Coordination Chemistry
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Lecture - 13
Coordination Equilibria – I

Hello everybody. Today we will be just talking about how the different equilibrium processes can control the complex formation.

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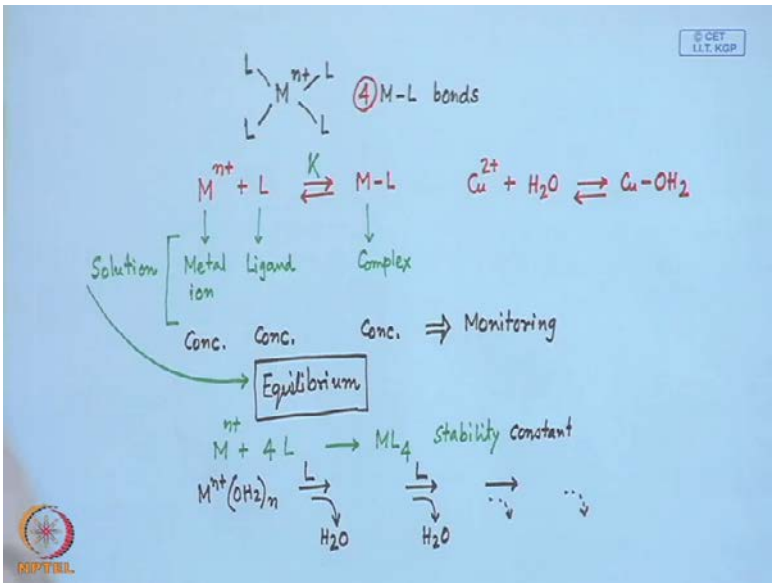

As we have seen that whenever we have a metal ion, and is forming some complex with the ligands, and if we just simply consider that there are four such metal ligand bonds which are present in the final product; that means the final complex. So, this number is very important; that means the four metal ligand bonds are forming and if we just think that M n plus was there which is forming first one metal ligand bond and if this particular process is reversible in nature; that means all these together. That means formation of one coordinate bond, these all the time we are considering it as a coordinate bond such that if we have copper two plus, the bivalent copper ion is present in the solution which is dissolved in water; in that case also we have the copper OH 2 bond and this particular thing is there, and they are in equilibrium.

So, we see that the metal ion, the ligand, and the complex, all these are present in solution. So, if they are in equilibrium and depending on the reaction condition and

depending on the medium, how we know that what percentage of the reaction is going from left to right; that means the corresponding affinity of the metal ion to react with the ligand to keep the corresponding complex species, at least one metal ligand bond is forming over there. So that equilibrium process, how we can monitor; that is the question that we know the corresponding concentration of the metal ion, so the monitoring of the concentrations of the ligand and the concentrations of the complex species.

So, if we can monitor all these species by some mechanism, so monitoring of these concentrations; so we can get some idea that how much metal complex is forming by reacting the metal ion with the ligand to give us the corresponding complex species. So during the complex formation, we can have that all the species starting from the complex the metal ion and the ligand; they are all in equilibrium. So in today's class, we will just consider how the equilibrium processes are taking place and how the different species can contribute for the equilibrium process, because this is a very important thing what we just can monitor in the solution stage.

So in solution, the complex which is giving us some equilibrium process and how we can monitor the corresponding equilibrium process such that we can evaluate some constant related to this particular complex formation; that means the equilibrium constant which can tell us that how quickly the corresponding metal complex will be forming from the individual components. So, that particular equilibrium constant for the forward reaction we can measure and the constant can be monitored for the different stages of the equilibrium.

So, we will be talking in this particular class about the coordination equillibria. So, we have more than one such equilibrium process; if we just consider that there are four ligands and one after another the ligands are coming and bound to the metal centre. So in that particular case, how we can talk about the stability of the corresponding complexes. How much stable the complex is; that means if we get this particular M L 4 species from the individual corresponding aquated or the solvated metal ion and how much of these species are forming immediately when we give the corresponding stoichiometric amount of that L; that means if we use M with 4L whether we get the corresponding ML's 4 species and how much this particular ML 4 species is stable that we can also monitor.

So, the stability of the complex can also be found out by monitoring this corresponding equilibrium process because if we see that this M n plus was there and we can have large number of bound water molecules. So, at different intermediate stages we just remove the water molecule as we react it with 1L; remove the second water molecule as we push the second ligand, similarly the third and the forth. So, these stages basically tell us that how quickly we can achieve the corresponding stable species because the other species like that of where we can have ML 1, ML 2, ML 3, etc, that are not so stable; only the ML 4 species had some stability compared to the intermediate species. So, then we can find out the corresponding stability constant for that particular process.

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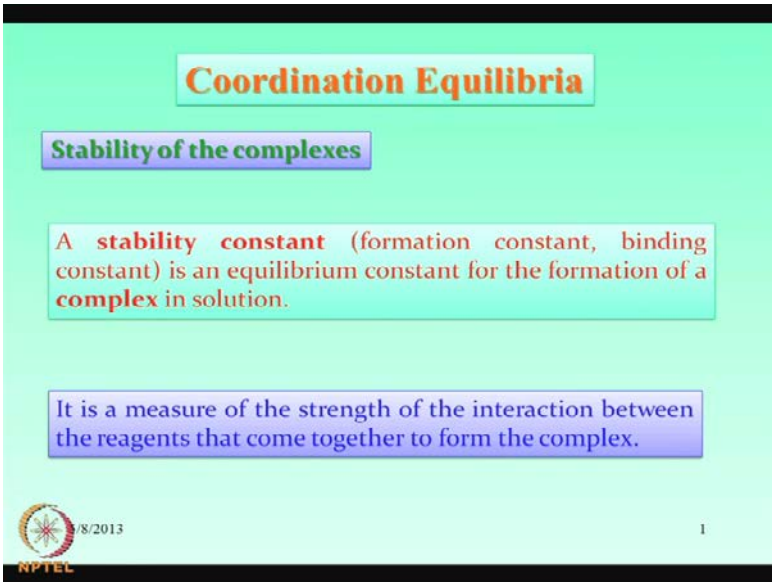

So, how we can find out the corresponding stability constant and determination of that particular stability constant for these complexes and give us some idea about the stability of the complex. So, in that way we can define a stability constant which also we can consider as a formation constant, that how the metal complex is forming in the solution, as well as the binding constant because the metal is binding the different number of ligands to it. So, we can consider it as the binding constant. So, when we are talking about the metal and the ligand system, we will be talking about the corresponding binding of the metal ion with that of the ligand; so it is therefore in equilibrium constant for the formation of the complex in solution.

So, how quickly we get the corresponding complex species in the solution. If it is a four coordinate one, how quickly we can achieve the corresponding four coordinate complex or of it a six coordinate complex, then whether we are able to get the corresponding six coordinate compound from the four coordinate one or some other mechanism can be operating over there such that we get the corresponding octahedral complex. So, situation is little bit different as we have seen that we can go up to a coordination number of sixteen, say. So, if we want to have a corresponding compound where the coordination number of twelve at least can be achieved around the metal centre. So, there will be definitely some twelve stages of formation of one after another metal ligand bonds.

