Rate Processes
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Module No. #01

Lecture No. #12

Theories of Reaction Rate (contd…)

Hello good morning everybody. So, we were discussing theories of reaction rates and it is a continuation of our last lecture.

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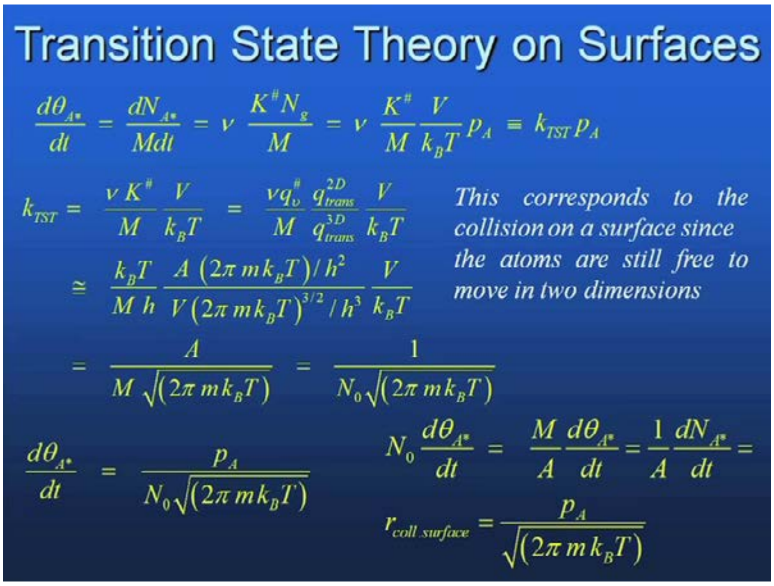

Transition State Theory on Surfaces

$$\frac{d\theta_{A^*}}{dt} = \frac{dN_{A^*}}{Mdt} = \nu\frac{K^{\#}N_g}{M} = \nu\frac{K^{\#}}{M}\frac{V}{k_BT}p_A \equiv k_{TST}p_A$$

$$k_{TST} = \frac{\nu K^{\#}}{M}\frac{V}{k_BT} = \frac{\nu q_\upsilon^{\#}}{M}\frac{q_{trans}^{2D}}{q_{trans}^{3D}}\frac{V}{k_BT}$$

$$\cong \frac{k_BT}{M\,h}\frac{A\,(2\pi mk_BT)/h^2}{V(2\pi mk_BT)^{3/2}/h^3}\frac{V}{k_BT}$$

$$= \frac{A}{M\sqrt{(2\pi mk_BT)}} = \frac{1}{N_0\sqrt{(2\pi mk_BT)}}$$

This corresponds to the collision on a surface since the atoms are still free to move in two dimensions

$$\frac{d\theta_{A^*}}{dt} = \frac{p_A}{N_0\sqrt{(2\pi mk_BT)}}$$

$$N_0\frac{d\theta_{A^*}}{dt} = \frac{M}{A}\frac{d\theta_{A^*}}{dt} = \frac{1}{A}\frac{dN_{A^*}}{dt} =$$

$$r_{coll\ surface} = \frac{p_A}{\sqrt{(2\pi mk_BT)}}$$

Now in our last lecture So, this is basically twelfth lecture. So, in our last lecture we talked about transition state theory on surface reaction. And in that case we discussed indirect adsorption process and we ended at this expression that d theta A star d t which is equal to P A pressure of a divided by N 0 that is the number density of sides available times twice pi M k T K B Tsquare root and this corresponds to the collision on a surface since the atoms are still free to move in two dimension that is on surface there is there is collision suppose this is the surface. So, atoms are moving around although they are weakly bound, but still they have the option to move like this. So, so there is a collision. So, expression is similar to you know what we got from the simple hard-sphere collision theory.

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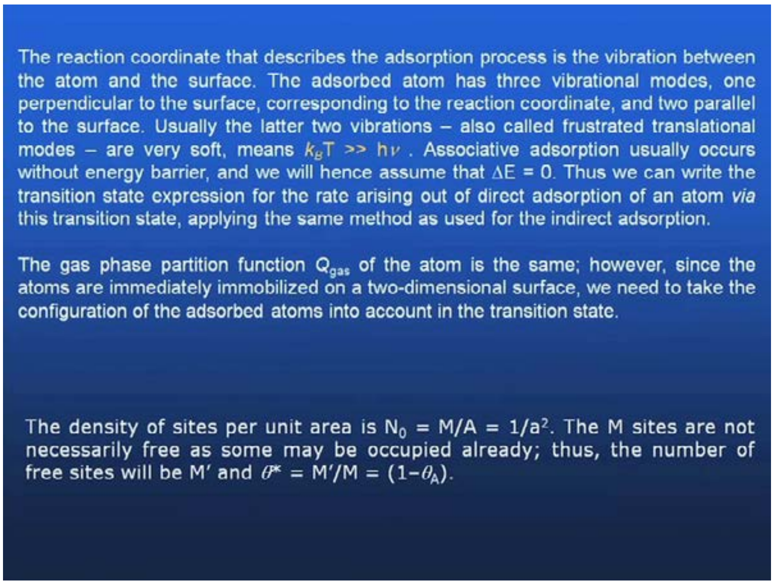

The reaction coordinate that describes the adsorption process is the vibration between the atom and the surface. The adsorbed atom has three vibrational modes, one perpendicular to the surface, corresponding to the reaction coordinate, and two parallel to the surface. Usually the latter two vibrations – also called frustrated translational modes – are very soft, means $k_BT >> h\nu$. Associative adsorption usually occurs without energy barrier, and we will hence assume that $\Delta E = 0$. Thus we can write the transition state expression for the rate arising out of direct adsorption of an atom *via* this transition state, applying the same method as used for the indirect adsorption.

