Rate Processes

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Lecture No. #24

Reactions in Solutions

Hi, good morning everybody. Today, I am going to talk on kinetics of reactions, which are occurring in solutions. So, before that, let us have a recapitulation of what we have learnt, you know, so far or maybe in the last couple of classes.

So, in our last class we have talked on a new topic, that is magneto kinetics, that is, effect of external magnetic field on chemical reactions and these chemical reactions are, are, you know, between, you know, radical species. So, what you, what you did over there is or what you have heard over there is, that you generate radical species by, by using, you know, brief pulse of radiation and that is, that is your light source from, from, you know, laser source or may be using flash light, you generate, you know, ensemble of radicals, I mean, a collection of radicals and that radicals undergo consecutive other reactions; one after another, it will undergo reaction and produce the desired product.

So, in that case, you know, we have seen, that if we apply external magnetic field depending on the spin orientation that that is, relative spin orientation of the partners of a radical pair, that is, radical pair is consisting of a pair of radicals; it is unpaired spins. So, maybe, both of them up or maybe, both of them down, maybe one up, one down like this. And I have shown using the vector atom model, I mean, vector model for those spins, how you know singlet state or maybe, how triplet state can be generated.

So, singlet state is basically like this, and they are in true sense spin opposed, like if this is your Z direction, then spins are oriented like this, exact line, it is doing this processional motion. So, these 2 spins having, are maintaining a phase difference of, phase angle of 180 degree with respect to one another. But for triplet state, the situation could be like this, could be like this, of course, along this z-axis or it could be like this. So, it is doing the processional motion about the z-axis and in this case, in this last case, the, the difference in phase angle is 0. So, they are maintaining a 0 phase angle. So, this is also a part of your, of your triplets. So, your triplet means 3 states.

And if you apply an external magnetic field, what is happening, that you induce a transition between these states, that is singlet and triplet and depending on the initial spin parentage, if the initial spin parentage is say triplet, that means, either this or that or maybe like this, one of, of these three could be a description of the triplet state. So, if you, if you apply an external magnetic field, that removes the degenerative between these three triplet levels and therefore, two-third of the total triplet population cannot interconvert to singlet, that is, possibility is reduced; only T 0 and S, you know, can do, do this inter conversion.

So, therefore, the ultimate result is, that if it is, it is the, you know, a radical pair, which is of triplet parentage, you will expect more of escape product. More of escape product means cage escape, that is, you will, you will get more free radicals. But, if your radical pair is of singlet parentage, the moment it is generated, it will tend to pair up the spin, that is, pair the spin means, that will tend to form a bond, that is, that is, your recombination, radical pair recombination, very fast recombination is going to take place, where the radical pair is a singlet, is of singlet parentage, I mean, singlet state, starting state is a single. Therefore, on, application of an external magnetic field, we will block the interconversion between singlet and triplet. Therefore, more of singlet state will remain and it will tend to, it will, this will tend to increase the recombination rate.

So, that happened and that happens and I gave typical examples, like you know, typical examples like, you know, using benzophen or maybe benzene, that is, that the, these two molecules, when are micellized in sodium dodecyl sulphate micelle. And then, you shine the sample with laser pulse, then radical pairs are generated. One partner, one of the, of these two radicals is from the ketyl radical, another is from, is the micelle component, that is, micelle transfers hydrogen to this excited state triplet benzophen or triplet benzyl. Therefore, therefore, you know, in presence of external magnetic field, their dynamic behavior has been found to get altered.

So, that means, in this case we have given a demonstration, that although it is known, that in general, that chemical reactions can be part upped by various external factors like pressure, temperature, means, if you increase the pressure, what is going to happen? That the number of effective collisions is increased, that is, collision frequency is increased, therefore reaction rate is enhanced. If you increase, I mean, because of the increase of pressure, what is happening that they are coming close and you know effective collisions are more.

In the same way, when temperature is increased, number of molecules having the minimum amount of energy that is required for crossing the activation barrier is increased and as a result of that, reaction rate is increased. So, that is the general trend and you can explain, that, that behavior using Arrhenius equation, that can nicely explain, why with increase of temperature, reaction rate is getting, getting altered and of course, in a positive sense. So, pressure, temperature, maybe volume, can indeed affect the rate of a chemical reaction.

But the last example, what we have given you, that is the, that is in the case of your, this case of your this spin chemistry. When you apply external magnetic field, it has been found to increase the, increase or maybe, alter; sometime it is increased, sometimes maybe, this recombination is decreased. So, that means, that means, pressure, temperature, external factor like the external magnetic field, if we deal with, you know, magnetic systems, I mean, paramagnetic system or, or, or spins, then you expect and specially when you use the confined system, like your radical pair is generated within the micellar cage, then this effect is very much enhanced, that is, you can indeed see it.

There is another, another example, that formation of exciplex. So, if this exciplex is, exciplex is basically, you know, formation of excited state complex and if that happens as a result of transfer of electron in the excited state, then it is again a case of, it is again a case of radical pair formation. And in and radical pair formation, so when this radical pair recombines, then you get some fluorescence. So, that is your exciplex emission and if you increase or decrease the, depending on if you increase or decrease the external magnetic field strength, depending on whether it is a single one or it is a triplet exciplex, your intensity, that is, fluorescence intensity may get enhanced or maybe sometime may get, should get reduced. So, that is also, also a, you know, case of observation of spin chemistry, that is, effect of external magnetic field on exciplex luminescence.

So, that is similar to this, you know, hydrogen atom transfer. That is, as I talked about in case of benzophen in SDS and of course, it is, it is done in, done using, using the technique of laser flash photolysis. So, so it is, it is a clear demonstration, that external magnetic field can influence this singlet-triplet evolution interconversion and thereby, thereby, your, you know, reaction yield is altered. In the same way, other factors, like say external factors, like ionic strength, pH, can indeed affect the chemical reaction rate.

