Advanced Chemical Thermodynamics and Kinetic
Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 35
Introduction to solution phase reactions dynamics 05

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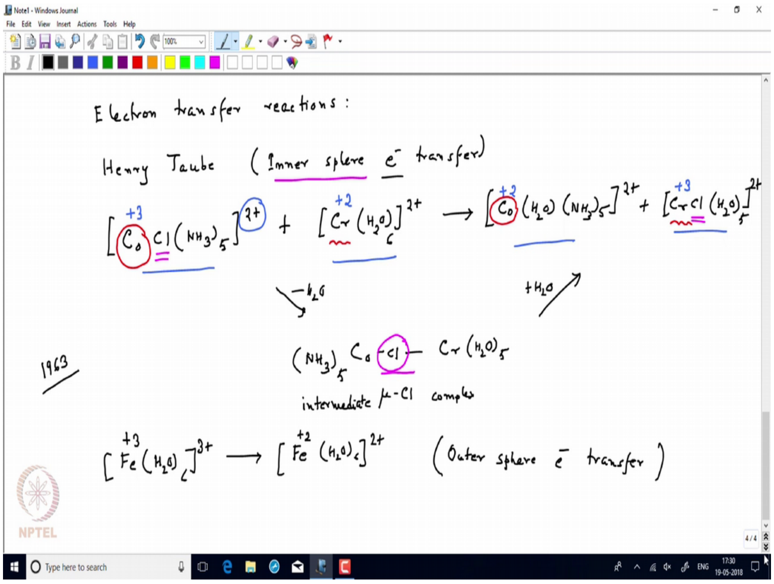

Electron transfer reactions :

Henry Taube (Inner sphere e^- transfer)

$$[\overset{+3}{Co}Cl(NH_3)_5]^{2+} + [\overset{+2}{Cr}(H_2O)_6]^{2+} \rightarrow [\overset{+2}{Co}(H_2O)(NH_3)_5]^{2+} + [\overset{+3}{Cr}Cl(H_2O)_5]^{2+}$$

$-H_2O$ $+H_2O$

$$(NH_3)_5Co-Cl-Cr(H_2O)_5$$

intermediate μ-Cl complex

1963

$$[\overset{+3}{Fe}(H_2O)_6]^{3+} \rightarrow [\overset{+2}{Fe}(H_2O)_6]^{2+}$$ (Outer sphere e^- transfer)

Let us now, start the discussion on electron transfer and electron transfer as we will see this kind of reactions are also dynamically influenced by the solvent. So, for electron transfer reactions, the mechanism for electron transfer reaction particularly involving these are transition metal ions was proposed by Henry Taube and this kind of mechanism is known as inner sphere electron transfer. I am just writing instead of electron, I am writing e minus.

Now, what is inner sphere electron transfer? So, let us consider an classic example, let us say these cobalt complex, cobalt chloride 2 plus and it reacts with chromium en cyclo complex to give rise to cobalt 1 water ammonia 5 2 plus plus chromium chlorine H 2 o o 5 these two these to whole 6 2 plus all right.

So, let us first figure out, which one is the oxidant and which one is a reductant in this equation. So, if you look at the cobalt complex first. Now you see there is a 2 plus charge and so, the chloride it is a negative 1 ammonia, is a neutral ligand. So, definitely the cobalt is in oxidation state of plus 3, now for chromium, it is very straight forward because water is a neutral ligand. So, chromium is in oxidation state of plus 2 this complex.

Now, in the product as you can see cobalt water and penta amine. So, these are all neutral ligands so, cobalt is oxidation state plus 2 and for chromium complex the chloride has minus 1 charge. So, it is in plus 3 oxidation state. So, as you can see that cobalt is undergoing here plus 3 to plus 2. So, it is reducing and the chromium is undergoing an oxidation and what is interesting here, which Taube noted is that these role of this chloride ion.

So, as you can see this chloride atom as if it is in this reaction is mediating the oxidation or reduction and this chloride ion, where it is located? It is located at the first coordination sphere, because this is a ligand directly attached to the metal atom. Initially, it was attached to the cobalt and finally, it is attached to the chromium and then Taube said to the electron transfer, in this case were actually we have redox couple and then the electron transfer is being mediated by this ligand, which is the chloride ligand Cl minus.