So, we have a pretty complex expression for the corresponding stability constant. So, how we get the corresponding stability constant; it also gives us some idea about the measurement of the strength of interaction between the reagent that come together to form the complex. So, when the reagents are metal and ligand we will be talking about the corresponding formation of the metal complex; it can be some other non-covalent interaction or some supramolecular interactions at the same time. In that particular cases we can have one component is binding to the other, then that case also the species what is forming on the right hand side due to the binding of the two fragments on the left; we call it as a complex species and in all these cases we can have the corresponding constant, which constant is known as the corresponding stability constant or the formation constant for the complex species.

So, it is true for some other physical system where we are not talking about the metal and the ligand, but some other biochemical reactions, some supramolecular interactions, some non-covalent interactions. In that particular case also the same type of expressions are useful to find out the corresponding equilibrium. So, first thing what we can see that we can have the interactions when we have the compounds which is forming from the metal ion and the ligands. So in these cases, we can have two kinds of complexes; when metal and the ligand is forming, it is one complex and the supramolecular complexes such as host-guest complexes and complexes of anions.

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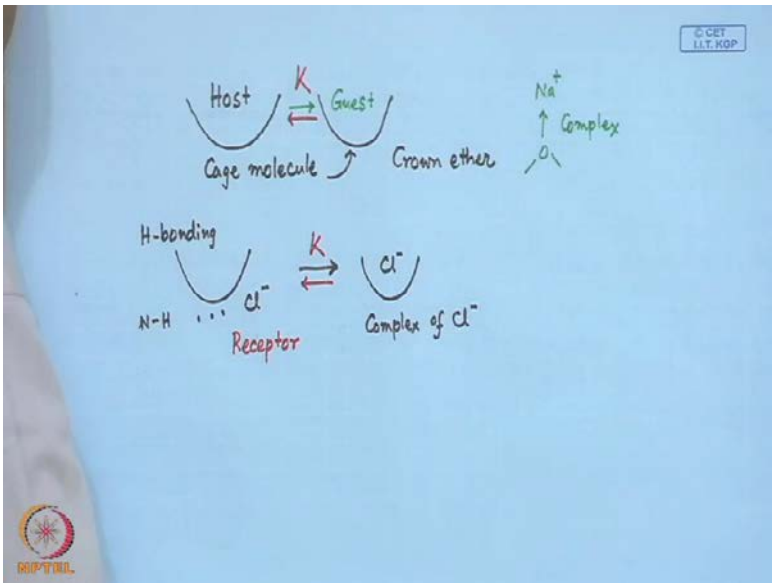

So, when we have no such physical quantity like metal and ligand, but we can have in host such as some big inorganic cage or some organic cage; so some cage molecule or some, say, crown ether. But in case of crown ether, we know that it has some donor groups; oxygen based donor groups which can coordinate to the metal centre like sodium, potassium, lithium, etc. So, in that particular case we can consider it as a complex equillibria. So, complex formation can take place, but within the cage molecule when it is basically trapping. So, if it traps the guest from some hydrogen bonding interaction or some hydrophobic interaction or some Van der Waals interaction. So, we get some interaction where the cage molecule, the same cage molecule can trap the guest.

So, if we have this particular species; that means if we have the guest plus host which are not bound and on the right hand side we have the guest which is bound to the host, then also we have this particular situation that complex is forming. Similarly we can have the anion binding; so some species which can also be there where we can have some hydrogen bonding donors. So, if hydrogen bonding can play some important role for some anion, say Cl minus. So, hydrogen bonding can use for some NH groups. So, these NH groups can interact with this Cl minus to go for the hydrogen bonding interactions and we get the corresponding complex species where this hydrogen bonded form of Cl minus is there. So, it can also be considered as the corresponding complex of Cl minus.

So, in this all these cases there are some equilibrium; how strongly they are bound to the corresponding host or this other anion binding site, because anions are also loosely bound in all bimolecular reactions also, in protein molecules, in DNA, in RNA, and all other cases. In the biological system also, this type of anion binding sites are very important and there we call them as the corresponding receptor sites for binding the corresponding anions. Because in true sense the Cl minus binding to some site where metal ion is not in involved, we cannot consider them as the corresponding formation of the metal complexes. So, in all these cases we can have the corresponding constant for this formation. So, we can measure the corresponding K values for these complex species.

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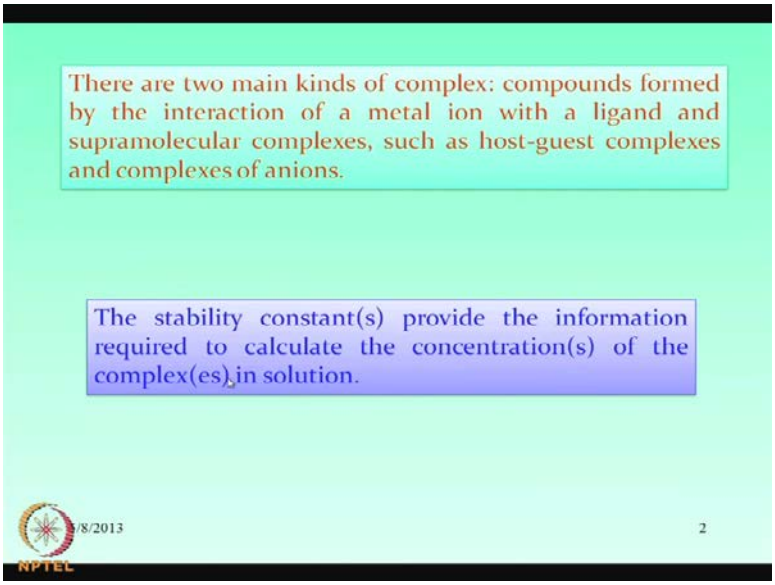

So, host cast complexes and complex anions are therefore very much important in this particular study and the stability constant or constants what we can get from the information's will be required to calculate the corresponding concentrations of the complexes in solution; that means if we know the corresponding concentrations of the reagents, then we can find out the corresponding concentrations of the complex species; that means at equilibrium we have the specific concentrations of the metal ion, the ligand, and the complex species. So, depending on the progress of the reaction towards the complex side, we can find out the percentage conversion of the metal ions to the desired metal complex and we can find out the corresponding equilibrium constant or the formation constant value for the binding of the metal ion to the ligand.

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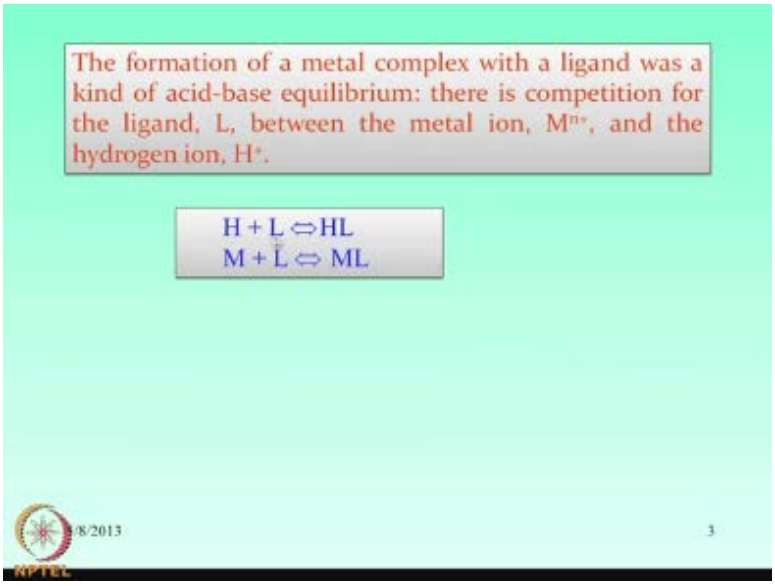

So, in that particular case the formation of a complex with ligand can be considered as a typical acid-base equilibrium and there is a competition for the ligand, L, between the metal ion, M n plus, and the hydrogen ion. Because we know that there are some sites, this is the cationic species; the metal ion is the cation and the hydrogen ion is also the cationic species. So, if the ligand is a lone pair donor or a base or typical anionic species, then the ligand can have some corresponding affinity to bind the metal ion as well as it can have the corresponding affinity for the H plus ion. So, we have these two processes; these two equilibrium processes are simultaneously operative between H plus L and between M plus L and for simplicity we have not added charge on the H and the charge on the M. So, the competition between the formation of H L and M L is important and if the ligand is an anionic one; so it basically gets back the corresponding proton to get the corresponding neutral ligand.