The gas phase partition function Q_{gas} of the atom is the same; however, since the atoms are immediately immobilized on a two-dimensional surface, we need to take the configuration of the adsorbed atoms into account in the transition state.

The density of sites per unit area is $N_0 = M/A = 1/a^2$. The M sites are not necessarily free as some may be occupied already; thus, the number of free sites will be M′ and $\theta^* = M'/M = (1-\theta_A)$.

Next we will move onto direct adsorption process of atoms now in this case the reaction coordinate that describes the adsorption process is the vibration between atom and the surface. So, you have got the surface like this and suppose you have got the atom which is bound over here. So, the reaction coordinate will be this particular motion say if this is your surface. So, reaction coordinate is this and the adsorbed atom has three vibrational modes one perpendicular like this, another like this way or maybe that way. So, these two modes these two correspond to you know on surface along the surface and this is perpendicular to the surface. And two parallel to the surface and one corresponding to the reaction coordinate which is perpendicular to the surface. Usually, the later two vibrations which are called the frustrated translational mode. So, these are somehow similar to translation. So, suppose translation suppose if a vibration occurs like this on surface. So, it may be very close to the translation on the surface and it is given a new name although it is not a true translation, but since it is really a vibration it is given frustrated translation mode and they are very soft this means your k T that is the thermal energy is much much greater than your frequency of vibration. Now associative adsorption usually occurs without energy barrier. So, that is in that case delta E for all practical purposes we can assume this to be equal to 0 thus we can write the transition state expression for the rate arising out of direct adsorption of an atom via this transition state applying the same method as used for the indirect adsorption. So, similar technique we will be following as did for indirect adsorption now the gaseous partition function which we would need to use in this case designated by Q gas.

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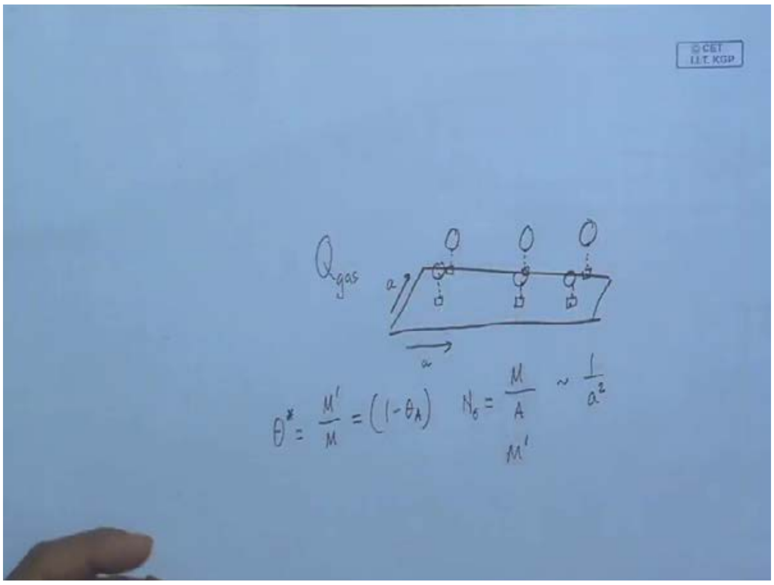

Designated by Q gas of the atom is the same; however, since the atoms are immediately immobilized. So, you have got the surface over here and your atoms are here. So, immediately after adsorption they they will find their own site that is you know the sites which are fixed for them. So, permanent site like that something like that it is not that in in unlike your earlier case that is indirect adsorption that th ey they will initially bind to the surface in a very weak fashion and then they will move around the surface and they will find a you know fixed positions fixed site. But here, now atoms will find their fixed positions initially at the very start of the process and they will get immobilized immediately on a two dimensional surface. So, this surface is a two dimensional one. So, you know some of them are here sticking out like this like this. So, it is a two two dimensional case.

And and we need to take the configuration of the adsorbed atom into account in the transition state. So, this is the situation. So, the density of sites sites means say this is one site this is another site say this is another site like this. So, density of sites per unit area will be equal to now as usual N 0 is equal to M total number of sites divided by area which goes as one by a square where a is the length this side and that side maybe something like that. So, M sites are now now the thing is that all these M sites are not necessarily free maybe when we started our counting of time maybe immediately before that some of the M sites are are occupied because of you know adsorption. So, in that case 100 percent of M M I mean say if initially suppose there were 100 M sites. So, maybe 90 of them are remaining free and maybe 10 out of out of on the 10 are you know at the very start they are occupied. Therefore, we give a new quantity which is defined as number of free sites which is equal to M prime. So, M prime is basically you know if you take a ratio. So, theta star is equal to M prime divided by M which is equal to 1 minus theta A that is you know fraction available for you know adsorption.

