Rate Processes

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Lecture No. # 25

Reactions in Solutions (Contd.)

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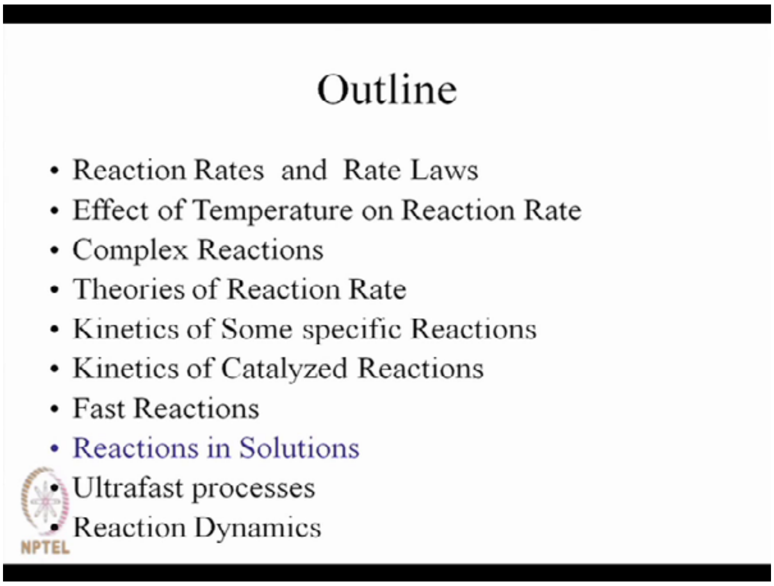

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

Hello good morning everybody. So, today we will continue with reactions in solutions. Now in the last lecture we were discussing associative and dissociative mechanisms.

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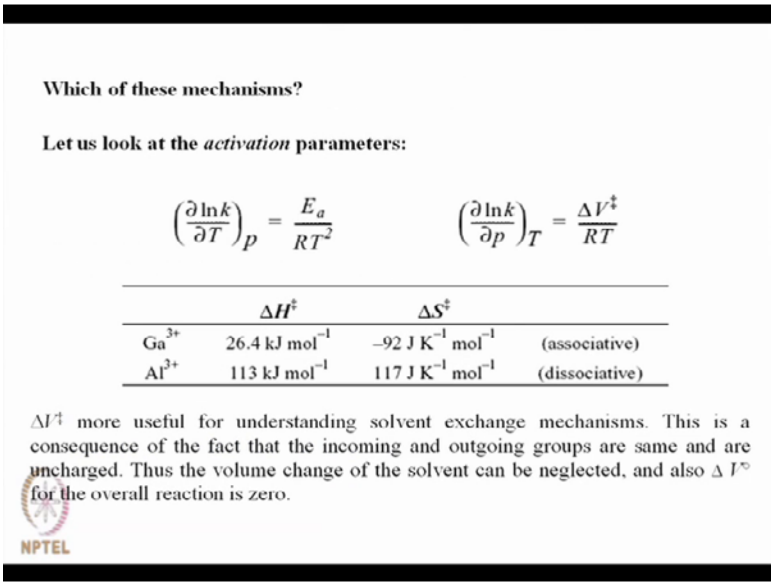

Which of these mechanisms?

Let us look at the *activation* parameters:

$$\left(\frac{\partial \ln k}{\partial T}\right)_p = \frac{E_a}{RT^2} \qquad \left(\frac{\partial \ln k}{\partial p}\right)_T = \frac{\Delta V^{\ddagger}}{RT}$$

	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	
Ga^{3+}	26.4 kJ mol^{-1}	–92 J K^{-1} mol^{-1}	(associative)
Al^{3+}	113 kJ mol^{-1}	117 J K^{-1} mol^{-1}	(dissociative)

$\Delta V^{\ddagger}$ more useful for understanding solvent exchange mechanisms. This is a consequence of the fact that the incoming and outgoing groups are same and are uncharged. Thus the volume change of the solvent can be neglected, and also ΔV° for the overall reaction is zero.

So, associative and dissociative mechanisms for solvent exchange reactions, now we talked about you know this which mechanism is operative. So, in that case we have to look into a this activation parameters and we have to make use of this equations that is a this del del t of l n k P which is equal to activation energy divided by RT square and also del l n k del p T is volume of activation divided by RT and c for means we have got an example two examples that for gallium 3 plus and aluminum 3 plus in one case. You know you know for both of them it is delta H is positive kilo joule 26.4 kilo joule per mol and it is 113 kilo joule per mol and delta S in one case it is minus 92 joule Kelvin inverse mol inverse and in other case it is plus 117 first case for gallium it is minus 92 and for aluminum it is 117.

So, looking at the sign of this delta S activation we can say that the first case of gallium is the associative one. What is associative suppose we have got two entities of this? So, they are they are different. So, entropy wise I mean there are two species. So, entropy is expected to be more compared to when they are combining. So, difference is a transition from this state to this state I mean like let us take this in one case state is this and second case state is this. So, initial state is this final state is this. So, entropy for this transition will be less I mean less means it is a negative it is more it is less so; that means, difference is negative and in reverse case it is like this to that this to that. So, it is less it is more. So, plus I mean positive value.

So, that is why you know we have termed this should be 117 case be dissociative and minus 92 case is to be associative and also we have talked that delta V activation is more useful for understanding the solvent exchange mechanism. This is the consequence of the fact that the incoming and outgoing group when they are same and you know same means if it is water coming and water out. So, there is not much change in volume of activation. So, it is neglected. So, that is for the overall reaction you know delta V activation is close to 0.

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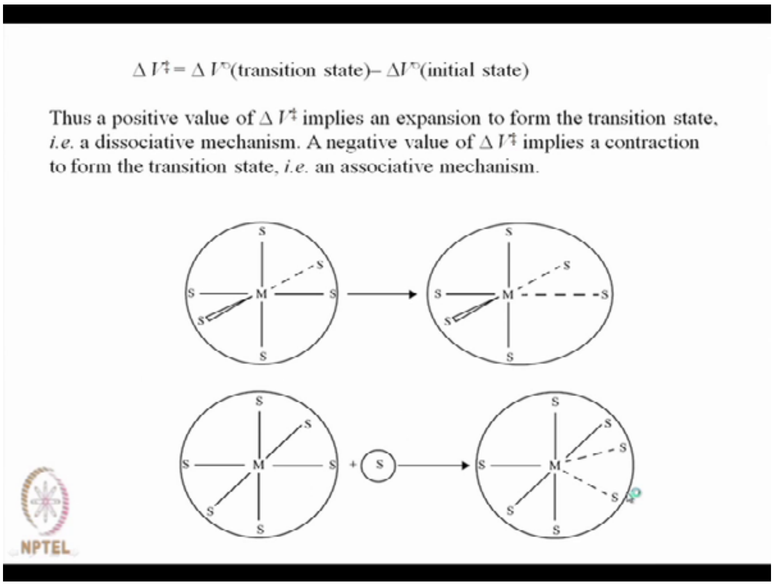

$\Delta V^{\ddagger} = \Delta V^{\circ}$(transition state)– ΔV°(initial state)

Thus a positive value of $\Delta V^{\ddagger}$ implies an expansion to form the transition state, *i.e.* a dissociative mechanism. A negative value of $\Delta V^{\ddagger}$ implies a contraction to form the transition state, *i.e.* an associative mechanism.

Now, volume activation is the volume delta V 0 transition state minus delta V 0 initial state thus for a positive value delta V activation implies an expansion to form the transition state that is a dissociative mechanism. Dissociative mechanism is from here to here and negative value of delta V activation implies the contraction to form the transition that is an associative mechanism. This is an associative mechanism and this is a dissociative mechanism. So, this bond stretched for dissociation. So, you see this initial volume is less final value is more here initial volume is this and plus this one. So, initial volume is total initial volume is more and this is compared to this.

You know this is compared to this is less this plus this is more than this volume. So, just by looking at this delta V activation, we can also predict whether the solvent exchange is a dissociative or whether is a dissociative or it is an associative one.