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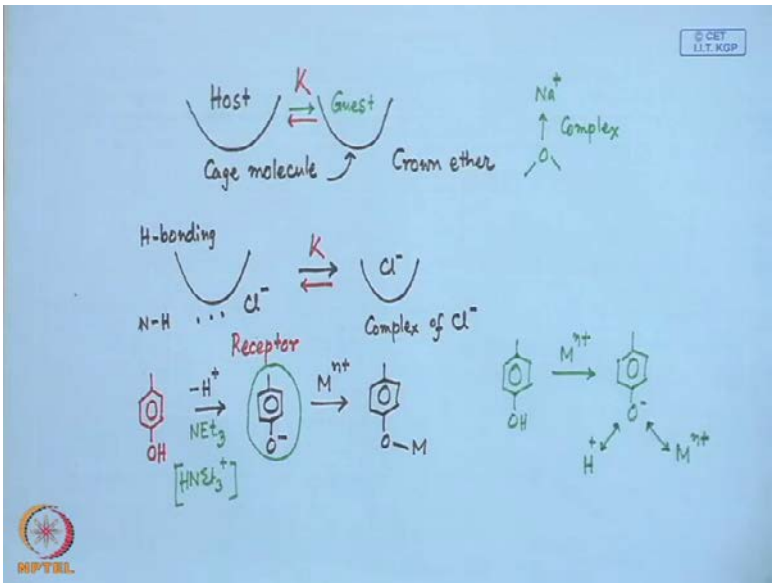

So if we have some site, it is also true for any amino acid or some biochemical reactions; that phenol part is available and this phenol part we can consider as that is the part of the corresponding amino acid and this particular one basically after deprotonation gives us the corresponding anion. So, after removal of H plus it gives us the corresponding anion; then it binds the corresponding metal ion centre in this form. So, this particular species which is there at the central part; that means the corresponding phenoxide ion, this will have the typical tendency; that means the competitive tendency to bind the M n plus or H plus. So, for deprotonation we use some organic base say NEt 3 and NEt 3 can take up the proton forming the corresponding NEt 3 H plus triethylammonium ion. So, this triethylammonium ion will be there and this will be free.

So, there will be no competition for this phenoxide ion to bind with the protons which were originally bound to the system because it has already been taken away by the triethylamine molecule. So, in that particular case only the added metal ion M n plus can bind to the ligand system and is forming one M O bond from the phenol unit. In that particular case only, we cannot have the corresponding competition for the L species for both H and M. But otherwise when we just simply add the ligand with that of the metal ion; that means if we just use the corresponding phenol unit with M n plus without considering and without thinking of the first step; that means the removal of the H plus then we will find that this O minus can have some binding tendency to H plus or to M n

plus. So, there will be two competitive pathways for binding the phenoxide ion to the M n plus and the protein.

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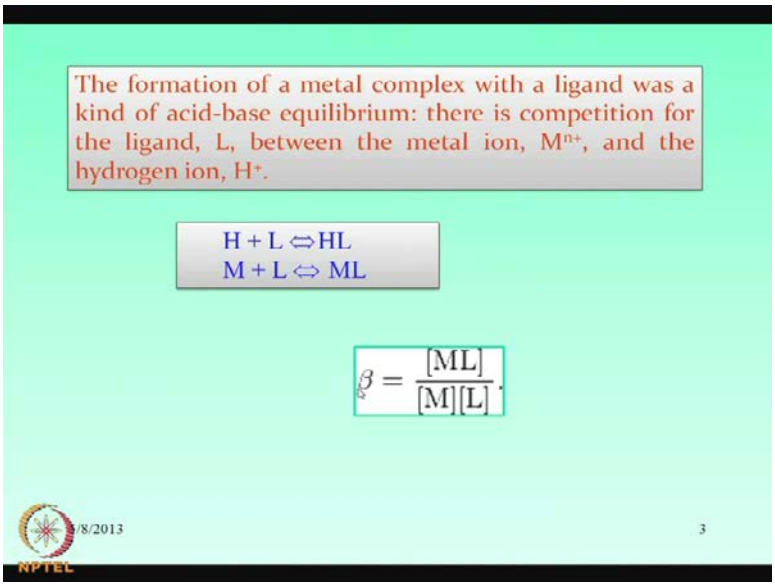

And therefore, we see that this H plus L and M plus L situation is there all the time and for the second case if we can consider that M L is forming out of M and L and if we can measure the corresponding concentrations of the fragment like ML as well as the starting concentration L and M, then at equilibrium what are the corresponding concentrations if we can measure; then we can write down the corresponding equilibrium constant which is nothing but the concentration of the complex formed the ML, the concentration of the ML, the concentration of the M left over at the equilibrium, and the concentration of the ligand at that particular point as equilibrium concentration of the ligand will give us a corresponding constant value as beta.

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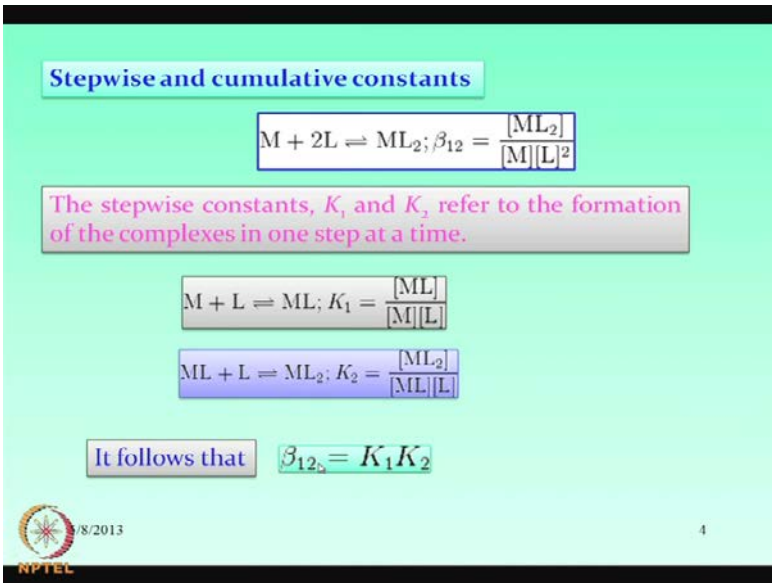

So in that particular case, we will find that both stepwise and cumulative constants are functioning when we can add more than one L to the metal ion; that means we can go from M plus L to M plus 2L. So, M plus 2L can give rise to ML 2 and where we get the beta one step and the beta 12 step; that means both the steps are operating and we have the corresponding cumulative constant which is beta 12 is the concentration of the final species which has been formed from ML, because this can be also written in the form of the ML plus L.