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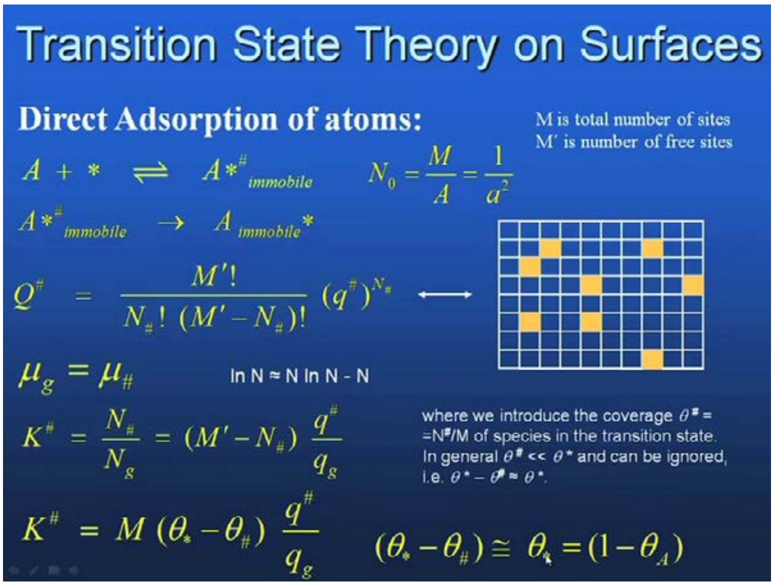

Transition State Theory on Surfaces

Direct Adsorption of atoms:

M is total number of sites
M′ is number of free sites

$$A + * \rightleftharpoons A*^{\#}_{immobile} \qquad N_0 = \frac{M}{A} = \frac{1}{a^2}$$

$$A*^{\#}_{immobile} \rightarrow A_{immobile}*$$

$$Q^{\#} = \frac{M'!}{N_{\#}!\,(M'-N_{\#})!}\,(q^{\#})^{N_{\#}} \longleftrightarrow$$

$$\mu_g = \mu_{\#}$$

ln N ≈ N ln N - N

$$K^{\#} = \frac{N_{\#}}{N_g} = (M'-N_{\#})\,\frac{q^{\#}}{q_g}$$

where we introduce the coverage $\theta^{\#} = N^{\#}/M$ of species in the transition state. In general $\theta^{\#} << \theta^{*}$ and can be ignored, i.e. $\theta^{*} - \theta^{\#} \approx \theta^{*}$.

$$K^{\#} = M\,(\theta_{*}-\theta_{\#})\,\frac{q^{\#}}{q_g} \qquad (\theta_{*}-\theta_{\#}) \cong \theta_{*} = (1-\theta_A)$$

So, direct adsorption now mechanism goes like you know like this. So, you see that A first it gets immobilised producing a transition state of this type and this then this gets into you know this is activated and then gives rise to immobilised star, but N 0 is equal to M by A where you know it is 1 by a square it goes as 1 by a square. So, M is the total number of sites available M prime is the number of free sites. So, you see these are occupied these yellow ones are occupied. So, out of say how many 1 2 3 4 5 6 7 8 9 10 and here 1 2 3 4 5 6 7 8; that means, out of 8 say 2 2 4 5 6 7 8 is shown to be occupied. So, 10 percent is occupied. So, remaining 90 percent is free for for other other you know molecule[s]- I mean other atoms to get adsorbed onto the surface. So, partition function overall partition function Q double dagger is given by this expression where M M primed factorial divide by N you know this is your activated factorial into M primed minus N factorial N double dagger factorial. So, this is your number of available sites and this is your say number of you know activated molecules are activated you know adsorbed sites. So, that mean I mean these these are the number of adsorbed gas molecules number of activated you know I mean molecules which are in activated state.

So, this is this is basically this corresponds to number of molecules which are I mean atoms which are adsorbed times your this since this is you know for your activated state. So, therefore, an N number of such activated activated atoms are there. So, therefore, your partition function will be corresponding q double dagger to the power N double dagger applying the same thermodynamical principle that you know chemical potential in the gas phase and chemical potential in the adsorbed state that is your double daggered state mu double daggered these are equal and applying the stirling’s approximation that l n N is equal to N l n N minus N for large N and we get the corresponding equilibrium constant for the you know the distribution of gas phase and the adsorbed phase. So, N double dagger divided by N g which is nothing, but after certain manipulation you will be getting this expression. So, K double dagger that is the equilibrium constant for this adsorption process which is equal to M is the total number of M sites times this here we do one thing we we introduce the coverage theta for your activated which is equal to N double dagger divided by M of species in the transition state these number of species I mean this is for the for your transition state and in general this one is much much less than you know this theta star state and this can be ignored and as a result of which you know theta star minus theta double dagger may be approximated to you know theta start. So, therefore, later on we will approximate these two simple theta star rather than writing these two because this is very small in comparison to your this step this is your activated state and this is your adsorbed state. So, activated means before means the moment it collides then it first forms this and then this immobilized one gets transferred to this and. So, this refers to this particular state. So, your expression you you know if I approximate these two then your theta star is nothing, but 1 minus theta a that is that is this is your this is the fraction that is in this state.

