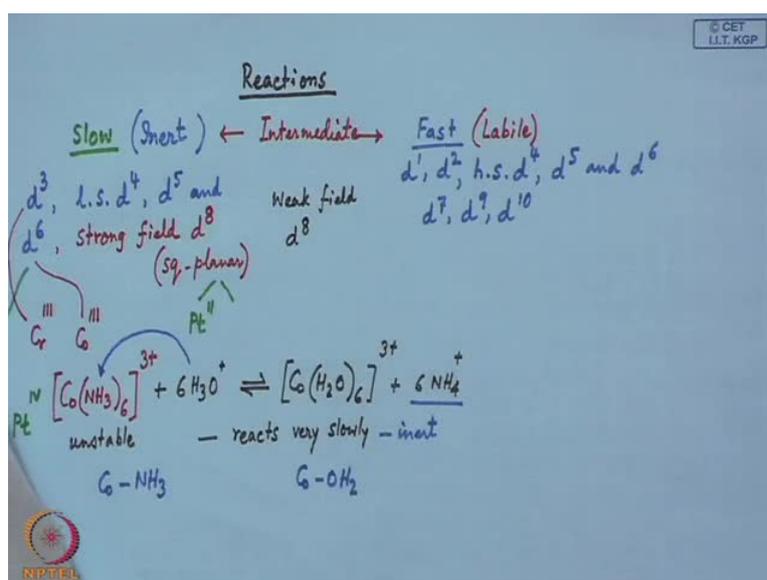


Coordination Chemistry
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Lecture - 37
Reaction Mechanism – III

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Good evening everybody. So, will still continuing with the mechanisms which can talk about the different types of reactions, and these reactions particularly happening when a metal is reacting directly with the ligands. So, today will be talking about the reaction mechanisms part 3 and in which particular mechanism we can use for two types of reactions. Some reactions are, can be categorized as slow that we have seen in our last class and some of these reactions we can considered as fast reactions. So, it is the inherent property of the metal ions as well as the ligands which can show some of these reactions.

So, when we have the slow reactions, we basically level the corresponding complexes which are participating in these slow reactions as some inert complexes. So, these inert complexes are definitely go for only slow kinetics, irrespective of its thermodynamic stability or unstability, they can go for only slow reactions when these reactions are very slow in nature. And several metal ion configurations such as d^3 low spin d^4 , d^5 , and d^6 will consider that these metal ions can give rise to very

slow reactions and the corresponding compounds we can call as inert metal complexes in terms of their ligand substitution reactions as well as some of them in strong field with d 8 electronic configuration. Definitely, in strong field d 8 configuration most of the cases we get the square planer complexes such as several platinum and palladium compounds.

So, this d 3 electronic configuration we all know that this is for chromium 3. So, if we have the corresponding chromium 3 compound and if we have only 3 unpaired electrons on the chromium orbital's the d orbital's, then this can react very slowly for the ligand substitution even for the water exchange reactions. Similarly, for d 6 configuration, we have the cobalt, the trivalent cobalt which we have seen also in case of the corresponding hexammine cobalt 3 compound which is substitutionally inert. And when this compound is reacting with acids say protons, giving rise to the corresponding substitution of all the ammonia ligands by water molecules to give us the corresponding hexaaquacobalt 3 compounds and 6 ammonium ion after protonation.

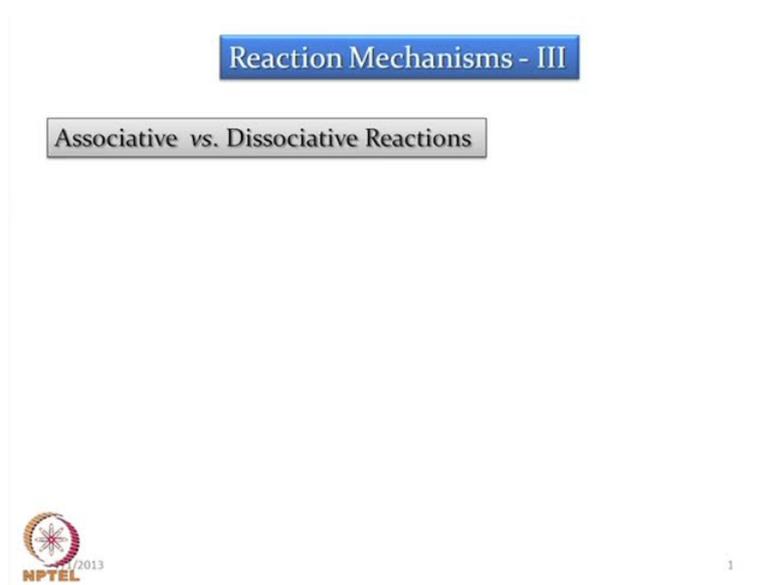
This compound is unstable in acid, but reacts very slowly with this acid very slowly with the acid. So, even we are considering the corresponding reaction of these that means the proton is attacking the corresponding ammonium ligands forming ammonium ion basically what we are going for? We are basically going for the corresponding substitution reactions where all the cobalt nitrogen bonds we have 6 cobalt nitrogen bonds from the ammonia ligands attached to the cobalt centre are substituted by cobalt hydrogen the attached to oxygen and then cobalt to oxygen. That means the cobalt oxygen bonds of the cobalt aqua group. So, these are reacts very slowly and therefore, we can level these as the inert compound.

So, this is there then for the strong field d 8 electronic configurations we can have. So, we can have platinum 2 for this particular one where is d 8 configuration and for this d 6 configuration we can have platinum 4, platinum in plus 4 oxidation states. So, this basically gives us some idea that what are the different types of the reactions we can consider as the corresponding slow reactions. And therefore, the other metal ions which are d 1 d 2 then not low spin, but high spin d 4, d 5, and d 6.