So, ML plus L also give rise to ML 2, but when we are directly getting all the species like M plus n number of L values; n is the coordination number. If it is 12, it can be 12L. So, we just see there that beta 12 will be the final concentration of the final species what we are looking for the corresponding compound and the metal ion remaining in the medium and the concentration of the L what is there at the equilibrium powered by the number of species what we are using. So, the stepwise constant; that means in first step that means addition of 1L which is also true, because this particular complex formation all we know is related to the corresponding binding of ammonia molecules to the silver ion.

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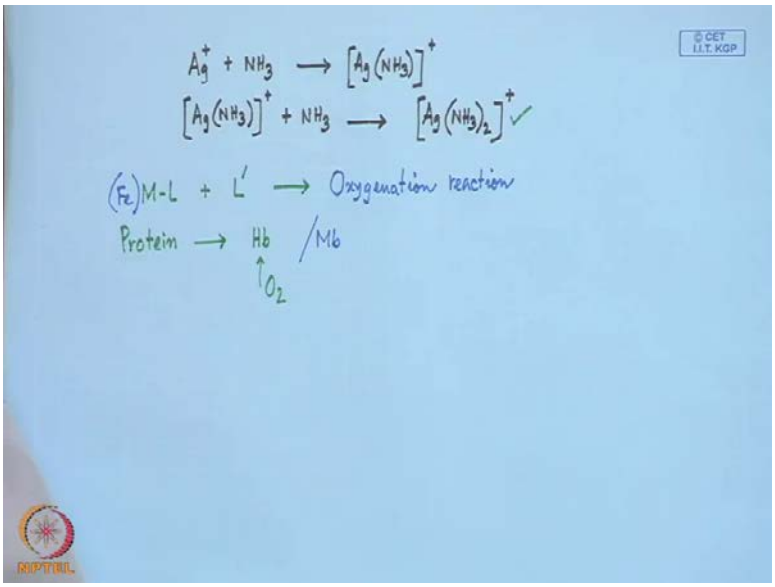

So, how the corresponding reaction what is taking place for silver one reacting with ammonia giving rise to; in the first step the silver amine complex or one amine is present, then in the second step it is reacting with the second ammonia molecule giving rise to Ag NH 3 whole 2 plus molecule. So, we should know about the corresponding concentration what is forming over there and the concentration what is remaining over during the equilibrium process as the corresponding silver ion concentration as well as the ammonia concentration. So in these two steps, we have K 1 and K 2 and we call them as the formation of the complexes in one step at one time; that means if both K 1 and K 2 is operating together we get only beta 12 in a single step.

So, when the first ligand the first ammonia molecule is coming and bound to the silver ion we get the K 1 value and when the second is coming to the first one; that means silver amine single species one NH 3 bound silver species plus another NH 3 giving rise to the silver diamine complex giving rise to the corresponding K 2 as ML 2 divide by ML and L, product of L. So, we get how this beta 12. So, the beta 12 is we are getting the product of these two. So, product of K 1 and product of K 2 is basically the beta 12. So, that gives us some idea that the beta 12 will be the K 1 and K 2; the product of the stepwise formation constants is the corresponding cumulative constant for the complex formation.

So, this particular expressions if we can have n number of this species; if the n value is equal to 4 or 6, we can have K 1 K 2 K 3 K 4 K 5 and K 6 like these. So, these types of expressions are also useful for any such reactions like that of when we get the species like that of the metal ligand species itself. So, if we have already the metal ligand species and if we can talk about further binding of any other ligand species; that means, the L prime or similar thing and when we find that this sort of things are also possible in some protein envelope, one such good example we will be talking in one of our future class also; that is the binding of hemoglobin during the corresponding oxygenation reactions, so O 2 binding by the hemoglobin molecule.

So, L prime would be our oxygen molecule and we have the metal centre as iron. So, this metal centre is our iron centre and this L prime is our O 2. So, the binding of the hemoglobin molecule of O 2 can also be studied in the same fashion by the different steps if there is more than one step. So in the biological system also, we can monitor the oxygenation reaction using the same procedure; that means the beta 12 beta 123 or beta 1234 can also be monitored for a reversible reaction like the oxygen binding to the iron centre in hemoglobin or in some cases also with myoglobin molecule. So, we have the beta values for different types of complex formation.

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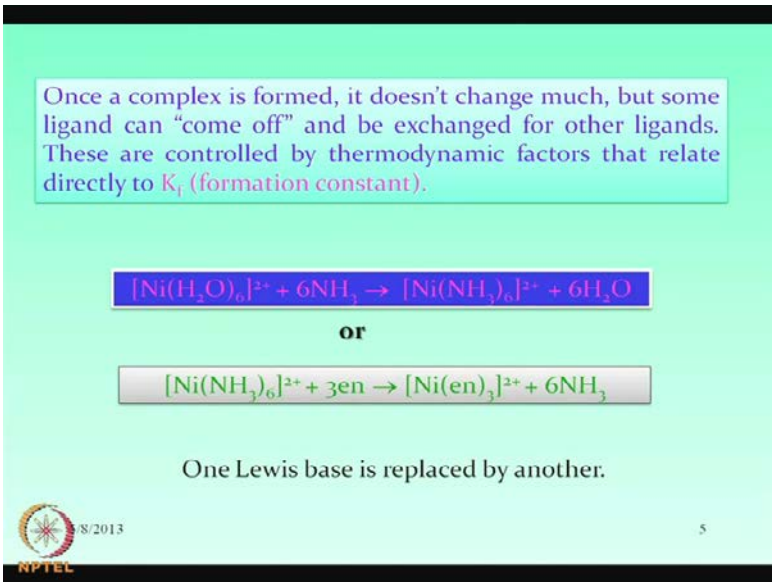

So, once the complex is formed. So, it can be the typical metal ligand assembly or it can be the bound oxygen to the hemoglobin or the myoglobin molecule. It does not change

much, but some of the ligand can come of or be exchanged for other ligands. So we see that, there is a ligand exchange reaction because typically when we go for some reactions like that of the corresponding water bound metal ion with some replacement with, say, ammonia molecule we find that water ligands; that means the aqua ligands are substituted by the amine ligands. And this particular transition from the aqua complex to the amine complex, there will be some control by the thermodynamic factor that relates directly to the K F values the formation constant values.

So we see that the water molecules, the 6 water molecules are bound to the nickel and is a ligand substitution reaction in a stepwise manner again; that means one after other amine molecules are coming and substituting the 6 water molecules already present to the nickel 2 ion giving rise to the corresponding binding of 6 ammonia molecules to the nickel centre and with the corresponding removal of 6 water molecules or we can consider that in another way; that we take some other ligand with that of the formed species; that means when we have the hexamine nickel 2 ion is formed from the hexaaquanickel 2 ion.

Then it is further reacting with 3 molecules of ethylenediamine and ethylenediamine is also nicely substituting all the 6 amine molecules; that means all the 6 NH 3 molecules are being replaced by these bidentate ethylenediamine molecules such that the binding potential, the binding strength of this bidentate chelating ligands; ethylenediamines are more compared to the binding of the ammonia molecules to the nickel centre. As a result we get trisethylenediamine nickel (II) ion with the removal of 6 ammonia molecules.