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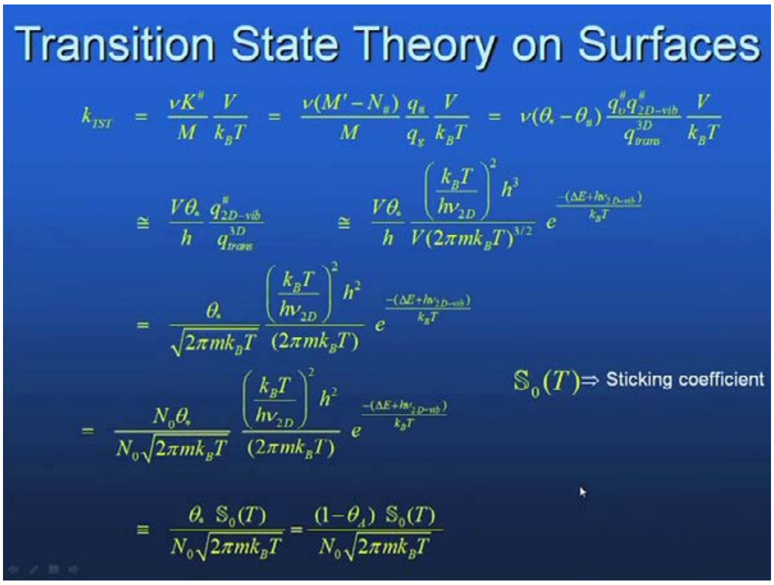

Transition State Theory on Surfaces

$$k_{TST} = \frac{\nu K^{\#}}{M}\frac{V}{k_B T} = \frac{\nu(M'-N_{\#})}{M}\frac{q_{\#}}{q_g}\frac{V}{k_B T} = \nu(\theta_* - \theta_{\#})\frac{q_0^{\#} q_{2D-vib}^{\#}}{q_{trans}^{3D}}\frac{V}{k_B T}$$

$$\cong \frac{V\theta_*}{h}\frac{q_{2D-vib}^{\#}}{q_{trans}^{3D}} \cong \frac{V\theta_*}{h}\frac{\left(\frac{k_B T}{h\nu_{2D}}\right)^2 h^3}{V(2\pi m k_B T)^{3/2}} e^{\frac{-(\Delta E + h\nu_{2D-vib})}{k_B T}}$$

$$= \frac{\theta_*}{\sqrt{2\pi m k_B T}}\frac{\left(\frac{k_B T}{h\nu_{2D}}\right)^2 h^2}{(2\pi m k_B T)} e^{\frac{-(\Delta E + h\nu_{2D-vib})}{k_B T}}$$

$$= \frac{N_0\theta_*}{N_0\sqrt{2\pi m k_B T}}\frac{\left(\frac{k_B T}{h\nu_{2D}}\right)^2 h^2}{(2\pi m k_B T)} e^{\frac{-(\Delta E + h\nu_{2D-vib})}{k_B T}}$$

$\mathbb{S}_0(T) \Rightarrow$ Sticking coefficient

$$\equiv \frac{\theta_*\ \mathbb{S}_0(T)}{N_0\sqrt{2\pi m k_B T}} = \frac{(1-\theta_A)\ \mathbb{S}_0(T)}{N_0\sqrt{2\pi m k_B T}}$$

So, your rate after your transition state theory is your this is you know nu times your equilibrium constant divided by in into V by k T because it it comes from your this P A factor. So, you recall your your earlier you know lecture on indirect adsorption let us go back to that th[at]- that will help you in recognizing the part. So, you see. So, if you if you just remove this one then your k T S T is this nu k double dagger m V by k B T. So, that we are using here that we are using over here therefore, this is your k because when you multiply this with your p a that will give you the overall you know rate that is D D D T of theta A star maybe. So, therefore, you know you write the appropriate expression for your K double dagger K double dagger is this this is your K double dagger. So, then this becomes theta star minus theta double dagger times your vibration one out of out of you know out of many one is taken out. So, you are taking out this that vibration that that vibration is perpendicular to the surface and. So, so you know and the other one is you know you know it has got this in the gas phase because it is in the gas phase. So, gas phase has got only since this is the case of atom. So, gas phase has got only three translation degrees of freedom. So, it is in three dimension. So, now, you then approximate this this 1 to theta star. So, you end up you end up to this expression because nu is equal to k T k T by h approximate you can approximate these 2. So, this is k T by h is thermal energy k T divided by h. So, you if you divide I mean if you write in place of nu equal to k B T by h then you end up this end up to this expression this is an approximation if you thing that this vibration which is responsible for you know reaction to occur has got the frequency you know you know k T by h that is k T means thermal energy divided by h that is an approximation that is why you write like this and then you if you write the respective expression if you write the respective expression for your for your this this one you get this one because you see this is two dimensional vibrational partition function and this is your translational partition function in three dimension and with with another exponential term is there. So, what we get from this we get this expression that k B T divided by h nu in 2 D for 2 D whole square because it is a two dimensional partition function. So, 2 two terms should be there and therefore, therefore, what we get is ultimately this expression. So, from this from this particular thing we get that it is theta it is proportional to theta star and and other terms are there. So, we write the respective expressions then simplify as as this and finally, k T S T comes out to be equal to this 1 theta star divided by N 0 and there is one term S 0 T it is called the sticking co-efficient what is sticking co-efficient I am coming to that. So, sticking coefficient which is which is a function of temperature divided by twice pi m k B into T. So, basically now you write in place of theta star 1 minus theta as as i as i told earlier.