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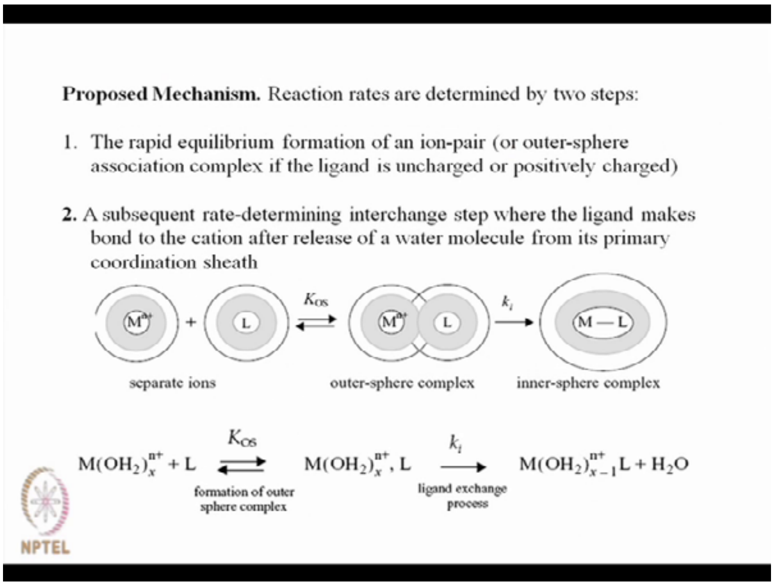

Proposed Mechanism. Reaction rates are determined by two steps:

1. The rapid equilibrium formation of an ion-pair (or outer-sphere association complex if the ligand is uncharged or positively charged)
2. A subsequent rate-determining interchange step where the ligand makes bond to the cation after release of a water molecule from its primary coordination sheath

$$M(OH_2)_x^{n+} + L \underset{\text{formation of outer sphere complex}}{\overset{K_{OS}}{\rightleftarrows}} M(OH_2)_x^{n+}, L \underset{\text{ligand exchange process}}{\xrightarrow{k_i}} M(OH_2)_{x-1}^{n+}L + H_2O$$

So, propose mechanism reaction rates are determined you know determined by two steps rapid equilibrium you know formation of ions. For an ion-pair case say even you are if it is you know your ligand is water or not. So, rapid equilibrium formation of an ion-pair or outer sphere association complex, if the ligand is uncharged or positively charged a subsequent rate determining interchange step where the ligand makes bond to the cation, after release of a water molecule from it is primary coordination sheath. So, this is this is an equilibration formation of the outer sphere complex then you know ligand exchange process. So, separate ions outer sphere complex inner sphere complexation.

So, you know this can be written in this form that M H 2 x n plus x number of H 2 is there with charge n plus ligand formation of an outer sphere complex producing this then ligand exchange process giving rise to M H 2 O x minus L plus. So, water is expelled out. So, initially an out-sphere association followed by you know in the subsequent rate determining step the ligand gets in and water is taken out. So, this is this is the this is proposed or it is a plausible mechanism for this ligand exchange process it may be a water it may be something else other than water as well.

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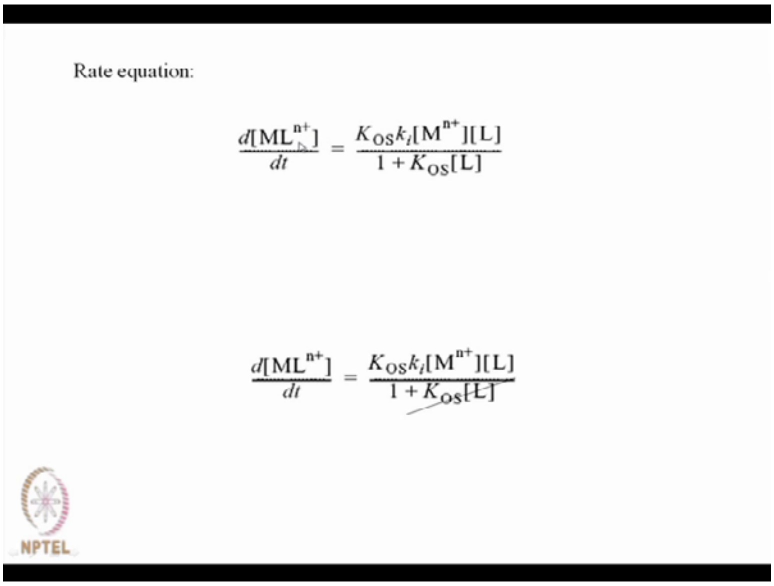

Rate equation:

$$\frac{d[ML^{n+}]}{dt} = \frac{K_{OS}k_i[M^{n+}][L]}{1 + K_{OS}[L]}$$

$$\frac{d[ML^{n+}]}{dt} = \frac{K_{OS}k_i[M^{n+}][L]}{1 + K_{OS}\cancel{[L]}}$$

So, rate equation is this. So, it is a two step process like as I talked about while I was discussing this you know diffusion control reaction where we have got the similar type of expression that d d t of M L n plus. That is rate of you know rate of change of concentration of this which is equal to K o s outer sphere complexation equilibrium constant then interchange. You know ligand exchange rate constant just look into this divided by 1 plus K o s, but when the concentration of ligand is less and generally K o s is small that equilibrium constant is small value then you can neglect see your expression becomes K o s, k i into this. So, it is rate is dependent directly on the metal concentration and also the ligand concentration provided this denominated this part K o s is small.

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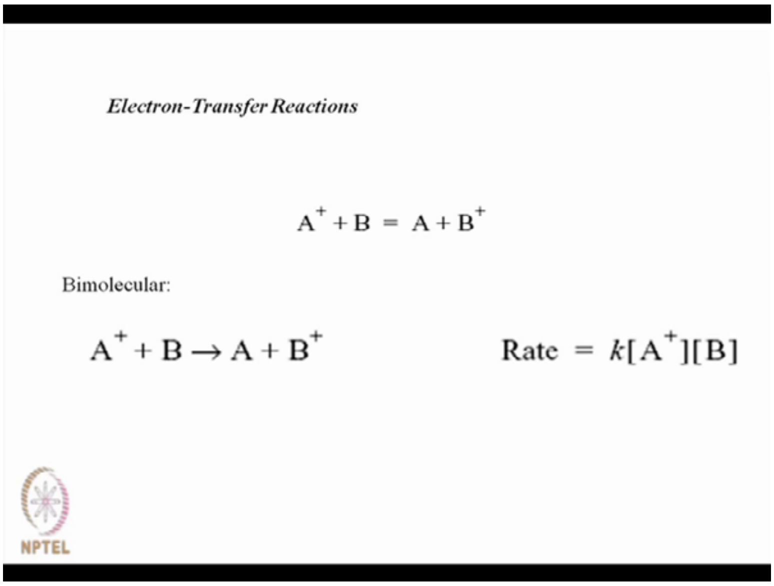

Electron-Transfer Reactions

$$A^+ + B = A + B^+$$

Bimolecular:

$$A^+ + B \rightarrow A + B^+ \qquad \text{Rate} = k[A^+][B]$$

So, this is the rate expression corresponding to this you know this mechanism that is corresponding to this proposed ligand exchange mechanism initially the formation of outer sphere complex then inner sphere complex formation. Then we will move on to electron transfer reactions. So, what is an electron transfer reaction electron transfer reaction is a reaction is typically a redox reaction oxidation reduction reaction there are there are many examples that you can think of say like copper sulfate. Copper sulfate is you know you mean electrolysis you know and copper sulfate solution is electrolyzed and solution and may be molten coppers sulfate and may be molten sodium chloride by using two electrodes then sodium plus is converted to sodium 0.

So, it is the reduction of sodium plus to sodium or may be ferric chloride ferric chloride plus a stannous chloride giving us to ferrous chloride and stannic chloride so; that means, in that case it is a reduction process of ferric to ferrous and oxidation process of stannous to stannic so; that means, what is happening that when it is an electron transfer process one entity is transfer electron to the other. So, the one which is giving out giving the electron to other entity is getting oxidize that is it becomes electron rich. Because it is accepting the electron and it is giving out the electron. So, electron deficient becomes electron deficient or maybe it is oxidation state is increased and its oxidation state is decreased.

That means, whenever there is an electron transfer process you can have a pair of substances or pair of chemicals which undergo oxidation and reduction process. So, electron transfer process is generally therefore, and redox process one entity is oxidized the other entity is reduced. So, this reaction this redox reaction can take takes place in ground state ground state means molecular ground. So, there is the lowest energies that may happen as I told you that ferric to ferrous and stannous to stannic it occurs in the ground state ground electronic state or in some cases this electron transfer may occur in the excited state. So, that is called excited state electron transfer process as what I have talked about you know in case of exciplex formation.