So, since it is a ligand, which is actually a part of the inner coordination sphere. So, this type of mechanism is known as inner sphere electron transfer and there actually Taube hypothesized and which was also found later experimentally correct that, some kind of a complex or the intermediate complex is formed, where you have the cobalt. And as you can see in the starting point that, cobalt I have 5 ammonia in the end also cobalt I have 5 ammonia and only thing is that 1 water molecule replaces 1 chlorine.

So, we can write it something like this, similarly for the chromium also as you can see that there are 6 water molecules and there are 1 chlorine and 5 water molecules. So, basically you can think that, this water molecule is basically replaced by the chloride ion and you have a chromium and the 5 water molecules are kind of intact and then you have a chloride ion, which is breezing this cobalt and chromium centers. So, this is called a mu bridging thing because it is the chloride ion is basically connecting the two centers.

So, this kind of mu chloride complexes is an intermediate in this case and as if what it is what is being what is being found here? What Henry Taube proposed is that this chloride atom or this this bridging chloride atom is as if the electron transfer is mediated through this bridging complex, which is mediated by this chloride atom.

So, finally, you will see this water molecule is here, it is being removed as you can see and again, it is being added. So, as if the reaction proceeded through, this pathway and this kind of electron transfer again as the name suggests it is a mechanism, it is obvious from the mechanism that it is mediated by the ligand, which is part of the inner sphere, for this work Henry Taube won the 1963 Nobel prize in chemistry.

But since we talked about the inner sphere electron transfer, there should be something known as outer sphere, but the inner sphere is kind of intact and the outer sphere. Let us just take an very simple example like say for example, this iron oxidation or reduction. So, iron from plus 3 oxidation state gets reduced to iron plus 2 oxidation state and as you can see the ligand of the inner sphere is still intact and this was basically, this kind of reactions which are which were categorized as from as evident from this stoichiometry.

As the outer sphere electron transfer, because people thought that electron transfer is mediated as if some external thing, which is right residing not in the inner sphere, but in the outer sphere, because the inner sphere is still intact, which is the 6 water molecules that forms the inner sphere. So, in this case it is a 3 plus complex, we just redraw it once again and then finally, we have a 2 plus complex and it is kind of a direct electron transfer not mediated by ligand.

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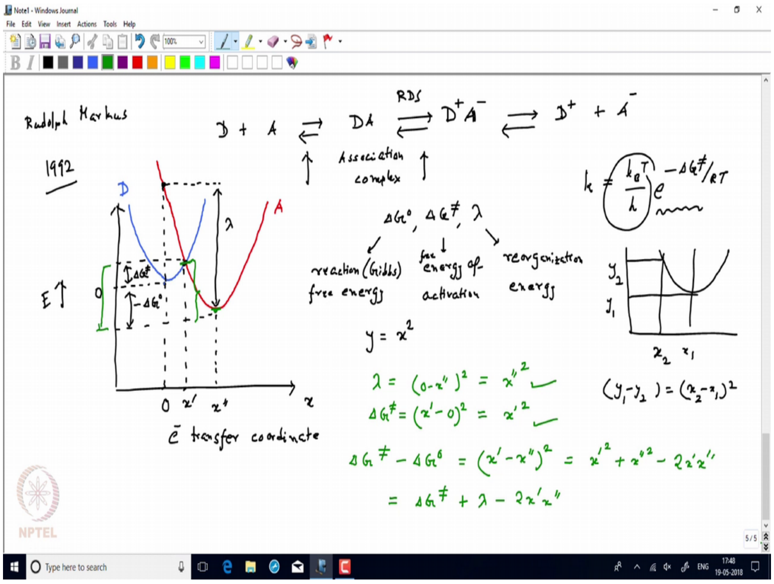

$$D + A \rightleftharpoons DA \xrightleftharpoons{RDS} D^{+}A^{-} \rightleftharpoons D^{+} + A^{-}$$