These can give rise to first reactions as well as d^7 d^9 and d^{10} which is a zinc $2+$. So, in this particular case where we have these metal ions and the metal ion configurations can tell us that the reaction would be fast that means the corresponding complexes are labile in character. So, these two extreme ranges we can have. So, one is either slower range and another is the corresponding faster reactions, but as some of these molecules can also come as intermediate between these two ranges. So, the metal complexes which can show some intermediate reactivity pattern or reaction rates.

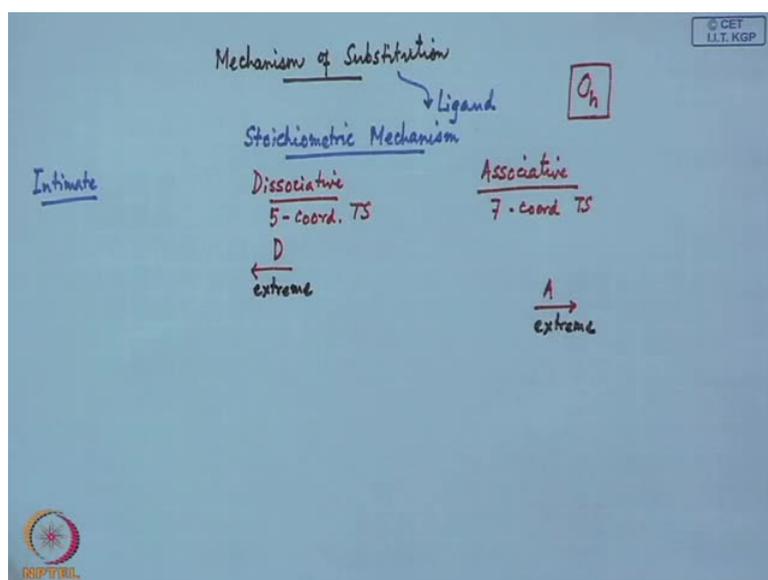
So, kinetics are telling us that it will have some intermediate rate of reaction if we consider it as for the corresponding ligand substitution reactions. And already we have consider these as the strong field d^8 system, but in this particular case we have the weak field d^8 system such as nickel $2+$ nickel $2+$ in the corresponding tetrahedral geometry we get is a corresponding weak field d^8 system. And that gives rise to the corresponding intermediate reaction rate for its corresponding ligand substitution reactions.

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So, what we will see that during these reactions we can have two different types of reactions. One is the associative another is the dissociative reactions. So, whatever we are talking about here is the corresponding mechanism of substitutions.

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So, if we have the corresponding mechanism of substitution, and we are talking about some of these ligands, so the ligands will come. So, you can consider it as the corresponding ligand substitution reactions around the metal centre and when we add the stoichiometric amount of metal and the ligand we have the stoichiometric mechanism. So, whatever mechanism we can have is based on stoichiometric amount of the addition of the ligand to the metal centre. So, in one case we have the intimate mechanism.

So, we have the intimate mechanism of reaction and we can have the dissociative that means one ligand is going away and the associative one, the differs one when one ligand is attaching to that particular system. So, if we are talking about the corresponding octahedral complex, so if one ligand is going away so in the transition state we have a five coordinated system in the transition state of reaction with that of the reactant.

So, transition state reactants can give rise to a 5 coordinated system. So, for the associative reaction in the similar way we can have 7 coordinated transition state for the octahedral reactants that means some ligand is reacting with the octahedral metal centre. So, we can have two different types of activation, the dissociative activation and the associative activation. And we have the mechanism known as D where we have in the extreme case we have the corresponding dissociative activation and we

get the corresponding 4 coordinated compound and the other end we have the associative reaction for the extreme cases. So, these two, that means D and A these are two extreme cases for these reactions. So, we have the associative versus dissociative reactions we can consider.

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Reaction Mechanisms - III

Associative vs. Dissociative Reactions

- Ligand substitution reactions are either associative or dissociative
- Associative: reaction intermediate has higher coordination number than reactants or products
 - Complexes of lower coordination number
 - Rates depend on the entering group
- Dissociative: reaction intermediate has lower coordination number than reactants or products
 - Octahedral complexes and smaller metal centers
 - Rates depend on leaving group

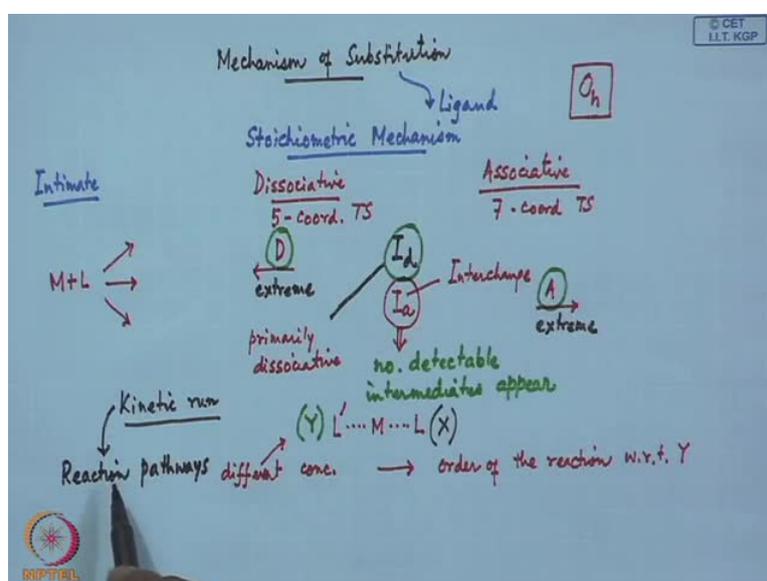
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And when we talk about the ligand substitution reactions they can either be associative or dissociative and when we have the associative reaction just now, we have seen that we can have an increase in coordination number. So, the reaction intermediate that means leading towards the corresponding transition state as higher coordination number than reactants or products. That means if the reactant is octahedral in nature we have 6 coordinated species and if the product is also a octahedral one the product is also 6 coordinated, but the transition state is 7 coordinated.

