Course on Analytical Chemistry
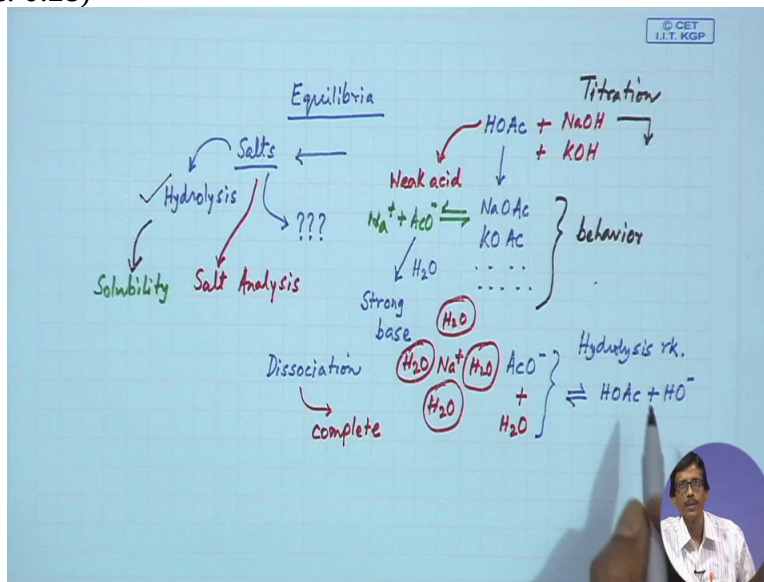**Professor Debashis Ray**
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Indian Institute of Technology Kharagpur
Module No 03
Lecture 15: Chemical Equilibria (Contd.)

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Good evening everybody, welcome to this class again and where we are talking about the typical equilibria process. And today we will just complete this part talking in terms of the fate of different salts. Okay? Because these salts are very important in terms of their formation as well as the reactions because as we are discussing that how these salts forming from typical reaction of acid and base, so a typical equilibrium is involved over there for a particular salt formation.

And there are different types of salts as we were saying that if we have symbol acetic acid CH3C00H and we know that it can give rise to salts like NAOAC as we all know is sodium acetate, then potassium acetate and other also such as save rubidium acetate, caesium acetate, all are possible to form from acetic acid. And these salts, today we will be talking about their behaviour in terms of hydrolysis.

That means whatever we are thinking now that we should also be able to understand the nature of this particular salt because we all know that when we talk in terms of the corresponding qualitative inorganic analysis, we are basically analysing the salts and that we also consider as

the salt analysis okay? So that is a typical different aspects but now if this particular salt is involved in a particular nucitalation process because we know that this sodium acetate formation and potassium acetate formation can take place from its reaction of acetic acid with that of sodium hydroxide and potassium hydroxide.

So at the same time we are talking, or we are thinking or we are discussing soma any aspects that when this salt is forming and when a particular salt we are getting from say weak acid, this is we all know that acetic acid is a weak acid. So when this particular salt or these salts, a family of these salts are forming, we will be interested to know about their behaviour and one such behaviour is your corresponding hydrolysis reaction.

Okay. So when these 2, that means we all know that the acid is reacting with base giving rise to salt plus water and this also we know that this is a typical neutralisation reaction and we can follow or we can monitor, or we can analyse this reaction for a typical neutralisation of unknown strength of acetic acid or unknown strength of sodium have outside.

That means, the titration, we will be talking today also again, the titration reaction, how this titration reaction will be useful to understand this particular neutralisation reaction, acid-based neutralisation reaction because this sort of neutralisation as they all know that the technique and tools, during our discussion of technique and tools what we have seen earlier that how burette and pipette and Alden Meyer flask are utilised for the formation of your corresponding salt and water molecule.

