Rate Processes
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Module No. #01

Lecture No. #13

Theories of Reaction Rate (contd…)

Hello good morning everybody. So, today we will continue with theories of reaction rate.

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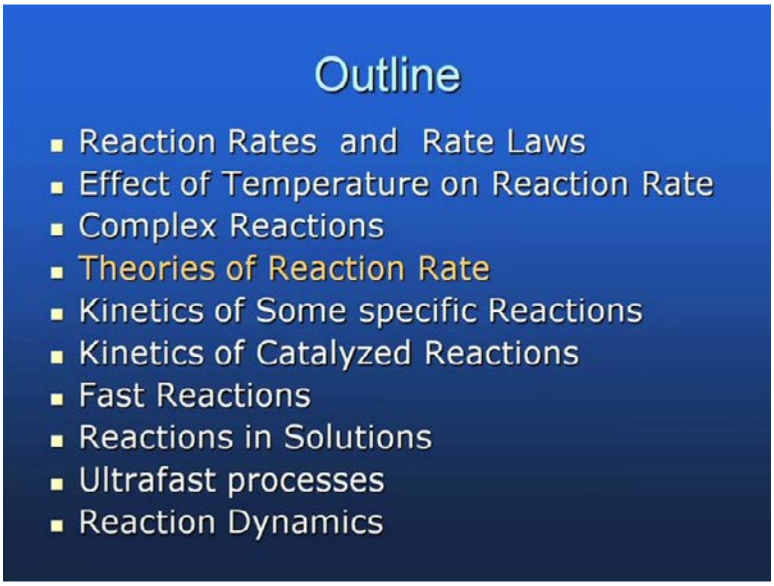

Outline

- 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, it will be the concluding part of this section that is theories of reaction rate. So, we were discussing this surface reactions surface means maybe say surface adsorbed molecules are undergoing some chemical transformation maybe carbon monoxide. So, when it gets adsorbed onto some metal surface then what happens to that maybe this this kind of reactions we were discussing.

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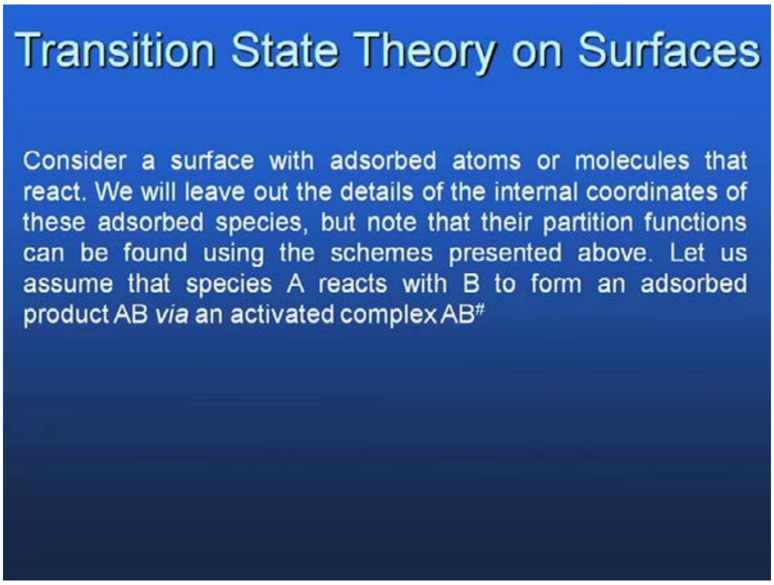

Transition State Theory on Surfaces

Consider a surface with adsorbed atoms or molecules that react. We will leave out the details of the internal coordinates of these adsorbed species, but note that their partition functions can be found using the schemes presented above. Let us assume that species A reacts with B to form an adsorbed product AB *via* an activated complex $AB^{\#}$

So, now, we were also trying to apply transition state theory on surface reactions now this time we will talk about a situation when adsorbed atoms or molecules which are they are on the surface they undergo chemical reaction that is chemical reaction on metal surface say there are two two atoms or molecules those those are adsorbed on metal surface. So, they will tend to react with each other. So, what could be the situation. So, that is consider a surface with with adsorbed atoms or molecules that react in this case we will leave out the details of internal coordinates of the of those adsorbed species,,, but note that their partition functions can be found using the schemes presented earlier that is I already talked about in earlier lectures let us also assume that species A reacts with B to form an adsorbed product A B via an activated complex A B double dagger or A B hash.

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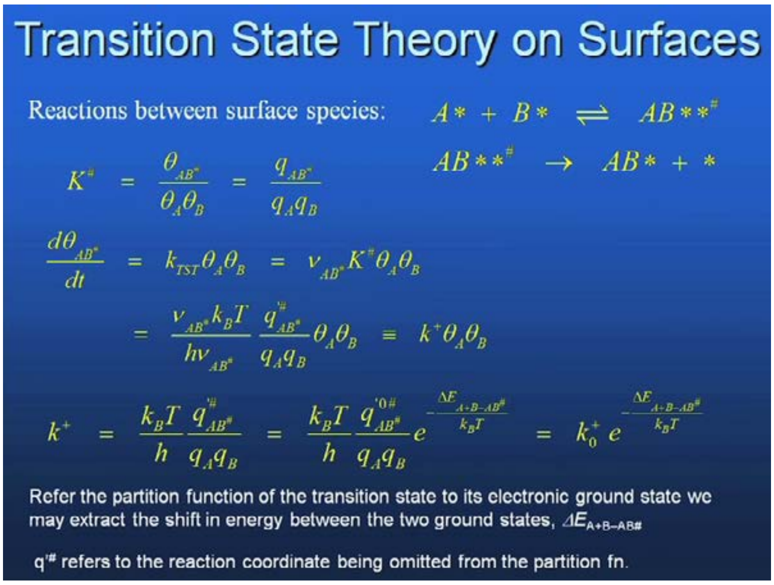

Transition State Theory on Surfaces

Reactions between surface species: $A* + B* \rightleftharpoons AB**^{\#}$

$AB**^{\#} \rightarrow AB* + *$

$$K^{\#} = \frac{\theta_{AB^{\#}}}{\theta_A \theta_B} = \frac{q_{AB^{\#}}}{q_A q_B}$$

$$\frac{d\theta_{AB^{\#}}}{dt} = k_{TST}\theta_A\theta_B = \nu_{AB^{\#}} K^{\#}\theta_A\theta_B$$

$$= \frac{\nu_{AB^{\#}} k_B T}{h\nu_{AB^{\#}}} \frac{q^{'\#}_{AB^{\#}}}{q_A q_B}\theta_A\theta_B \equiv k^{+}\theta_A\theta_B$$

$$k^{+} = \frac{k_B T}{h}\frac{q^{'\#}_{AB^{\#}}}{q_A q_B} = \frac{k_B T}{h}\frac{q^{'0\#}_{AB^{\#}}}{q_A q_B} e^{-\frac{\Delta E_{A+B-AB^{\#}}}{k_B T}} = k_0^{+} e^{-\frac{\Delta E_{A+B-AB^{\#}}}{k_B T}}$$

Refer the partition function of the transition state to its electronic ground state we may extract the shift in energy between the two ground states, $\Delta E_{A+B-AB\#}$

$q^{'\#}$ refers to the reaction coordinate being omitted from the partition fn.

So,. So, schematically it is basically A star plus B star. So, these two are adsorbed onto onto surface. So, that is why it is a star plus b star.