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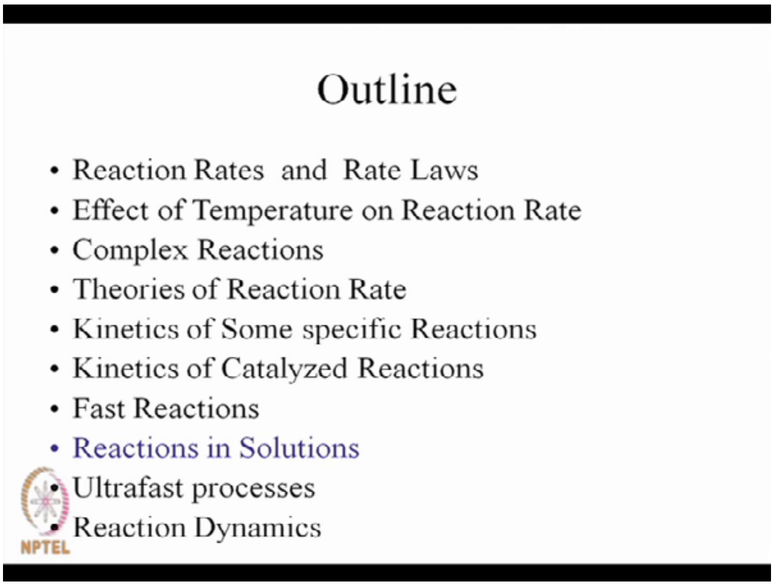

Outline

- 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

So, next, what we are going to talk about is reactions in solution. So, solution reactions are very important because if you think of, you know, reactions, what you study in chemistry, in many cases you encounter solution phase reaction, say hydrolysis of ester giving rise to acid, I mean, if it is an acid catalyzed reaction, then it will lead to acid. And the alcohol, if it is a best catalyzed reaction, then you will get the salt of the corresponding acid. So, the point is and in the same way, means there are other examples, many examples, plenty of examples of this solution phase reaction, as for example, hydrolysis of RX, that is, alkyl halide giving rise to alcohol. It is a bit, is, it is a nucleophilic displacement reaction, that your, that your nucleophile, maybe, which hydroxide, you know, depending on the mechanism, whether it is a sonar SN2. If it is SN1, then initially your carbo-cation is generated and then, this carbo-cation is attacked by, by your base or maybe, a backside attack for SN2 case of your nucleophile, nucleophile, and displacing the halide from, from, from the other side, so this is also another solution phase.

There are, there are also plenty of reaction, maybe, some, it is, it is, these are organic reactions, maybe in organic reactions, reactions of ions, those are very important. So, so, solution phase reaction is very important and it is, it is, you know, characteristically different, that if you think of gas phase reaction and if you think of solution phase reaction, these two differ a lot because solution in, in, in solution phase, you know, your reacting species, that is, your maybe, your molecule, maybe your ions are surrounded by solvent molecules. But in case of your gas phase, you know, it is, it is a rarified situation because it is a gas. Therefore, it is a very dilute; maybe in some cases you can consider this to be a dilute case. I mean, dilute case means, it behaves like a dilute solution, very dilute solution, that, that reacting molecules or atoms or species are far apart and collision maybe, maybe a mode for, for you know, reaction to take place. So, for gas phase reaction they will collide and then subsequent reaction will take place, maybe wall collision in some cases is, is could be very important. So, you know, technically there are, there are lots of differences, you know, between solution phase and gas phase reactions.

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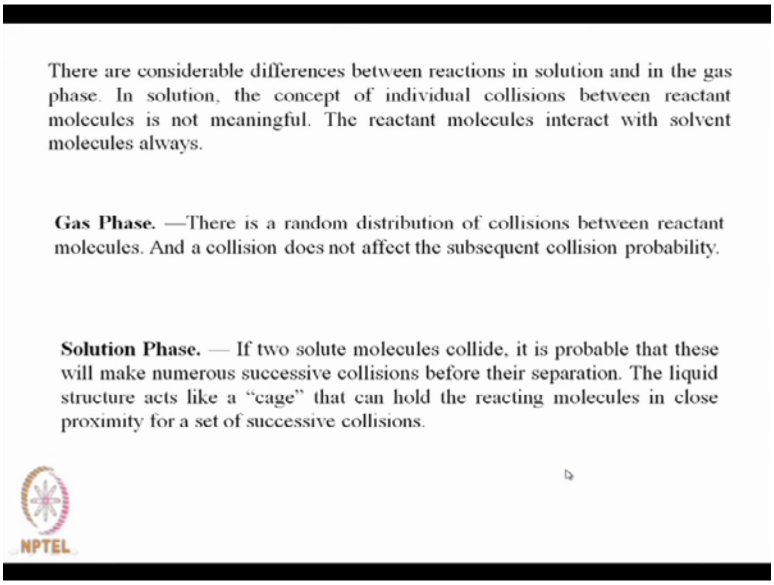

There are considerable differences between reactions in solution and in the gas phase. In solution, the concept of individual collisions between reactant molecules is not meaningful. The reactant molecules interact with solvent molecules always.

Gas Phase. —There is a random distribution of collisions between reactant molecules. And a collision does not affect the subsequent collision probability.

Solution Phase. — If two solute molecules collide, it is probable that these will make numerous successive collisions before their separation. The liquid structure acts like a "cage" that can hold the reacting molecules in close proximity for a set of successive collisions.

There are considerable differences between reactions in solution and in gas phase. In solution, the concept of individual collisions between reactant molecules is not meaningful. Reactant molecules interact with solvent molecules always because it is always surrounded by solvent molecules. Suppose, it is a, it is, if you consider a reaction where there is some, some electrostatic contribution, that is, you know a reaction between ionic species. Ionic species means, you have got, say 1 plus component, 1 minus component or maybe both minus or maybe both plus. So, what is happening, that when they are coming close to each other, if they are opposite, I mean, if they are oppositely charged, then they will be attracted, they will be attracted, I mean, like this; so, the closer the, the more is the attraction. That is, this attraction or interaction is guided by Coulomb’s law. But suppose, if in between these two attractive, I mean, attracting, you know, molecules, solvent molecules enter and suppose the dielectric constant is high, then this will tend to, you know, what is happening, that tend to solvate both the charges. Therefore, solvated ions will result and in that case the, you know, isolated or unsolvated ions and, and a pair of solvated ions, they will interact differently.

Therefore, interaction, if the interaction is occurring in a different, you know, different extent or maybe, interaction is less or more, then of course, the result is expected to be different. That is, interference of solvent in between solvent molecules, in between these two interacting ions or maybe, suppose if you, if you introduce a solution containing lots of ions, then those ions, other ions like, maybe salts, they will tend, this will tend to solvate or maybe, maybe you know, you know, this, this charge or maybe, other charges is surrounded by other ions, as a result of which the effective charge on this, on this ion originally, and that one originally will be, will be altered, will be reduced. So, interaction is naturally less. Therefore, therefore, you know, therefore, they are considerably different, you know.

Now, gas phase reaction, there is a random distribution of collisions between reactant molecules. And the collision does not affect the subsequent collision probability. So, so, random distribution of collisions between reactant molecules, so it is distribution of collision occurs in a random fashion and you know previous collision is not going to affect the later collision. So, there is no, you know, there is no influence. Suppose, they, right now a collision has happened, so that collision is not going to affect the, the next collision with this molecule and other molecule. So, collisions are independent, independently, you know, behaving.

