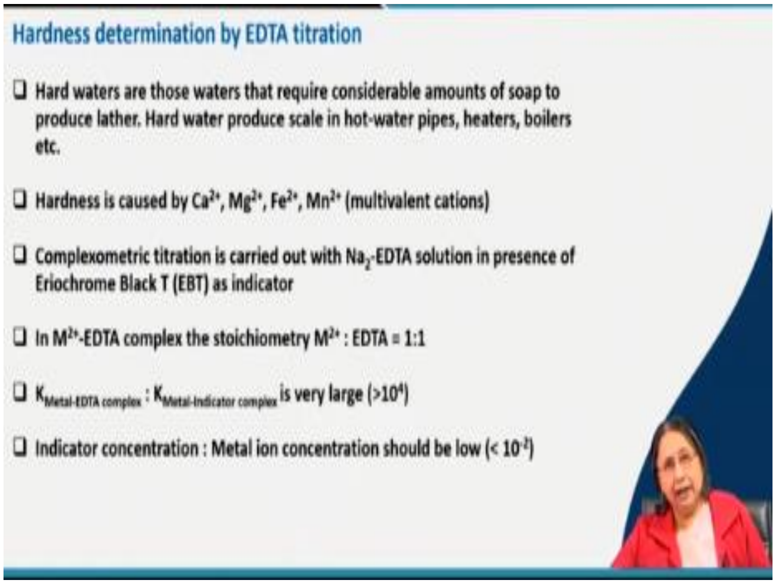

Hardness determination by EDTA titration

☐ Hard waters are those waters that require considerable amounts of soap to produce lather. Hard water produce scale in hot-water pipes, heaters, boilers etc.

☐ Hardness is caused by Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} (multivalent cations)

☐ Complexometric titration is carried out with Na_2-EDTA solution in presence of Eriochrome Black T (EBT) as indicator

☐ In M^{2+}-EDTA complex the stoichiometry M^{2+} : EDTA = 1:1

☐ $K_{Metal\text{-}EDTA\ complex} : K_{Metal\text{-}Indicator\ complex}$ is very large ($>10^4$)

☐ Indicator concentration : Metal ion concentration should be low ($< 10^{-2}$)

Now let us come to the hardness determination. We always do the hardness determination by EDTA (Ethylene diamine tetra acetic acid) titration. We all know that hardness is caused by multivalent cations. Although many people think that it is caused by calcium ion or magnesium ion but actually it can be caused by other ions also which are multivalent like iron, or maybe manganese or even may be strontium (Sr^{2+}), barium (Ba^{2+}) etc. But usually strontium, barium do not occur in nature. But iron, manganese usually occurs in nature. In many cases we see that Mn^{2+} is present in the ground water. Same is true for iron. In many places you see that groundwater contains iron in huge quantities. Now the hard waters are those waters that require a considerable amount of soap to produce lather and hard water produce scales. Why? It is so because in hot water pipes, heaters, boilers because of the formation of calcium salt deposited. Now when we determine the hardness, we determine the calcium, magnesium ions and we use the indicator which is called Eriochrome Black T(EBT) and we do the titration by disodium salt of EDTA. Many people say that we do the titration with EDTA, but it is not true. It is so because as EDTA is not soluble, it is a weak acid. We now all know that weak acids are weak electrolytes. So, they do not get solubilized in water that is why we use disodium salt or tetra salt of EDTA. Now what is happening? We take the hard water in a conical flask then we add a few drops of EBT and then EBT color is blue. Actual original color of EBT is blue, but because there is some calcium, magnesium ions present in the water the color of the complex is rose red. We maintain the pH in alkaline rains by ammonium hydroxide ammonium chloride buffer. After that, we start our titration by EDTA. We start with EDTA. Now what will happen? EDTA is a very good complexing agent. So, it complexes with free calcium magnesium ions present in the conical flask that is sample water. Now slowly EDTA concentration is increased. All the calcium, magnesium ions get complexed with the EDTA by then while reaching the end point. All the calcium magnesium ions will be consumed by EDTA to complex formation. Now what will happen? Now two, three drops of extra EDTA will attack the complex formed between Eriochrome Black T and the calcium magnesium ions. Then the calcium, magnesium ions will be captured by the EDTA and then the Eriochrome Black T will remain free. Then you will get back the blue colour. Now the question is that why EDTA finally is breaking this complex (EBT calcium, magnesium ion complex)? Here another thing is very important to mention that in the in this metal and EDTA complex, the stoichiometry is 1 is to 1. It is breaking this complex because metal EDTA complex is much more stable. So, who is more stable that will be persist. And if you compare the value of equilibrium constant (K) you will see that K value for metal EDTA complex is to K metal indicator complex is very large. It is more than 10,000. That means it is very stable. So EDTA will break this complex.