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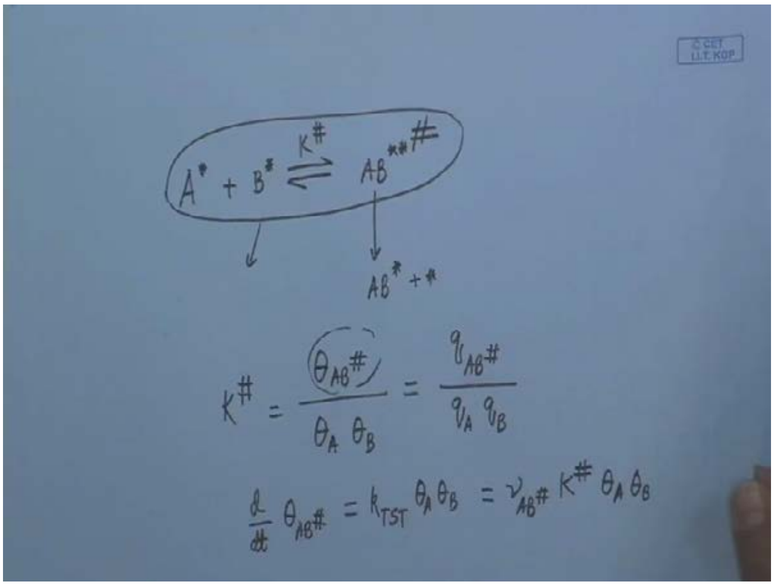

So, giving rise to A B that is both adsorbed and hash then what what will happen to this is that this will undergo reaction to give you A B star plus star means you know they combine to to form A B adsorbed and your the position which was occupied say by a is now left open like this. So,. So, this this first step is the equilibrium so; that means, you have to have one K double dagger or maybe K pound or K hash. So, K hash will be equal to theta A B it is related to you know coverage theta A theta B which is nothing,,, but equal to q A B divided by q A times q B. So, rate of change of theta A B this rate of change of this how can you write you can write d d t of theta A B which is as as per with with transition state theory k T S T k T S T times theta A theta B. So, in that case you can write your nu A B the same treatment we did earlier K this theta A theta B.

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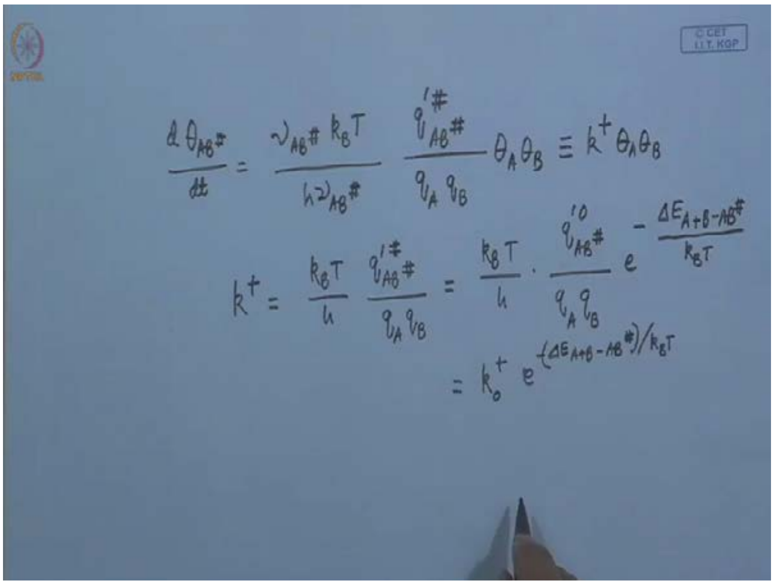

$$\frac{d\theta_{AB^\#}}{dt} = \frac{\nu_{AB^\#} k_B T}{h\nu_{AB^\#}} \frac{q'^{\#}_{AB^\#}}{q_A q_B} \theta_A \theta_B \equiv k^+ \theta_A \theta_B$$

$$k^+ = \frac{k_B T}{h} \frac{q'^{\#}_{AB^\#}}{q_A q_B} = \frac{k_B T}{h} \cdot \frac{q'^{0}_{AB^\#}}{q_A q_B} e^{-\frac{\Delta E_{A+B-AB^\#}}{k_B T}}$$

$$= k_0^+ e^{(\Delta E_{A+B-AB^\#})/k_B T}$$

So, which will ultimately turn out to be d theta A B d t which is equal to you can write nu A B double dagger k B T that is your thermal energy k B k boltzmann times t divided by h nu A B of course,,, this activated times q A B primed; that means, one mode is taken off. So, one mode less that is why it is primed divided by q A q B theta A theta B and you can write this to be equal to like k plus theta A theta B that is for the forward process k plus. So, basically k plus is equal to is equal to k B you can write k plus is equal to k B T divided by h into. So, because these two will get cancelled. So, q A B primed q A B primed divided by q A q B which is equal to k B T by h times q A B primed zero divided by q A q B into exponential to the power minus delta E A plus B minus A B double dagger divided by k B T. So, basically we refer here the partition function of the transition state to its electronic ground state to its electronic ground state and we may extract the shift in energy between the two ground states by this much delta E A plus B minus A B double dagger or the A B pound. So, here we are referring this partition function of the transition state to its electronic ground state that is why this term is here and q primed refer double dagger refer to the reaction coordinate means one reaction means the basically basically one mode is taken off that is that is the reaction coordinate which is taken off and that reaction coordinate along which this reaction is taking place maybe one vibrational mode is converted to a translation. So, that is why it is primed. So, basically it is it is now equal to k you refer this k 0 plus e to the power minus delta E A B B minus A B double dagger divided by k B T. So, this is the expression for your k plus.

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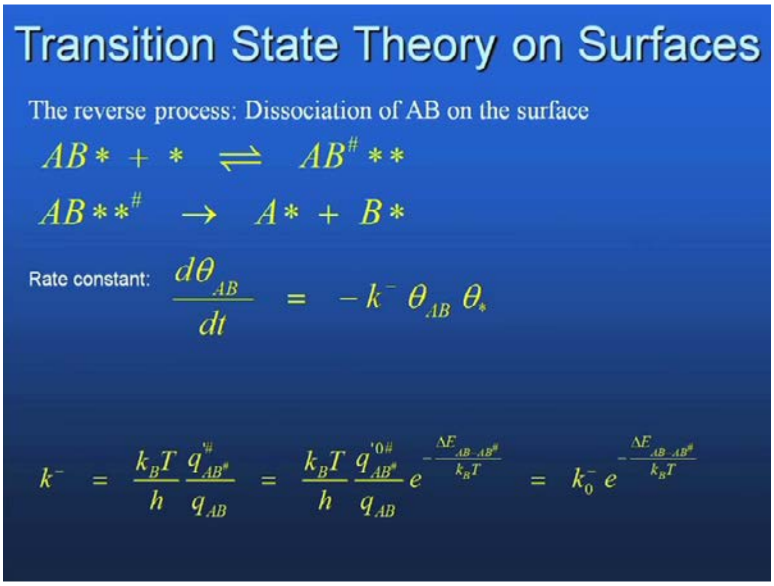

Transition State Theory on Surfaces

The reverse process: Dissociation of AB on the surface

$$AB* + * \rightleftharpoons AB^{\#}**$$

$$AB**^{\#} \rightarrow A* + B*$$

Rate constant: $\frac{d\theta_{AB}}{dt} = -k^{-}\theta_{AB}\theta_{*}$

$$k^{-} = \frac{k_B T}{h}\frac{q'^{\#}_{AB^{\#}}}{q_{AB}} = \frac{k_B T}{h}\frac{q'^{0\#}_{AB^{\#}}}{q_{AB}}e^{-\frac{\Delta E_{AB-AB^{\#}}}{k_B T}} = k_0^{-}e^{-\frac{\Delta E_{AB-AB^{\#}}}{k_B T}}$$

Next reverse process reverse process means the dissociation of A B on surface. So then the the scheme will be like the scheme will be like this that A B star plus giving rise to A B.