Solution phase, what is happening? It is of course, different from gas phase because it is, it is, you know, your molecules interacting entities are surrounded by, interacting entities are surrounded by, you know, solvent molecules. So, if the situation is, of course, lot different compared to gas phase reaction and gas phase reaction is sometimes very simple, but the moment solvent enters into the, complexity comes into action. Maybe, solvent molecule helps in doing some kind of, you know, transfer, transfer of energy from one entity to another or maybe transfer of one atom to the other; it may be acting as a mediator.

So, if two solvent molecules collide, it is probable, that these will make numerous successive collisions before their separation, it is a probable situation. The liquid structure acts like a cage and it can, it can hold the reacting molecules in close proximity for a state of successive collisions. So, it is acting like a cage. So, once you put a molecule or a, or an ensemble of molecule into, into solvent, say in water, then water will tend to cage it. So, water molecules are in the, in the cage; I mean, the solvent molecules are in the cage of water. So, it will, it will tend to remain over there for a considerable period of time because you know, changing over from one case to another will require certain amount of energy and that may not be available. So, therefore, and that is why, liquid structure acts like a cage and it can hold the reacting molecules in close proximity, say, say like a geminate recombination.

As I talked about in the last lecture on, on magneto kinetics, that when you shine your sample with laser light, the radical pair is generated, I mean, benzophen goes to the excited state, singlet, triplet. This triplet abstracts the hydrogen form micelle and immediately, radical pair is generated. And this radical pair so generated remains within one cage, which is called the geminate cage, I mean, single cage that is called the geminate pair, geminate pair of radicals. So, that means, this radical pair is caged by the solvent or maybe caged by, by the micelle itself. So, these reacting molecules are, are held by the solvent cage allowing successive collisions to take place and maybe, who knows, that out of such successive collision, maybe collisions, maybe, 1 collision will be effective for the reaction to take place. So, in this way, you know, solution phase, that is, solute, I mean, solvent molecules help in, you know, promoting the reaction.

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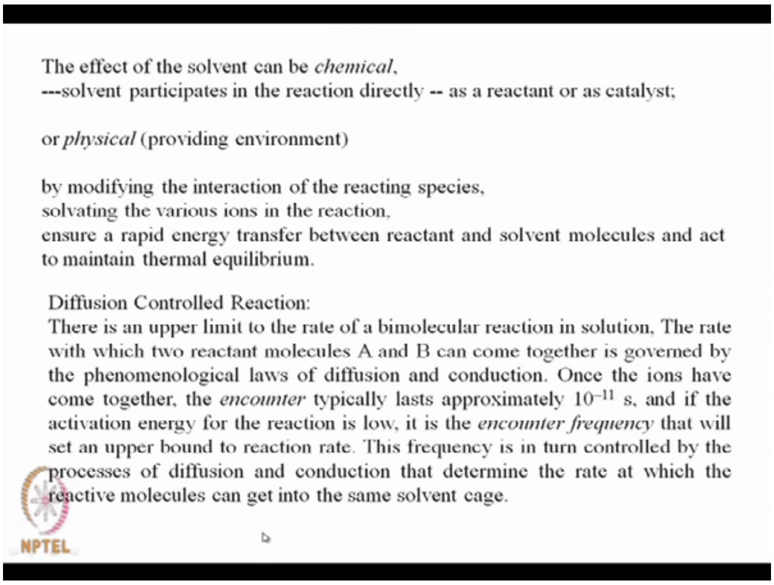

The effect of the solvent can be *chemical*,
---solvent participates in the reaction directly -- as a reactant or as catalyst;

or *physical* (providing environment)

by modifying the interaction of the reacting species,
solvating the various ions in the reaction,
ensure a rapid energy transfer between reactant and solvent molecules and act to maintain thermal equilibrium.

Diffusion Controlled Reaction:
There is an upper limit to the rate of a bimolecular reaction in solution. The rate with which two reactant molecules A and B can come together is governed by the phenomenological laws of diffusion and conduction. Once the ions have come together, the *encounter* typically lasts approximately 10^{-11} s, and if the activation energy for the reaction is low, it is the *encounter frequency* that will set an upper bound to reaction rate. This frequency is in turn controlled by the processes of diffusion and conduction that determine the rate at which the reactive molecules can get into the same solvent cage.

So, effect of solvent, what can be the role of solvent? So, effect of solvent can be chemical; chemical effect means, it may directly participate in reaction. Say, for example, if you add, say water, water with NaOH, NaOH solid, then, what is happening? Heat is generated, sodium plus gets solvated and OH minus also getting solvated. So, you, you generate NaOH equated or maybe, think of, say, say a reducing agent or an agent, which can abstract hydrogen from, I mean, which can, which, which can generate hydrogen from water, say for example, hydrides or maybe, say, you, you, if you think of reaction of sodium with water. So, what is happening, that the moment you add sodium or, or I mean, when the moment sodium touches water, it catches fire. So, that means, NaOH is generated and, and you know, hydrogen is liberated.

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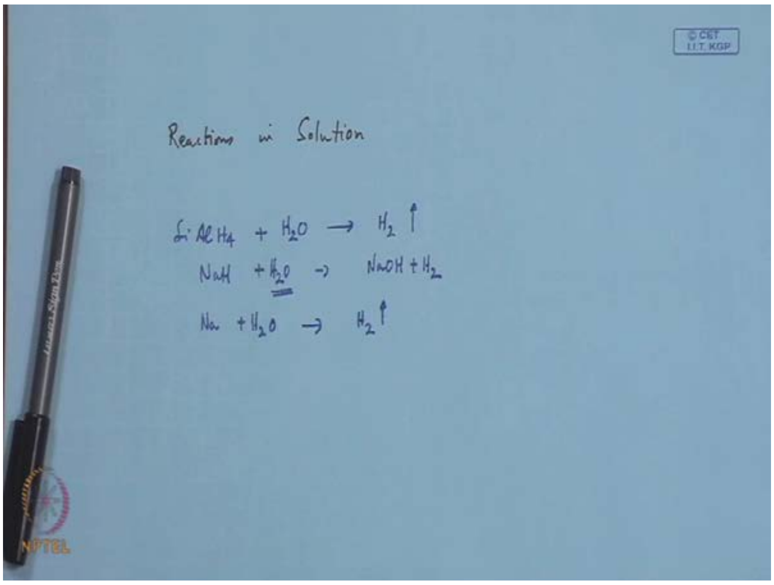

Reactions in Solution

$LiAlH_4 + H_2O \rightarrow H_2\uparrow$

$NaH + \underline{\underline{H_2O}} \rightarrow NaOH + H_2$

$Na + H_2O \rightarrow H_2\uparrow$

So, therefore, so the thing is, that the water, water can itself act as, as your reactant, like say for example, say lithium aluminium hydride. If it comes in presence of water, then hydrogen is liberated and of course, you know, lithium hydroxide or say sodium hydride plus water, so NaOH plus H 2. So, that means, water is acting as, as a reactant or it may be physical. It may be physical, means such chemical reactions may not take place, Na plus water, so you may expect evolution of hydrogen. So, therefore, the point is, it is a case where water is acting as, as, as a, as, as a reactant, so it can, it can participate in chemical reaction directly, it may act as a reactant or maybe, in some cases, the solvent maybe catalyst. So, it, it is regenerated after the reaction, so it may be catalyst or it may be physical. I mean, into you know, involvement is as a physical involvement by modifying the interaction of the reacting species.