So now if we consider that these are the corresponding acids, so some of these acids are giving rise to a different type of salts, so this nature of this salt also whether this particular salt can undergo hydrolysis reaction or another aspect we will be talking also related to that of their solubility. Why we are talking about this particular solubility? Because we all know that this is a salt of weak acid, strong-based. This will be hydrolysed almost completely and as we all know that this can give rise to NA plus and ACO minus.
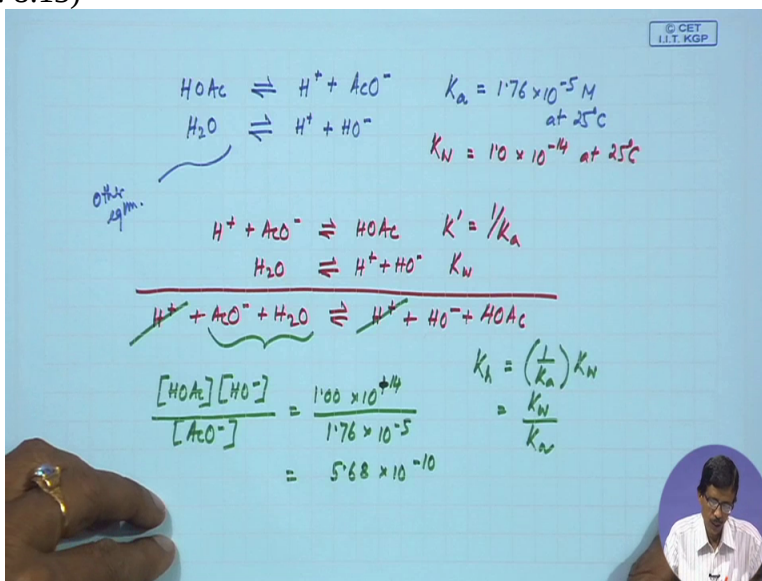
So how far this particular hydrolysis reaction is going, that we can understand. So this equilibrium process where we can consider this acetate ion, this acetate ion is therefore a strong base. So this nature is known to us and we all know that whenever you have a weak acid, its

corresponding conjugate base would be a strong base. So if we take this, any of them, that means sodium acetate, potassium acetate or others, that means the caesium acetate or the rubidium acetate and we dissolve it in water, what will happen and the fate of that corresponding dissociation because now we are thinking about the dissociation.

So dissociation will take place and we have a almost completely dissociated acetate ion in the medium and if it is sodium or if it is potassium, it will be surrounded by so many water molecules around it, so many water molecules will be surrounding this sodium ion. And it will be basically isolated from this acetate ion. So it will be completely dissociated. So dissociation will be complete. So this complete dissociation can give rise to this hydrated sodium ion, all the water molecules will be within its hydration spheres.

As we all know the charge by radius ratio rule that how many water molecules can surround this sodium ion in the solution but we were talking something related to the hydrolysis of this acetate ion. So what is that particular hydrolysis reaction? So this acetate ion, so many water molecules are surrounding sodium ion, in the same way you can have also the surrounded water molecules around this acetate ion and whether the available water molecule is there such that it can go for some reaction where it can be within again a chemical equilibrium forming our acetic acid back and the corresponding amount of hydroxide ion. So this particular reaction is therefore can be termed as the hydrolysis reaction.

(Refer Slide Time: 8:13)

Why we study this particular hydrolysis reaction, that we will see because this can give rise to some important idea to us that whether we can utilise this particular reaction thinking of a corresponding dissociation as we all know that the acid dissociation for the 1st tab giving rise to H plus and acetate ion and we all know it is corresponding KA so KA is 1 dollar 76 into 10 to the power minus 5 molar at 25 degrees centigrade. Then we have to consider this water molecule and its corresponding dissociation.

So this dissociation of water molecule is therefore come into play for this particular reaction where it can give rise to again H plus and HO minus. So just now what reaction or the equilibrium we are talking about that this acetate ion will bind this H plus okay? So this is their when this is the source from sodium acetate or potassium acetate, so available acetate ion will bind this H plus from the water molecule giving some equivalent amount of hydroxide ion.

So what should be the corresponding PH if we consider or if we think of the other equilibrium? So this is the 2nd equilibrium. So other equilibrium we have to consider over there. So what is therefore happening? That Hplus plus acetate ion, so if we rearrange and this dissociation we all know that this constant is known as KW and its value is 1 into 10 to the power minus 14 at the gain 25 degrees centigrade. So how this KW can control the corresponding hydrolysis reaction for this KA values?

So how we get this particular hydrolysis reaction because for the hydrolysis reaction, we can have a constant which can be considered that for its reaction with water molecule giving rise to the equivalent amount of hydroxide ions. So if we rearrange this thing like H plus and acetate ion from left to right giving rise to the undissociated acetic acid and it will be 1 upon this 1 upon KA, the K prime will be 1 by KA because we have rearranged in a different way.

And then we add up this water like this what is the, we have written over there because we are thinking or we are talking in terms of the corresponding reaction between this acetate ion and the water molecule. So this we all know that H plus and HO minus and you have the KW value. So if we add up this together, so we will have Hplus plus acetate ion plus H2O giving rise to Hplus plus HOminus plus HOAC, acetic acid.