So, this particular types of associative reactions are possible when we have the complexes of lower coordination number. If the coordination number is less it can accept one more bond or two more bonds to form the higher coordination number for the transition state and rate depends on the entering group. That means the group which is coming and attaching to the metal centre will control the corresponding reactivity pattern as well as the rate of the reaction.

Similarly, when we go for the corresponding dissociative reaction the reaction intermediate has lower coordination number than reactants or products is typically opposite to that of the associative reaction. And octahedral complexes can give rise to that dissociative reaction and small or metal centers that means metal centers having less coordination number compared to octahedral also. And in this particular case the rate of the reaction is dependent on the leaving group that means the group which is leaving to give rise to the 5 coordinated species will control the rate of the reaction. So, when we have these two that means D in the extreme end and A in the other end.

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We have two other intermediate reactions which is known as intermediate dissociative as well as intermediate or interchange associative. So, one is I small d and I small a and this I is the interchange. So, we can have in these two particular cases when the incoming ligand is presumed to assist the reaction, but no detectable intermediates appear. So, no detectable intermediates appear that means the transition state has not very much a (()) life to corresponding appearance and as corresponding detection in the corresponding state.

So, in the case of the other one that means I d the degree of assistance is small and the reaction is primarily dissociative. So, the reaction what we get from there is primarily dissociative in nature primarily dissociative in nature. So, when the

incoming ligand in case of this I_a when the incoming ligand begins forming a bond to the central atom, that means intermediate associative that means some weak interaction is taking place the central atom with that central atom before the departing ligand bond is weakened appreciably. So, one bond is forming weakly to the metal's ligand when L' is coming and the other bond which is already present is there which is weakened appreciably.

So, this ligand metal bond will be weakened appreciably compared to that particular bond which is forming in a newer way. So, there are many reactions which can be described as I_a and I_d mechanism rather than typical A and D. So, we can have therefore, we can consider that we have the reactions which we can consider as D and A at two extreme ends or the two intermediate cases I_a and I_d. When the kinetic evidence is present products to association or dissociation, but detection of intermediates is not possible we get either D or A or I_a or I_d.

So, when we bring these that means this L' can be a capital Y. So, we can have the different kinetic experiments and that kinetic experiments can consider that large X of the incoming reagent Y that means if this is a X and the incoming reagent Y is there then we can analyze the kinetic data for the progress of the reaction for a particular kinetic run. So, we use the kinetic run of the reaction which will consider that it also dependent on the temperature of the reactions at different concentrations.

So, initially when we consider the rate of the reaction how it is affecting when we consider that different concentrations of Y, can use different concentrations of Y then what we get? We get the corresponding order of the reaction with respect to Y. So, if we are able to find out the corresponding order of the reaction from the kinetic data we can find out that how the variation in the concentration of Y can affect the rate of the reaction, and whether this Y that means the term the concentration term Y is involved in the corresponding rate law for the corresponding reaction.

So, we can have from this kinetic run we have the kinetic rate law and the kinetic consequences of reaction pathway. So, whatever we are talking over here is the different reaction pathways. So, we want to know what particular pathway is giving a particular type of product when you do a particular reactions say M plus L and if we can have different pathways for the reactions to take place where L is reacting

with M then we can find out the corresponding possible reaction pathways and it is corresponding kinetic consequences, and we try to find out the corresponding kinetic rate law.

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Patterns of Reactivity

- Formation constants tell us about thermodynamics
- Kinetics requires a different measure: nucleophilicity
- Ligand displacement are nucleophilic substitution reactions

– The rate of attack on a complex by a given ligand (Lewis Base) relative to the rate of attack by a reference base

- Rates span from 1 ms to 10^8 s

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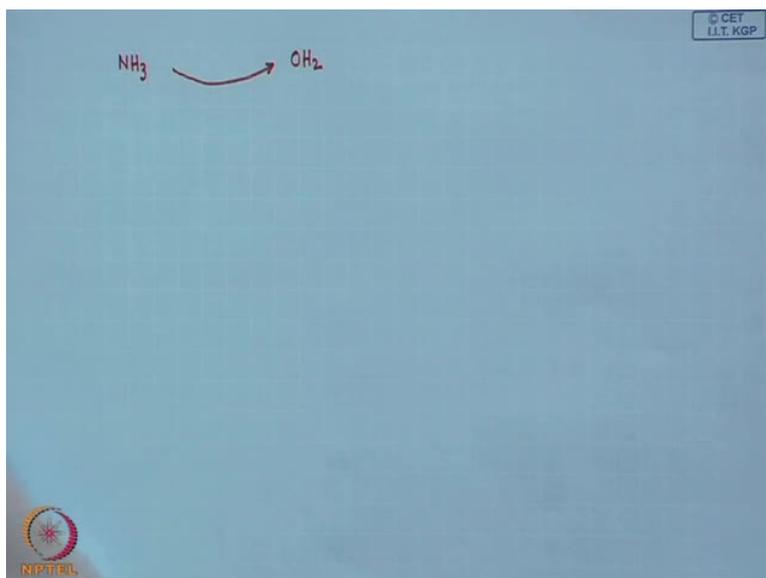
So, the how this rate law can help us in understanding the corresponding values for these reactions where we can consider that the reactivity pattern for a particular metal ion with the different ligands are different. So, the different patterns what we can see that the formation constant tell us about the thermodynamics. That means the k value the equilibrium constant or the formation constant values tell us about the corresponding thermodynamic stability of the metal complex.