So, 6 ammonia molecules will be removed from the system and we will be ending of with the corresponding tris-chelate of the nickel molecule. So, one Lewis base is replaced by the other. So, we have the first step the monodentate ammonia molecules are there; monodentate ammonia ligands they are also Lewis bases, they are bound to the nickel centre. In the second step, we are considering as the ligand substitution reaction by another chelating base which is removing the bound ammonium groups around the nickel ion.

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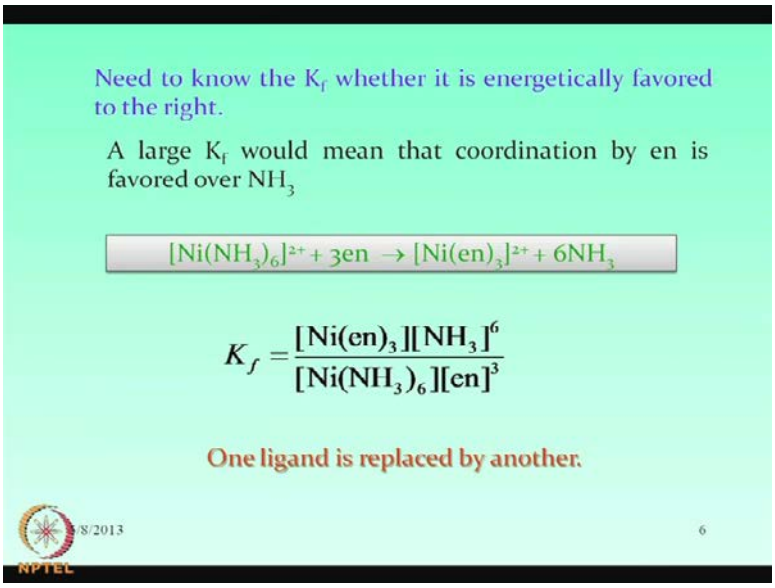

So, we want to know the corresponding K value; that means the formation constant value how this K value is favoring us from left to right towards the formation of the tris-chelate for the compound. A large K value would mean that coordination by en is favored over ammonia. So, if we are able to measure that experimentally these values can be measured, if we are able to measure the corresponding K value in solution for the reaction of ethylenediamine with NH 3. We can consider that the binding of ethylenediamine; that means the coordination of ethylenediamine is favored over NH 3, that is why ammonia molecules are leaving behind and those positions are taken up by the ethylenediamine molecule.

So, we find that the binding of three ethylenediamine to this system. So, how we write the corresponding formation constant value is that the formation constant value is the species which are present on the right hand side by the species which are there in the left hand side; that means all the species, the formation of this hexamine compound which was been taken place in the first step as well as the formation of the new chelate complex as well as the corresponding concentration of the two different ligands. So, this also gives us some opportunity to find out the corresponding K value during the replacement of one ligand by another.

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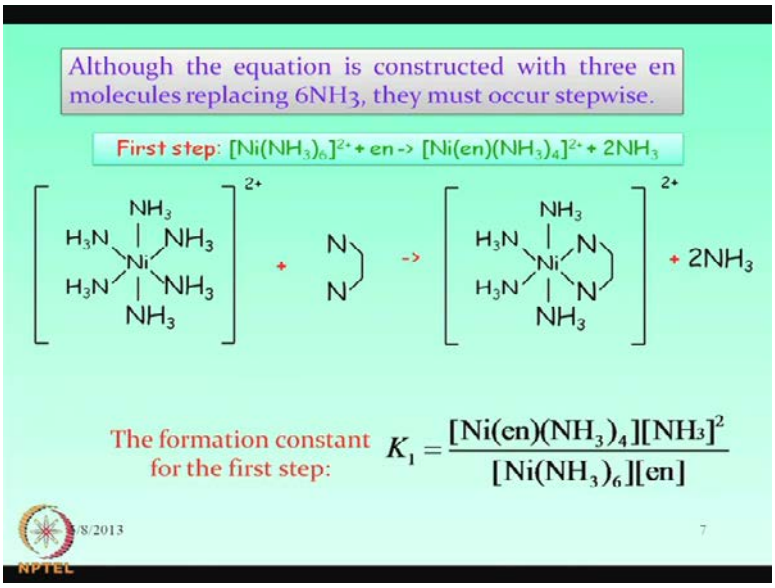

So, this is the situation where we see that the six ammonia molecules are attaching to the nickel centre and ethylenediamine is coming. So, in the first step what is happening? Two adjacent ammonia molecules are being replaced by one ethylenediamine. So, this will have some attached H 2 molecule groups also. So, these are NH 2 CH 2 CH 2 NH 2. So, this is the ethylenediamine unit which will replace two ammonia molecules. So, this equation we thus constructed with the 3 en molecules replacing 6 NH 3, they must occur in a stepwise fashion. Therefore, we consider that in the first step one ethylenediamine molecule is attaching to the molecule, but it is very difficult to isolate in the solid state and characterize by some structural methods or by some spectroscopic methods to identify the species where the nickel centre is bound to four ammonia molecules and one ethylenediamine.

Because this is some kind of some intermediate species which is forming within the solution and the stability of this particular intermediate is not so high such that we can isolate this particular intermediate by using some other anion. So, first step is definitely we can write in this form that 4 ammonia molecules and 1 ethylenediamine removing 2 ammonia molecules from there. So, the formation constant for the first step would be the concentration of this species; then two ammonia molecule concentration of this is what is coming out there the concentration term for the ammonia and the hexamine complex and the ethylenediamine. So, this would be the K 1, because we are breaking the entire reaction what is forming in a single step for the K value for that tris-chelate formation.

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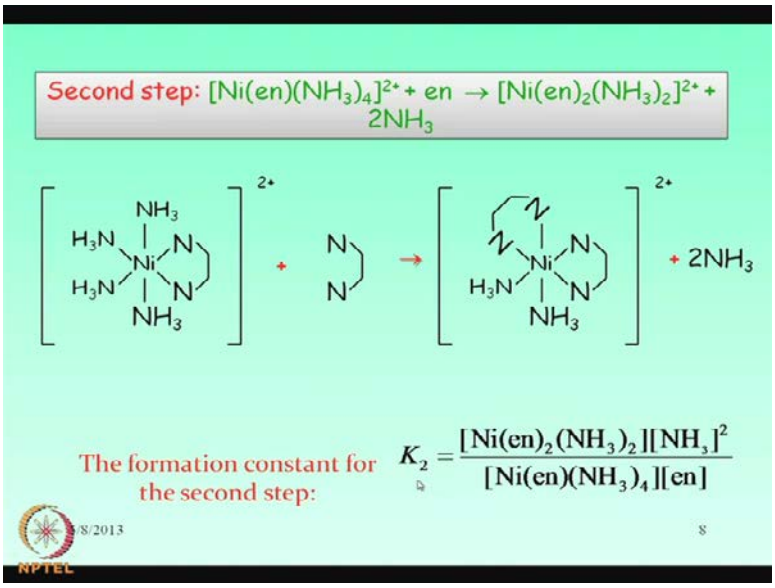

So, in the second step we utilize the second ethylenediamine molecule. So, second ethylenediamine molecule will come and bound by replacing two more ammonia groups from these two sites they are cis positions and they are adjacent to the first chelate ring. So, the second chelate ring is also attaching to the molecule and we can write this particular equilibrium. So, how we can break the entire reaction basically? By utilizing the reaction for Ni en NH 3 whole 4 2 plus plus en giving rise to Ni en 2 NH 3 whole to 2 plus plus 2 NH 3 molecules which were present.