So for this particular hydrolysis reaction, what we are talking about, we have to show this. So this will go, this will go. So we will end up with the corresponding reaction of this ACO minus with the H plus giving rise to H0 minus and the acetic acid. And so for this equilibrium, so again we are talking about other equilibrium, so this particular equilibrium which is renowned as the corresponding constant for the hydrolysis reaction.

So it is termed as KH. So this KH for the hydrolysis reaction will be there for 1 upon KA into KW. So it will be KW by KA. So for this particular reaction, so the equilibrium condition will be the concentration of the formed acetic acid, then concentration of generated hydroxide ion what is there, divided by this acetate ion because this water is there as the solvent. So water concentration we do not have to consider. So is giving rise to 1dollar 00 into 10 to the power minus 14, the KW value, like that.

So this is the corresponding KW value of the reverse one. So this is plus, so it is 1 dollar 76 into 10 to the power minus 5. So it will be equal to, this is minus 14, so it is 5 dollar 68 into 10 to the power minus 10.

(Refer Slide Time: 13:34)

A **sparingly soluble salt** is completely dissociated --- means that the very small amount that does go into solution dissociates completely

When an excess of barium iodate is equilibrated with water

$$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2IO_3^-(aq)$$
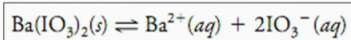
$$K = \frac{[Ba^{2+}][IO_3^-]^2}{[Ba(IO_3)_2(s)]}$$

So this way we can also consider and we can use all these expressions to find out several other things, that means what should be the PH if we think or if we consider the corresponding PH value for this reactions, what should be the corresponding PH value of say 0 dollar 1 molar solution of ACOK, the potassium acetate in water at 25 degrees centigrade. So if we think of the 3rd should be the PH because this is a salt and which is getting hydrolysed so this PH can be known if we can have some idea about the corresponding hydroxide ion concentration.

So this hydroxide ion concentration, that means if we have the total hydroxide ion concentration which will be equivalent to that of your hydroxide coming from the acetate ion, from the acetate, and this acetate concentration also will be equivalent to concentration of the used acetate, that means the used salt. So all these things and all these manipulations can basically giving rise to some relationship where the hydroxide ion concentration will be dependent on your KH into concentration of your acetate ion.

So just now we have determined the corresponding KH value. In our previous side that KH value what we are getting for this corresponding acetate ion, so it will be 5 dollar 68 into 10 to the power minus 10 is the KH value of this acetate ion into the corresponding salt what we are considering is the corresponding concentration of the potassium acetate salt. So therefore we can calculate it out. The hydroxide ion concentration will be equivalent to 5 dollar 73 into 10 to the power minus 6 molar.

So these are the things, so these are the different equilibria we can use and we can manipulate for the calculation of the hydrolysis of the acetate ion and the amount of hydroxide ion forming over there. So what we know from here is that not only the corresponding acid and the based iteration, we can have the corresponding this salt, this salt of strong base, salt of weak acid and strong base is basic in nature. That we all know. So it can be titrated with acid.

So the equivalent amount we can is can be found by titrated with some acid. So this salt concentration and all these things because whenever we talk in terms of this corresponding reactions, that means the reaction is taking place, this acetic acid is reacting with some base, acetate ion is forming and within the reaction medium, again we see that there several other chemical equilibria is operating where the corresponding acetate ion is present in the corresponding acetic acid.

So the composition, that means the combination of this acetate ion and acetic acid will give rise to some interesting phenomena that we will see and that we will discuss in terms of the corresponding buffered solutions okay?

So before we go to that, what we see that some of the type of fault which we consider as the sparingly soluble or the difficultly soluble salt, so what is that? So sparingly soluble salt, unlike your sodium acetate or potassium acetate. So what does it mean? Sparingly soluble salt is also completely dissociated. So we should be very much careful while defining this sparingly soluble salt and the corresponding salt what we are getting from the acetic acid as sodium acetate or potassium acetate that here also, that a very small amount that go into solution, the amount that is basically going into the solution is dissociating completely.

That means the whatever solubility you have and that particular amount will be in the dissociated form. So when we have a salt like barium iodate, we all know that the sulphate ion can be detected or can be estimated by reaction with barium ion in the form of barium chloride where barium sulphate is precipitated as insoluble precipitate but that is also not insoluble what we call the precipitate, the amount of precipitate what is forming is dependent upon its nature which we consider here as the sparingly soluble salt.