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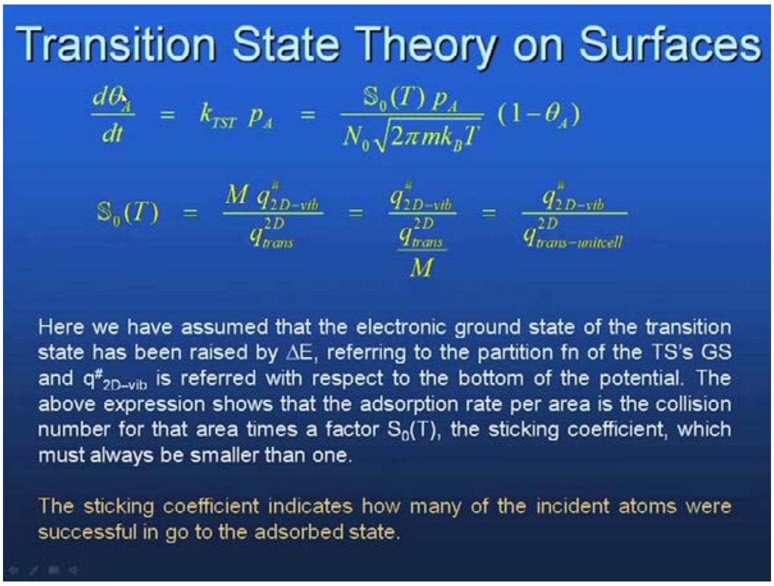

Transition State Theory on Surfaces

$$\frac{d\theta_A}{dt} = k_{TST}\, p_A = \frac{S_0(T)\, p_A}{N_0\sqrt{2\pi m k_B T}}(1-\theta_A)$$

$$S_0(T) = \frac{M\, q^{\#}_{2D-vib}}{q^{2D}_{trans}} = \frac{q^{\#}_{2D-vib}}{\frac{q^{2D}_{trans}}{M}} = \frac{q^{\#}_{2D-vib}}{q^{2D}_{trans-unitcell}}$$

Here we have assumed that the electronic ground state of the transition state has been raised by ΔE, referring to the partition fn of the TS's GS and $q^{\#}_{2D-vib}$ is referred with respect to the bottom of the potential. The above expression shows that the adsorption rate per area is the collision number for that area times a factor $S_0(T)$, the sticking coefficient, which must always be smaller than one.

The sticking coefficient indicates how many of the incident atoms were successful in go to the adsorbed state.

So, so what do we get we get d theta A d t that is rate of reaction which is equal to k T S T into P A and you write the respective expression for k T S T from the previous slide that S 0 T P A S 0 T P A S divided by N 0 twice pi m k B T into 1 minus theta A where S T is given this expression q double dagger 2 D vibration divided by q translation of the unit cell in two dimension because unit cell means it is a two dimensional case therefore, your unit cell will be a two dimensional one because it is on a surface. So, here we have. So, and there is the of course, there is an exponential term in your k t s t which is which we already shown this exponential term. So, so here what we have done we have assumed that the electronic ground state of the transition state has been raised by delta E and we are referring to this to the partition function of the transition state's ground state that is transition state has got the lowest level. So, that we are referring and q double dagger 2 D vibration is referred with respect to the bottom of the potential and the above expression shows that the adsorption rate per area per unit area is the collision number for that area times the factor S T S 0 T. So, so the. So, the adsorption rate is basically your collision rate the rate with which it is colliding with you know with the wall times times your this sticking co-efficient now this sticking sticking co-efficient you you know indicates how many incident atoms were successfully successful in going to the adsorbed state that is not of them not all of them are in the adsorbed state. So, suppose 10 atoms are colliding. So, out of 10 10 will not stick to the surface maybe say 50 percent is sticking and maybe 50 percent is going out. So, therefore, therefore, we we are just introducing it is a kind of probability factor I mean not probability it is it is an you know it is a factor that reflects that not all the collisions are successful in in making you know those atoms adsorbed onto the surface. So, therefore, the sticking co-efficient indicates how many of the incident atoms were successful in going to the adsorbed state. So, it it represents a fraction of course, it is a fraction because suppose there are 100 collisions. So, 100 collisions per unit time. So, theoretically 100 should get attached 100 atoms should get attached to the to the surface, but that does not happen it is less than 100 and that takes care you know this is 0 T takes care of that and of course, it is a it is a function of temperature because these are these partition functions are in the functions of temperature therefore, it is S 0 T.