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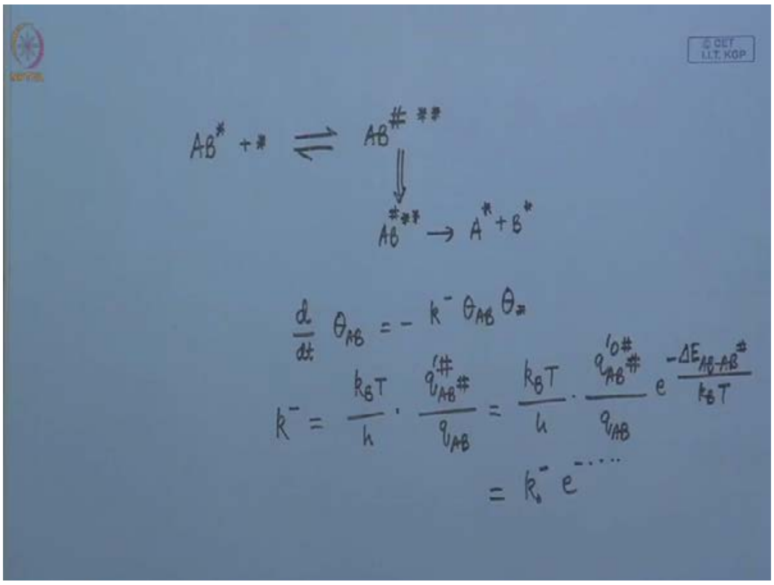

$$AB^* + * \rightleftharpoons AB^{\#**}$$

$$\Downarrow$$

$$AB^{\#**} \rightarrow A^* + B^*$$

$$\frac{d}{dt}\theta_{AB} = -k^-\theta_{AB}\theta_*$$

$$k^- = \frac{k_BT}{h}\cdot\frac{q'^{\#}_{AB^{\#}}}{q_{AB}} = \frac{k_BT}{h}\cdot\frac{q'^{0\#}_{AB^{\#}}}{q_{AB}}\, e^{-\frac{\Delta E_{AB-AB^{\#}}}{k_BT}}$$

$$= k_0^- e^{-\cdots}$$

Then, this will dissociate that is the it is it is basically the reverse process A B star star you know double dagger this give this gives rise to A star basically this is this thing A star plus B star. So, rate constant d d t of theta A B is equal to minus k minus theta A B theta star that is the uncovered region that is your surface. So, you can write as usual means as in the in the former case you the same way you can write k minus is equal to k B T by h into q A B double dagger primed double dagger divided by q A B is equal to k B T by h into double dagger primed 0 double dagger divided by q A q B or q A B into exponential to the power minus delta E delta E E has got the similar significance as I talked about A B double dagger divided by k B T which is nothing,,, but equal to you can write k 0 minus e to the power minus whatever I wrote over here the same same quantity will be here. So, this is the rate constant for the you know reverse process.

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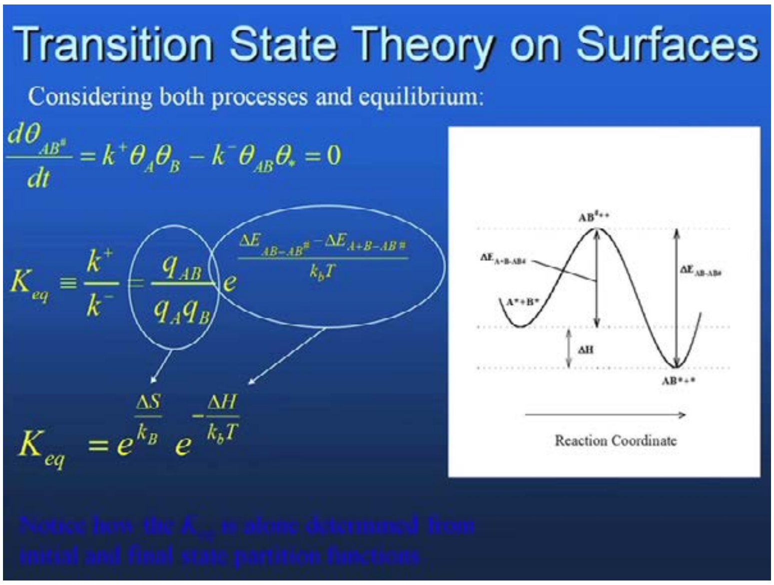

Transition State Theory on Surfaces

Considering both processes and equilibrium:

$$\frac{d\theta_{AB^{\#}}}{dt} = k^{+}\theta_{A}\theta_{B} - k^{-}\theta_{AB}\theta_{*} = 0$$

$$K_{eq} \equiv \frac{k^{+}}{k^{-}} = \frac{q_{AB}}{q_{A}q_{B}} e^{\frac{\Delta E_{AB-AB^{\#}} - \Delta E_{A+B-AB^{\#}}}{k_bT}}$$

$$K_{eq} = e^{\frac{\Delta S}{k_B}} e^{-\frac{\Delta H}{k_bT}}$$

Notice how the K_{eq} is alone determined from initial and final state partition functions

So, when we consider that both steps are under equilibrium. So, then then what can can we write we can write that is like a steady-state approximation considering both processes and and an equilibrium approximation.

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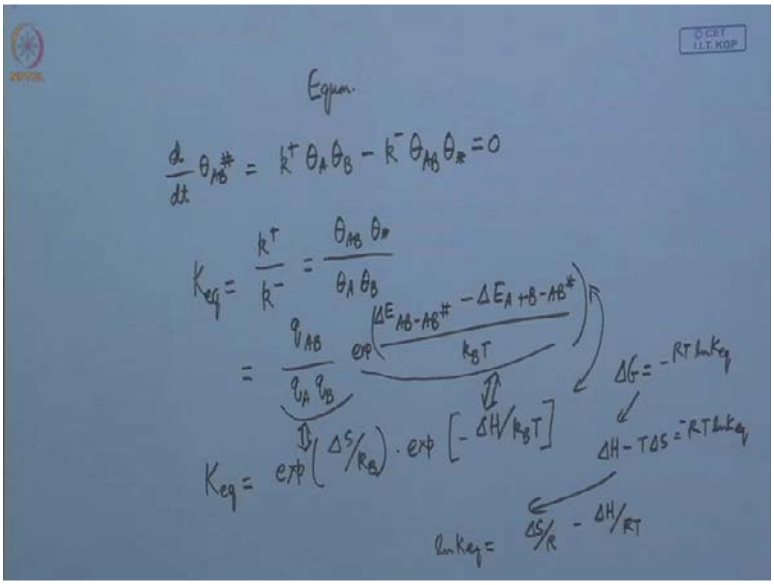

Equm.

$$\frac{d}{dt}\theta_{AB}^{\#} = k^{+}\theta_{A}\theta_{B} - k^{-}\theta_{AB}\theta_{*} = 0$$

$$K_{eq} = \frac{k^{+}}{k^{-}} = \frac{\theta_{AB}\,\theta_{*}}{\theta_{A}\,\theta_{B}}$$

$$= \underbrace{\frac{q_{AB}}{q_A q_B}}\ \underbrace{\exp\left(\frac{\Delta E_{AB-AB^{\#}} - \Delta E_{A+B-AB^{\#}}}{k_BT}\right)}$$

$$K_{eq} = \exp\left(\Delta S/k_B\right) \cdot \exp\left[-\Delta H/k_BT\right]$$

$$\Delta G = -RT\ln K_{eq}$$

$$\Delta H - T\Delta S = -RT\ln K_{eq}$$

$$\ln K_{eq} = \Delta S/R - \Delta H/RT$$

We can write d d t of theta a b which is equal to you know this is for your plus means forward process theta A theta B minus k minus theta A B theta star which is equal to 0 because it is it is equilibrium equilibrium; that means, rate of forward reaction and rate of backward reaction these two will equalize. So, that is why we put this to 0 we put this to

0. So, what do we get that it is equilibrium constant we can write K equilibrium that is equilibrium constant if we write equilibrium constant that is equal to k plus divided by k minus which will be equal to you know from this you can if you put this so; that means, k plus by k minus means basically theta A B theta star divided by theta A theta B this way you can write and this will ultimately come out to be like q A B divided by q A q B into exponential to the power delta E A B minus A B pound or A B hash delta E A plus B minus A B this divided by this is exponential divided by k B T now what is this term means what what is the significance of this term means how can we relate this term with some other known quantities. So, to do that.