$$k = \left(\frac{k_B T}{h}\right) e^{-\Delta G^{\ddagger}/RT}$$

ΔG^{0}, $\Delta G^{\ddagger}$, λ

reaction (Gibbs) free energy; free energy of activation; reorganization energy

$$y = x^2$$

$$\lambda = (0 - x'')^2 = x''^2$$

$$\Delta G^{\ddagger} = (x' - 0)^2 = x'^2$$

$$\Delta G^{\ddagger} - \Delta G^{0} = (x' - x'')^2 = x'^2 + x''^2 - 2x'x''$$

$$= \Delta G^{\ddagger} + \lambda - 2x'x''$$

$$(y_1 - y_2) = (x_2 - x_1)^2$$

Now, for this Rudy Marcus actually developed a theory, which is very widely known as the Marcus theory, Rudolph Marcus and this theory was developed in the age 1950's, now this is the same Marcus, who developed the RR KM theory. And there is a connection because, this is also related to the transition state theory, because if you remember the Marcus theory, which we again did not discuss in it is full glory and because of this was very much out of scope for the for this course.

Now, we only showed what at the Marcus expression, but we emphasize that Marcus made a connection of the RRK model, which was based on the model that, we have yes uncoupled harmonic oscillators. So, that model 2, he said basically it is connected, there is a connection with the this harmonic oscillator model with the transition state model and he successfully made that connection.

So, in the electron transfer theory also he basically, borrowed the idea of a transition state and the potential energies for a potential energy surface that, we will see in a moment. So, this was developed in 1950's onward, but for that has got a Nobel Prize in 1992. It took long years because of some reason and we will discuss also what is the reason. Now suppose for any general electron transfer reaction suppose I have a donor and I have an acceptor and what happens is that first the donor and acceptor comes close together and then they form a kind of complex, this is known as association complex.

Now, once this association complex is formed then, there is a electron transfer from the donor to the acceptor. So, then the donor gets a positive charge, because of the electron loss and the acceptor gets a negative charge, because of the gain in electron and then they get separated. So, if the reaction, the rate determining step is this step that the formation of the association complex, then the entered thing is basically controlled how the reactants are coming closer together.

So, again this will be something like diffusion mediated the rate will be diffusion mediated; however, if this is the rate determining step were actually, the electron transfer from donor acceptor is the rate determining step then, actually the question is how depending on the free energies of the donor and the acceptor the rate of the reaction will change and that we are going to discuss. So, you are assuming that this step is the rate determining step, you can actually write it all these steps as a reversible steps in the sense that, there could be association complex and they can fall apart.

There could be electron transfer and there could be back electron transfer on all these things. So, we are assuming this in this case that, the rate determining step is the electron transfer step itself. Now, let us think what are the free energies or the relative free energies for the donor and the acceptor. So, we will just draw a diagram and few notations for that. So, again the donor has some electronic energy, let us say this is a donor electronic energy and I am leveling my energy scale, which is shown here.

As the 0 of energy which were actually the donor energy is minimum and also this ordinate and now this coordinate is the electron transfer coordinate. Now again it could be a combination of many vibrational modes. So, this coordinate is the electron transferred coordinate and this coordinate may be a combination of many vibrational degrees of freedom or vibrational modes. It may not be a single coordinate, but those combinations we are showing if it is a linear combination of this vibrational coordinate, which gives you an effective one dimensional, a reactive coordinate which is the electron transfer coordinate and again where the donor electronic energies are minimum I call that position as say 0.

So, that now the donor will of course, have some vibrational motion with respect to the this reorganization of the solvents around it and I am just assuming here that this vibrational motions are all harmonic in the sense that I have a parabola, this is just like the intra molecular vibration. So, we are this is basically, the same thing applied for the inter molecular vibrations, but the assumption is the same that, I have a harmonic motion there and also I have a harmonic motion here.

So, this is basically the donor parabola. So, I am just labeling it as D, maybe we can use some other color just to make sure that we have a sufficient distinguishing feature. So, this is suppose the donor parabola, this drawing is not very good. So, you can try drawing once again the donor parabola. So, it will be something like this is better and then we also have an acceptor parabola, which is something like this. So, this is acceptor parabola and this is the donor parabola.

Now, again where the acceptor energy is minimum so, that coordinate let us call it as x double prime so, again x is the electron transfer coordinate and e is the free energy and also we see that at a point the donor and the acceptor potential energy surfaces, these are all 1 dimensional potential energy surfaces with the harmonic approximation. And that intersection let us call it as position x prime and now we see that, we have several things.