So, if we have $M + L_n$ or $M + L_6$ we can determine the corresponding equilibrium constant or the formation constants for the different steps that stepwise formation constants for the thermodynamic parameter that means the equilibrium constant value as well as corresponding ΔG values. But in case of it is corresponding formation rate the kinetics for this particular reaction requires a different measures where you considered the nucleophilicity, how it is looking the ligand, how it is looking for the metal centre which is the corresponding nucleophilic centre.

So, the nucleophilicity, how we can consider for the corresponding kinetics of the reaction? So, in all these cases the ligand displacement reactions are nucleophilic substitution reactions. So, one L is substituting other L which is attaching to the

nucleophile that means the corresponding metal centre. So, we get the corresponding nucleophilic substitution reactions for these ligand substitution reactions. So, we have the rate of attack on a complex by a given ligand; that means the Lewis Base is attacking the corresponding metal centre relative to the rate of attack by a reference base.

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So, if we consider that means if we just simply consider the corresponding substitution reaction where the given ligand is our say ammonia which is a Lewis Base and the reference ligand which is also a reference base is the water molecule. So, if we can go for the substitution of these water molecules for the metal aqua bond by the metal amine bond, how this particular new Lewis Base can attack and the move these water molecules from the metal centre that we can find out and how quickly they are happening that we can find out from the corresponding rate of the reaction.

So, in this particular case so we can have two different reactions, one is the slow reaction and another is the corresponding fast reaction. So, the different rates which can spend from 1 millisecond to 10 to the power 8 second. So, when we have 1 millisecond to 10 to the power 8 second which is in the lower range to the higher range. So, in this particular window we can measure the corresponding reactivity

pattern that means the rate of formation of the product and its corresponding dissociation by some mechanism.

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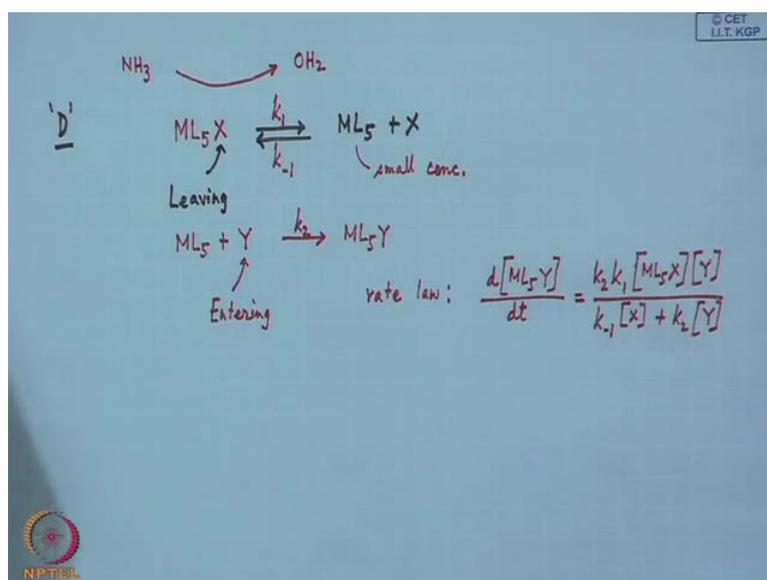
Ligand Labels for Nucleophilic Substitutions

- Three types of ligands can be important:
 - Entering Ligand: Y
 - Leaving Ligand: X
 - Spectator Ligand

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So, this particular thing can give us that ligand levels we can have and these ligands we can use for it is corresponding nucleophilic substitution reactions. So, three types of ligands we can consider that we have the entering ligand Y, we have the ligand which is leaving from the system as X and the spectator ligand which are present there as L. So, we can have the kinetic information for the different cases and we can use to find this kinetic (()) for the different types of the mechanisms.

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So, if we have a corresponding system like $M L_5$ where X is present over there which will be the corresponding leaving ligand. So, $L X$ can leave the system which is leaving ligand and this mechanism is dissociative in nature. That means the mechanism is D and we can have two ways of this reaction for this dissociation where we get $M L_5$, where L are the spectator ligands and X is completely dissociating from the system.

So, we can have a very small concentration what we can assume as these hypothesis for a steady state approximation that this can have a very small concentration with the progress of the reaction. Then this $M L_5$ can react with Y which is our entering ligand, Y is our entering ligand and this is also forming $M L_5 Y$. So, the rate of formation of these $M L_5$ and $M L_5 Y$ all these are dependent on the rate of this particular dissociation that means k_1 and reverse of these reaction is k_{-1} and the rate of this particular attachment of the entering ligand is k_2 .

So, this particular thing ultimately give rise to the corresponding manipulations and all these giving us the corresponding rate law as d/dt of the corresponding $M L_5 Y$. That means the formation of these the product $M L_5 Y$ with time. So, the formation of these the rate of change concentration of the new compound which is forming through the introduction of Y is therefore is dependent on $k_2 k_1$, these two k_2 and

k_1 is dependent on these two steps and the concentration of $M L_5 X$ and the concentration of Y .