So, basically from other you know already already studied you know expressions. So, already I told told those expressions that K equilibrium can be written in terms of you know like exponential to the power delta S divided by k B into exponential to the power minus delta H divided by k B T. So, if we compare these two together means if we compare this equilibrium constant as we have obtained considering this surface processes that I just talked about and already already you know the older expression already we we talked about this expression earlier that equilibrium constant you can write in terms of your delta S and delta H you can write in this way or maybe it is a classical equilibrium constant expression because delta G is equal to minus R T l n K equilibrium. So, basically delta G is equal to you can write from here delta H minus T delta S is equal to R T with a minus sign R T l n K equilibrium. So, from this we can write l n K equilibrium K equilibrium is equal to is equal to delta S by R R and minus delta H delta H by R T. So, if you take exponential of both sides then you will be getting this expression. So, now, you compare these two these two.

So, what do we get that comparing these two this this is you see this is an energetic term energy term and this is something different you know it is not exactly an energy term it is it is a ratio of partition functions. So, if it is a ratio of partition function and you know already I talked about in earlier lecture one of the earlier lectures that this this part that is prefactor this prefactor term has got a connection with entropic term and this has got a connection with an energetic term. So, therefore, we we compare this part with this one and this part with this one so; that means, this entropy of activation term or maybe entropic term is basically coming from your ratio of your partition functions and this is coming from this energetic term. So, you see if we look into the diagrammatic representation then this is your potential well for A star plus B star this is your activated complex or that is your transition state that is A B A B hash star star. So, that is these are adsorbed and they for these two adsorbed A and adsorbed B these two will form an activated complex. So, that that is why it is represented A B star double double dagger star star and then it will come down to here giving rise to A B star plus star star means one maybe one position one chair is made vacant.

So, what is this this is the energy difference between this activated state and the adsorbed A B star that is why adsorbed A B star and what is this this is the energy difference between your activated A activated B and this complexed I mean activated activated I mean adsorbed A adsorbed B with your this activated complex adsorbed activated complex. So, this is your adsorbed activated complex this is your adsorbed A and adsorbed B this is your adsorbed A B and one one site is kept vacant. So, this is the energy that is why it is written this gap is your delta E A plus B minus A B pound or double dagger and this is your delta H of reaction that is your energy of this state and difference in energy of this state and this state. So, that is why you know you see that if this is a reaction between A star plus B star giving rise to A B star plus star through this through this activeted state or through this transition state then your equilibrium constant can be expressed in this way where this is a ratio of you know ratio of the partition functions and this is your energy difference term exponential of energy difference term and therefore, this energy difference term can directly be related to the heat of reaction and this this ratio term can directly be related to your entropic term. So, that is why equilibrium constant can alone be determined from the initial and final state partition functions. So, initial state and final final state and initial state partition functions.

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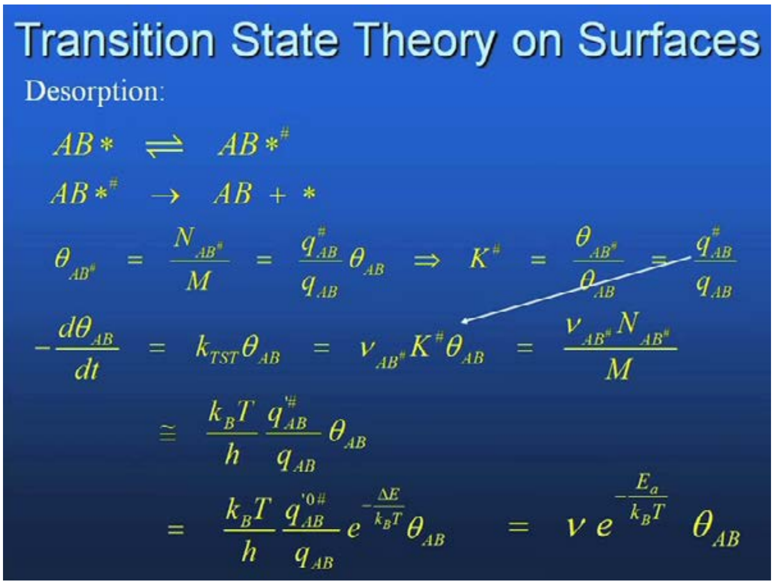

Transition State Theory on Surfaces

Desorption:

$$AB* \rightleftharpoons AB*^{\#}$$

$$AB*^{\#} \rightarrow AB + *$$

$$\theta_{AB^{\#}} = \frac{N_{AB^{\#}}}{M} = \frac{q^{\#}_{AB}}{q_{AB}}\theta_{AB} \Rightarrow K^{\#} = \frac{\theta_{AB^{\#}}}{\theta_{AB}} = \frac{q^{\#}_{AB}}{q_{AB}}$$

$$-\frac{d\theta_{AB}}{dt} = k_{TST}\theta_{AB} = \nu_{AB^{\#}}K^{\#}\theta_{AB} = \frac{\nu_{AB^{\#}}N_{AB^{\#}}}{M}$$

$$\cong \frac{k_BT}{h}\frac{q'^{\#}_{AB}}{q_{AB}}\theta_{AB}$$

$$= \frac{k_BT}{h}\frac{q'^{0\#}_{AB}}{q_{AB}}e^{-\frac{\Delta E}{k_BT}}\theta_{AB} = \nu e^{-\frac{E_a}{k_BT}}\theta_{AB}$$

Now we will move onto desorption once this reaction is complete that is formation of A B star is complete then it should desorb from the surface. So,. So, this prescription you know prescription is A B star in equilibrium with A B star double dagger or A B star hash.

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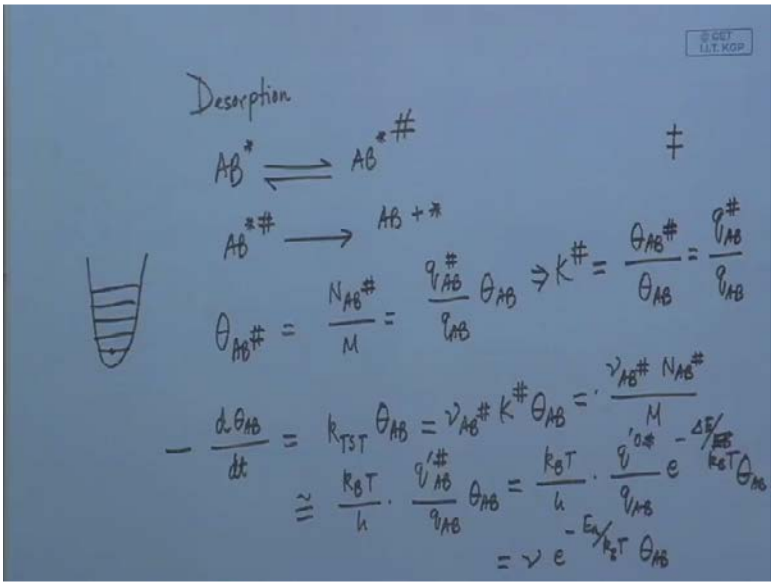