So when it is equilibriated with water, what happens therefore? That means this is a sparingly soluble salt, the barium iodate like that of our barium sulphate, so the amount which is going into the solution they will completely dissociate that particular part is completely dissociated into bivalent barium ion and 2 of the iodate ion. So barium iodate is giving these 2 ions and we get something, that means this is also a typical equilibrium process like that of your reaction what we get for the salts.

So here also, K for this solubility of any sparingly soluble salt, that we can also consider as the corresponding concentration of barium ion and iodate ion and the corresponding amount which is there as the corresponding solid, sparingly soluble part of the typical salt as the barium iodate.

(Refer Slide Time: 19:47)

The **common ion effect** reduces the solubility of an ionic precipitate when a **soluble compound** containing one of the ions of the precipitate is added to the solution in equilibrium with the precipitate

$$AgOAc(s) \rightleftharpoons Ag^+(aq) + OAc^-(aq)$$

When $AgNO_3$ is added to the test tube, the equilibrium shifts to the left to form more AgOAc

So this number of moles of barium iodate what we are getting is divided by the volume of the solid barium iodate's constant. So by the not volume, this is the weight basically. Since it is solid, since it is a the corresponding weight of the barium iodate is considered is a constant, so no matter how much excess solid is present, so this ratio basically, the dissociated form and the undissociated form, so this ratio will always be constant. So that will again be defined in terms of a corresponding constant.

So that constant again will follow from some amount of equilibrium. So this particular one, so this concentration, these 2 concentrations what we are getting in the solution, so in this solution,

the concentration of the bivalent barium ion and the concentration of the iodate ion, the product of these 2 is basically giving you K multiplied by the corresponding concentration of the solid barium iodate giving rise to a new constant which we consider as the solubility product constant or KSP value.

That we all consider, these 2 things are there that like barium sulphate, like silver chloride, so the amount is there, so silver ion and the chloride ion, so if the product is exceeding this KSP value, so the extra amount which is exceeding this particular value, will be precipitated as solid. So here also, this particular solid. So in a reverse way, if we consider the solubility of that particular salt, that will also come under this particular equilibrium thing.
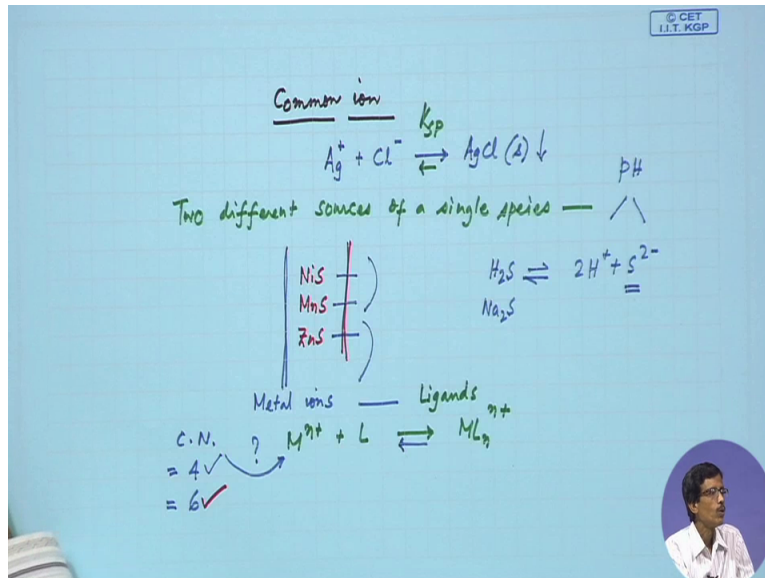
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The **common ion effect** reduces the solubility of an ionic precipitate when a **soluble compound** containing one of the ions of the precipitate is added to the solution in equilibrium with the precipitate

$$AgOAc(s) \rightleftharpoons Ag^+(aq) + OAc^-(aq)$$

When $AgNO_3$ is added to the test tube, the equilibrium shifts to the left to form more AgOAc

So this equilibriation process is again related to something which we will consider now as a corresponding common ion effect. So what is that common ion effect? So the name itself tells us that we are supplying something which is common into the ions what is getting formed or what is forming over there for this particular reaction. So if we all know that we can detect the presence of chloride ion by addition of silver nitrate to any solution containing chloride ion such that we will get the corresponding presentation of silver chloride which is a solid and which is coming out from the solution as precipitated.