As I told you, that the moment you add water, that moment, the moment water is coming in between, you know, reactant species, then the interaction between these 2, these 2 entities will, will get altered, will be altered, solvating the various ions in the reaction in a different extent, say lithium ion is, is getting, you know, solvated in a, in a different way or in a different amount than sodium ion. So, it, it depends on the ionic potential and ensure a, it ensures a rapid energy transfer between reactant and solvent molecule. So, water, say, it, it is providing a cage where, you know, intimate, intimate contact between the reacting molecules and the solvent will ensure the, the transfer of energy in between in between them and act to maintain the thermal equilibrium. So, it, it is acting as a bath, thermal, I mean, maintaining a constant temperature. So, this sort of role solvent can, can perform.

Now, diffusion controlled, for diffusion controlled reactions, which I already have talked about in several occasions, that there is an upper limit to the rate of bimolecular reaction in solution. The rate with which two reactant molecules, say A and B, can come together is governed by the phenomenological laws of diffusion and of course, conduction. So, it is guided by how easily they can diffuse. So, for a reaction to take place, they will have to come close. So, so, if other factors are not important, only this factor is important for the reaction to take place, then the rate is guided by this time required for these entities to come close via diffusion. Once the ions have come together, the encounter typically last approximately for about 10 to the power of minus 11 second and if the activation energy for the reaction is low, it is the encounter frequency that will set an upper bound to reaction rate. This frequency is in turn controlled by the process of diffusion and conduction that determine the rate with which the reactive molecules can get into the same solvent cage. So, therefore, this diffusion of the entities and you know, their conduction is very important and that can set up, you know, set an upper bound to the reaction rate.

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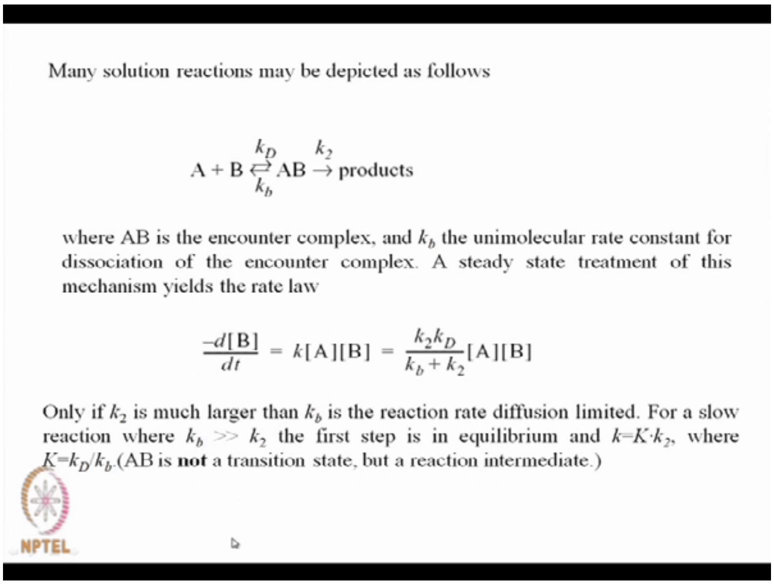

Many solution reactions may be depicted as follows

$$A + B \underset{k_b}{\overset{k_D}{\rightleftarrows}} AB \overset{k_2}{\rightarrow} \text{products}$$

where AB is the encounter complex, and k_b the unimolecular rate constant for dissociation of the encounter complex. A steady state treatment of this mechanism yields the rate law

$$\frac{-d[B]}{dt} = k[A][B] = \frac{k_2 k_D}{k_b + k_2}[A][B]$$

Only if k_2 is much larger than k_b is the reaction rate diffusion limited. For a slow reaction where $k_b >> k_2$ the first step is in equilibrium and $k = K \cdot k_2$, where $K = k_D/k_b$.(AB is **not** a transition state, but a reaction intermediate.)

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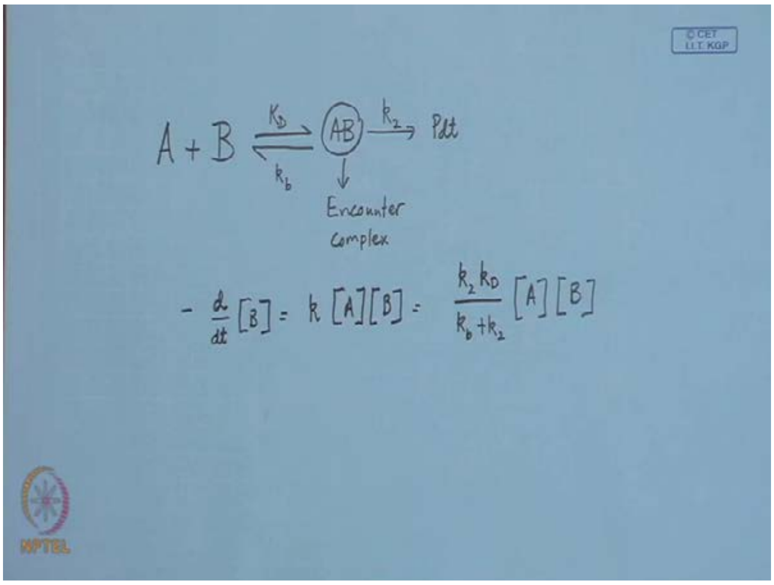

$$A + B \underset{k_b}{\overset{K_D}{\rightleftharpoons}} \boxed{AB} \xrightarrow{k_2} Pdt$$

$$-\frac{d}{dt}[B] = k[A][B] = \frac{k_2 k_D}{k_b + k_2}[A][B]$$

Now, many solution reactions can be depicted as follows, that is, A plus B, A plus B equilibrium K D and K B giving rise to AB and then K 2 products. So, this is your encounter complex; encounter complex. K B, the unimolecular rate constant for the dissociation of the encounter complex. And if you apply a steady state treatment, then you end up, end up with this rate law, minus d d t of B is equal to k, which is equal to k 2 k D divided by k B plus k 2. So, you have to apply steady state approximation onto this encounter complex, you have to apply. So, applying steady state approximation to this, what you get? This expression, that it is a bimolecular, bimolecular, I mean, you know, concentration of it is dependent on the concentration of A and concentration of B, this is your overall rate and this expression is this. So, only if k 2 is much larger than k B, then the reaction is diffusion limited. If larger, then you can neglect this one and k 2 k 2 gets canceled. So, this is basically formation of your encounter, encounter complex, this is your diffusion rate k d. So, that means, if k 2 k D divided by k B plus k 2, if you write this to equal to k 2 k D divided by k 2, that means, these two gets, get, these two get, I mean, k 2 gets canceled, then it is k D. The reaction is said to be, you know, the reaction rate is diffusion limited.