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Desorption

$$AB^{*} \rightleftharpoons AB^{*\#} \qquad \ddagger$$

$$AB^{*\#} \longrightarrow AB + *$$

$$\theta_{AB^{\#}} = \frac{N_{AB^{\#}}}{M} = \frac{q^{\#}_{AB}}{q_{AB}}\theta_{AB} \Rightarrow K^{\#} = \frac{\theta_{AB^{\#}}}{\theta_{AB}} = \frac{q^{\#}_{AB}}{q_{AB}}$$

$$-\frac{d\theta_{AB}}{dt} = k_{TST}\theta_{AB} = \nu_{AB^{\#}}K^{\#}\theta_{AB} = \frac{\nu_{AB^{\#}}N_{AB^{\#}}}{M}$$

$$\cong \frac{k_BT}{h}\cdot\frac{q'^{\#}_{AB}}{q_{AB}}\theta_{AB} = \frac{k_BT}{h}\cdot\frac{q'^{0\#}}{q_{AB}}e^{-\Delta E/k_BT}\theta_{AB}$$

$$= \nu e^{-E_a/k_BT}\theta_{AB}$$

So, A B it is a desorption process desorption process A B star equilibrium A B pound then A B star pound or star hash giving rise to A B plus the site is vacant now now has now become vacant. So, this is purely a desorption process. So, now, what is theta A B hash which is equal to N A B divided by M the significance of N and M is already told. So, that is why it is this by that then q A B divided by q A B theta A B from this it can be written that K hash or K double dagger theta A B. So, in some books you will be finding in means in place of this hash is symbol like this double dagger. So, that is why we may call this as hash or maybe double dagger or maybe sometimes it is called as pound symbol. So, K double dagger is equal to this by theta A B which is equal to q A B divided by q A B. So, rate of desorption or you know rate of the process is nothing,,, but minus d theta A B. So, it is decreasing that is why it is minus sign d t which is equal to which is equal to k T S T into theta A B. So, this k from T S T has always to be included which is equal to nu A B this K double dagger theta A B so; that means, this is your nu N A B N A B double dagger divided by M and you can approximate these two to k B T boltzmann constant temperature divided by h times q primed A B divided by q A B into theta A B which is equal to k B T divided by h into same treatment as I did just earlier from now divided q A B exponential to the power minus delta E K B T sorry k B k B T theta A B so; that means, your nu into e to the power minus E a by k B T into theta A B. So, this is the net rate expression. So, this is your energy of activation I mean exponential activation energy divided by k B into T.

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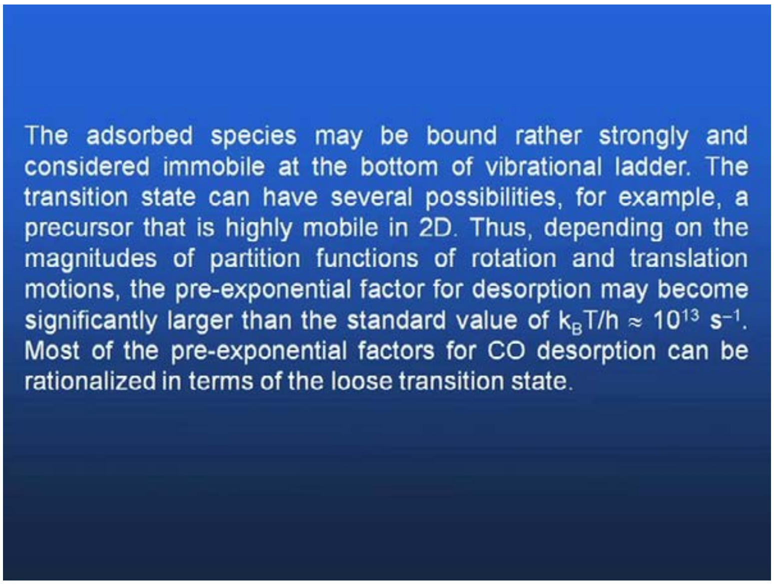

The adsorbed species may be bound rather strongly and considered immobile at the bottom of vibrational ladder. The transition state can have several possibilities, for example, a precursor that is highly mobile in 2D. Thus, depending on the magnitudes of partition functions of rotation and translation motions, the pre-exponential factor for desorption may become significantly larger than the standard value of $k_B T/h \approx 10^{13}\ s^{-1}$. Most of the pre-exponential factors for CO desorption can be rationalized in terms of the loose transition state.

So, the adsorbed species maybe bound rather strongly and considered immobile at the bottom of the vibrational ladder the transition state can have several possibilities. So, once this species is adsorbed and bound rather strongly and when it is considered immobile; that means, it is at the bottom of the vibrational ladder; that means, if we have this vibrational ladder like this this is your ladder. So, this is your this is the bottom of the ladder. So, here you know motion is you know less that is why it is more or less less mobile or immobile the transition state can have several possibilities for example, a precursor that is highly mobile in 2 D thus depending on the magnitudes of partition functions of rotation and translational motions the pre-exponential factor for desorption may become significantly large than the standard value k T by h which is of the order of ten to the power 13 per second so; that means, depending on the magnitude of the partition functions of the of the rotation and translational motions the pre-exponential factor for the desorption process maybe maybe large and most of the pre-exponential factors for CO desorption can be rationalized in terms of loose transition state.

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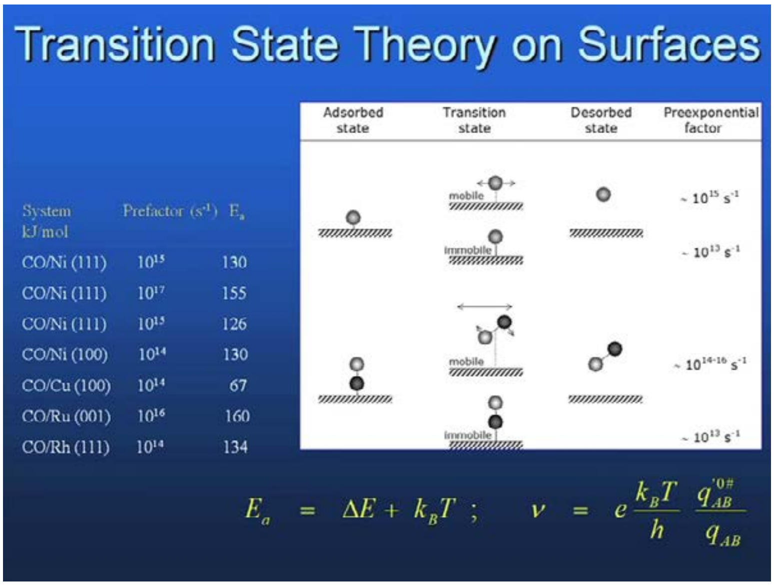

Transition State Theory on Surfaces

System kJ/mol	Prefactor (s^{-1})	E_a
CO/Ni (111)	10^{15}	130
CO/Ni (111)	10^{17}	155
CO/Ni (111)	10^{15}	126
CO/Ni (100)	10^{14}	130
CO/Cu (100)	10^{14}	67
CO/Ru (001)	10^{16}	160
CO/Rh (111)	10^{14}	134

$$E_a = \Delta E + k_B T \; ; \qquad \nu = e \frac{k_B T}{h} \frac{q_{AB}^{'0\#}}{q_{AB}}$$

So,. So, let us have various systems that system with you know like you know different system that is as if the your here it is carbon monoxide is adsorbed onto various you know planes of different metals that is 1 is 1 1 11 plane or maybe 1 0 0 or maybe 0 0 1 like that and. So, the system is this prefactors per second is this and energy of activation is kilo joule per mole this much of kilo joule per mole. So,. So, in the first case you see that when carbon monoxide is adsorbed onto nickel 1 1 1 plane cristal plane. So, it has got the pre-exponential prefactor of 10 to the power 15 it is it is high and energy of activation is 1 30 for nickel 1 1 1 you know it is 10 to the power 17 and 155 then there are there are various options you know you can have then carbon monoxide nickel 1 1 0 it is you see that 10 to the power 14 and it is 1 30 and then it is carbon monoxide C U and 1 0 0 it is 10 to power of 14 and 67 carbon monoxide ruthenium 10 to the power 16 1 60 carbon monoxide rhodium 1 1 1 it is 10 to power of 14 1 34.