So, we have also an acceptor minimum, which is somewhere here and since we called that donor energy to be 0.

Let us say that the acceptor is stabilized by an amount which, I am calling is as this energy gap as delta G 0, now delta G 0 is the free energy for the reaction donor to accepter. Now the way I have drawn it actually the delta G 0 is negative. So, that gap or the absolute value of the gap is minus delta G 0 and then again, we will define one more quantity that is how much energy you need for the donor to cross this donor acceptor, I mean cross point.

So, that is kind of the activation energy for this and we will since this is an activation energy, we will use a similar notation. I will write it as delta G dagger notation. So, we have delta G dagger and we have delta G 0, already defined and there is also one more interesting parameter and that is if you think that, if I just excite the donor vertically and if you see that excitation of donor vertically means, it is an electronic excitation again.

So, if I move it vertically, which means actually I am not, I am thinking that the solvents are not reorganizing meaning at this energy, where I have, I mean a cone basically, I draw a vertical line from the donor minimum to a point, where actually just crosses the acceptor then, I see that point means actually this is some energy with respect to the again, the donor this is energy of the acceptor, but this energy is basically the acceptors energy for the same configure same solvent configuration for the donor minimum.

So, basically you can think let me first draw this and label this energy. So, this is this energy and that is known as reorganization energy or you call it as a lambda. So basically, lambda tells it is the energy required for the acceptor to go to the same solvent and vibrational, I mean inter intra molecular as well as inter molecular degrees of freedom so, that tuning of that freedom so, that it has the right configuration of the donor ground state geometry. So, if we supply that much energy from the acceptor to the donor then from the to the acceptor.

Then the acceptor will have some energy, which has the same configuration as the donor has and initially there are a lot of discussion people are thinking that this reorganization energy, how it basically takes into part how the out basically expert into this electron transfer rates and people thought that, if I particularly excite the donor. And I basically reach the acceptor curve then, actually electron transfer will take place, but this is not true because what we will see that usually most of the electron transfer reactions are thermally activated not electronically activity.

But we will still see that these reorganization energy or the lambda actually takes part into the dynamics. So, basically this is the reaction free energy; a free energy of the reaction. So, again this free energy means actually, this is reaction Gibbs free energy delta G dagger is nothing, but the energy of activation or again it is a free energy of activation. And lambda, one of the most important parameter is known as solvent reorganization energy or simply reorganization energy.

Now, we will find a simple relation between these terms and keeping in mind that the rate constant for electron transfer according to the iden equation, which is a transition state theory is given by k B T by h into e to the power minus delta G dagger by acting. And if you remember there was a equilibrium here between these once we did all this interesting calculation and then we showed, when you talked about the thermodynamic interpretation of the activation the transition state theory then, we actually arrived at a relation over actually, we had this kind of relationship at this equation.

Now, this k B T by h again is coming from the iden equation and this delta G dagger is the free energy of activation. So, you all we want is an expression for the delta G dagger with respect to the delta G 0 and then we are done. So, let us now try to figure out or I mean these are all parabolas. So, we can actually write the equation like the equation for parable as you know that is Y equal to x square. So, actually it is Y equal to x square with some constant.

But we have drawn it in such a way that, everything is scaled to one meaning the constant is already absorbed within x. So, then we can write the all the energy equations will be something like Y equal to x square. Now following let us first follow the parabola for which is for say minus let us just try to figure out what is first the reorganization energy lambda. If you follow the acceptor parameter so, suppose let me just draw on this side.

Suppose I have a parabola like this and this is the center of the parabola suppose, this is x 0 and I am asking this question, what is the value at say x 1? So, what do you do is that at the value this thing suppose, this is y and this is basically Y 1 this is y 2. So, I can just write y 1 minus y 2 is nothing, but if I just change the notation here as x 2 and x 2. So, it is basically x 2 minus x 1 squared. So, in the same token I am writing that, y 1 minus y 2 in this case is the lambda.

So, the reorganization energy lambda is nothing, but let me use some different color for the equations. So, the reorganization energy in this case is nothing, but x double prime minus x prime. So, that again, the lambda the x prime here or the other coordinate as you can see it is basically 0. So, let me use the same notation as I am following x prime minus 0 double prime minus 0 square. So, this is nothing, but x double prime square. So, similarly if you this is following the accepter parabola.