So if we consider so in this, not single headed arrow but also we consider that you can have a reversible sign because this will be in equilibrium and you have a corresponding KSP value also for this particular reaction. So again now, how the corresponding addition if we externally add another ion, either chloride or silver ion, what will happen to this equilibrium? So addition of some common ion is not so this is not any other thing, that means you can have a uncommon ion, that means which is not common to these 2 ions which is responsible for this precipitation reaction.

So if we have 2 different sources of single species, so if we can have 2 different sources of a single species and in that particular reaction can take place over there, so you have this and you can have the another equilibrium, so equilibrium of both may shift the concentrations. So this particular equilibrium, so if we increase the concentration of chloride, so we get this particular,

the shifting of the equilibrium from one side to the other, how it can affect the corresponding reaction.

So by definition, this common ion effect we can consider from a typical textbook definition is that it will reduce the solubility of the ionic precipitate. So we are giving the example that the corresponding silver chloride precipitate or the barium sulphate precipitate or barium iodate precipitate, so these are the typical precipitates, when they are coming as the corresponding precipitate when we add one reagent to the analyte, so we get something when a soluble compound containing one of the ions of the precipitated is added to the solution in equilibrium with the precipitate.

So that is the actual act what is happening. So we are talking about something, that means we will be supplying this particular species for the silver chloride, so if we add again the silver nitrate, so that silver nitrate is your soluble compound and it has one common ion, that means the corresponding silver ion of the precipitate is added and solution of the equilibrium of the precipitate will change. So will take another example, instead of silver chloride precipitation, we will take the precipitation of silver acetate.

So like that of your barium iodate, this silver acetate can also be soluble partly by giving you silver ion as well as the acetate ion. So giving of this, giving you of this, that means the silver ion and hesitate ion can also tell us that when we can change this particular concentration because this product of these 2 concentrations, that means the product of these 2 ions, that means the silver ion and the acetate ion, when it exceeds the KSP value, and therefore we can have the corresponding precipitate as a solid silver acetate.

So if we take these 2 in a typical test tube, so this is the thing, you have the saturated solution and we get the corresponding precipitate of silver acetate. Now in the 2nd step, in the 2nd test trip, we are doing something related to supply of common ion. So supply of common ion what is happening? The supply of that particular common ion will be responsible for shifting the precipitate from the right-hand side to the left-hand side, so more and more of this silver acetate can be precipitated due to the presence of that common ion.

So this is a typical analytical aspect of underlying principle when we have to control the corresponding ions in the solution that we all know the precipitation of metal ion sulphides like nickel sulphide, like manganese sulphide, zinc sulphide, et cetera. And for all these in group analysis we all know that for group analysis what we are having these that these are precipitated, that means the sodium sulphide we provided or if we pass H2S for acetic medium of this NA2 plus or MN2 plus or zinc 2 plus, so their corresponding KSP values, so each individual precipitate can have the corresponding KSP value.

And once the KSP value basically exceeds the corresponding concentration of sulphide ion required for the precipitation of nickel sulphide or manganese sulphide, so these will be precipitated out. So by this we can control the corresponding thing, that means we can control the corresponding dissociation of H2S when H2S is supplying to for the precipitation or sometimes NA2S sodium sulphide can be added and this can we all know that twice of H plus plus sulphide 2 minus.

So the acidity control or the acid for this particular reaction, the amount of acid added to this, will also control the available sulphide concentration in the medium. So if we can have 2 groups of these metal ion sulphides for a particular range of KSP for one group of metal ions and another KSP value for another group of metal ions, what we can see that we just control the corresponding sulphide concentration. So if we control the corresponding sulphide concentration, in one case we can precipitate one particular family, in another case, we can control the precipitation of the other sulphides.

So by addition of these acid, extra acid, so that means you can have 2 of these cases by controlling the simple pH. So control of pH basically control the available sulphide ion concentration for the precipitation of these metal ion sulphides. So the same thing is also happening over there when we have the precipitate of silver acetate, we see that this silver acetate is precipitating like that of your addition of silver ion by any form, so this addition of silver ion to some acetate ion giving rise to silver acetate.

Now silver nitrate can be added to this 1st test tube. So a solution of silver nitrate can be added to the 1st test tube and this particular equilibrium, so equilibrium for this corresponding solubilisation or corresponding association what we can see can go to thereafter due to the

addition of silver ion more and more silver ion which is coming out from the silver nitrate. So as silver nitrate is added which is a soluble component because it is soluble in water. So that solution we are simply adding.