So, these are the these are the various values of you know prefactors now if you look into this that here you your this is your adsorbed state this is your transition state this is your desorbed state and these are the pre-exponential factor you can you can see that if the adsorbed state is like this that is it is adsorbed onto the surface then it can have two option one is mobile another is immobile when it is mobile then it can move around in two dimensional surface on the metal maybe carbon monoxide or so or maybe I mean maybe nickel or maybe copper it depends means whether if it is if it is mobile then it can have two dimensional motion because third dimension this one you know you know third motion this motion is not possible because this site it is bounded or it maybe immobile that is it does not have any option to move around maybe x y x or y direction and the desorbed state fore both of these is like this that is distance is increased a little bit and the pre-exponential factor comes out to be you you see that it is 10 to the power of 15 and it is 10 to the power 13. So,.

So, basically you know basically you see that for immobile case it is the value is less prefactor prefactor is less,,, but for it is if it is mobile then prefactor is high what about this say diatomic system. So, it can have a mobile mobility mobility or it can it may not have mobility. So, if it is mobile if if its adsorbed state is I mean transition state is this this is your adsorbed state then it will have motion like this this motion it is a rotational motion or maybe a a translational motion. So, basically it is a mobile mobile situation and for immobile you see it does not have any option to you know either rotate or maybe translate in this direction. So, it is immobile and your adsorbed desorbed state this is your adsorbed state or this one is adsorbed state. So, desorbed state means when it it leaves the it leaves the surface then it it is like this and for your mobile case it is 10 to the power 14 to 10 to the power 16 it is high and for immobile case it is 10 to the power 13 you see for both cases when it is you know atom or maybe molecule you see the immobile case your pre-exponential factors are close and of course,,, this is lower than corresponding mobile case and activation energy is delta E plus k B T.

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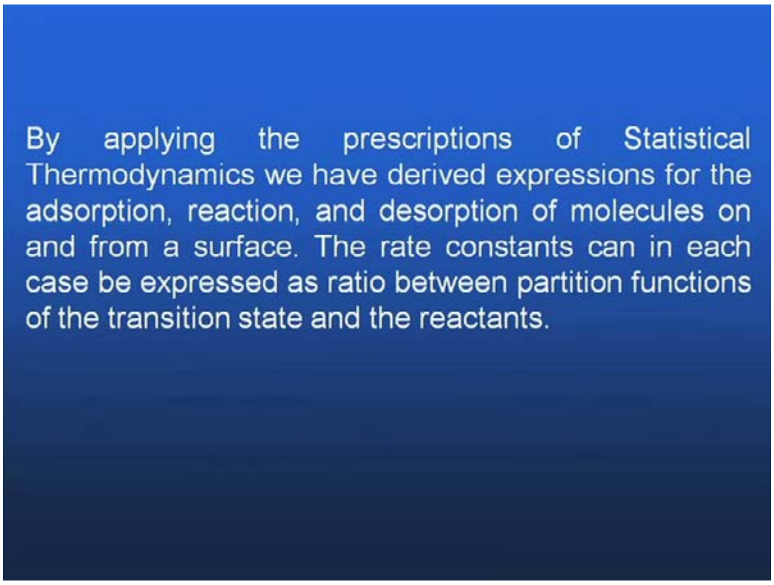

By applying the prescriptions of Statistical Thermodynamics we have derived expressions for the adsorption, reaction, and desorption of molecules on and from a surface. The rate constants can in each case be expressed as ratio between partition functions of the transition state and the reactants.

Next. So, through this discussion it is it is clear that that we have been able to understand we have been trying to understand this surface reactions and application of transition state to surface reaction and in that case what we have done is we have applied the prescriptions of statistical thermodynamics we have derived expression expression for the adsorption reaction and desorption of molecules or atoms on and from the surface the rate constants can can in each case be expressed as the ratio between the partition functions of the transition state and reactants. So, we have expressed the rate constant in terms of the partition functions of the transition state and the reactant states and here we have tried to tried to utilize the statistical thermodynamical prescriptions to find you know the to find the partition function which we have applied which we have employed in finding out the the rate constant of the process.

So,. So, in this particular lecture what we have particular part of the lecture because next we will move onto this next we will move onto a diffusion controlled reaction before that what we what we did this in this part that we have we have invoked the idea of surface reaction it is not simply the adsorption and desorption process once these molecules get adsorbed onto metal or on onto onto some surface then there is every possibility of reaction why every possibility of reaction because at par with tran I mean this collision collision theory that when there is a collision then there is a possibility of reaction; that means, they must come in proximity to each other like they will come close to each other and then there will be reaction and in this case these are gas phase molecules when they

they collide they are they are truly gas phase molecules,,, but when the question of a of a metal surface comes into action then these two molecules are now in a state of adsorption like this say these two are adsorbed onto the metal surface say this is your metal metal surface. So, these two are adsorbed.

So, this this two I mean may have motions like this maybe like this or maybe like this or something like this so; that means, they may have mobility or they may not have mobility,,, but the thing is that when they are they are absorbed onto the same metal surface they have the option to come close to each other; that means, an option of reaction on surface that is a reaction of absorbed molecule molecules on metal surface and that we have tried to tried to implement that is reaction between surface species and we have got we have got some expression of the overall rate of the process and when there is there is adsorption when there is forward process there is equal probability I mean there is there there is some probability of the back reaction to occur therefore, we have also also included that possibility. So, and we have we have got some some expression for rate constant for the for the dissociation of A B on surface as well because the forward reaction was was the formation of A B back reaction will be will be dissociation of A B into A and B and we have we have applied the concept of equilibrium equilibrium because at equilibrium forward and backward reaction both are both are forward and backward reaction rates are identical therefore, we we employed that and we got the expression for the equilibrium constant in terms of the energetic an energetic term and you know partition function and ultimately ultimately we we compared this with expression for equilibrium constant and we come out with a conclusion that this q A B divided by q A and q B it is your entropic term.

So, this this pre-exponential term this pre-exponential term is related to your entropic term and your exponential term is related to energetic term and has got some some relation with your with your energy of activation and then we have employed desorption process that once this molecule I mean A B is formed this may undergo desorption that is leaving the metal I mean metal surface. So, desorption process. So, from that we also have got the rate expression for the desorption process. So, depending on whether it is you know highly mobile or less mobile whether you know whether it is you know whether the magnitude of the partition functions that is the rotation and translation these are are you know very high or low the pre-exponential factor for desorption may become significantly high. So, pre-exponential factor significantly high means there is a high probability of you know desorption rate that is it I will contribute contribute you know contribute considerably and we have got some you know typical values of the pre-exponential factor prefactor and we have given also the diagrammatic representation of various adsorbed states for atoms and also for molecules and we have also tried to you know rationalize why this pre-exponential term is you know high because you know pre-exponential term high means your it is related to it is related to entropy and since you know for the mobile case although it is adsorbed onto the metal surface this metal surface,,, but what is happening that you know this this has this mobility option in this direction or maybe in this direction.