Similarly, we can follow the donor parabola and we can easily figure out that this delta G dagger is nothing, but if you follow this thing it will be x prime minus 0 squared. So, that is nothing, but x prime square. So, ideally for this reorganization energy, if we follow exactly the way I have drawn it is basically, the originators x double prime. So, it will be 0 minus x double prime square, but since you are squaring it is the same.

Now, we have already expression for lambda and delta G dagger. So, then what we are left to with is now think about it like what will be this gap. So, delta G dagger plus this negative of this free energy change. So, delta G dagger minus delta G 0 so, basically this energy cap now, we are talking about now following again, we can actually use this for any to evaluate that, since these are all parabolas. So, you can actually use it for any energies.

Now, you can easily see that these following the acceptor parabola, we can say that a n you just follow this x 2 minus x 1 thing. So, this is nothing, but the value of the acceptor parabola here, minus value of the acceptor parabola here. So, all I have to take is that x prime minus x double prime square of that and that I now can expand. So, it will be nothing, but x prime squared plus x double prime squared minus 2 times x into x prime x prime into x double prime. Now, we can actually substitute the values of x double prime and x prime squared.

So, x prime squared I know that it is delta G dagger and then what we have here is x double prime square is nothing, but the reorganization is actually lambda and then, I also have the 2 x x prime. So, that I can just write it as like this, it is not x x prime it is x prime and x double prime.

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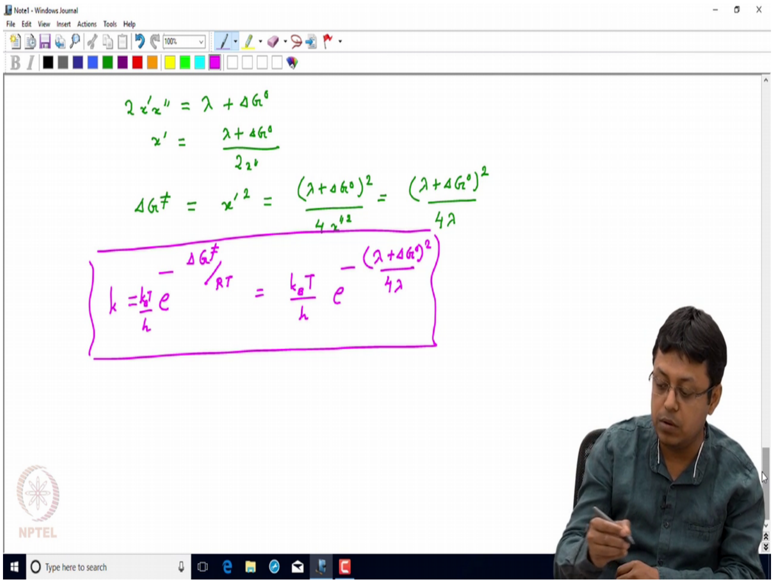

$$2x'x'' = \lambda + \Delta G^0$$

$$x' = \frac{\lambda + \Delta G^0}{2x''}$$

$$\Delta G^{\neq} = x'^2 = \frac{(\lambda + \Delta G^0)^2}{4x''^2} = \frac{(\lambda + \Delta G^0)^2}{4\lambda}$$

$$\boxed{k = \frac{k_BT}{h} e^{-\Delta G^{\neq}/RT} = \frac{k_BT}{h} e^{-\frac{(\lambda + \Delta G^0)^2}{4\lambda}}}$$

So, we can actually get a very simplified relation that, we can see here that this delta G dagger term cancels out. So, what we have is that 2 x prime x double prime, I am just writing the expression for this term is nothing, but lambda plus delta x 0 and then I can solve it for x prime.

So, x prime is nothing, but lambda plus delta G 0 divided by 2 x double prime and x double prime again is nothing, but the square root of lambda, but we are just keeping it like that and. So, x prime is we all we want is this quantity delta G dagger because, remember that we are going to use the adding equation for this. So, this equation, but actually I have delta G dagger. So, the expression for delta G dagger as we see here is nothing, but x prime square. So, I have to take the square of this entire thing, which is lambda plus delta G 0 squared divided by 4 x double prime squared.