So, it is an excited state complex formation via electron transfer from one entity to other, but not in the ground state it is in the excited state not in the ground state, but in the excited state that is say your molecule fast get excited to the to some level and in the exited state the species has got. You know tendency, more tendency to you know transfer the electron or to excited the electron since excited state properties are lot to more different than the ground state properties it has been found in most of the chemicals, most of the molecules that excited state properties differ considerably from the ground state property.

Because excited state electron distribution within the molecules different that is orbitals different then what is in the ground state that is why the excited state properties are different therefore, excited state electron transfer or electron acceptance in this tendencies are different. So, that is about your exciplex or excited state complex formation.

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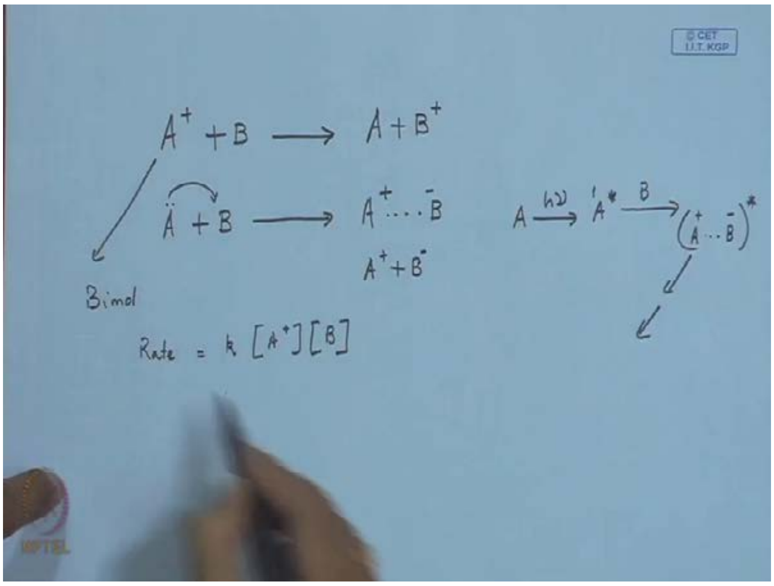

A typically reaction I mean scheme for electron transfer is like this. A plus I mean charge A plus you know A plus I mean plus charge plus B giving rise to A plus B plus or maybe say A plus B. Say electron is transfer from here to here giving rise to A plus B minus or may be A plus B minus. So, it is a by molecular case by molecular reaction. So, rate of the process is equal to k into concentration of A plus into concentration of B. So, if it is an elementary state then since two species are involved therefore, rate is equal to k times A plus into B. And also may be if it is it was an elementary reaction is same you can write. So, this is typical you know representation of an electron transfer process what happens in case of excited state process see we have got a molecule which does not react in the ground state.

Then what we have to do we shine with radiation appropriated radiation it moves on to excited state may be singlet. Then in the excited state, if you have got say some suitable electron acceptance such that. Say maybe electron acceptor of this then you get A B may be plus minus and maybe it is a complex. So, this complex formation occurs in excited state it is just called the (( )) excited state complex and then it will undergo various other reactions may be some photo physical process or may be some photochemical process it will undergo some photochemical and may be some photo physical process. So, this is about your excited state process this is about may be the ground state process electron transfer reaction can happen in the ground state or may be in the excited state as well.

So, depending on this species is concerned it is not that for all species you know ground state electron transfer will take place in some place, it does not found that in ground state there is no reaction, but if you shine with radiation the reaction takes place. Because in that case excited state the redox properties are different than the ground state redox property. That is why you need to excite the sample and then redox properties are altered and then other reactions will automatically occur.

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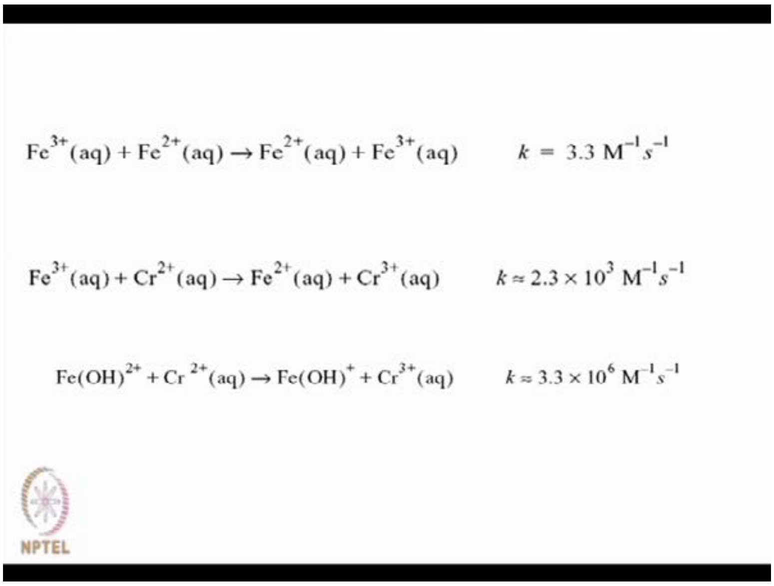

$Fe^{3+}(aq) + Fe^{2+}(aq) \rightarrow Fe^{2+}(aq) + Fe^{3+}(aq)$ $k = 3.3\ M^{-1}s^{-1}$

$Fe^{3+}(aq) + Cr^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cr^{3+}(aq)$ $k \approx 2.3 \times 10^{3}\ M^{-1}s^{-1}$

$Fe(OH)^{2+} + Cr^{2+}(aq) \rightarrow Fe(OH)^{+} + Cr^{3+}(aq)$ $k \approx 3.3 \times 10^{6}\ M^{-1}s^{-1}$

Typical examples ferrous, ferric case ferric aqueous plus ferrous aqueous giving rise to ferrous aqueous, ferric aqueous. There is an electron transfer between you know ferrous, ferric it is 3.3 mol inverse to second inverse. Ferric plus chromium 2 plus chromous then ferrous plus chromic it is a rate of electron transfer is about 10 to the power 2.3and 10 to the power 3 mol inverse second inverse. For ferrous ferric it is 3.3 mol inverse second inverse. Now what happens with ferrous hydroxide with chromous then it becomes I mean ferric hydroxide, if you which 2 plus. It is basically ferric with one which and chromous then you see it is giving rise to F e O H plus and chromic. So, because it is which presents of which you see its values of high 3.3 into 10 to the power of 6.

Whereas, only equated or hydrated ferric is doing in at lower rate. So, therefore, you know this redox properties are very much dependent on you. See from this you can say that since these two although this is iron 3 plus, this is also iron 3 plus, but you see it is the rates are considerately difference means, it depends on the this electron transfer tendency. Electron transfer is very much dependent on the ligand concern not only on the not only on the oxidation state or state for the charge, but also on the ligand present is very important.

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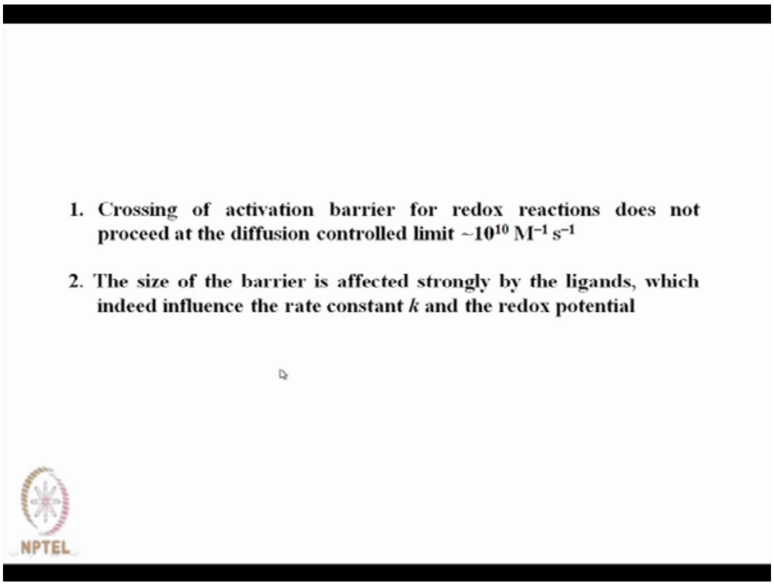

1. Crossing of activation barrier for redox reactions does not proceed at the diffusion controlled limit ~10^{10} M^{-1} s^{-1}
2. The size of the barrier is affected strongly by the ligands, which indeed influence the rate constant *k* and the redox potential

So, the crossing of activation barrier for redox reactions does not proceed diffusion controlled limit say 10 to the power 10 mol inverse second inverse. Also the size of the barrier is affected strongly by ligand, as I told you means from this example the size of the barrier is affected strongly by the ligand which indeed influence the rate constant k and the redox potential. So, ligand play in fight a role in controlling the rate of electron transfer, that is you know crossing of barrier is very much very much dependent on the ligand and also the crossing of activation barrier for redox solution does not proceed at the diffusion control limit. Which is of the 10 to the power 10 mol inverse second inverse this is another, you know observed situation?