So, in this particular case also we should be able to write the formation constant by knowing the corresponding concentration of this particular species which is forming as the intermediate species. So, at the intermediate species if we are able to know the corresponding concentration of the intermediates, the very transient species which are very fastly disappearing from the solution medium because it is immediately reacting with the third ethylenediamine molecule. So, if we are able to find and able to determine the corresponding concentration of this particular species which is transiently forming in the reaction medium. We should then be able to find out the corresponding value for the second step; that means, the K 2 value for the reaction

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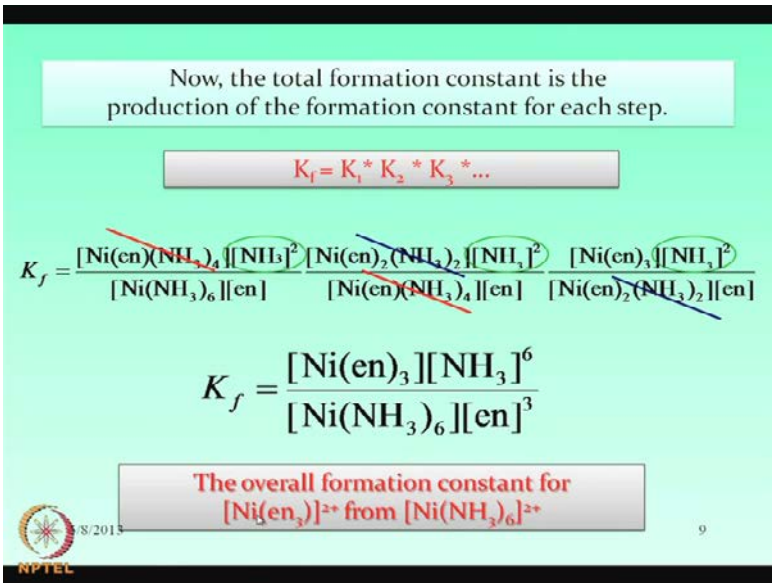

Now we see that the entire K value; that means the K value will therefore be the product of the corresponding K en value for the formation of the species by the attachment of one ethylenediamine molecule. Then the formation of second species; that means, the K 2 value with two ethylenediamine group attaching to the nickel centre, and then third the K 3 value for the formation of the tris-chelate and the other individual; that means the species; that means the concentration on the species what we are utilizing to write down those expressions on the right hand sides. So, there are some common things. So, this will cut with these two will cut and this are basically NH 3 power 2 NH 3 power 2 and NH 3 power 2 will give rise to NH 3 powered 6.

So, we get basically the K value, this overall formation constants, the cumulative constant for the formation of the tris ethylenediamine nickel (II) will therefore be this one Ni en 3 concentration, then NH 3 powered 6 and Ni NH 3 6 concentration and en concentration powered by 3. So, we can find out the K for the single step reaction where tris ethylenediamine nickel complex is forming from the hexaamine nickel 2 species. So, the total formation constant is therefore what we can conclude from this particular part that the total formation constant the K f is nothing but the product of the formation constant for each step. So, if we have three steps like K 1 K 2 and K 3 we get the K value as the product of K 1 into K 2 into K 3. So, we have the K f K 1 product K 2 product K 3 product and so on.

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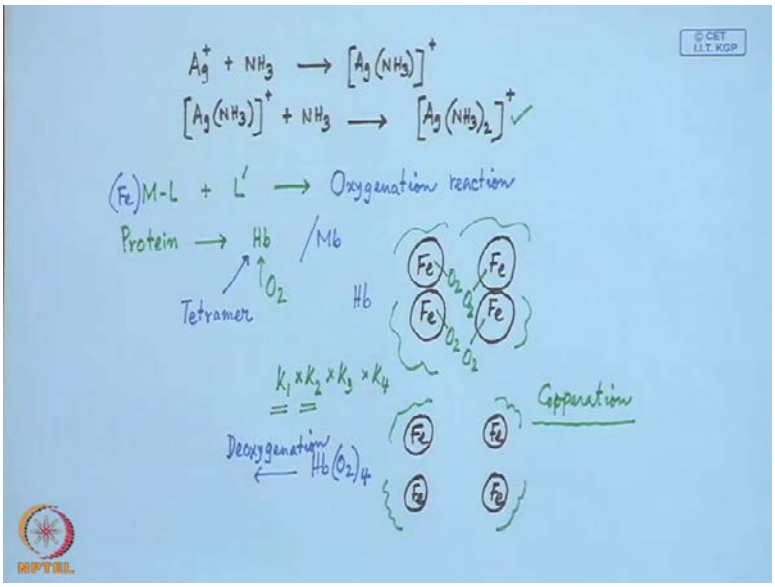

So, in this particular case also where we know that hemoglobin molecule is nothing but is a tetramer species. So, tetramer means immediately we can see that we can have four iron sides. So, it is the hemprotein type thing. So, four; it has some quaternary structure. So, the quaternary protein structure of hemoglobin tells us that it has four iron centre and all those four iron centre can be utilized for binding of iron. So, this oxygenation reaction of the tetrameric hemoglobin molecule can be considered as a corresponding binding of the O 2 in a stepwise manner. So, we have the corresponding K 1 value for the binding of first O 2 molecule to the first iron centre. Then the second O 2 molecule to the second centre which will be K 2, then the third one is to the third centre which is K 3 and the forth one which will be the corresponding K 4.

So, how these values are interrelated that will be seen if we just know the corresponding protein envelop of the entire tetrameric structure. So, there will be a cooperativity; that means the cooperation is taking place when first centre is getting oxygenated; that means when K 1 is there. So, when first centre is oxygenated; so there will be a certain movement in the protein structure which allows the corresponding binding of the second O 2 molecule feasible; that means the dependence of the K 2 value on K 1 is seen from this kind of cooperative binding of O 2 molecule to the hemoglobin centre. So, altogether we have the K 1 K 2 K 3 and K 4 and is a very complex process for the oxygenation reaction, but the cooperativity of the hemoglobin molecule for oxygen binding which we

can consider as when we have hemoglobin which is in the deoxy form to that of our hemoglobin by binding of 4 O 2 molecule at four different steps.

So, four different steps will be required to get the fully oxygenated hemoglobin molecule from the deoxyhemoglobin and the steps required for the oxygenation reactions are dependent to each other which will also be known to us the way the reaction goes for the corresponding reversible way for the deoxygenation because this can go and this can deliver these oxygen to these myoglobin molecules. So, myoglobin molecules are then the acceptors and these oxyhaemoglobin molecules can go for deoxygenation reaction. So these are all interrelated, but for the time being, we will come back again on this aspect of binding of the biological system where we see again that these K 1 K 2 K 3 and K 4 values are clearly observable in case of hemoglobin molecule for binding of O 2. So, the overall formation constants for Ni en 3 2 plus from Ni NH 3 whole 6 2 plus can be directly written like this K value. Once we write the direct reaction of Ni NH 3 whole 6 2 plus with ammonia in presence of ammonia and the formation of the corresponding Ni en whole 3 molecule.