So, if it has got the mobility mobility option then your entropic term will contribute significantly. So, entropic term entropic term contribute significantly means it will surely give you some higher value that is why that is why this you see that pre-exponential factor for the mobile case mobile transition-state case it is you see I mean about about hundred times more than your this pre-exponential pre-exponential factor where this is immobilized this adsorbed stuff stuff is immobilized. So, this motion or this motion or maybe rotational motion for molecules it is not possible therefore, you know it is associated with a reduction in entropy. So, reduction in entropy means for sure your pre-exponential factor will be less the same can be concluded means we can we can we can have the similar conclusion and similar explanation when we consider adsorption of molecules onto onto the surface and in that case you see that if it is a mobile situation then your pre-exponential factor this pre-exponential factor is you know quite high about 10 to the power of 14 to 10 to the power 16 why it is it is still you know about how much about about 10 to the power 3 times more 10 to 10 to the power 3 times 10 to 1000 times more depending on on which molecule is adsorbed; that means, when entropic term contributes considerably then your it contributes towards a high pre means it it leads leads to a high pre-exponential factor; that means,; that means, throughout throughout this discussion of the surface reaction and application of transition state theory we have tried to apply the statistical thermodynamics thermodynamical thermodynamical expression to to derive the you know relation that relates the adsorption process or reaction or desorption process with you know with partition function.

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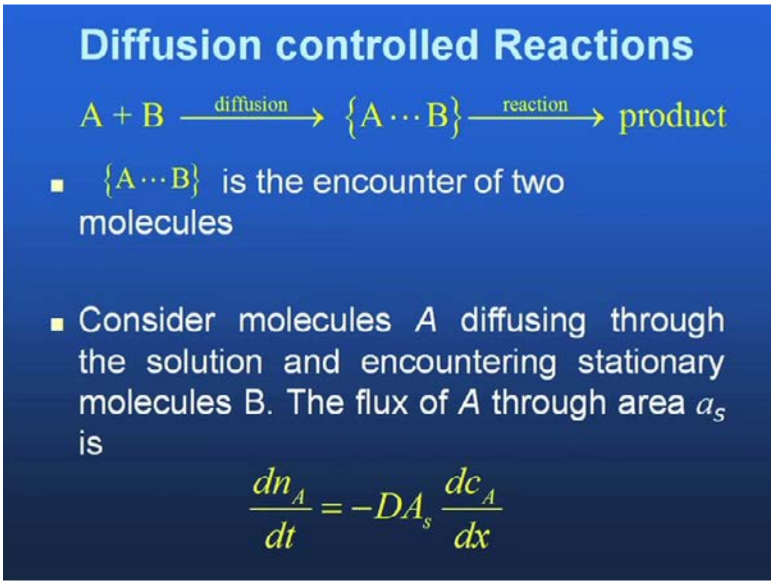

Diffusion controlled Reactions

$$A + B \xrightarrow{\text{diffusion}} \{A \cdots B\} \xrightarrow{\text{reaction}} \text{product}$$

- $\{A \cdots B\}$ is the encounter of two molecules
- Consider molecules *A* diffusing through the solution and encountering stationary molecules B. The flux of *A* through area a_s is

$$\frac{dn_A}{dt} = -DA_s \frac{dc_A}{dx}$$

Next will be next will be we will move onto another specific specific reaction because if we if we go to you know the very first slide that we have just completed this theories of reaction rate we have explained you know gas phase reaction we have tried to explain the solution phase reaction and now we have explained we have we have discussed we have discussed the surface reactions. So, now, we will move onto another topic that is kinetics of some specific reactions specific type reaction that is your diffusion controlled reaction what is that diffusion controlled reaction consider a reaction say a simple reaction say hydrolysis of a star acid catalyzed hydrolysis of A star to give you to give you acid acid acid means the organic acid and your alcohol.

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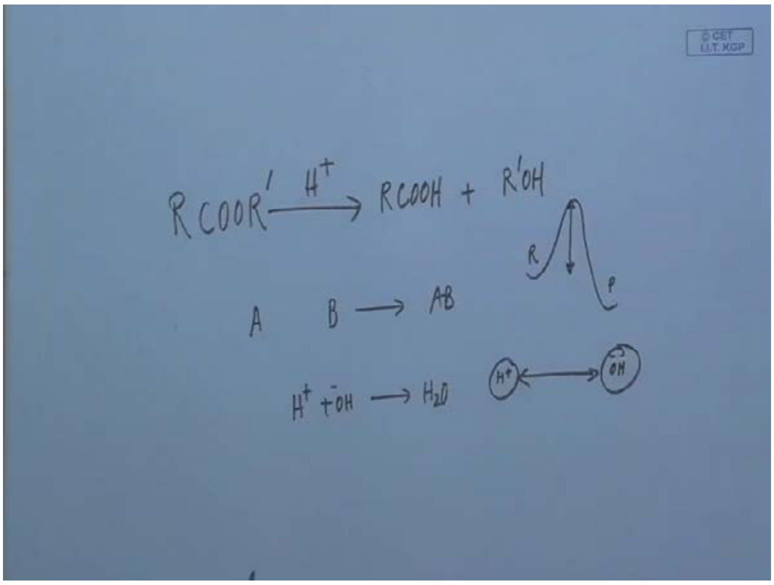

So, that is your R C O O R H plus giving rise to R C O O H plus R primed. So, this is at acid catalyzed hydrolysis of a star. So, if you measure if you measure the reaction I mean rate of reaction then you will be finding that you will be finding that it takes time it is not very fast it happens slowly you (( )) I mean a concentration of this R C O is that is acid concentration slowly rises with time. So, it does not happen all on a sudden it is it does not happen like a like a you know like like a like an explosion. So, it takes time,,, but suppose if we have if we have the situation that we have got reactant A and reactant B if they come close to each other it will form A B immediately means it does not take it does not take any time; that means, we can say that possibly we can we can assume that maybe this barrier reaction barrier is not there possibly reaction barrier is not there reaction barrier means you know this one this is your reactant this is your product and say this is your forward reaction barrier or activation activation barrier is probably not there if the activation barrier is not there probably then these two will immediately combine to produce B that is if you have the option to bring A and B close to each other then with one collision maybe if we if we consider that you know collision theory is the theory by which we can explain everything or if we just think of collision then in a single collision it it will make a bond like if you think of you know this H plus and O H minus reaction that is to produce water plus O H minus acid base reaction to produce water.

So, it is a very fast reaction now the question is question is that what type of reaction is this your thing is that these very fast reactions are generally you know its its rate is diffusion limited it it says that its rate is diffusion limited diffusion limited means it is you know of the order of nanosecond minus 9 or minus 10 seconds it is a 10 or or its rate is very high 10 to the power 9 10 to the power 10 or 10 to the power 11 per second. So, it is it is a truly a diffusion if it is a truly diffusion controlled reaction then suppose you have got one H plus over here and one H minus O H minus over here and then what you do you mix them together,,, but there is a separation physical separation like they are at some distance then what will happen now even if these two are present in in single same pot same container they may not form water at at such a separation they will not form water at such a separation they have to come. So, coming or coming close to each other this process. So, they have to swim and they will move towards each other. So, if you know if the if the viscosity say of this solvent is if it is very high then flow I mean flow of this O H minus or movement of O H minus from here to this position or maybe H plus from here to this position will really affect it that is will become slowed down will become become slowed down so; that means, even if this reaction is very fast,,, but it will take time and that that rate is determined by the you know viscosity or in turn it will be determined by how easily these two ions will diffuse to each other. So, it is. So, rate is called diffusion limited rate.