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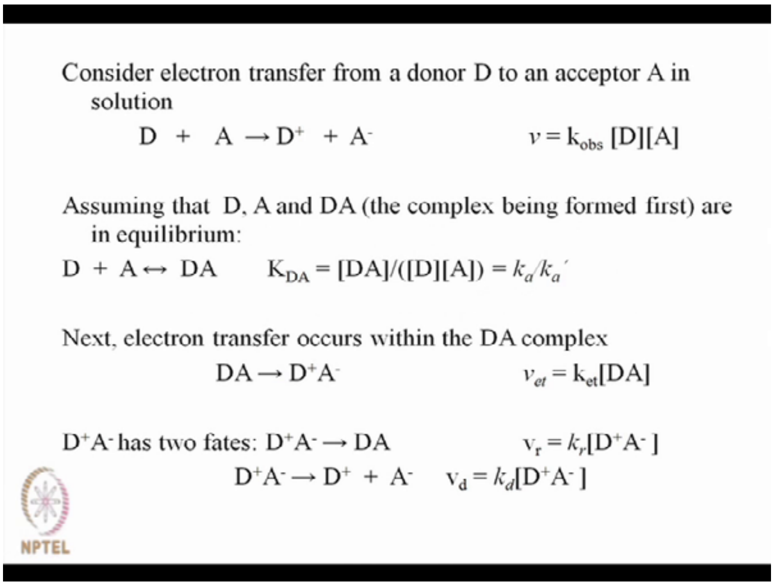

Consider electron transfer from a donor D to an acceptor A in solution

$D + A \rightarrow D^+ + A^-$ $\quad v = k_{obs}[D][A]$

Assuming that D, A and DA (the complex being formed first) are in equilibrium:

$D + A \leftrightarrow DA$ $\quad K_{DA} = [DA]/([D][A]) = k_a/k_a'$

Next, electron transfer occurs within the DA complex

$DA \rightarrow D^+A^-$ $\quad v_{et} = k_{et}[DA]$

D^+A^- has two fates: $D^+A^- \rightarrow DA$ $\quad v_r = k_r[D^+A^-]$

$D^+A^- \rightarrow D^+ + A^-$ $\quad v_d = k_d[D^+A^-]$

Now, let us again consider this electron transfer from a donor to an acceptor D plus and A minus where velocity of the reaction. Velocity of the reaction is since it is an elementary process as I told you started with A plus plus B, but here we are uncharged state to a charged state. So, velocity is k observed into concentration of A into I mean D into concentration a. Also we assume that it is proceeds via formation of D A complex that is donor acceptor concepts followed by electron transfer, that is an equilibrium is establish between A plus D to A D or D plus A to D A and equilibrium is establish then electron transfer takes place to give rise to your D plus a minus. So, equilibrium constant will be like you know this an equilibrium K D A is equal to D A divided by D, A which is your k a divided by k a prime k is the association constant and k prime is the dissociation constant.

Next is the state is the as I told you that it is the electron transfer within D A complex. So, the thing is that these two entities initially will form a complex see this is the complex and then after this is formed. Since now orbital of say donor and orbital of acceptor they somehow they interact proximity, because of the proximity. So, now, it is this interaction is well suited when they form D A complex and then transfer of electron from one to another takes place. So, that is why next is the electron transfer that is occurring within DA complex. So, rate of electron transfer means the rate of reaction electron transfer reaction is basically v electron transfer is equal to k electron transfer into consideration D A.

Now this D A, D plus A minus has to fates one is back electron transfer or reverse electron transfer and then other option is the dissociation. So, dissociation of this D plus A minus. So, moment the electron is transferred from donor to acceptor they become charged one becomes plus another becomes minus. So, there hailed by they are hailed by electrostatic force of attraction and then solvent cage what that will do that will interfere in between. So, that followed by they will separate I mean they solvent inter in between in between D plus and A minus and there attraction force becomes less. So, that they tend to separate out, but in the meantime other situation may happen immediately after the electron is transferred from on to another that is D to A reverse electron transfer may take place or the back electron transfer that may take place.

So, that is defecated here I mean that is written here as v reverse is k reveres D plus A minus. So, that the contact D appear is regenerated the other option is that as I told you that after the electron is transfer they will I mean D plus A minus will separate out producing isolated D plus and isolated A minus. So, that rate is dissociation of your D plus A minus is k d into concentration of D plus A minus. So, what has happened is started with a donor and an acceptor your result is D plus plus A minus separated overall rate is k observe is I mean d observe is k observe tend to D A. So, what is happening that it occurs via formation of a D A complex?

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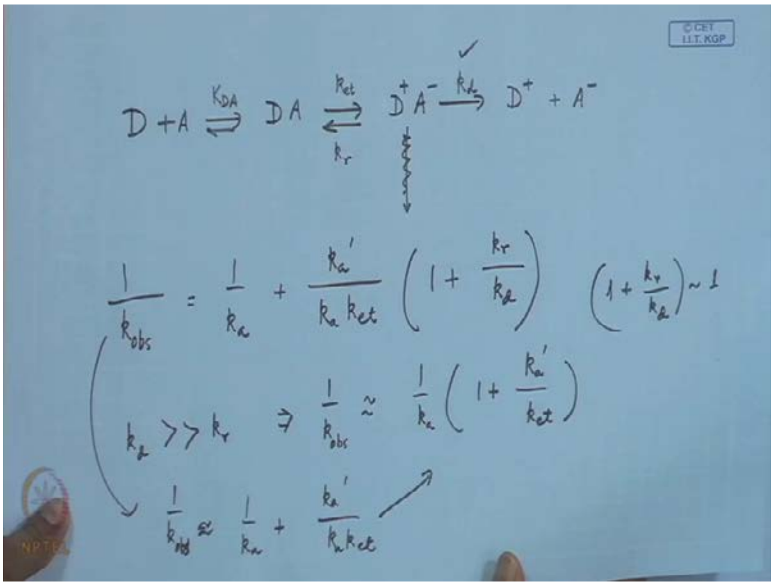

$$D + A \overset{K_{DA}}{\rightleftharpoons} DA \underset{k_r}{\overset{k_{et}}{\rightleftharpoons}} \overset{+}{D}\overset{-}{A} \xrightarrow{k_d} D^+ + A^-$$

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{k_a'}{k_a k_{et}}\left(1 + \frac{k_r}{k_d}\right) \qquad \left(1 + \frac{k_r}{k_d}\right) \sim 1$$

$$k_d >> k_r \Rightarrow \frac{1}{k_{obs}} \approx \frac{1}{k_a}\left(1 + \frac{k_a'}{k_{et}}\right)$$

$$\frac{1}{k_{obs}} \approx \frac{1}{k_a} + \frac{k_a'}{k_a k_{et}}$$

So, like this D plus A, D A then D plus A minus then it has got two option or maybe I can write it like this reverse electron transfer D plus plus A minus. So, it is your k e t this is you k r this is your k d and this equilibration this is you know k D A equilibrium constant.