But I know that x double prime square is nothing, but the reorganization energy. So, I have to write it as lambda plus delta G 0 squared divided by 4 lambda. So, we have already got an expression for delta G dagger. So, the rate constant of the expression for the rate constant will be k is e to the power of minus delta G dagger by RT or if I am talking about not in terms of 1 mole. So, I can use k B T relation also.

But let us just use the RT expression with k B T by h pre factor. So, this is nothing, but k B T by h e to the power minus lambda plus delta G 0 squared divided by 4 lambda so, this is the expression we get for Marcus theory. Now this is not a very rigorous derivation of Marcus theory, there has been a few approximations that, you make and those are basically, there is no tight coupling between these electronic states of the donor and the acceptor and also this will hold if the donor of the acceptors are not too close with each other.

So, now we are going to see what is what are the consequences of the Marcus theory? Now, everything if I keep on increasing the delta G 0 will how the rate constant behaves well depend on this interesting relationship between delta G 0 and the lambda.

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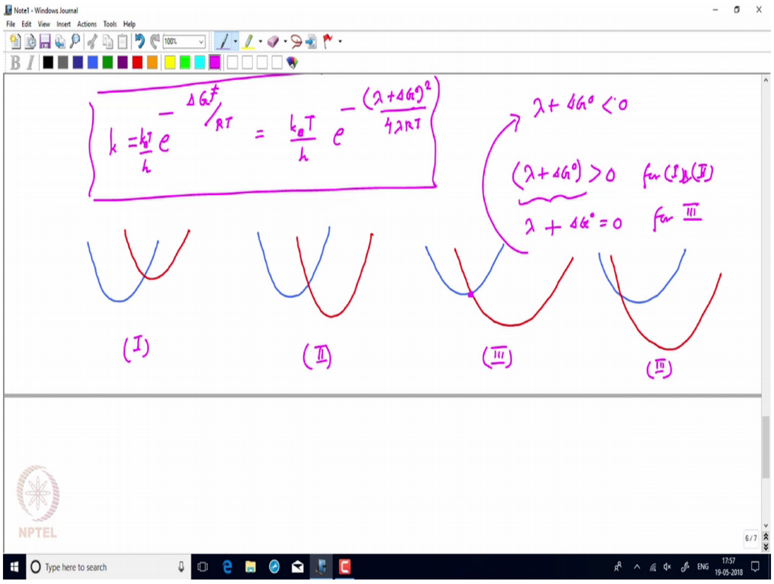

$$\boxed{k = \frac{k_BT}{h} e^{-\Delta G^{\ddagger}/RT} = \frac{k_BT}{h} e^{-\frac{(\lambda+\Delta G^0)^2}{4\lambda RT}}}$$

$\lambda + \Delta G^0 < 0$

$\underbrace{(\lambda + \Delta G^0)} > 0$ for (I) & (II)

$\lambda + \Delta G^0 = 0$ for III

Now suppose we will consider 4 different scenarios where we will be using this Marcus theory. Now, what are these 4 different scenarios? Suppose actually, I have a high negative values for let us say are slightly positive value for delta G 0, now what do you mean by that? So, let us think that the parabolas look like something like this. So, I was using a different color. So, let me also stick to the same color. So, situation number 1 is, I have donor parabola like this and then I have acceptor parabola, which is situated like this and then another situation, where I have the donor like this and the acceptor is like this.

So, in these two cases what we see here is that the, this term which is basically lambda plus delta G 0 this term. So, what is the sign of this term? Now lambda is always positive, now if the way I have drawn here in the first figure as well as in the second figure is that this delta G 0 is positive in the first figure; in the second figure, it is slightly negative. So, if it is slightly negative or positive overall, this term is greater than 0 for 1 and 2.

So, then what will happen, if I increase the delta G 0 in this case? So, the reaction rate, actually decrease because it is a highly negative number as we can see it will be all lambda RT. So, with just the so, that if I just plot the reaction rate with delta G 0, we will see that this zone, if I have relationship between this free energy and the reorganization energy something like that. So, that this term is always positive then, I will have always e to the power minus negative.

So, the reaction rate is not very high. Now the reaction it will become maximum when this lambda is perfectly balancing the delta G 0, now in that case, if I want to draw the parabola it is will be something like this, I have a donor parabola and I have the acceptor parabola right here. Now you can see this is the situation 3, where I have the maximum range. So, the reaction rate will be maximum, but you can think also in this way that, this is basically the cross point is right at the bottom of the donor.