So, in this case that means for the dissociative case it is dependent on the concentration of the compound which is reacting as well as the corresponding concentration of the entering ligand. And the corresponding decrease in concentration of this dissociation is $k_{-1} X + k_2 Y$. So, this particular rate law is critically giving us the corresponding rate law for this dissociative mechanism.

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Ligand Labels for Nucleophilic Substitutions

- Three types of ligands can be important:
 - Entering Ligand: Y
 - Leaving Ligand: X
 - Spectator Ligand
- Species that neither enters nor leaves
- Particularly important when located in a *trans* position, designated by T

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So, we have therefore, three different types of ligands which is entering, which is leaving and which is their remaining as the spectator ligand. So, this species that neither enters nor leaves the what are these spectator ligands? So, spectator ligands are those ligands which is not entering into the system or not leaving in the system and particularly important when we find them as located in a *trans* position designated by T.

This will considers in some way that when we were talking about the corresponding substitution reaction in octahedral complexes we do not find any effect from the corresponding spectator ligand. But for the corresponding square planar complexes like that of our platinum or palladium or for some strong field ligand around the

nickel centre like cyanide we have this ligands which are trans to that particular system.

That means whether that particular position is the leaving position or the position is utilized for entering the ligand trans to that and these spectator ligands, we can consider as the T ligand which can see the corresponding reaction and can control the corresponding reactivity pattern for these centers.

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The slide contains two main sections. The first section, titled 'Stoichiometric Mechanisms', lists three types: Associative - A (two steps), Dissociative - D (two steps), and Interchange (continuous process). The second section, titled 'Rate Determining Steps', describes the rate dependence for associative and dissociative mechanisms. The NPTEL logo and the year 2013 are visible in the bottom left corner, and the number 4 is in the bottom right corner.

Stoichiometric Mechanisms

- Associative - A (two steps)
- Dissociative - D (two steps)
- Interchange (continuous process)

Rate Determining Steps

- associative – the rate depends heavily on the entering group
- dissociative – the rate is independent of the entering group

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So, when we have since we are talking about these stoichiometric reactions and the stoichiometric mechanisms what we can see. So, we have these associative in two steps and dissociative in two steps and the interchange which is a continuous process. That means at two extremes what we have seen just now that associative thing we can consider at one end and dissociative and other and in between we have the interchange of the corresponding mechanism.

So, the rate determining steps which are very important how we can find out from the rate law? In case of associative mechanism, the rate depends heavily on the entering group. The group which is entering is dependent on that particular concentration that means when we go for the two ligands, the ligand which is coming up which is being associated to the metal complex to giving a (()) and coordinated intermediate or after dissociation it is coming and attaching to the metal centre.

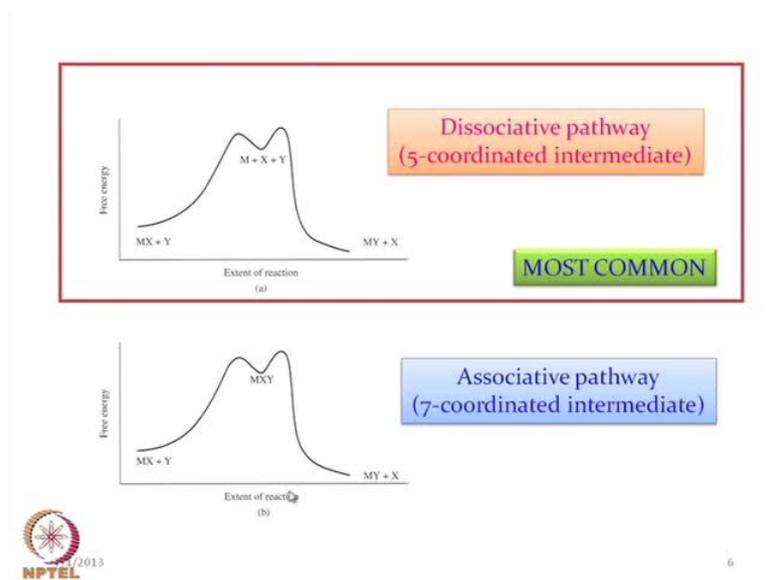
dissociative type. So, in other case which is associative in nature that means where the incoming ligand can go and attach to the metal centre forming the $M(L)_5XY$.

So, in this particular case this is the slow step, this is also the slow step, but in this particular case the dissociation is the slow step or the slowest step and slowest step is the rate determining step that means the rate of the reaction is dependent only on the slowest step that means the dissociation path. Similarly, since this is the slowest step that means the rate of the reaction is dependent on the associative pathway which is dependent on the rate constant k_1 .

Therefore, the rate equation in this particular case would be r is equal to k_1 into $M(L)_5X$ into Y . That means it has the contribution of both the two that means the concentration of the starting complex that means $M(L)_5X$, and the concentration of the entering group that means the Y when both these two concentrations are involved over there we can consider it as some kind of associative mechanism is operating and the second step for the removal of X is pretty fast.

So, it has no contribution. So, in the rate law there is no contribution for k_2 , but for some other cases where we consider as the interchange for these reactions. That means I_a or I_d whether it is associative interchange or dissociative interchange we can have the corresponding reactions where the rate law can involve both k_1 and k_2 as well as the concentration of the intermediate as well as the starting compound and the product concentration.