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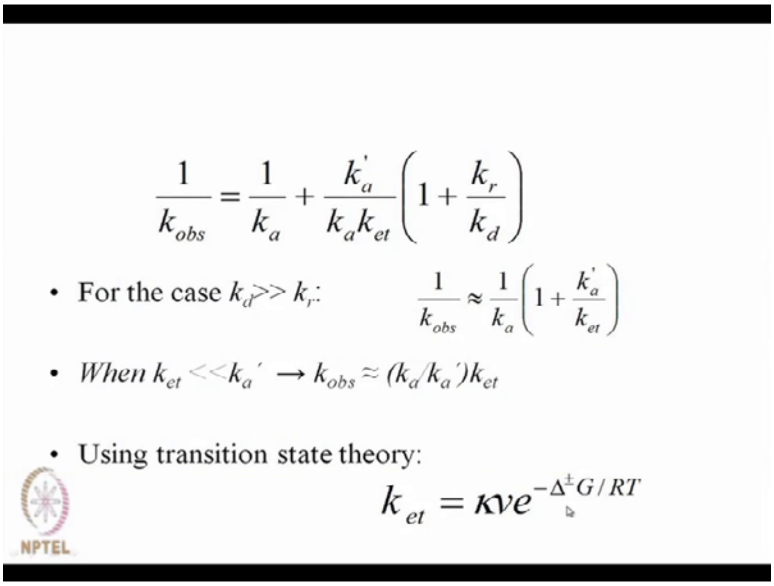

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{k_a^{'}}{k_a k_{et}}\left(1 + \frac{k_r}{k_d}\right)$$

- For the case $k_d >> k_r$: $$\frac{1}{k_{obs}} \approx \frac{1}{k_a}\left(1 + \frac{k_a^{'}}{k_{et}}\right)$$
- When $k_{et} << k_a{'} \rightarrow k_{obs} \approx (k_a/k_a{'})k_{et}$
- Using transition state theory: $$k_{et} = \kappa \nu e^{-\Delta^{\pm} G/RT}$$

So, we can finally, write like this that 1 by k obs equal to 1 by k e 1 by k o b s observe is equal to 1 by k plus k a prime divided by k a, k e t times 1 plus k r by k d. When k d is very greater than k r what is k d? k d is dissociation rate compared to your reverse electron transfer rate k d is much greater than k r. Then what you can write 1 by k 1 by k a into 1 plus k a prime by k a t. When k d is very very greater than k r. So, this is one case given this is high. So, means from this you can you can get this expression with the idea that k d is much greater than k r. When k d is much greater than k r means you know this is negligibly small. This is negligibly small means in that case this one plus k r by k d can be approximated to one therefore, you just you just have this one.

So, this one can be written as one by k obs which is equal to one by k a plus I mean approximated k a prime divided by k a, k e t. Which gives you this one what about the other situation what about the other situation that when k e t is very very less than k a prime. When k e t is very very less than k a prime means what is k a prime? k a prime is the this is the association rate constant divided by dissociation of a.

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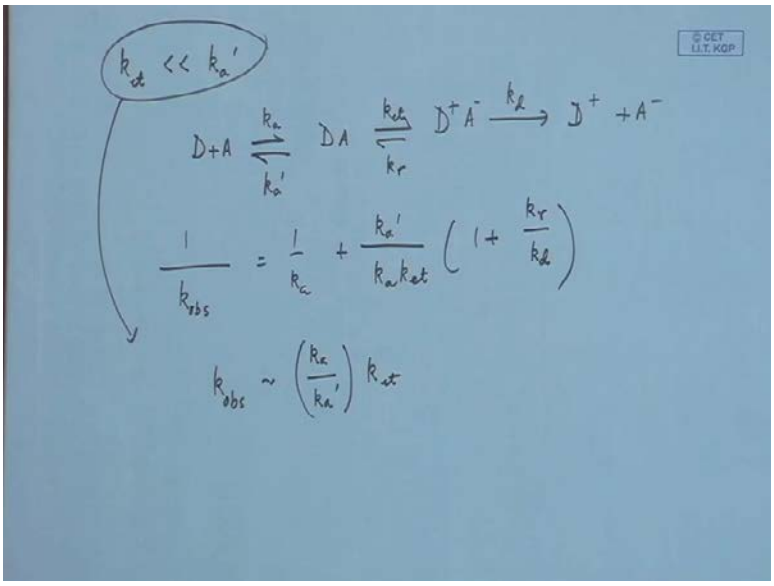

$$k_{et} << k_a'$$

$$D + A \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} DA \underset{k_r}{\overset{k_{et}}{\rightleftharpoons}} D^+A^- \xrightarrow{k_d} D^+ + A^-$$

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{k_a'}{k_a k_{et}}\left(1 + \frac{k_r}{k_d}\right)$$

$$k_{obs} \sim \left(\frac{k_a}{k_a'}\right) k_{et}$$

So, your expression is when k e t is much less than k a prime. So, your original scheme was like D plus A original scheme was D plus A. Your k a and your k a prime D A, k e t, k r, D plus A minus k d, D plus A minus. So, this one this situation this situation means if this one is very high compared to the forward reaction then what would you get your original expression was 1 by k obs is equal to 1 by k a plus k prime divided by k a, k e t 1 plus k r by k d. So, k obs will become in this case after applying this over here k will become k a by k prime into k e t. That means, if k prime is very high compared to this one, and then if this is a very high quantity then compared to other this is major.

So, this part is the major share. So, therefore, this expression can be approximated, that means, 1 by k observed is equal to your k prime divided by k e t just this part. So, that will give you this one and using the transition state theory k e t electron transfer you can write like this like this.

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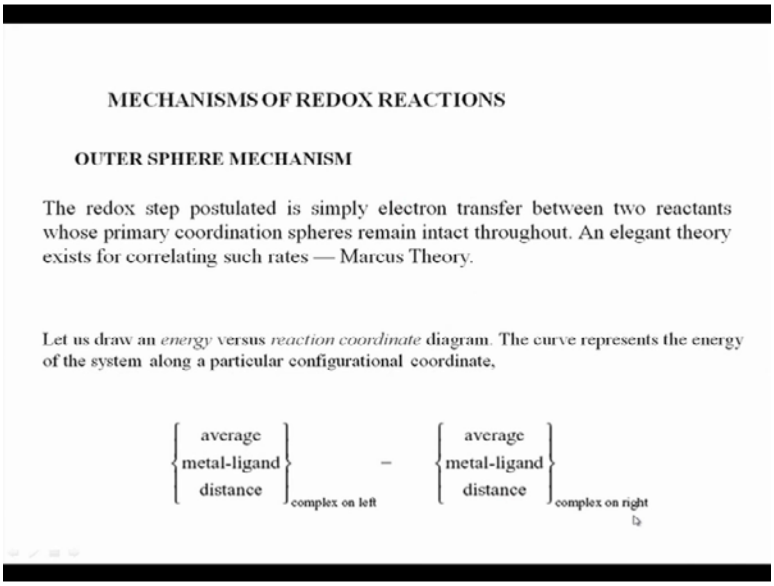

MECHANISMS OF REDOX REACTIONS

OUTER SPHERE MECHANISM

The redox step postulated is simply electron transfer between two reactants whose primary coordination spheres remain intact throughout. An elegant theory exists for correlating such rates — Marcus Theory.

Let us draw an *energy* versus *reaction coordinate* diagram. The curve represents the energy of the system along a particular configurational coordinate,

$$\left\{\begin{matrix}\text{average}\\ \text{metal-ligand}\\ \text{distance}\end{matrix}\right\}_{\text{complex on left}} - \left\{\begin{matrix}\text{average}\\ \text{metal-ligand}\\ \text{distance}\end{matrix}\right\}_{\text{complex on right}}$$

Now, mechanism of redox reaction it is come to mechanism outer sphere mechanism the redox step postulated, simply the electron transfer between reactants. So, primary coordination sphere remain intact throughout an elegant theory is based on you know this coordinating the Marcus theory. So, primary coordination sphere is not affected only the outer part is you know affected. So, it is your outer sphere mechanism, now let us draw energy versus reaction coordinate diagram energy level diagram the curve represents the energy of the system along a particular configurational coordinate. Configurational coordinate will be averaged metal ligand distance, which is complex in the left hand side in your reaction scheme and the averaged metal ligand distance in the complex which is in the right hand side.