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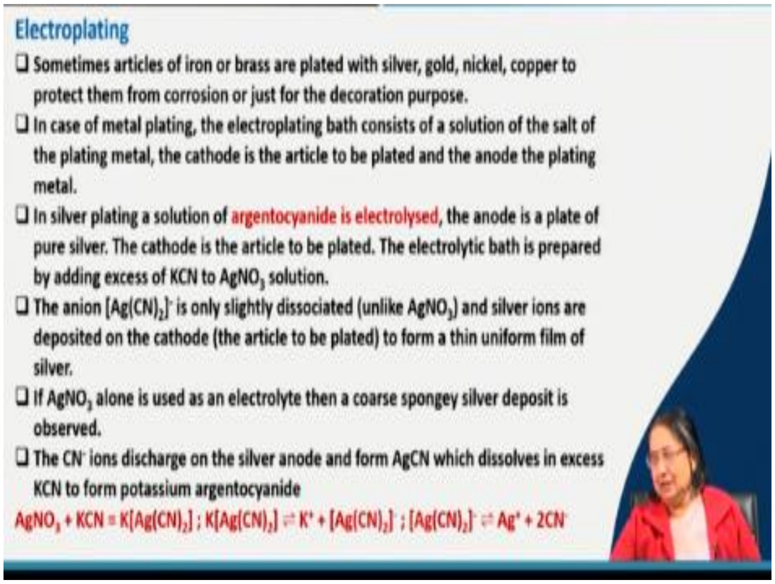

Electroplating

☐ Sometimes articles of iron or brass are plated with silver, gold, nickel, copper to protect them from corrosion or just for the decoration purpose.

☐ In case of metal plating, the electroplating bath consists of a solution of the salt of the plating metal, the cathode is the article to be plated and the anode the plating metal.

☐ In silver plating a solution of argentocyanide is electrolysed, the anode is a plate of pure silver. The cathode is the article to be plated. The electrolytic bath is prepared by adding excess of KCN to $AgNO_3$ solution.

☐ The anion $[Ag(CN)_2]^-$ is only slightly dissociated (unlike $AgNO_3$) and silver ions are deposited on the cathode (the article to be plated) to form a thin uniform film of silver.

☐ If $AgNO_3$ alone is used as an electrolyte then a coarse spongey silver deposit is observed.

☐ The CN^- ions discharge on the silver anode and form AgCN which dissolves in excess KCN to form potassium argentocyanide

$AgNO_3 + KCN = K[Ag(CN)_2]$; $K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^-$; $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$

Now, electroplating is another example where following equilibrium is used.:

$AgNO_3$+KCN=$K[Ag(CN)_2]$………………(1)

$K[Ag(CN)_2] \leftrightharpoons K^+ + [Ag(CN)_2]^-$……………(2)

$[Ag(CN)_2]^- \leftrightharpoons Ag^+ + 2CN^-$…………………..(3)

I will tell you later but this type of equilibrium is used for electroplating of some metal utensils or metal like silver or gold or copper or nickel. So why do we do that the plating? It is so because to protect the metal (maybe iron or brass) or we want to make it beautiful by gold plating or silver plating so we use this.

Now the important part I will tell you that in case a metal plating the electroplating bath consists of a solution of the salt of the plating metal by which you will plate. Say, for example silver or gold. So, the salt is there in the metal electroplating bath. And we use a cathode. What is a cathode? It is the article to be plated on which you want to plate the silver or gold. On the other hand, the anode is the plating metal that you want to make it with. In the silver-plating solution, argentocyanide (argento means silver) is electrolysed. It is not silver nitrate but it is argentocyanide. Potassium argentocyanide is often used. The anode is a plate of pure silver. As you want to do silver plating and cathode is the article to be plated, the electrolytic bath is prepared by adding excess KCN to AgNO3 solution. So, when you add excess KCN to $AgNO_3$ it will definitely form argentocyanide. Now so in your electroplating bath you have argentocyanide which will be electrolysed as the cathode and you are using something which you want to electroplate and in the anode you will use the silver. Now if silver nitrate alone is used what will happen? That is the main topic here. The anion $AgCN_2^-$ is a complex. You can see it is a cyano complex of silver. It is only slightly dissociated. It is not completely dissociated like silver nitrate. Silver nitrate is a strong electrolyte. It will 100% dissociate. But $AgCN_2^-$ is slightly dissociated. And once it is slightly dissociated so it will be deposited on the electrode to form a very thin uniform film. So, it will go on in a very slow process and then it will form a very thin uniform film of silver. If you use silver nitrate as the electrolyte then you will get a coarse spongy silver. It is so because silver nitrate is a strong electrolyte and the electrolysis will go on fast and you will get a spongy silver deposit. This is the beauty of this electroplating with silver. The cyanide ion discharges on the silver. Then what will happen? In the anode the cyanide ion will be discharged to form silver cyanide. This silver cyanide will again dissolve in the KCN that you have taken in the bath to form potassium argentocyanide. The reaction is shown ((1)-(3)).