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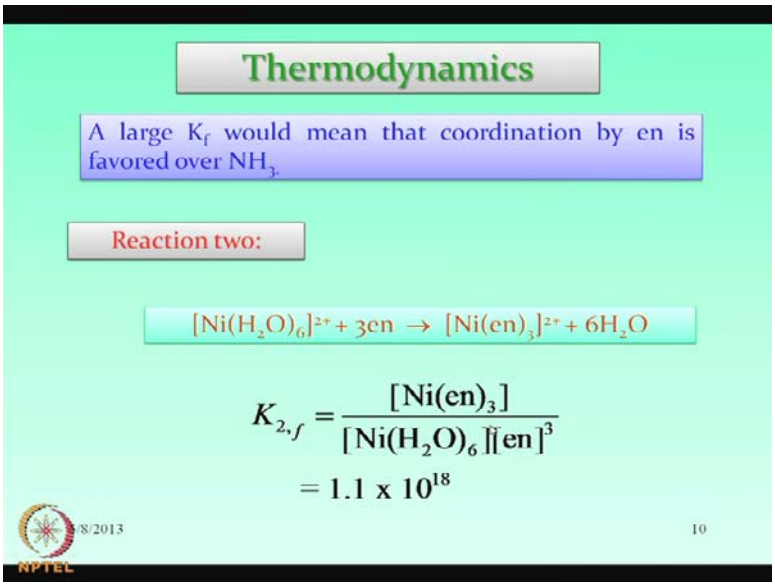

So, what are the thermodynamic roles for the formation of these species; that we will see from some thermodynamic comparison for the formation of these different steps. So, a value which is related to the coordination equilibrium; that means the equilibrium is there due to the coordination and a large K f value will mean that coordination by

ethylenediamine is favored over NH 3. So, if we are able to monitor the corresponding K f value due to the binding of the ethylenediamine on the amine complex of nickel, we can simply assume that the binding is favored for the chelate ring. So, the reaction what we can see for the other one; that means where we see that the echo complex is binding directly with ethylenediamine. So, that is also possible.

So, directly from the echo species we get the formation of the tris-chelate of the bivalent nickel and we find out the corresponding values for the formation of these and for the reaction which is directly forming; from the echo complex we can find out the corresponding K value as 1.1 into 10 to the power 18. Just we simply compare the magnitude of these values. So, the numerical values of these constants can give some idea that how the reaction is favored from left to right, how the K values are higher if we are just simply taking about the corresponding monodented substitution reactions of ammonia ligands which are replacing the water molecules or in other case the ethylenediamine molecules are replacing the water molecules. So, straightway when we are getting the corresponding tris-chilate from the echo complex, we have a corresponding K value of the order of 10 to the power 18.

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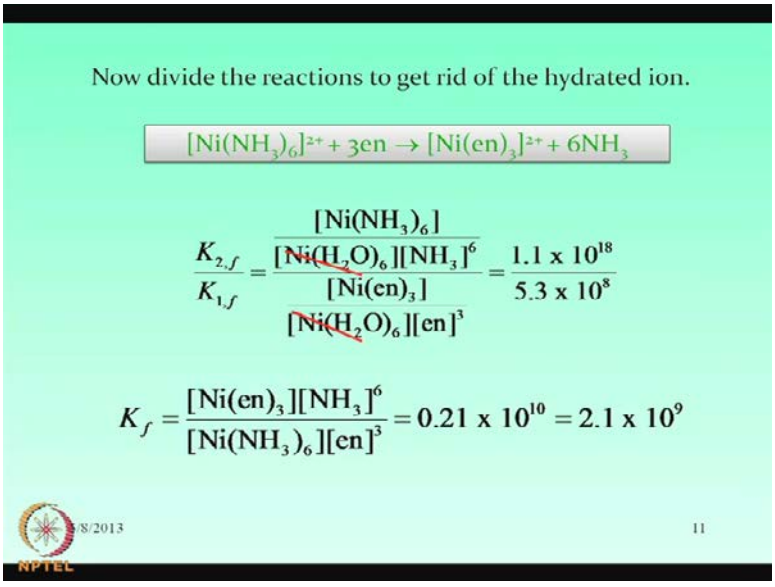

So, we see that when we have the corresponding K value from the amine complex, we get the corresponding value for this where the 6 amine groups are there which are substituting with ethylenediamine giving the tris-chelate and this tris-chelate is

responsible for the removal of 6 NH 3 groups. So, in these two steps; that mean this was the first one; that means if we just get the values for the formation of these; that means the formation of the corresponding values for this K 2, and the formation of the corresponding K F values for the K 1 for the amine complex and the ethylenediamine complex. Both of them are forming from the echo complex.

We get some ratio like this which is 1.1 into 10 to the power 18 by 5.3 into 10 to the power 8 and this value is definitely nothing but the formation of the tris-chelate from the amine complex. So, that way we get the corresponding formation constant value for the direct formation of the tris ethylenediamine complex from the hexaamine complex and in that particular case we find the corresponding value as 2.1 into 10 to the power 9. So, in case of the corresponding formation of these values for this corresponding tris ethylenediamine starting from the water molecule, that means the echo complex or from the amine complex. So, these values basically gives us some idea that how we get the corresponding values for the thermodynamic stabilities of these complexes.

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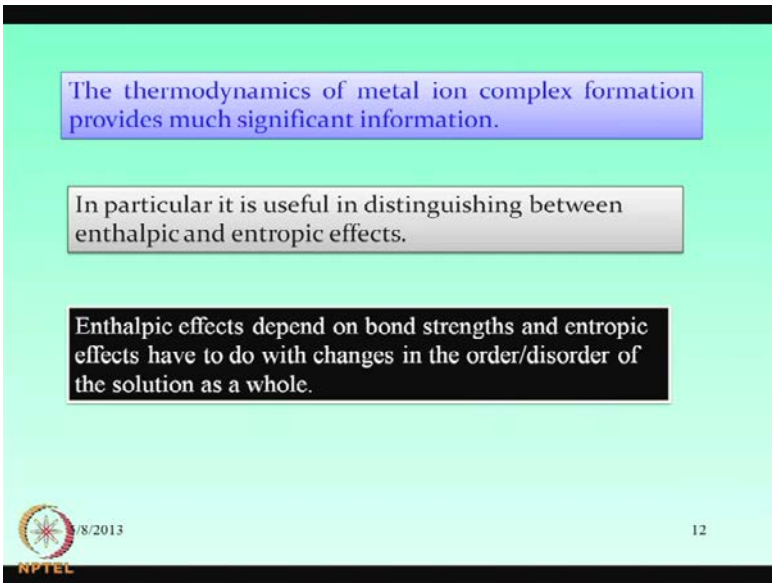

So, it gives us some information that the thermodynamics of the metal ion complex formation provides some significant information about the stabilities of these complexes and in particular it is useful in distinguishing between the two parts. So, the thermodynamic stability constants can have two parts; one is the corresponding enthalpic term and another is the corresponding entropic effects. So the enthalpic effects, what is

the heating effect, how the corresponding enthalpy values are responsible to detect the corresponding formation of the complexes, and these enthalpic values depend on the bond strength and entropic effects have to do with the changes in the order and disorder of the solution as a whole. So, how strong bonds we are able to form such that when the ethylenediamine is reacting with the nickel centre.