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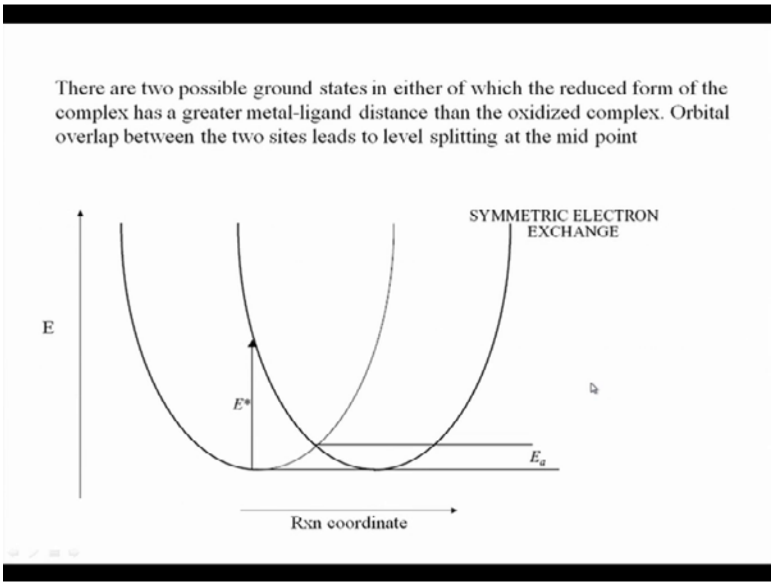

There are two possible ground states in either of which the reduced form of the complex has a greater metal-ligand distance than the oxidized complex. Orbital overlap between the two sites leads to level splitting at the mid point

So, the possible this is your energy this side is energy this side your reaction coordinate and this is your energy of activation and this is symmetric electron exchange case there are two possible ground states in either of which the reduced from the complex has a greater metal ligand distance than the oxidized may be greater. You know metal ligand distance the orbital overlap between the two sites leads to level splitting at the midpoint. So, it is a case of symmetric electron transfer and this is your energy of activation. So, this is E star and then it will move from this potential surface to this potential surface. So, this much of energy has to be applied over here for you know for transition from here to here.

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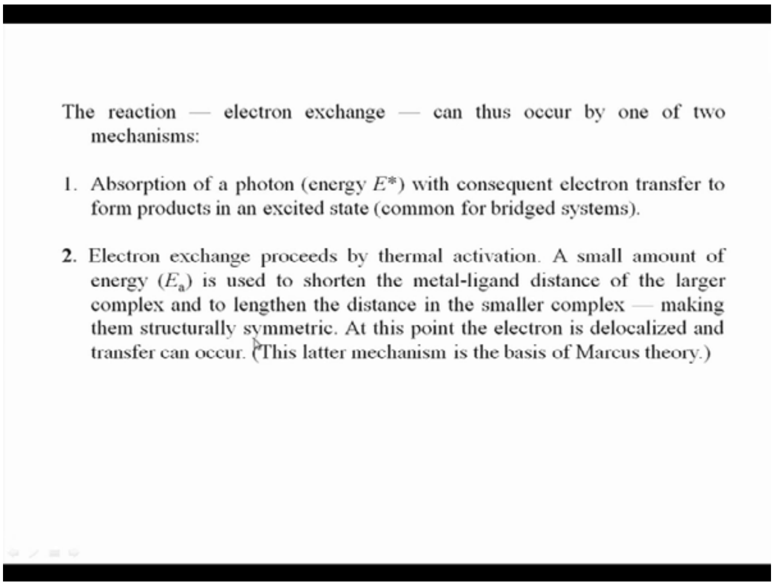

The reaction — electron exchange — can thus occur by one of two mechanisms:

1. Absorption of a photon (energy E^*) with consequent electron transfer to form products in an excited state (common for bridged systems).
2. Electron exchange proceeds by thermal activation. A small amount of energy (E_a) is used to shorten the metal-ligand distance of the larger complex and to lengthen the distance in the smaller complex — making them structurally symmetric. At this point the electron is delocalized and transfer can occur. (This latter mechanism is the basis of Marcus theory.)

So, the reaction electron exchange reaction can thus occur by one of two mechanisms as I told you that may be E star means the amount of energy that may be supplied by a photon or may be or may be by (( )). So, absorption of a photon that is energy E star with consequent electron transfer from product to from the products in an excited state, that is common to the bridged system that is the system absorption the photon and then electron transferred as I told you in case of your that exciplex formation. So, absorption of photon with energy is there by the system is transferred from you know E state of a given. You know oxidation state to another state.

So, that is occurring by electron exchange or electron exchange proceeds by thermal activation. So, it is a photochemical activation small amount of energy is used to shorten the metal ligand distance of the larger complex and to lengthen the distance in the smaller complex making them structurally symmetric at this point, the electron is delocalized and transfer may occur and so, this is the basis of Marcus theory. So, it may be by thermal means or as I told you to may be by a photochemical means. So, electronic exchange may be by this means or may be by the small energy that is supplied from you know thermal energy that is available within the system that is k t.

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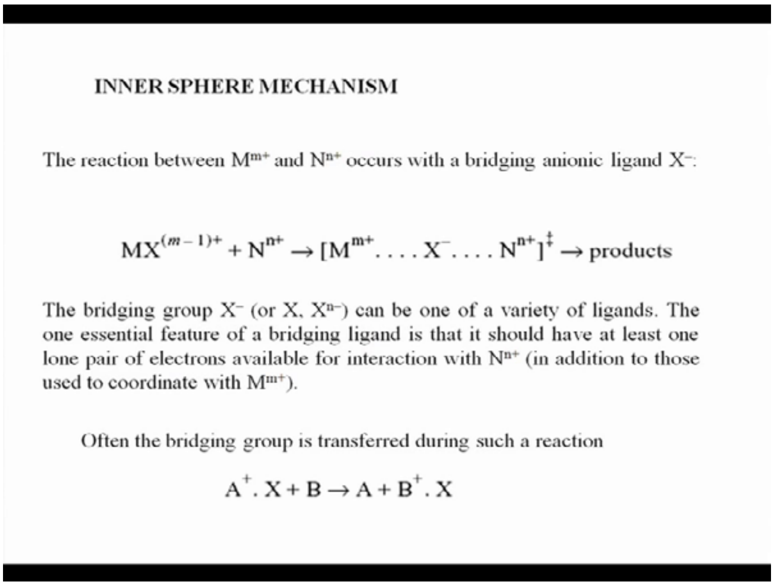

INNER SPHERE MECHANISM

The reaction between M^{m+} and N^{n+} occurs with a bridging anionic ligand X^-:

$$MX^{(m-1)+} + N^{n+} \rightarrow [M^{m+}\ldots.X^{-}\ldots.N^{n+}]^{\ddagger} \rightarrow \text{products}$$

The bridging group X^- (or X, X^{n-}) can be one of a variety of ligands. The one essential feature of a bridging ligand is that it should have at least one lone pair of electrons available for interaction with N^{n+} (in addition to those used to coordinate with M^{m+}).

Often the bridging group is transferred during such a reaction

$$A^{+}.X + B \rightarrow A + B^{+}.X$$

What about the other mechanism inner sphere mechanism the reaction between M m plus plus N n plus occurs with a bridging anionic ligand x minus. So, there is X minus. So, which bridges that bridge may be water I mean O H minus or may be water likes and water like not exactly water; it is not a good bridging one. So, cannot be water cannot be very good and on a some cases there examples, but water compared to which minus is a is a poorly bridging, which minus is a good bridging one the bridging group X minus can be one of a variety of it. The one essential feature of a bridging ligand is that it should be have at least one lone pair of electrons available for interaction with N n plus in addition to those used to coordinate with M m plus.

So, this X minus will coordinate with a pair and then there may be additional pair which will coordinate with n plus. So, it should sufficient option to coordinate with both m and n that is why the bridging group. Bridging group as the essential feature that it should have one lone pair of electrons available for interaction with N n plus, in addition those used to coordinate with N n plus M m plus. So, often bridging group is transferred during (( )) electron transfer process like as I have given over here that A plus dot X, I mean it is it is initially coordinated plus B then electron is you know transferred I mean this one has got transferred from A to B and of course, the electron has been transferred from b to a thereby making A plus to A 0 and B 0 to be plus X. So, I mean it occurs in inner sphere mechanism. So, it happens via you know this reaction happens via bridging ligand X minus.