So when they add this silver ion in the form of a solution of silver nitrate, what we find that the amount of precipitated, what precipitate? The amount of the precipitate of silver acetate is increasing. So earlier what was happening? That due to the establishment of this equilibrium for this particular reaction, you can have more amount of acetate ion in the medium. That means your solution is having more amount of acetate ion but it is not exceeding the corresponding product of KSP value of silver acetate.

But we have to increase the corresponding concentration of silver ion, so that silver ion is exceeding your KSP value, so the extra amount of that silver acetate what is forming due to the addition of silver ion is precipitated, so from left to right we are getting more and more you see, from the top also more amount of this silver acetate is getting precipitated. So we basically control the amount of precipitation which can take place due to the addition of some common ion to a reaction medium.

So this can also happen nicely for this equilibrium process. Why we are studying all these things? So this can also be useful to see for metal complex formation. So metal ions are there we all know and in the complexation reaction or the coordination compound formation, we know that there are certain ligands. So like, this can be considered I told you previously also that this can be considered as your typical acid and this can be a base.

So this can react, so M is there, MN plus is there and L and this L can be a neutral one, can be charged one, that means it can be anionic one for this reaction with the cationic metal ion for the metal complex formation which is MLN with some charge, again N plus. So this particular reaction, so if it is forming, so like that of our typical other acid-based reaction, so this can also be considered as equilibrium process, so for the formation of this particular species, that means the 1st species, we have to consider the corresponding equilibrium for the attachment of the 1st ligand to this metal ion.

Why we are talking about this 1st ligand because all this complexation reaction, it is not like your typical precipitation reaction like silver chloride or acid-based reaction but the reaction is 1 is to 2 but depending upon the nature of this corresponding thing, that means what should be the corresponding coordination number of this metal ion, so depending on that, the number of L we will be attaching to this particular metal ion centre.

And if the metal ion, that means the coordination number is 4, we can see that one after another, L will go and attach this particular metal ion centre. Similarly you can have a coordination number of 6. So one after another, that means 1, 2, 3, 4, 5, 6 of these L can go and attach these metal ion centre. So 1 when is attaching 1, you have ML1. That means one ligand is attaching. Then you can have the 2nd one, you get the ML2.

So we can have either 4 for a coordination number of 4 or 6 for a coordination number of 6, that means different equilibrium constants we can have. So one such example is the reaction of in the 1st case, that means we have any copper salts such as copper sulphate is dissolved in water and this is a very typical reaction we all follow from your school days you are knowing that thing. The corresponding formation of this hexa aco copper 2 species.

So what is that hexa aco copper 2 species? If you have a solid copper sulphate, we all know the copper sulphate pentahydrate also because in the solid state, the formula we write as the copper sulphate having 5 water of crystallisation. So when that is dissolved in water, this copper centre is surrounded by 6 water molecules and this we cannot stop. When we do any such a reaction, this particular species, so whatever we are at the starting point, that means what is there that the copper ion in water or iron ion in water or nickel ion in water, they will all be aquated species.

So this aquated species anything but the corresponding hexa aco or the tetra aco species of the metal ion. So what we want to follow is the corresponding equilibrium constant for the formation of this particular reaction when we attach the ammonia. So ammonia is your incoming ligand because already you have this water molecule, so you please try to understand over here that when you dissolve it in water, your water molecules are also ligand because a lone pair of electrons on the water molecules are coordinating to this water centre.

Now when we add ammonia, these water molecules will be replaced by this ammonia giving rise to 1 equilibrium condition because we are reacting in 1 is to 1 stoichometry. The stoichometry of this particular reaction can only permit the replacement of one of the water molecule out of those 6 water molecules surrounding this copper centre, that means this water molecule will be taken away from the coordination sphere of this copper centre giving rise to a corresponding penta aco mono amine copper 2 species.

So like typical acid-based reaction, we can have the corresponding K1 value we can write, the equilibrium constant we can write for this particular case, is that of our reaction, that means the right-hand side what we can have a new species which is not the hexa aco but is a Penta aco species, the concentration of the Penta aco species what is forming over there is and the water which is going away divided by the corresponding concentration of the copper hexa aco species and the ammonia concentration.

So in the 2nd step also, if we have, if we put the corresponding ammonia for the 2nd time for this reaction, so it will replace one more water molecule giving rise to the 2nd K2 value. So what we see that whether we will have the corresponding replacement of all 6 water molecules or it can stop at some point, that means after the replacement of the 4, that means your copper species is only stable with the Tetra amine complex form, so we can have only K1, K2, K3 and K4. So that we will see in our next class, okay? Thank you very much.