For a slow reaction where, you know, in other case, if a slow reaction, where k B is greater than k 2, very, very greater than k 2, slow reaction, why? Because this one is high, this back reaction is high, that is, unimolecular decomposition of your encounter complex to give rise to A and B for a, for a slow reaction, where k B is very, very greater than k 2, then your expression comes out to be, to be equal to, you know, k 2 k D divided by k B. So, what is k D by k B? k d by k B is nothing, but your equilibrium constant. So, you can write, k 2 into k equilibrium, where k equilibrium is k D by k B. AB is not a transition state, but it is a reaction intermediate. So, remember, that AB is not a transition state, but a reaction intermediate.

So, what you see, that for a fast reaction, if, if it is forming the product very fast compared to the back reaction, compared to the, you know, dissociation of your encounter complex, then this is a diffusion limited case; it is a diffusion limited reaction. So, so, physically, that the moment they are, the moment these two entities, say these two entities are coming, they will immediately do the reaction giving rise to say, product of this sort or maybe, say product of this sort. Say, this is a product, so that means, these two steps, I mean, consecutive steps k D k 2, they are occurring, you know, very fast compared to the back reaction, that is, k b, k b step and under that situation you can call, that this reaction to be diffusion limited. That is, this is so fast, k 2, so fast, that this is negligibly small like your, you know, reaction between H plus and OH minus, the moment it is coming, generating your water. So, there is no chance, that the back reaction is taking place. Maybe, water dissociates to form H plus and OH minus, but that is very small. So, that is why, k 2 is very high compared to k b, but when opposite situation happens, then the reaction is, you know, it is a fast equilibrium followed by a slow decomposition of your encounter complex to produce, to produce your product. So, situation, these two situations are, you know, different in one case, it is, you know, diffusion limited. In other case, it is it is not diffusion limited, but the, this fast equilibrium, quick equilibration between AB, I mean, reactant and your encounter complex, there is equilibrium between them.

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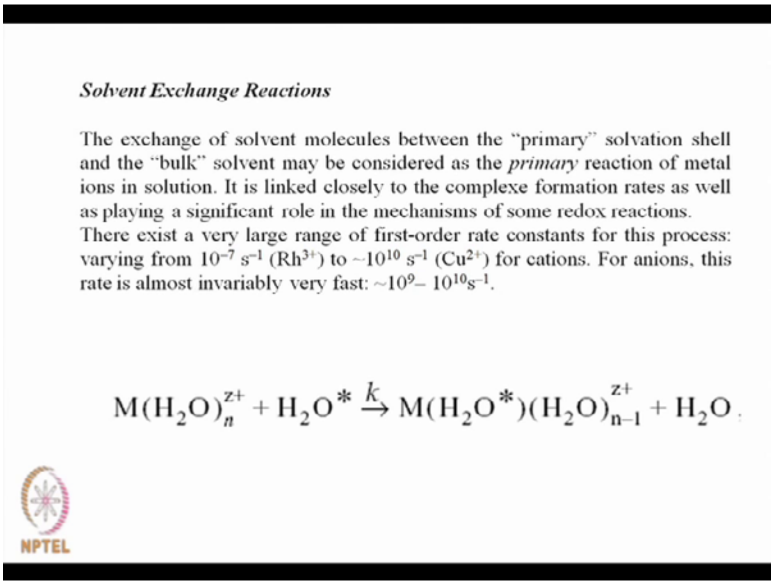

Solvent Exchange Reactions

The exchange of solvent molecules between the "primary" solvation shell and the "bulk" solvent may be considered as the *primary* reaction of metal ions in solution. It is linked closely to the complexe formation rates as well as playing a significant role in the mechanisms of some redox reactions. There exist a very large range of first-order rate constants for this process: varying from 10^{-7} s^{-1} (Rh^{3+}) to ~10^{10} s^{-1} (Cu^{2+}) for cations. For anions, this rate is almost invariably very fast: ~10^{9}– $10^{10}s^{-1}$.

$$M(H_2O)_n^{z+} + H_2O^* \xrightarrow{k} M(H_2O^*)(H_2O)_{n-1}^{z+} + H_2O.$$

Now, let us come to solvent exchange reaction. So, what is that? It is basically the exchange of solvent molecules between the primary solvation cell and the bulk solvent maybe considered as the primary reaction of metal ions in solution. So, solvent exchange means, your metal ion is there, it has got a primary solvation cell very close to your metal ions primary solvation and maybe, bulk is somewhere here. So, these solvent molecules are considerably different than these molecules, which those, which are in the, in the bulk, away from your charge. So, the exchange of the solvent molecules between primary solvation cell and the bulk solvent may be, may be considered as, as the primary reaction of metal ions in solution. So, it is linked closely to the complex formation rates, as well as, playing a significant role in the mechanism of some redox reactions. So, why it is that? Because when complex is formed, then maybe, these solvent molecules are replaced by the ligand or maybe, water can be, can be ligand as well. So, it is linked directly to the complex formation rates, as well as playing a significant role in redox reactions.

Redox reactions are nothing but, you know, electron transfer reaction, electron exchange reaction, where you know, one oxidation state is, is getting converted to another; maybe, say, chromium 3 to say chromium 0, maybe iron 2 to iron 3, nothing but, this is nothing but the redox reaction. But these redox reactions are considerably affected in presence of, in presence of solvated; I mean, you know, solvent molecules, that is, solvent molecules, which are surrounding your metal ion. So, there exists a very large range of first-order rate constants for this process, varying from 10 to the power minus 7 to 10 to the power 10 for cations. And for anions this is almost invariably very fast, that is, 10 to the power 9 to 10 to the power 10 second inverse; it is close to, you know, diffusion limited.