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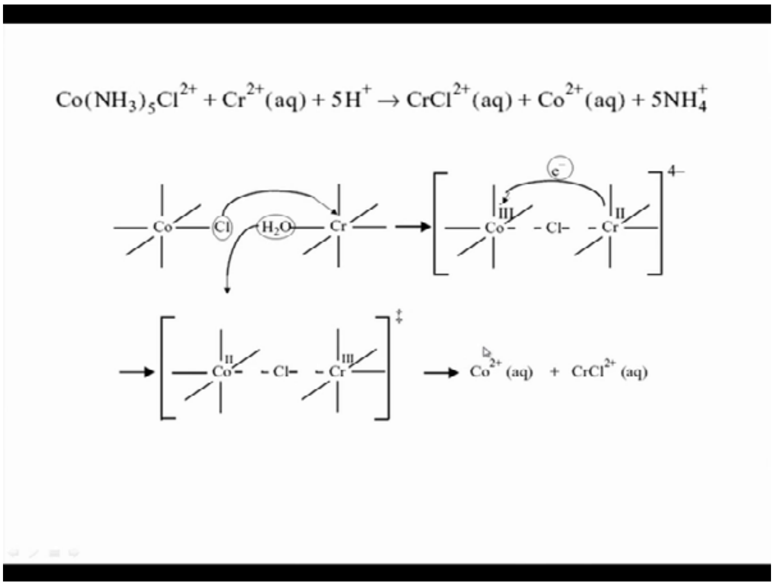

$Co(NH_3)_5Cl^{2+} + Cr^{2+}(aq) + 5H^+ \rightarrow CrCl^{2+}(aq) + Co^{2+}(aq) + 5NH_4^+$

Now, typical example I am (( )) over here is say is a cobalt N H 3 plus C l 2 plus plus chromium 2 plus equated plus 5 H plus giving rise to this. So, what is happening over here you know this chloride this is coordinating over here? So, chloride has got I mean chlorine has got lone pair of electron. So, if you see as I mentioned over here that at least it should have at least one lone pair of electrons available for interaction with N n plus, in addition to those used to coordinate with M m plus. You see here this chloride is already coordinate to cobalt. So, now, it has got a lone pair. That lone pair is given to here, I mean this outer circle. You know represents here lone pair I mean electron cloud and of course, lone pairs are present.

So, that lone pair is donated over here and of course, this bound will be a little strengthens, because now this is going to become a bridging ligand. So, it comes over here and then automatically, you know it is a kind of you know as I told you like associative mechanism kind of thing, the moment the chloride comes they this bound may be lengthen and then it is this water is expelled. So, this attacks over here then water is expelled it is you know kind of you know (( )) to although it is not from the may not be from back side. So, that happens and then now what is happening that because of this bridge formation these two interacting entities are now in close proximity.

So, now, it is good time for them to transfer electron because they are now in close proximity, because in some cases solvent mediated electron transfer may happen, but probability wise that is less, but with the one which is more probably that when this interacting entities are made to come close to each other then this electron transfer is rather electron transfer from here to here. This is happening because of say such bridging interaction. So, for sometime this chloride will tend to bring these two entities here like cobalt and chromium in proximity and then electron is getting transferred. So, electron is getting transferred. So, this is the typical transition state that chloride is bridging one. So, after this transferred initially cobalt, it was cobalt 3 chromium 2.

Now it is electron transfer means it is getting oxidized and it is reduced. So, redox reaction, I mean electron transfer has occurred via this bridging chloride and then ultimately this will separate out. So, of course, it will separate out and ligand lids cobalt as I told over here that often bridging group is transferred during reaction. So, the example here is you know this bridging group is transferred over here. You see also this bridging group initially; it was associated with cobalt now it is a part of chromium. So, bridging group is transferred from cobalt to chromium along with the electron transfer, which results in redox between cobalt 3 chromium giving rise to cobalt to chromium 3.

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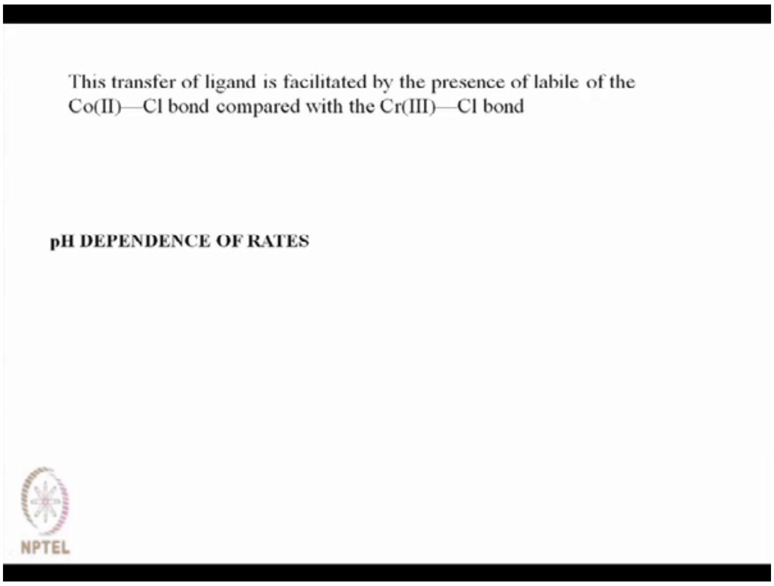

This transfer of ligand is facilitated by the presence of labile of the Co(II)—Cl bond compared with the Cr(III)—Cl bond

pH DEPENDENCE OF RATES

So, this transfer of ligand facilitated by the presence of you knows this does not always happen. So, the moment this chloride is a part of chromium you know this transfer is possible, because of the labile cobalt chloride bond compared with chromium cobalt. I mean chloride bond cobalt 2 chloride bond is more labile compared to chromium chloride bond. So, depending upon whether this bond is stronger or this bond is stronger the ligand, I mean the bridging ligand will either remain to it is original side or maybe it is transferred to other side. So, this there are there are plenty of examples that you may find in literature or may be in many books where you will be finding bridge, you know involvement of bridging ligand like. Which minus is also very good bridging ligand, but not you know what it is not that as good as which minus it is poorly bridging.

So, bridging ligand is very important part for you know inner sphere electron transfer process to occur.

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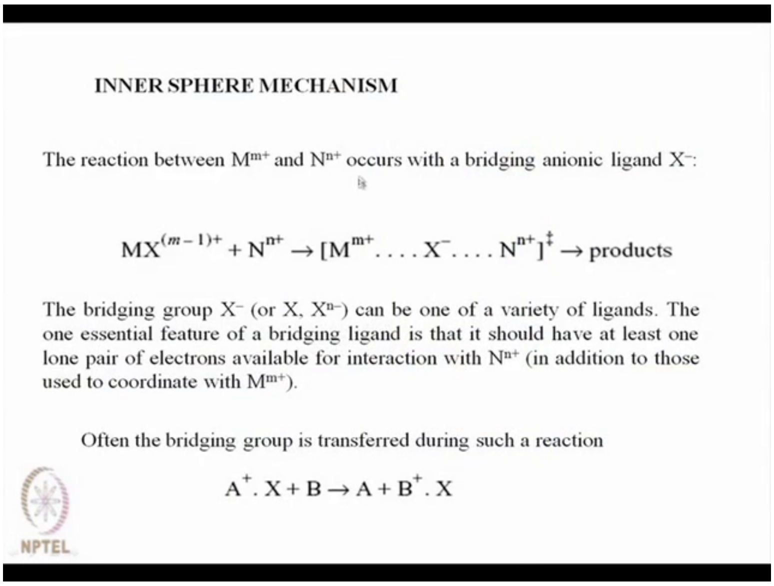

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$$A^+ . X + B \rightarrow A + B^+ . X$$

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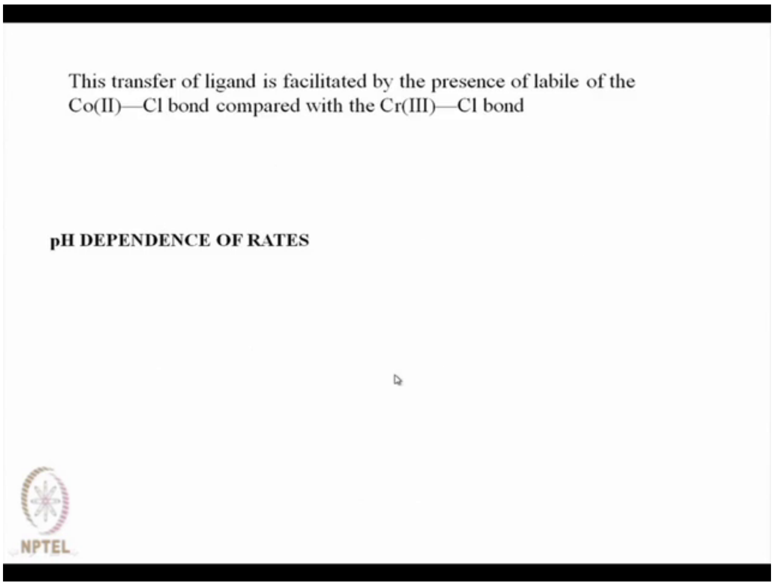