So, I have 0 activation energy and this is very clear from this picture. So, delta G dagger itself is 0 and or mathematically, you say that the activation energy is nothing, but the reorganization energy is nothing, but equal to the negative of the free energy change in this reaction and then, if I move this parabola. So, what I am doing, I mean in this drawing is that I have a donor variable and have an acceptor parabola. So, as if I started to accept a parabola here and then I am actually moving it down.

So, then if I move it from the down then, I am actually, basically, I am increasing the delta G 0 further then, I will hit a very very interesting situation where, I will have a situation like this because I am moving it down the rate parabola. Now you see that in this case, what will happen? The delta G 0 actually is so, high negative that the lambda the reorganization energy is much smaller and the lambda plus delta G 0, together is again negative and then the e to the power this term will again become the negative and then we will have less activation energy.

So, in the fourth case is very interesting now, what do we see here is that the lambda plus delta G 0 again will be very much positive in the sense that in this case, the delta G 0 is highly negative it is not slightly negative and the positive, then actually we will have the positive region of this Marcus theory and then the reaction rate will again fall because.

So, we have the 4 situation here. Now, let us consider the fourth and most interesting situation.

So, before going to that let me actually write the conditions for all of them. So, in the first case, we had first and second case we had this and for the third case, we had lambda plus delta G 0 was actually 0. So, we had maximum rate and now we are considering another situation, but basically we are moving the acceptor parabola much down so, that I have an crossing somewhere here, now in this case delta G 0 is very very negative and if it is very very negative lambda plus delta G 0 maybe, I can write it here for case 4, lambda plus delta G 0 is negative here. And since we are considering actually square of that term again, that is a positive number and then what we will have again the reaction rate will fall as we increase the delta G 0.

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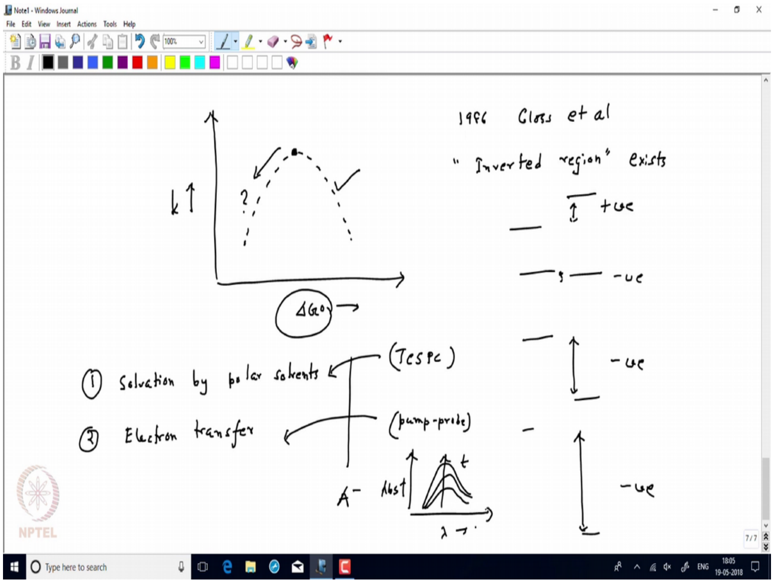

1986 Closs et al

" Inverted region" exists

① Solvation by polar solvents

② Electron transfer

So, if I plot actually delta G 0 versus the reaction rate will have a very very interesting plot. So, this is delta G 0 this is the reaction rate and if delta G 0 is small or negative or slightly negative as is discussed. So, the reaction rate will first increase and then at a perfect positioning of the reorganization energy with respect to the delta G 0 will see a maximum reaction rate.

But then again if we keep on increasing the delta G 0, which means actually this is more and more positive or more and more negative in either case, we will have the drop in the reaction rate. Now this region is basically known as Marcus inverted region and for a long time people found that, when I am having this kind of situation like this situation 1 and 2, where delta lambda plus delta G 0 is positive meaning that, delta G 0 is slightly negative or delta G 0 is positive meaning this region, it was well known to people.