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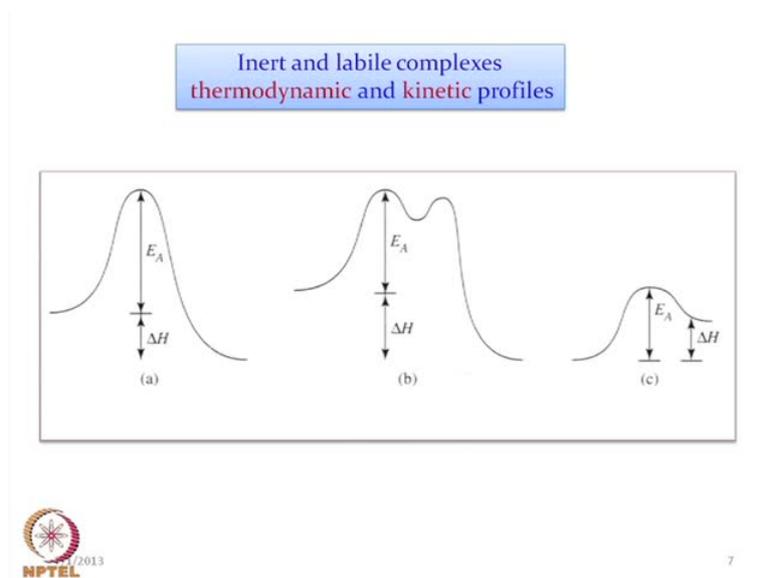
So, we see the corresponding energy profile, how we consider it as the corresponding free energy change for these reactions. So, the free energy change for the reaction this is L_5 has not mentioned over here, this is the $M L_5 X Y$ is there then $M L_5$ plus X plus Y as the intermediate where it is the dissociative pathway. That means $M L_5$ is forming and $M L_5$ will have some stability at this particular point. So, this de this particular stabilized point has $M L_5$; that means the dissociated form has some stabilization then it is reacting with Y forming the product which is $M L_5 Y$.

Here also due to the extent of the reaction the associated form has some stability. So, if we are able to detect these if we have certain stability for these. That means the steady state approximation was not valid in this particular case where we are not assuming that these two intermediate has very low concentration. But it has certain amount of measurable concentration then we can have the corresponding intermediates, and we can involve the corresponding rate law for the involvement of these species for the progress of the reaction.

So, this one that means the dissociative pathway is the most common one where this $M L_5 X$ is reacting with Y giving $M L_5 Y$ plus X and is 5 coordinate intermediate in this particular case and in the other case we have the 7 coordinated intermediate is forming. That we have discussed so far and the corresponding free energy and the

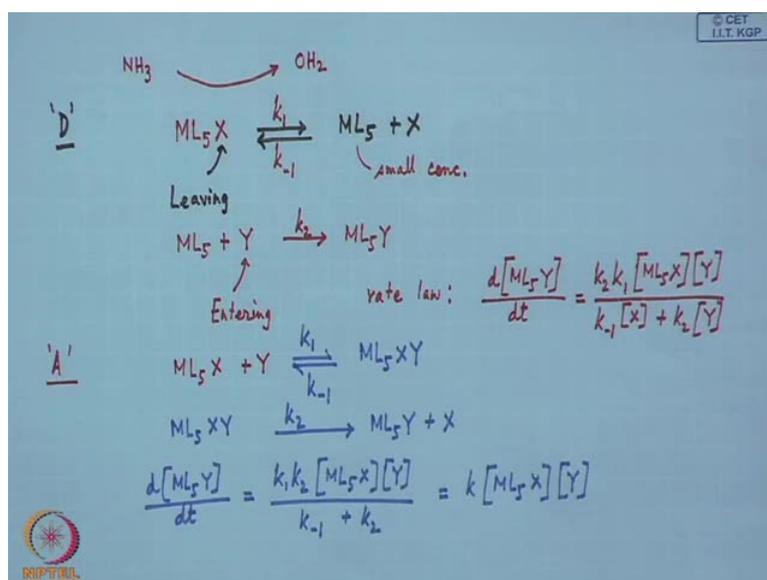
path for the corresponding extent of reaction can also be monitored in that way for to find out the corresponding rate law.

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This we have already discussed in detailed that means how we can consider the different inert and labile complexes. One is the corresponding thermodynamic part and another is a corresponding kinetic part. So, when we have these things that means the corresponding reactions, one is we are considering as the dissociative path another we are considering the corresponding associative path and when we consider these reaction profiles such as when we have these particular case as D.

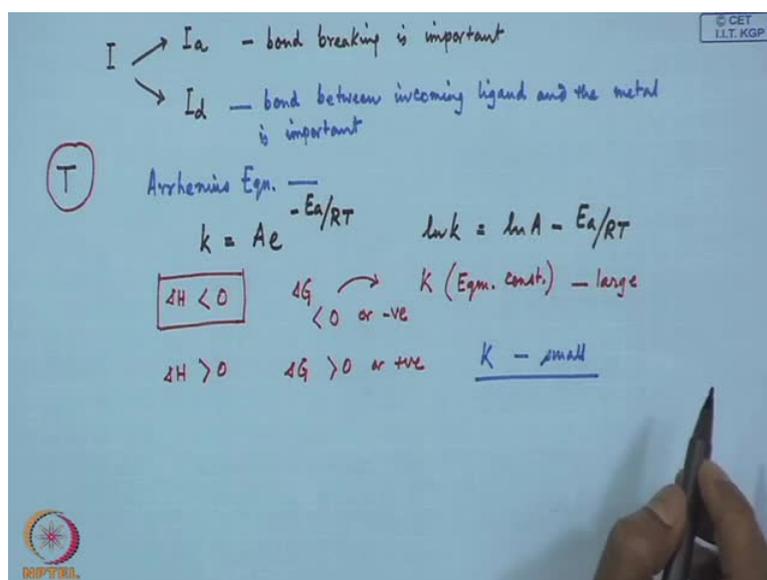
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We can also the reaction as the corresponding associative pathway where ML_5X is reacting straightway with Y and both way reaction can give rise to ML_5XY . That means the associated form we have this k_1 and k_{-1} in the same way as that of our dissociative pathway. Then in the second step this particular associated form that means ML_5XY is going for the elimination of the X giving rise to ML_5Y plus X and the rate of the reaction, the rate law for the reaction. That means d of ML_5Y dt would be equal to $k_1 k_2$ again ML_5XY and $k_{-1} + k_2$.