So, reaction is M H 2 O n Z plus is the charge plus water, water means, this water is star means, it is, it is in the bulk water with a, with a rate constant of k giving rise to M H 2 H 2 O star H 2 O n minus 1 Z plus plus water. So, this, you know, unstarred water is coming out. So, it is basically exchange of outer water going into inner primary solvation cell and the inner primary solvation cell water is going out, that is why, M H 2 O 3 are n number of waters in the, in, in very close to M having Z plus charge on metal ion. So, it is, you know, solvent exchange, it is a typical solvent exchange reaction. And, and you know, for, for cations, it varies significantly from 10 to the power of minus 7 per second, very slow, to 10 to the power 10, very fast for cations. And for anions, the rate is almost invariably very, very fast, 10 to the power 9 to 10 to the power 10, this solvent exchange, you know, reaction.

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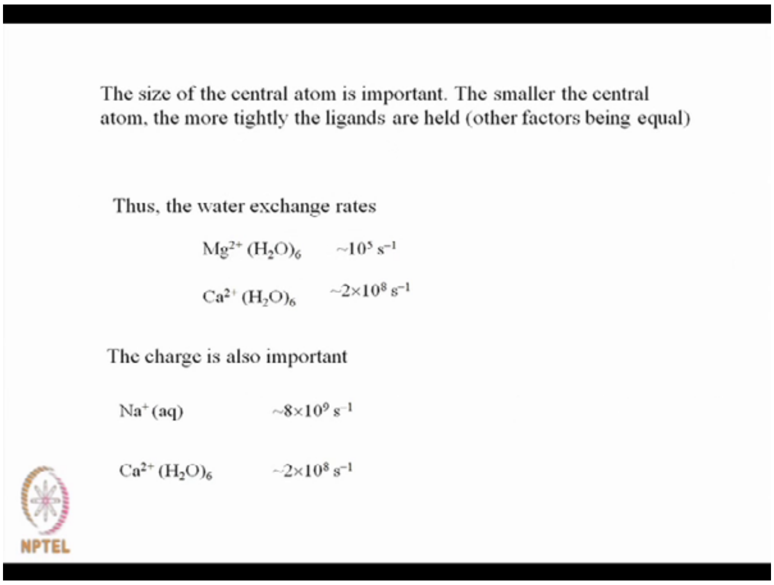

The size of the central atom is important. The smaller the central atom, the more tightly the ligands are held (other factors being equal)

Thus, the water exchange rates

$Mg^{2+}(H_2O)_6$	$\sim 10^5\ s^{-1}$
$Ca^{2+}(H_2O)_6$	$\sim 2\times10^8\ s^{-1}$

The charge is also important

$Na^+(aq)$	$\sim 8\times10^9\ s^{-1}$
$Ca^{2+}(H_2O)_6$	$\sim 2\times10^8\ s^{-1}$

So, in this case, the size of central atom is very important. The smaller the central atom, the more tightly the ligands are held. Other, other factors being equal when you consider, when you compare, then other factors should be, should be unaltered, otherwise you cannot compare. The size of central atom is important because if the size is, you know, high, then effective, you know, potential of that central atom will be less. So, therefore,

therefore, you know, solvent molecules are less tightly held, but for smaller central atom, the more tightly the ligands are held.

So, thus, for water exchange rates magnesium and calcium, see, that for magnesium 2 plus it is 10 to the power 5, but for calcium it is 10 to the power 8. So, so in case of magnesium, see it is, rate is, you know, rate is smaller, but for calcium, the rate is higher. So, you can correlate, you can correlate the statement, the size of central atom is very important and also charge is very important. So, sodium plus equated, for sodium plus equated you see, charge is plus 1 and for calcium 2 plus, the charge is 2 plus. So, the rate for sodium plus equated or hydrated sodium, it is 8 into 10 to the power 9 per second, but for calcium 2 plus, it is 2 into 10 to the power 8. It is much less compared to sodium plus. So, you know, charge is also important and the size is also important. So, why I have told other factors being, you know, held equal. That means, for magnesium it is 2 plus, calcium it is 2 plus, so the charge factor is kept held, I mean, kept constant.

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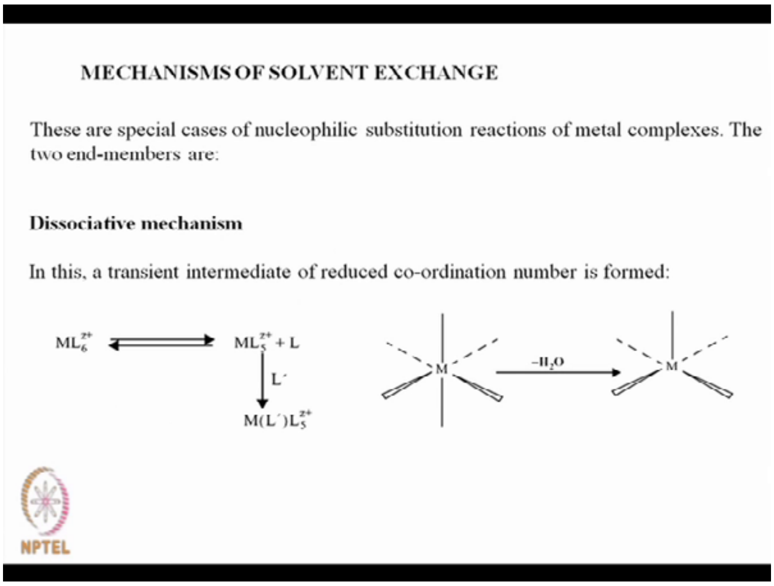

MECHANISMS OF SOLVENT EXCHANGE

These are special cases of nucleophilic substitution reactions of metal complexes. The two end-members are:

Dissociative mechanism

In this, a transient intermediate of reduced co-ordination number is formed:

$$ML_6^{z+} \rightleftharpoons ML_5^{z+} + L \xrightarrow{L'} M(L')L_5^{z+}$$

Now, let us come to mechanisms of solvent exchange process. Now, these are special cases of nucleophilic substitution reaction of metal complexes and the 2 end-members are, you know, like, like as I, as I, you know explained over here, I mean, given over here. So, it is a dissociative mechanism. In this case, a transient intermediate of reduced coordination number is formed, that is, the two end-members, I mean, this, the, the, is a reduced coordination state. So, this is one member, this is another member and water has been taken off. So, it is ML Z plus 6 legends, then ML 5, same number of charge plus ligand, then adding another ligand, you are having 6, I mean, 6 ligands; of course, the other ligand is L primed. So, what is happening here? That you have got in originally 6 water molecules, say now this water is lost giving rise to, you know, a 5-membered species. It is a square pyramid, it is an octahedral, it is an octahedral geometry; it is a square pyramid in geometry. So, it is an, it is a dissociative mechanism, that this bond is dissociated, giving rise to this one and associative mechanism the, the other way.