Silver nitrate and excess KCN which will form the complex $K[Ag(CN)_2]$. After that this complex will ionise to form K^+ and $[Ag(CN)_2]^-$. Then cyano complex of silver will again ionise in a slow manner to produce Ag^+ which will be deposited in the cathode to make the silver plating. But if you use silver nitrate then this type of thin film will not be produced instead you will get a spongy silver deposit which is not wanted. So, this is a very good example of the complex formation. The same you can do with gold also to make some gold plating or something. This is a very nice example.

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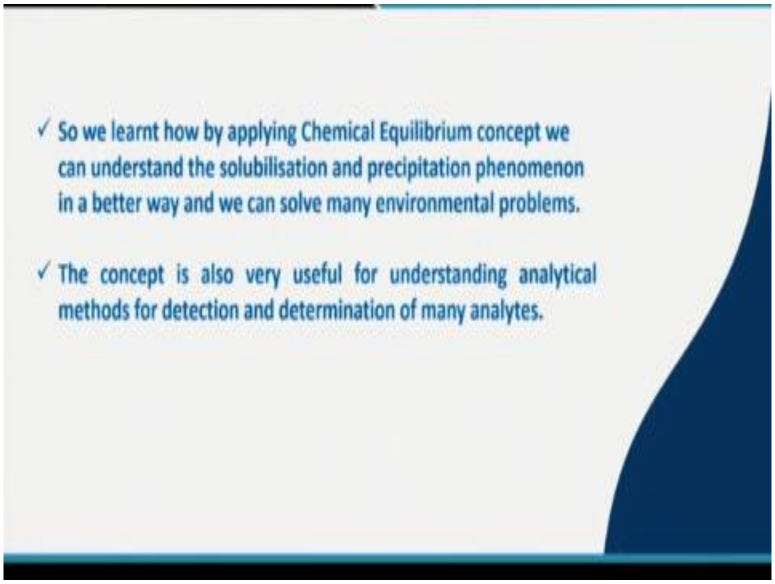

- ✓ So we learnt how by applying Chemical Equilibrium concept we can understand the solubilisation and precipitation phenomenon in a better way and we can solve many environmental problems.
- ✓ The concept is also very useful for understanding analytical methods for detection and determination of many analytes.

So, from the chemical equilibrium chapter, we have learned many things. So, we learn how to apply chemical equilibrium concept to understand the solubilisation and precipitation phenomena in a better way and we can solve many environmental problems. The concept is also very useful to understand the analytical methods for detection and determination of many analytes.

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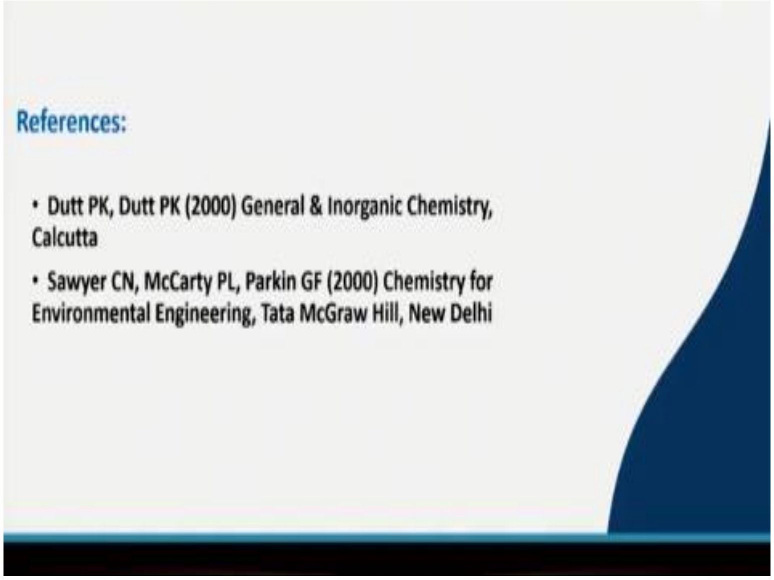

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- Sawyer CN, McCarty PL, Parkin GF (2000) Chemistry for Environmental Engineering, Tata McGraw Hill, New Delhi

And we must know how to form the equilibrium expressions and what is the impact. You can learn from different books. But I have taken many examples from two books mentioned in the last slide. You can read these two books to get even better idea. Thank you.