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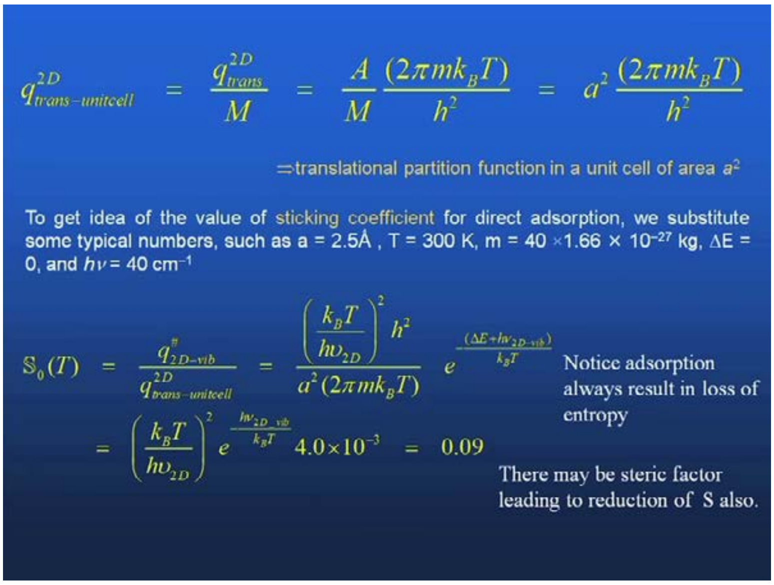

$$q^{2D}_{trans-unitcell} = \frac{q^{2D}_{trans}}{M} = \frac{A}{M}\frac{(2\pi m k_B T)}{h^2} = a^2\frac{(2\pi m k_B T)}{h^2}$$

$\Rightarrow$translational partition function in a unit cell of area a^2

To get idea of the value of sticking coefficient for direct adsorption, we substitute some typical numbers, such as a = 2.5Å , T = 300 K, m = 40 ×1.66 × 10^{-27} kg, ΔE = 0, and $h\nu$ = 40 cm^{-1}

$$S_0(T) = \frac{q^{\#}_{2D-vib}}{q^{2D}_{trans-unitcell}} = \frac{\left(\frac{k_B T}{h\upsilon_{2D}}\right)^2 h^2}{a^2(2\pi m k_B T)} e^{\frac{(\Delta E + h\nu_{2D-vib})}{k_B T}}$$

$$= \left(\frac{k_B T}{h\upsilon_{2D}}\right)^2 e^{\frac{h\nu_{2D\_vib}}{k_B T}} 4.0\times10^{-3} = 0.09$$

Notice adsorption always result in loss of entropy

There may be steric factor leading to reduction of S also.

Next is next is. So, q translation of the unit cell in two dimension which is you know basically basically this trans divided by M say unit cell. So, unit cell means that is a squared cell in two dimension. So, you can write this q trans unit cell ultimately to this a square divided by h square twice pi m k B into T. So, this is nothing, but the translational partition function in a unit cell of area a square that is that is if you can find a an atom within an unit cell then how its you know partition partition function will look like. So, that is represented over here now to get idea of the value of the sticking coefficient that i talked about for direct adsorption we substitute some typical number and see means what is what is that coming out to be. So, whether this is very close to unity or it is less than unity or maybe it is much much much less than unity that we we we would like to know for some typical numbers for for some typical situations. So, we substitute some typical numbers and such that your A this a is equal to 2.5 angstrom temperature is equal to 300 kelvin mass is equal to 40 into 1.66 into 10 to the power minus 27 kg for some typical (( )) delta E is 0 and h nu is 40 centimeter inverse and if we substitute these number if we plug in this number over here then you will end up to getting like 0.09 . So, it is much much less you see it is much much less than unity. So, it it reflects that maybe out of 100 if it is 0.09 then out of 100 9 collisions are successful and remaining 91 91 is of no use although they are colliding atoms are colliding onto the surface and one more important point that we should think of is the is the adsorption process and corresponding change in entropy you see that something if something is adsorbed onto onto the surface like this before adsorption it had you know more degrees of freedom to move now since it sticks to the surface. So, its you know restriction is more its freeness to movement is reduced. So, if its freeness to movement is reduced then of course, its entropy should reduce. So, adsorption always results in you know reduction in entropy and there maybe steric factor leading to reduction of s as well.