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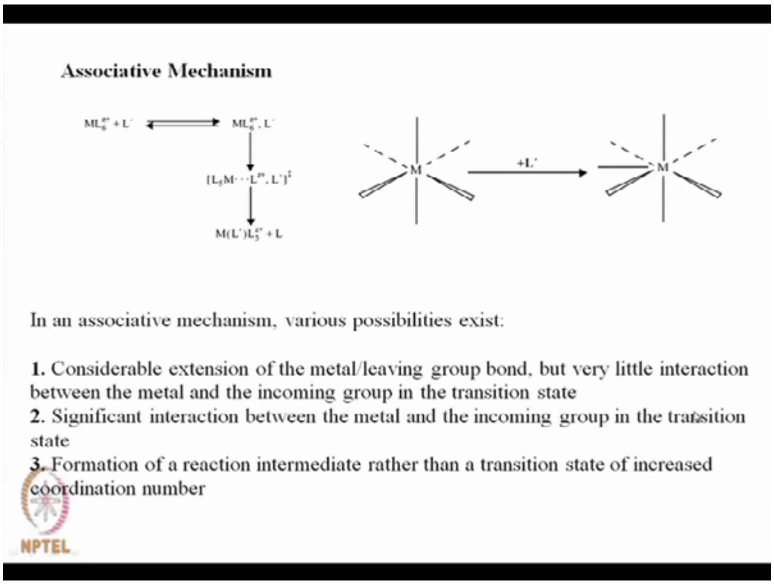

Associative Mechanism

$$\begin{tikzcd} ML_6^{z+} + L' \arrow[r, shift left] & ML_6^{z+}, L' \arrow[l, shift left] \arrow[d] \\ & {[L_5M\cdots L^{z+}, L']^{\ddagger}} \arrow[d] \\ & M(L')L_5^{z+} + L \end{tikzcd}$$

In an associative mechanism, various possibilities exist:

1. Considerable extension of the metal/leaving group bond, but very little interaction between the metal and the incoming group in the transition state

2. Significant interaction between the metal and the incoming group in the transition state

3. Formation of a reaction intermediate rather than a transition state of increased coordination number

So, originally, I mean, previously it is dissociative, means, you see, that 1st the ligand gets dissociated and then, this position is vacant, then this, then the 2nd ligand comes in. So, it is basically exchange of ligands.

So, next case, what is happening? It is an associative, means all the 6 ligands remain over there, then the 7th ligand comes in and coordination number increases from 6 to 7. So, it is a 5-membered plane, so pentagon and pyramidal shape. So, it is an octahedral. So, you see, that here ligand comes, it is producing like this, something like M L 5 L. Then, L primed, then maybe this bond is lengthened and this ligand is included in the, in the activated complex. This is your activated complex, then activated complex rearranges itself and releases this, this ligand, that is L. Now, what is happening, what has happened is, M L primed L 5 Z plus, it is, it is, it is similar to SN 2 kind of mechanism, that, that your, you know, the transition state is a, like, say for your tetrahedral carbon atom, it is it is now becoming a 5-membered, I mean, 5 coordinated species in the transition state and then the 5th ligand is lost. But, but, the dissociative mechanism is similar to your SN 1, where the halide gets, you know, dissociated fast giving rise to a carbo-cation and then, carbo-cation gets, you know is attacked by your nucleophile.

So, in an associative mechanism various possibilities exist, considerable extension of the metal and leaving group bond, but very little interaction between metal and incoming group in the transition state is there. So, that means, something of this sort may happen, significant interaction between metal and the incoming group in the transition state, it may happen. There are, there are various possibilities, formation of a reaction intermediate, rather than a transition state of increased coordination number. So, these are the possibilities for an associative mechanism.

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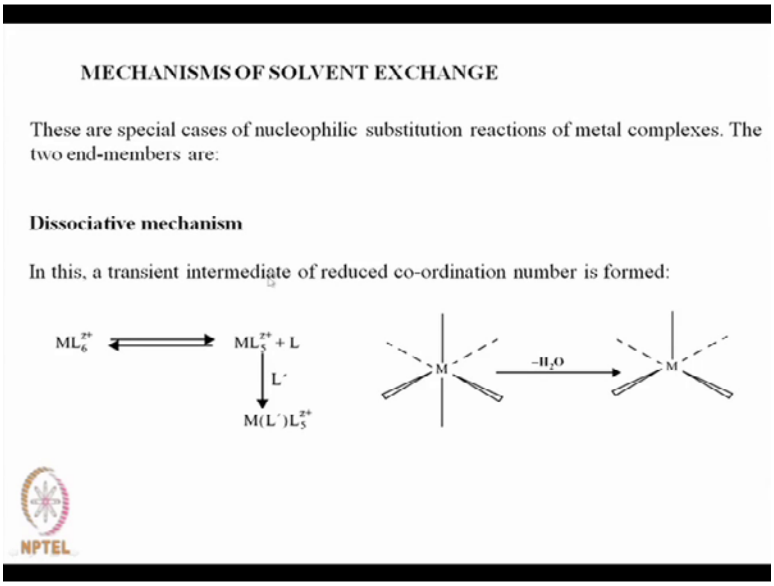

MECHANISMS OF SOLVENT EXCHANGE

These are special cases of nucleophilic substitution reactions of metal complexes. The two end-members are:

Dissociative mechanism

In this, a transient intermediate of reduced co-ordination number is formed:

$$\begin{tikzcd}
ML_6^{z+} \arrow[r, shift left] & ML_5^{z+} + L \arrow[l, shift left] \arrow[d, "L'"] \\
 & M(L')L_5^{z+}
\end{tikzcd}$$

So, again, if you go back to dissociative, you see ML 6 ML 5 L. So, 6th position is vacant ligand and I mean the 2nd ligand and L primed has the option, option to attack now. So, it attacks and giving rise to M L primed L 5 Z plus charge, but here it, it is a little bit different than, than the earlier one, that this 6th ligand remains and then it leaves. So, this type of intermediate is a possibility and then it rearranges itself in such a fashion, that I mean, it rearranges itself and producing M L primed L 5. So, these are the 2 situations, that is, one is associative, another is dissociative mechanism for, you know, ligand exchange.