This transfer of ligand is facilitated by the presence of labile of the Co(II)—Cl bond compared with the Cr(III)—Cl bond

pH DEPENDENCE OF RATES

p H each dependent is also this electron transfer is also very much dependent on p H of the medium. So, p H can also play a crucial role in determining the electron transfer it. So, as we have a talked about here that electron transfer reaction is very you know crucial reaction that is the redox reaction. So, in chemical also in biochemical systems electron transfer plays, you know is a very important role now. Because of electron transfer a species is oxidized or reduced and corresponding of the other species is reduced in oxidized.

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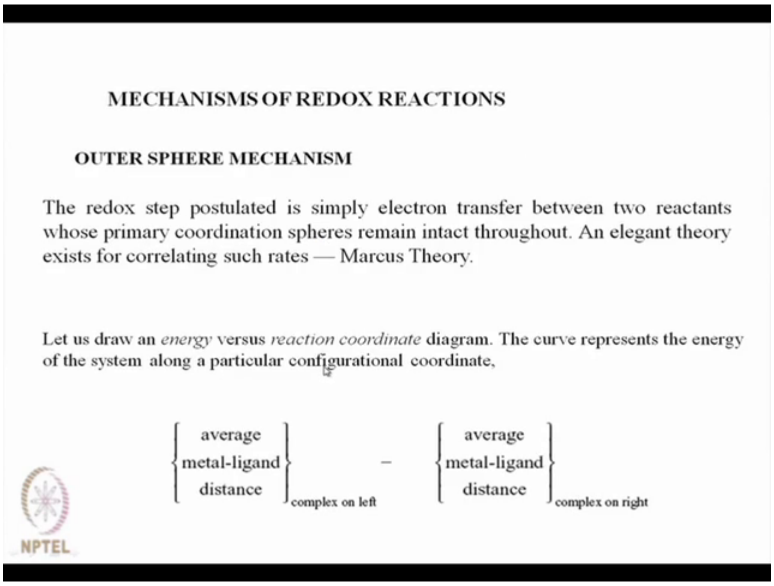

MECHANISMS OF REDOX REACTIONS

OUTER SPHERE MECHANISM

The redox step postulated is simply electron transfer between two reactants whose primary coordination spheres remain intact throughout. An elegant theory exists for correlating such rates — Marcus Theory.

Let us draw an *energy* versus *reaction coordinate* diagram. The curve represents the energy of the system along a particular configurational coordinate,

$$\begin{Bmatrix}\text{average}\\ \text{metal-ligand}\\ \text{distance}\end{Bmatrix}_{\text{complex on left}} - \begin{Bmatrix}\text{average}\\ \text{metal-ligand}\\ \text{distance}\end{Bmatrix}_{\text{complex on right}}$$

So, you will be finding a plenty of biochemical reactions like you know in case of respiration. So, what I mean oxygen is used to oxidize and as a result of oxidation enormous amount of energy is released. So, that is also a redox process which occurs you know inside our ceels. So, energy is released and that energy is used up used up for doing some work and that is why you eat and we gain energy out of the food. So, in biochemical reactions or biochemical processes this electron transfer processes is a very crucial reaction apart from other. You know very I mean there are other reactions like hydrolyses then I know may be ligation or whatever.

So, those are those are also important, but this reaction specially in respiration is very very important reaction and apart from this biochemical processes may be chemical for chemical processes as well redox reaction play a paramount role may be industrial processes this you know electron transfer reaction is a very important reaction. Let us come back and what we have learnt over here in you know this under the heading reactions in solutions. Now we have talked about this solvent exchange reaction associative or may be dissociative solvent exchange reactions.

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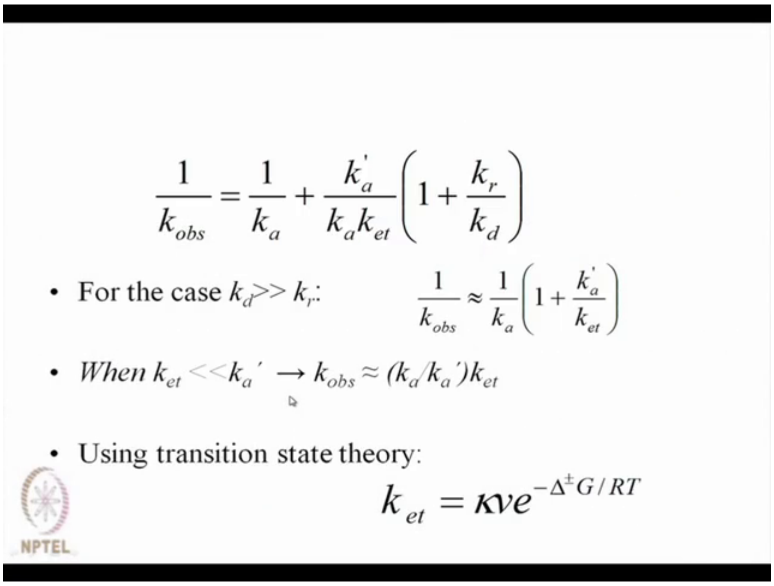

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{k_a^{'}}{k_a k_{et}}\left(1 + \frac{k_r}{k_d}\right)$$

- For the case $k_d >> k_r$: $$\frac{1}{k_{obs}} \approx \frac{1}{k_a}\left(1 + \frac{k_a^{'}}{k_{et}}\right)$$
- When $k_{et} << k_a' \rightarrow k_{obs} \approx (k_a/k_a')k_{et}$
- Using transition state theory: $$k_{et} = \kappa \nu e^{-\Delta^{\pm} G/RT}$$

Now we can identify by looking at the activation parameters with that the reaction is an associative solvent exchange or it is a dissociative solvent exchange and by the use of the thermo dynamical concept of entropy the entropy is basically nothing, but it is a major of degree of disorder. So, when activated complex is formed if it is an associative mechanism; that means, may be more than one species they combined to form an activated complex. So, initially you have two finally, you have one. So, there are you know more option for this two molecules, I mean the system can be represented in many ways that is there are many ways of realizing the system, but when it is only one species that ways will be reduced.

When it is an associative case then of course, entropy is reduced because entropy is a measure of degree of disorder. So, when it is associative reduction in entropy when it is dissociative more species increase in from this we can find out. You know looking at that activation parameter, we can find out you know whether it is an associative or dissociative and from the volume activation. We can also from the volume activation; we can also know whether when it is a negative or whether it is value is positive. Can you know find out whether it is an associated or associative or dissociative process?

We have talked about the proposed mechanisms the rate equations then we jumped on to an electron transfer reaction. This is a very important phenomenon in especially in solution phase. We discussed that with you know several examples and we also talked about you know their you know kinetics and how that can be affected factors that is going to affect and different situations like when k d is very very greater than k r or when k electron transfer is very very less than k dissociation of your accepting a contact complex. We also try to know understand the various mechanisms with outer sphere or may be inner sphere and possible means of reaction, whether it is you know absorption process I mean whether it is by absorption of photon or by thermal means inner sphere mechanism.

We also try to explain and in that case we have taken the example of this where chloride is acting as a bridging ligand for facilitating electron transferred and the end of reaction chloride is getting transferred from cobalt to chromium. So, that is all about electron transfer reaction. Next in the in a next piece of lecture we will talk on electro kinetics because electrochemical reactions that is occurring at the electrodes because you know at the electrode electron transfer takes place of metal ion becomes metal or metal dissolves into solution. So, that is a very important reaction, which is I mean important part of kinetics study that is the kinetics of reaction that is occurring at the electrode.

So, we will take up that in the next lecture that is the electrode kinetics. So, that is all for today.