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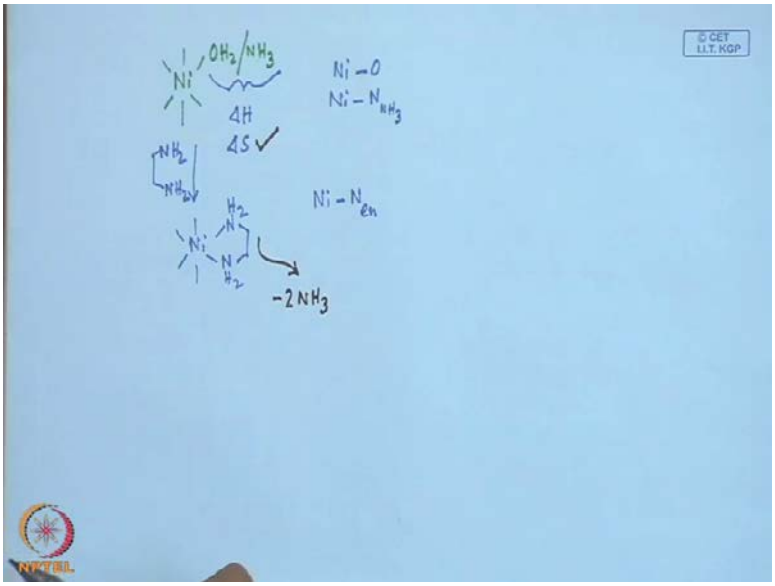

So, we have all this positions whether it is bound to the water molecule or ammonia molecule. So, we have the corresponding values for delta H also and the corresponding values for delta S. So, we have the contribution from the enthalpy as well as the entropy, but in this particular case we are replacing the water molecule by the ammonia molecule. But the nature of these bonds from Ni-O to Ni-N we are changing and this nitrogen bond is coming from the ammonia molecule. And in the second step when we are utilizing the ethylenediamine is forming the chelate ring and in that particular case the Ni-N bond of different type which is coming from the ethylenediamine is forming.

So, we can have the relative contribution of the bond strength and the order-disorder phenomenon related to the more ordered form of these two groups' in this particular case when one ethylenediamine is binding towards the nickel 2 plus ion it is removing 2 NH 3 molecules. So, more number of molecules is removing from the system. So, we should have some contribution from the entropy term. So, this entropic effect will have some changes on the order and disorder of the solution as a whole; so how the entropy effect

can contribute for the solution thermodynamics for the binding of the chelate ring to the metal ion.

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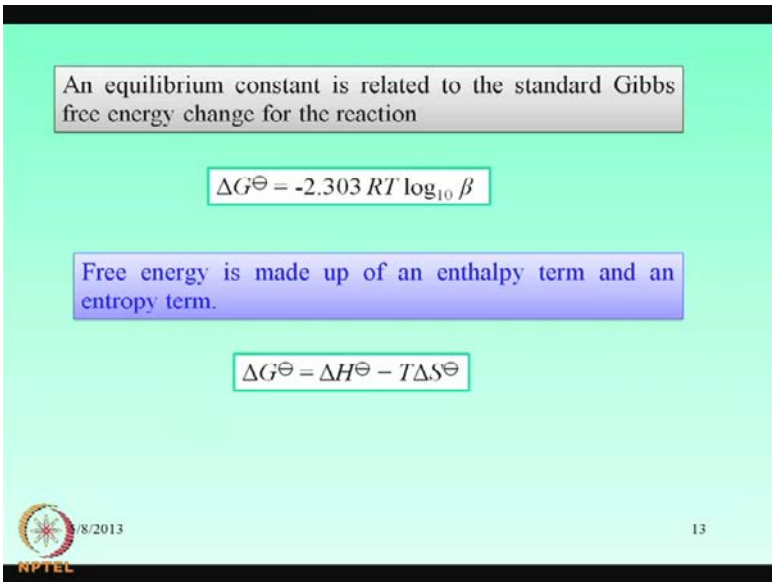

So, for that equilibrium constant which is related to the standard Gibbs free energy; so both delta H and delta S they are related to the delta G standard particularly. So, when the standard G values the delta G values are they which should be related to the corresponding enthalpy term and the entropy term by the corresponding equilibrium constant value which is the beta value. So, delta G 0 value will be equal to minus 2.303 RT log to the base 10 beta.

So, this is the constant value what we are looking here for the determination of the stability constant and the formation constant. And these determination of beta value can also give us some idea about the corresponding delta G 0 value for the reaction system, where we know the corresponding temperature and the temperature effect can also be monitored. Because we know if the corresponding beta value is known we can find out the corresponding delta G 0 values for these reactions, such that the free energy is made up of an enthalpy term and an entropy term; that we all know that it has two parts.

So, how this delta G 0 is taking up their individual contributions from the entropy term and the enthalpy term; that we will just see if we just can monitor or equate this delta G 0 values with the delta H 0 value or the minus T delta S 0 values for the different standard conditions. These are called the different standard conditions. So, once we measure these

values for the free energy change, we can correlate them for the corresponding enthalpy term and the corresponding entropy term for the binding of say ammonia molecule around nickel as well as the binding of the corresponding ethylenediamine molecule to the system.

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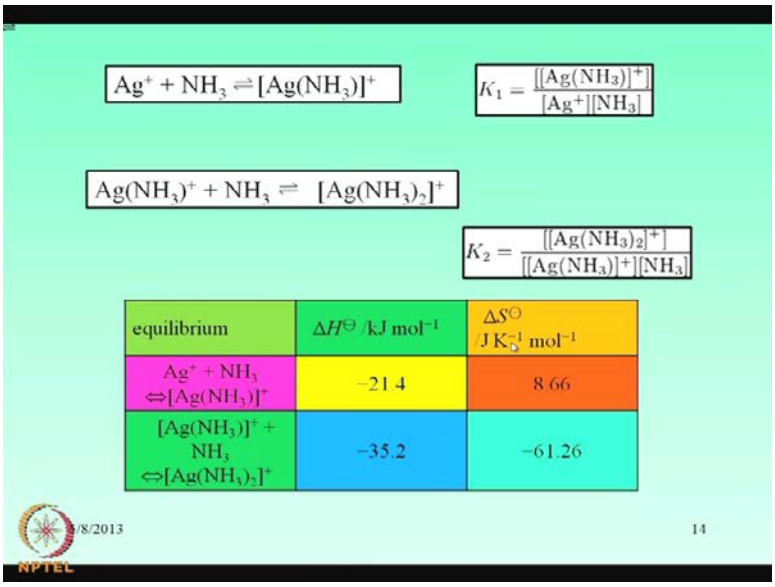

So, these values basically can give us some idea for the corresponding silver amine complex where we get the corresponding K 1 value for the silver amine complex as well as for the corresponding values for the second step. So, we get both K 1 and K 2 values for these cases and the different values for the equilibrium as well as the enthalpic contribution and the entropic contribution. So, for the formation of the corresponding silver amine complex with a coordination number of two, we will find these two contributions that the enthalpy contributions are favored; that means both these two cases though the steady crowding is not much.

So, they are favored both for this enthalpy contribution and the entropy contribution is mostly favored in the second step not in the first step due to the formation of a corresponding silver amine complex with a coordination number of two. And in this particular case which we are not talking about the corresponding chelate formation, we do not have some opportunity; we do not have the corresponding opportunity to see how these delta S values can contribute only for the chelate formation.

Thank you very much.