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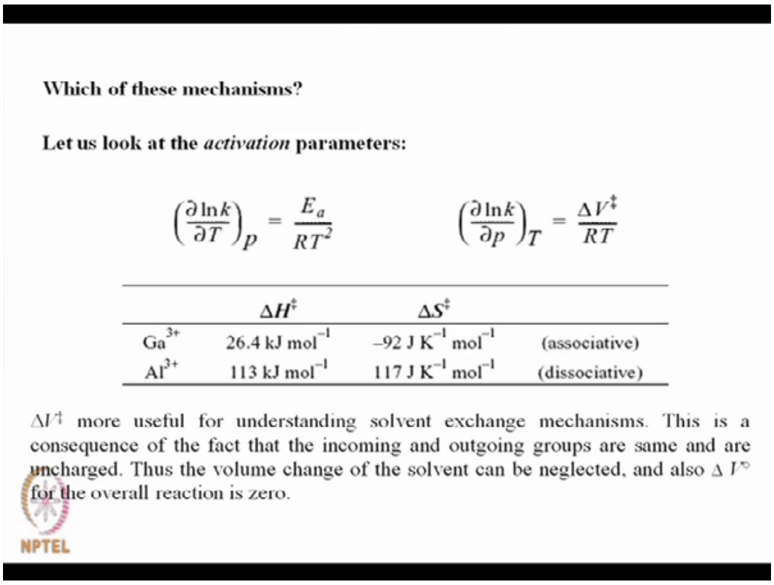

Which of these mechanisms?

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.

Which of these mechanisms, how can we, can we judge, that whether it is an associative mechanism or a dissociative mechanism? Now, again, you see, that you have got in this case, your water is lost, so you generate a species, single species to a double species, I mean, this plus water or maybe, this plus ligand. In this case, this plus ligand to a single species, so 2 species forming a single species during activation process. So, let us look at the activation parameters.

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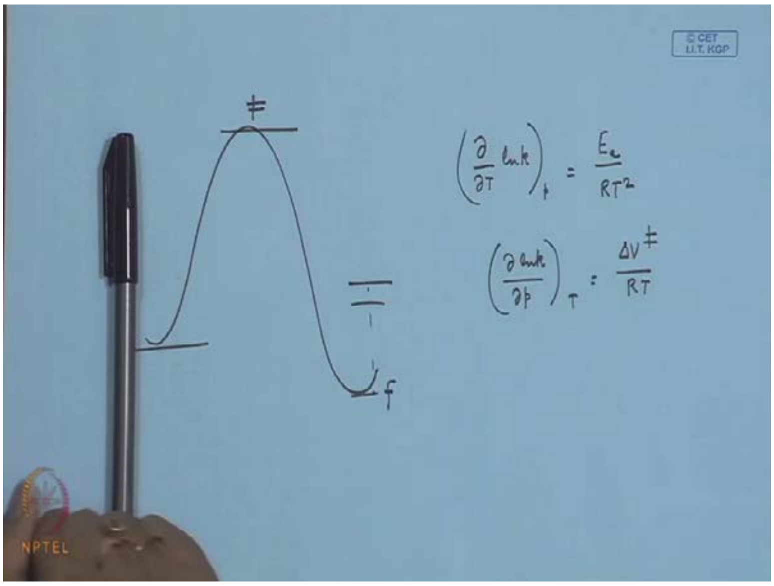

Activation parameters means, so initial state, this is your activated state and then, maybe somewhere here your product state maybe here or here or here whatever. So, like this, maybe, this is your activated state, this is your initial state and this is your final state. So, so, the expression is del lnk del T p del del T p of lnk is equal to E a by RT square and del lnk del p T is equal to delta v by RT. So, this is energy of activation, this is volume of activation.

So, what is happening here? So, when it is the case of associative mechanism, that means, because of this activated state formation, activated state formation, I mean, 2 to 1, there is a loss in, there is a loss in entropy. So, entropy of activation will be, will be less; entropy of activation will be less, I mean, negative in negative sense. But for, if it is a dissociative, then you may expect entropy to be increased rather. So, therefore, just by looking at the, looking at the, you know, delta s, double dagger delta s activation and its sign magnitude and its sign, you can in principle judge, whether it is, it is a case of associative or it is a case of dissociative mechanism. So, delta v is also more useful for understanding the solvent exchange mechanism. This is a consequence of the fact that the incoming and outgoing groups are same and are unchanged. Thus, volume change of solvent can be neglected and also delta v 0 for the overall reaction is 0, but in some cases, that may also change.

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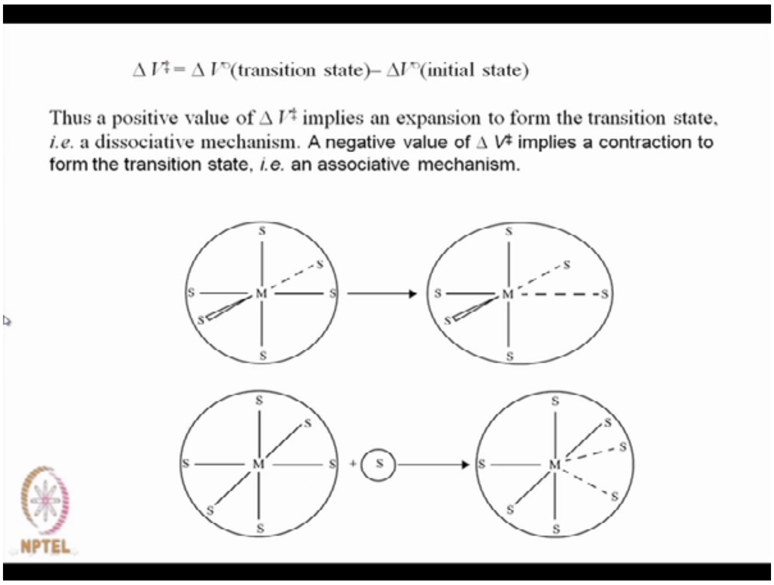

$\Delta V^{\ddagger} = \Delta V^{\circ}$(transition state)– ΔV°(initial state)

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.

So, delta v double dagger is, is the volume of the transition state minus the volume delta v of the initial state. So, therefore, delta v double dagger is also useful in, in, you know, understanding, that is, pressure dependence of lnk will give you the delta v; that will also give you the idea of, you know, whether it is an associative or it is a dissociative case. But when the incoming and outgoing groups are same, then this is difficult, you know, I mean volume change can be neglected, but if these two are different, then you may not, you may not, you know, ignore it.

So, so, I guess, today I will have to stop over here and maybe, I will have to elaborate this delta v activation in the next lecture. But before that, let us sum up, that you know, I have today, I have, we have talked about solvent exchange reaction and it is the exchange of bulk solvent to your primary solvation, I mean, primary solvation cell. It is the, it is the exchange of, you know, molecules, which are in the primary solvation cell and in the bulk solvent. And how this is changing the factors like, you know, charge and also, the size is important and mechanisms are like dissociative mechanism and could be an associative mechanism and that can be well judged with thermodynamic parameters, like this activation parameters. So, I guess, today I will stop. So, in the next lecture, I will talk on this delta v activation and also on the, on the electron transfer reactions. So, till then, have nice time.

Thank you.