So, this particular rate law can also be considered when we have very small values for this k_{-1} and k_2 values these are the very first reaction. And when we consider there this particular one when we these are very small this k_2 and k_2 this is very small, k_2 and k_2 can cancel out. And we can have for all these products; we can have the corresponding one constant which is k which is ML_5X and Y . So, this particular case also the rate law is dependent on both the concentration of this particular species and the concentration of the corresponding incoming ligand or the entering ligand which is attaching to that particular metal centre.

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So, where we see that due to these two that means the D and I we can have also these intimate reaction where the interchange is taking place where we have I_a as well as I_d, so dissociative interchange and the associative interchange. So, these associative interchange is taking place if the breaking of the bond between the leaving ligand and the metal is important. So, bond breaking is important in this particular case.

And in the second case which is dissociative one where the bond formation, the bond between incoming ligand that means bond between incoming ligand and the metal is important. So, for these different types of reactions we just now bring the corresponding temperature parameter. So, far we are talking about the corresponding rate law and the concentration change for the different reactive patterns. That means the corresponding X concentration and the Y concentration, the leaving ligand and the entering ligand we are talking about.

Now, if we consider the temperature we can have the corresponding Arrhenius equation. So, Arrhenius equation can play some important role over there where the rate of the reaction k is equal to $Ae^{-E_a/RT}$. E_a is the energy of activation and k is the rate of the reaction and A is the constant or $\ln k$ is equal to $\ln A - E_a/RT$.

So, these basically gives us some of these plots where we can find out that how the corresponding parameters. That means where the k values we know that these are the rate of the reaction which has some dependents on the thermodynamic stability for the corresponding k value that means k forward reaction divided by k backward reaction will give us the corresponding equilibrium constant value. But this particular E_a value is nothing but the corresponding energy of activation in the corresponding potential energy barrier.

How quickly we can cross the corresponding energy barrier in terms of the energy of activation that gives rise to the corresponding rate of the reaction. So, we can have three different types of these plots depending upon the E_a . E_a is a small E_a definitely is a energy of activation with respect to the enthalpy of the reaction. If the enthalpy of the reaction is less that means ΔH is less and which is less than 0 we can have a corresponding large equilibrium constant, because we know that if we have ΔH is less than 0 we can talk about the corresponding ΔG also.

Because these ΔG is related to ΔH through $T \Delta S$ and the temperature effect is on the entropy term, but this corresponding heat of reaction is directly related to the corresponding free energy change of the reaction and if this is negative also this is less than 0 or negative. So, we can have the corresponding k value which is a equilibrium constant and these equilibrium constant would be large. So, we have large equilibrium constant. So, whenever we have this ΔH less than 0 our ΔG is also less than 0 and we have large equilibrium constant.

So, in these two first two cases where we have this ΔH is small here also the ΔH is small. So, we have this large equilibrium constant that means it has the thermodynamic stability that means these two cases we are considering as the stable complexes, stable metal complexes. But when we talk about it is kinetic profile we should consider it is corresponding the E_a values the energy of activation, how much you have the corresponding barrier to cross from the left hand side which we have considered so far as $M L 5 X$ to get ultimately to $M L 5 Y$, that means the corresponding product formation.

So, this is the corresponding barrier where it has to be crossed such that you can have in some cases you can have the intermediate and in some other case you do not

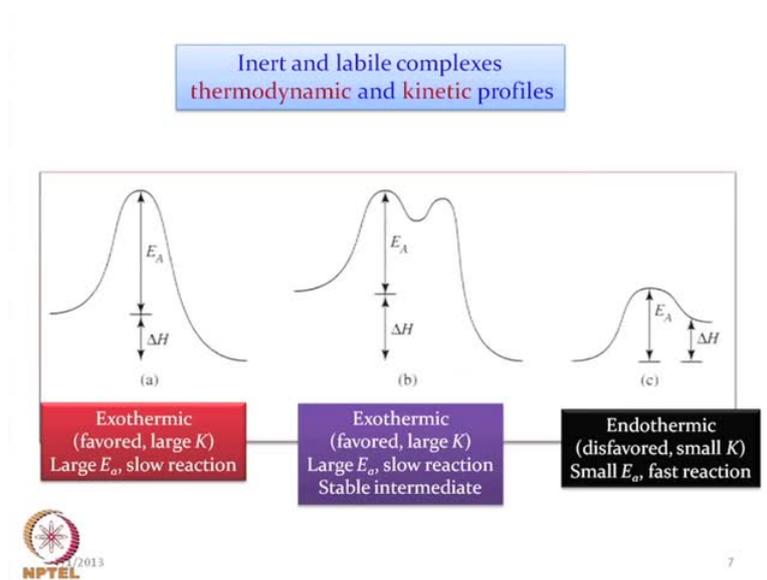
have the intermediates that means if it is the through going through the dissociative mechanism we have the corresponding dissociated form that means the 5 coordinated species is the intermediate. But if it is the associated form that means the 7 coordinated species would be the intermediate. But these two cases the E_a values are large that means we get the corresponding reactions for these as the very slow reactions.