But this region was a question and we had to wait for nearly 30 years to find that actually, there is a inverted region that the reaction rate, it was contrary to the below age 35 decrease the free energy gap. So, probably the reaction rate will increase, but what Marcus theory showed, no actually the reaction rate will again fall in this region not actually increase, if I further decrease the free energy between the reactant and the products. And this is nicely explained in this way we derived the parabolas and then this region was unknown until in 1986 or so when, Claus and co workers found that yes experimentally, they verified that this inverted region in Marcus theory that was explained in Marcus theory or that was basically Marcus actually predicted this version that inverted region exists.

And they found it experimentally and then in 1992 Marcus was given the Nobel Prize in chemistry for this fantastic work. So, let us summarize that what we discussed under this section. So, we talked about the dynamic effect of a solvents and we first talked about salvation; salvation by polar solvents and there we talked about that as what the polar solvents does is that, what a polar solvent does to a solute? Is that it stabilizes its electronic energy states, but this stabilization happens over time.

So, what will happen here, is that if we can collect the emission from each of these state as the system is stabilizing due to reorganization of the solvent, I will get the fluorescence spectrum coming from the blue edge to green and to red edge, which is evolving over time and that time evolution of the fluorescence spectrum directly correlates with the motion of the solvents around the solute molecule.

So, that we know talked about the dynamics of stoke shift or time resolved fluorescence stoke shift measurements and secondly, we talked about electron transfer and under the electron transfer. We talked about first the inner sphere electron transfer when, ligand which is a part of the inner coordination sphere can actually participate directly in the electron transfer reaction as if it is mediated by a ligand exchange. I mean the and by formation of a of a mu bridging complex and as opposed to the outer sphere electron transfer were actually the electron inner sphere is intact, but somehow this electron gate is transferred through space and that was described by Marcus theory.

And where we saw that this Marcus theory shows, I mean very correctly actually, accounts for the fine balance between the free energy and the reorganization energy. So, long story short this free energy between the reactant and the product it does not always mean that, if I have a smaller and suppose what we are discussing. So, far is that whether this free energy thing or let us say, I have a donor and then I acceptor and then if the acceptor has a higher free energy, this was case 1 or slightly negative free energy. So, this was case 2.

And then I have a very high free energy or somewhere actually it is we can actually have the 0 activation energy and then very very high, but actually again I will have a like the decrease in the reaction rate and everything if here in this case, we are plotting with respect to the free energy only, it is negative, it is then more negative and it is more negative something like that and then the crucial factor here is not the free energy alone.

But the lambda the reorganization energy and for all these plots, we said that the lambda is kind of constant in this case and we just vary it the free energy by varying the just vertically moving the acceptor parabola with respect to the donor parabola. And if we do that then, you figured out that at a perfect balancing condition the reaction rate will be maximum, when the reorganization energy perfectly, I mean basically counteracts the free energy of the reaction.

However, if the free energy of the region is even more negative, you will not gain in the red constant in increasing the rate constant actually, the rate constant will drop and that is successfully captured in Marcus theory. So, we stop our discussion on these reaction dynamics the reaction dynamics in solution portion. So, where we have covered a great deal of a reactions starting from the diffusion limited reactions and then we also talked about the reactions between ions and then we talked about briefly the dynamic role of solvents.

And again one can ask how this is measured we did not discuss again this dynamic, how this is measured? One thing we mentioned when we talked about the kinetic measurements is the TCSPC technique and by TCSPC technique one can actually measure the simply by electronics, how to basically get the fluorescence spectrum or construct the fluorescence spectrum at different time. From that you can actually, calculate the salvation time correlation function there are also sophisticated techniques like fluorescence of conversion and many other techniques that we did not discuss.

And the electric on transfer for example, we can study with say pump probe technique, where suppose after electron transfer regenerate and acceptor spaces and these acceptor spaces has suppose characteristic absorption. So, we can initiate the electron transfer with some optical pulse or infrared pulse and then you can actually, watch how this acceptor band is increasing over time. And how this acceptor absorbance is increasing and from that, actually you can calculate the rates of the reaction and you can actually infer you can have a lot of insights regarding the dynamics. So, we will stop our discussion on these reaction dynamics in liquid phase here and then the we will give you an summary of the course afterwards.

Thank you.