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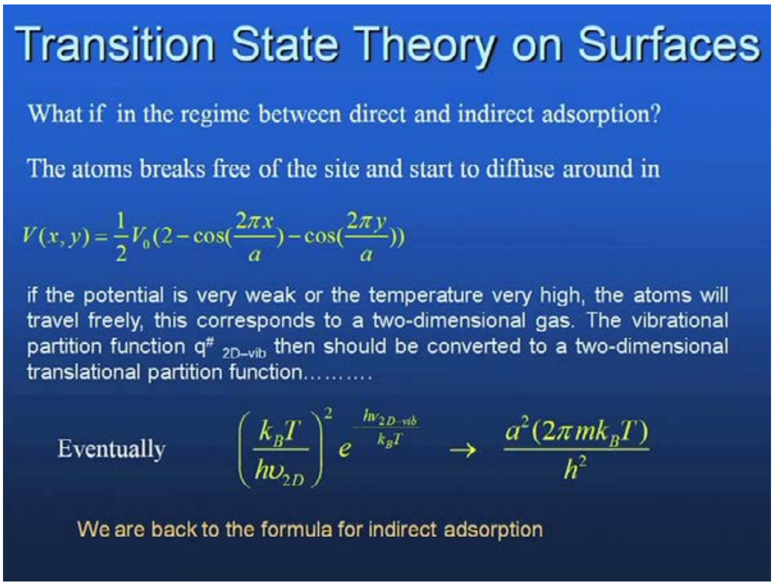

Transition State Theory on Surfaces

What if in the regime between direct and indirect adsorption?

The atoms breaks free of the site and start to diffuse around in

$$V(x,y)=\frac{1}{2}V_0(2-\cos(\frac{2\pi x}{a})-\cos(\frac{2\pi y}{a}))$$

if the potential is very weak or the temperature very high, the atoms will travel freely, this corresponds to a two-dimensional gas. The vibrational partition function $q^{\#}_{2D-vib}$ then should be converted to a two-dimensional translational partition function……….

Eventually $$\left(\frac{k_BT}{h\upsilon_{2D}}\right)^2 e^{\frac{h\nu_{2D-vib}}{k_BT}} \rightarrow \frac{a^2(2\pi mk_BT)}{h^2}$$

We are back to the formula for indirect adsorption

Next is what if the regime between direct and indirect adsorption if we are in between these two because we have discussed two extreme situations one is your direct adsorption means we talked about that you know in our earlier class and I earlier lecture and right now discussed direction adsorption now what happens if we are in between. So, the atoms atoms break break I mean atoms break free of site and starts to diffuse. So, atoms are now detached and becomes free and it will start to diffuse now if the potential is very weak or temperature is very high potential means the force which binds the atom onto the onto the surface if this potential is very weak potential or the form this V x y since it is in two dimension. So, its x y potential has the form this cosine function to cosine function I mean it is a cosine function there is another cosine function. So, if temperature is high or if the you know if the potential is weak then atoms will travel freely. So, atoms will travel freely means here and there it will it will travel because temperature high means temperature high means. So, h nu by k T or k T k B T S you know much much greater than h nu so; that means, they will have the option to move around the surface here and there in two dimension. So, it is basically a two dimensional gas although in kinetic theory of gas we have seen that atoms or the gas particles may move within your container here and there in three dimension so, but here since out of three degrees of freedom one is you know taken off. So, therefore, this situation can be regarded as regarded as a two dimensional gas and the vibrational partition function q double dagger two D vibration then should be converted to a two dimensional part you know translational partition function because it is moving around on the surface and eventually the you know this part will have to be replaced with this one. So, what we get out of this that we are back to the formula for indirect adsorption. So, direct adsorption when we are in the regime between direct and indirect adsorption situation is such that your potential is very weak the force which binds your atom onto the surface that is the potential surface I mean potential function is you know the amount of potential or the force is weak that is why it is called your potential is very weak that is the force with which it is attracting towards the surface is weak or if temperature is high high temperature means there there you know restriction is reduced because its thermal motion is increased. So, thermal motion will tend to compete with the attractive force and ultimately if it is very high that is if the thermal motions or the thermal energy is very high then they should get free free means the restriction is not there therefore, your you know your direct adsorption where initially those atoms were confined they are immobilized are now are now a kind of mobile. So, that is why the situation is a two dimensional gas and your corresponding partition functions are now you know reduced like this you know we have to replace this with corresponding translational partition function.

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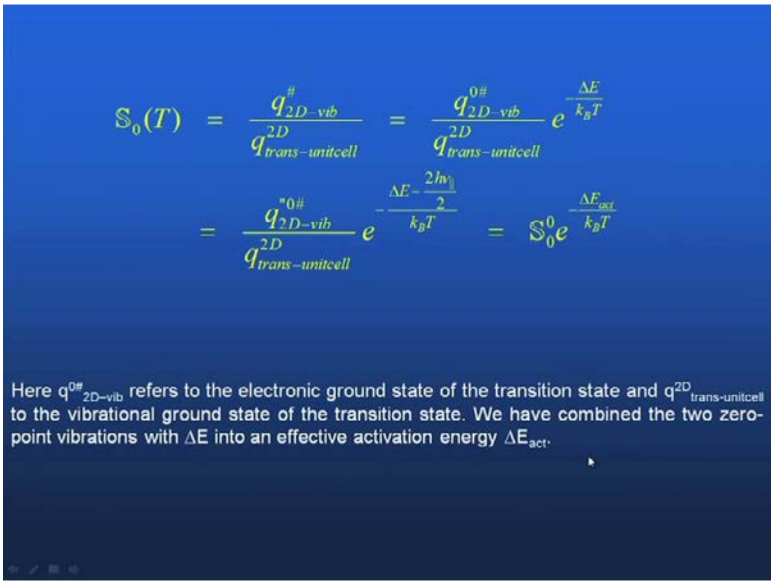

$$\mathbb{S}_0(T) = \frac{q^{\#}_{2D-vib}}{q^{2D}_{trans-unitcell}} = \frac{q^{0\#}_{2D-vib}}{q^{2D}_{trans-unitcell}} e^{-\frac{\Delta E}{k_B T}}$$

$$= \frac{q^{"0\#}_{2D-vib}}{q^{2D}_{trans-unitcell}} e^{-\frac{\Delta E - \frac{2h\nu_{\parallel}}{2}}{k_B T}} = \mathbb{S}^0_0 e^{-\frac{\Delta E_{act}}{k_B T}}$$