So, we get the very slow reactions for these, so kinetically they are where is as a stable. So, it has large equilibrium constant. So, thermodynamically they are stable, but it is very slow reaction so it is a very inert compound. So, the complexes are typically inert, but in this particular case we have both these cases we have in this where ΔH is greater than 0, ΔH is positive. That means when the ΔH is positive is greater than 0, ΔG is also greater than 0 or positive. So, when ΔH is greater than 0 and ΔG is positive.

So, we have the corresponding k value that means the equilibrium constant is therefore, small. So, it is thermodynamically not very stable. So, it is thermodynamically unstable compound, but what about its corresponding energy of activation? This E_a value compared to these two is also small. So, there corresponding barrier for activation is also small, so if the barrier of activation is small we get a corresponding very fast reaction.

That means it is therefore, a corresponding labile compound, it is, it will react very fast way and the rate of the reaction is also very fast. So, the energy of activation is giving us some idea that whether this particular reaction can give rise to the corresponding separation for these two cases. That means the corresponding energy of activation and that energy of activation can give rise to the corresponding these two thermodynamic and kinetic parameters.

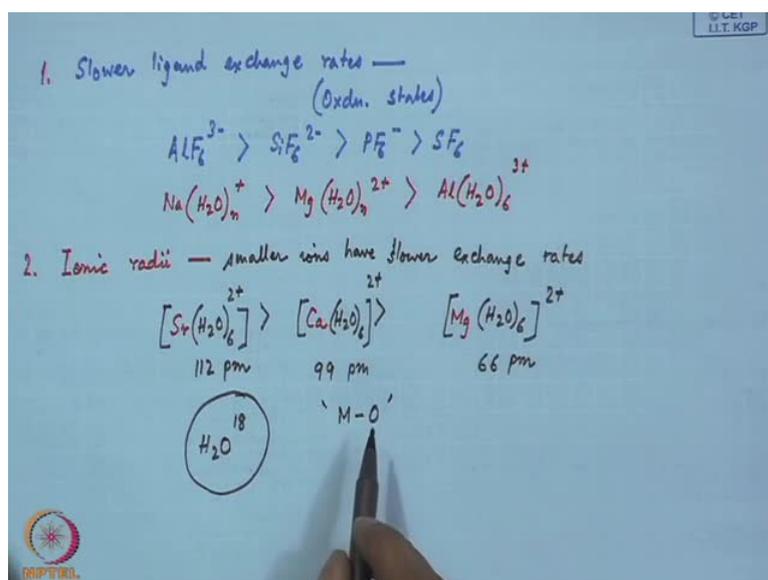
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So, we find that in this particular case we have this exothermic one which is favored as large K , a large E_a therefore, we have a very slow reaction. In the second case we have, this is also exothermic favored by large K large E_a a slow reaction, but it has some stable intermediate. The difference between a and b is nothing but here we do not have some depression, and we have no such stable intermediate, but here in this particular case we have some stable intermediate.

So, we can consider though everything is same, but we can consider that the type of or the nature of the reaction is different because in this particular case we have the stable intermediate. And in the third case we have endothermic reaction because your ΔH is greater than 0. Therefore, the reaction is disfavored which has a small k value, small k value also tell us about the corresponding positive value for the free energy change, but at the same time our E_a value the energy of activation is also small and we get a very fast reaction. So, this basically gives us some important idea about the different types of reactions. So, if we have certain reactions.

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So, you have some slower ligand exchange rates we can consider and which is dependent on the oxidation states. So, depending upon the oxidation states we have very slower ligand exchange rate than the rate of the reaction for the water exchange also and other ligands. So, if it is dependent on simply the oxidation state therefore, the rate of the reaction is greater than for hexafluoroaluminate to SiF_6^{2-} where we have the corresponding oxidation state is different, then PF_6^- which is greater than SF_6 where 6, 5, 4, 3.

So, where we have this particular one where we have the higher oxidation state where the corresponding rate is also slow. Similarly, for the water exchange reaction for these also can change for monocationic sodium which is hard than that of our magnesium aqua compound which is bivalent and which is greater than that of our aluminum 3 plus. So, as we change the corresponding oxidation state so rate of the reaction is also decreasing and we have the highest possible rate of exchange, ligand exchange whether it is a fluoride exchange or water exchange is for the other oxidation state. Similarly, it has also depends on this is case one and this is case two for ionic radii.

So, you can have the ionic radii for strontium we can have the ionic radii for calcium and we can have the corresponding ionic radii for magnesium and all these has some particular order. So, if we consider the corresponding rate for these exchange

reaction so the smaller ions. So, those ions which are smaller that means magnesium is smaller than calcium than strontium, so smaller ions have slower exchange rates. So, the smaller ion is magnesium hexaaqua which is 66 picometer only which is less than calcium 2 plus which is 99 picometer and then strontium which is 112 picometer.

So, if we just consider the corresponding water exchange rate, the rate of water exchange we can consider for the water molecules which are bound to the metal ion to the bulk water molecules which is surrounding the system. And if we then sometime level this water this H₂O can be leveled by O 18, and we can some experiments which we can consider that how this leveled water can exchange with these metal ions.

So, it is typically dependent on the corresponding oxidation state and we can find out the depending upon these basically where we can have the corresponding strong metal oxygen bond. And if the nature of the metal oxygen bond can predict some of the strength for this metal oxygen bonds and the corresponding rate of the reactions. So, in our next class we will consider about the corresponding effect for these trans ligands, how it can control the different rate of the reactions.

Thank you very much.