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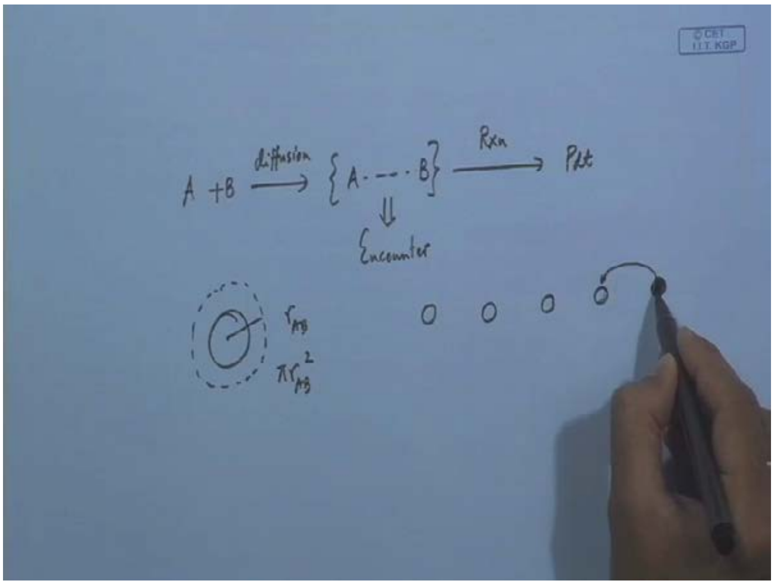

So, schematically schematically it is it is shown like this A plus B plus B giving rise to A B which is called an encounter complex or encounter of two molecules this is this is designated by this. So, it is diffusion and then this this will form your product this is your reaction. So, this is called your encounter of encounter of A B. So, what is happening happening actually consider molecules a diffusing through the solution and it is encountering say A stationary B molecule. So, it is like like your collision between two gas molecules so; that means, since the molecules are are having or the atoms are having some definitive volume therefore, it will it will have a sphere of influence and when this sphere this atom is moving this sphere of influence is also moving. So, when a second atom or molecule is within this sphere of influence. So, what will happen that is that is the sphere then there there will be a collision; that means, this this diameter of this this sphere will be you know or the radius of this sphere will be sum of the individual radii.

So, the flux of A through the area a s suppose you have got this this atom and say this is a s why a s because a s is basically your r A plus B r A B. So, a s is this pi r A B hole square. So, flux through the area a s means through this area a s means if there is any B molecule within this area then there will be collision there will be encounter complex and that will lead that will that will lead to the product formation. So, flux of a through the area a s is given by d n A d t is given by d n A d t is equal to minus of D A s d c A d t. So, where is this is your diffusion constant diffusion coefficient.

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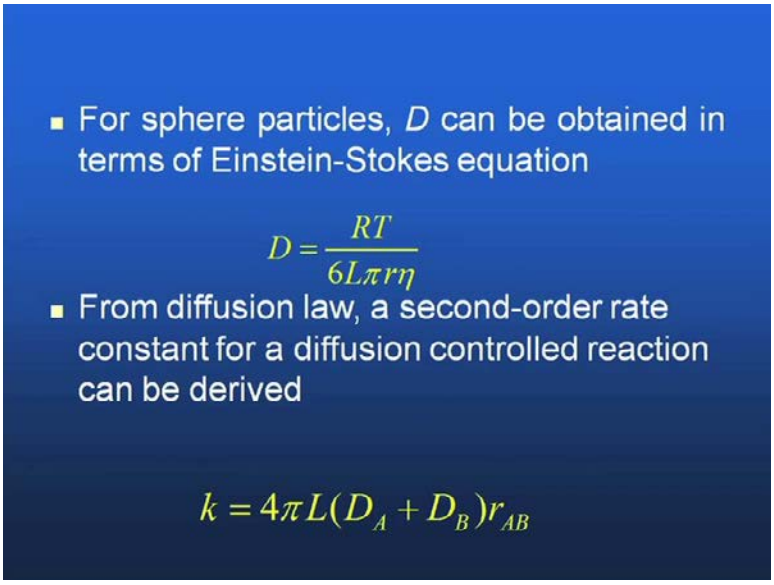

- For sphere particles, *D* can be obtained in terms of Einstein-Stokes equation

$$D = \frac{RT}{6L\pi r\eta}$$

- From diffusion law, a second-order rate constant for a diffusion controlled reaction can be derived

$$k = 4\pi L(D_A + D_B)r_{AB}$$

So, for for spherical particle D can be obtained in in terms of Einstein-Stokes equation it is a famous equation it was it was named after einstein and stokes because these these two scientists worked on this. So, your diffusion constant is R into T divided by 6 L pi r eta. So,. So, eta is the is the is your coefficient of viscosity and from diffusion law second order rate constant of the diffusion controlled reaction can be derived that k is equal to 4 pi L D A plus D B times r A B. So,. So, this is this is a special type of reaction when I will talk more about this diffusion controlled reaction maybe in the in the next lecture,,, but the thing is that this reaction is of great importance since you know when there is no barrier there could be barrier and there could be barrierless process. So, when there is no barrier barrier means no activated rate process then simply you know this reaction will be very much dependent on how easily these you know reactant species are coming close to each other how easily and that easiness is very much dependent on several factors like temperature temperature will increase the average motion because thermal energy when when it is put onto the system.

So, their relative I mean mobility will be more then of course,,, on the viscosity of the medium of course,,, on the viscosity of the medium if viscosity is more then the reaction rate I mean the you know diffusion process will will be slowed down diffusion process will be slowed down. So,. So, you know these factors are you know to be taken into consideration consideration with you know with with great importance. So, like like I I gave you the example of H plus and O H minus combination. So, its rate is very fast and you cannot you know simply you cannot simply measure this reaction rate by you know by like we what we do for conventional kinetic studies because it is a very fast the moment you will mix H plus with O H minus all on a sudden means the moment these H plus O H minus will come close to each other it will just make water so. So, therefore, these particular type of reaction where the rate is very fast because it does not there is no barrier apparently there is no barrier.

So, if there is no barrier only barrier is the diffusion barrier and diffusion is basically you know you have got say diffusion can be regarded as see you have got several holes in within within say liquid and say your molecule of your your your entity that is that has to be transported from here to here what what do you require that you have to jump you means you have to put this over here therefore, this position is will be vacant and this position will be occupied again this will jump from here. So, this way so; that means, if there is one molecule already occupied then what will happen that it has to leave this space and it has to remove this means the the already occupied o- occupied molecule so; that means, that will require require some energy and you know so; that means, it is it is your if it is a diffusion barrier that is responsible for slowing down the process. So, diffusion is ultimately a very important and determining factor for this very very fast reaction these are called fast reactions I will come to this fast reaction means how these rates can be measured that is for the first reaction which is called the method is called you know stopped flow technique.

So, that I will talk about maybe towards the end this you know the series of lectures you know where I will also discuss the techniques by which you can measure reaction rate techniques means maybe analytical maybe spectrophotometric maybe maybe you know other other methods like stop flow maybe plug flow maybe temperature jump method there are many methods. So, that we will discuss. So, we have just started this specific type of reaction that is your diffusion controlled reaction. So, in the in the - next lecture we will continue to this diffusion controlled reaction and then we will move onto the one important factor that is that is you know what happens when salt is added onto chemical you know chemical reaction that is if the reaction is carried out in medium containing salt added salt from outside then what is going to happen does it really affect the overall rate of the reaction or no and what are the factors means what are the conditions that you will be getting some influence of salt added salt that we will that we will discuss in the next lecuture. So,. So, till then have nice time thank you.