Here $q^{0\#}_{2D-vib}$ refers to the electronic ground state of the transition state and $q^{2D}_{trans-unitcell}$ to the vibrational ground state of the transition state. We have combined the two zero-point vibrations with ΔE into an effective activation energy ΔE_{act}.

So, S T S 0 T will have this expression. So, S 0 T is S 0 0 into e to the power minus some delta E act activation. So, overall it is a kind of overall. So, there is delta E and plus there is another you know vibr[ation]- you know perpendicular vibration frequency for your perpendicular vibration. So, here you know this q 0 dagger 2 D vibration refers to the electronic ground state or the transition state and q 2 D trans transition- transition state unit cell to the vibrational ground state of the transition state this refers to and we have combined the two zero point vibrations with delta E into an effective activation energy this is called your effective activation energy this is your effective activation. So, you see we have combined this 1 delta 0 with two zero-point vibrations because you see zero-point vibration is h nu divided by 2 half h nu into 2. So, it is basically we we are referring to two two zero-point vibration because we have converted your two dimensi[onal]- in two dimensional case your two vibrations into translation. So, that is why in effect we have added this much of energy to the overall activation energy and that gives you this you know this expression and additional exponential term.

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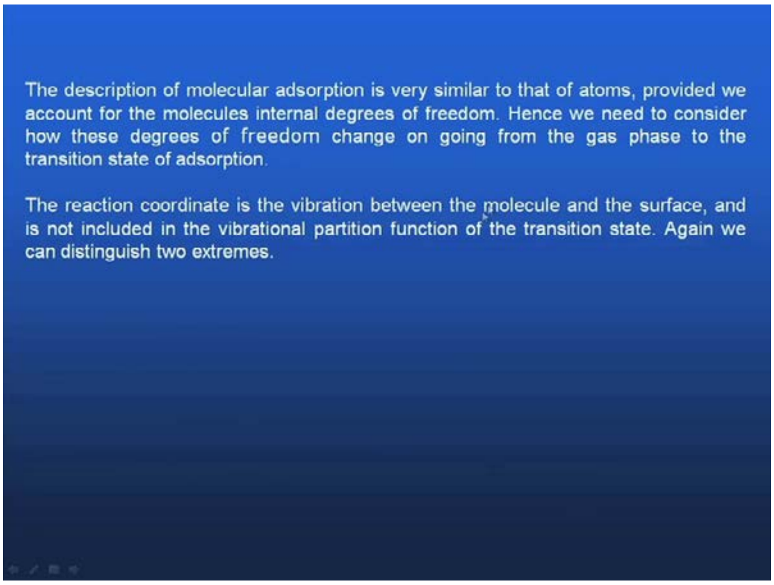

The description of molecular adsorption is very similar to that of atoms, provided we account for the molecules internal degrees of freedom. Hence we need to consider how these degrees of freedom change on going from the gas phase to the transition state of adsorption.

The reaction coordinate is the vibration between the molecule and the surface, and is not included in the vibrational partition function of the transition state. Again we can distinguish two extremes.

Now, the description of molecular adsorption is very similar to that of atoms now we will move onto molecular adsorption. So, this description of molecular adsorption we started with discussion on atom adsorption onto the molecular onto the metal surface maybe or maybe on onto the surface now what if we replace a polyatomic entity atoms are maybe in most of the cases monoatomic entities in gas phase especially although there are exceptions to this. So, in general for simplistic cases atoms are you know thought to be monoatomic, but if it is if it is polyatomic; that means, maybe if it is a molecule or if it as an aggregate of atoms then what will happen. So, description of molecular adsorption is very similar to that of atoms provided we account for the molecules molecular internal degrees of freedom when you account we have to we have to account for the internal degrees of freedom because in case of atoms there is no degrees of freedom internal degrees of freedom like you know vibration or maybe you know rotation. So, hence we need to consider how these degrees of freedom change on going from gas phase to the transition state of adsorption that is the moment the atoms I mean molecules are in the gas phase it gets adsorbed onto the surface. So, what is the what what will be the fate of these you know fate of this internal modes that is you know vibration. So, the reaction coordinate is the vibration between the molecule and the surface. So, this is say this is your molecule say this is your molecule and your reaction coordinate will be like this is your reaction coordinate. So, if this is your surface. So, this is your reaction coordinate like this. So, you know this distance distance changes. So, as it does like this. So, the reaction coordinate is the vibration between the molecule and surface and is not included in the vibrational partition function of the transition state and again we can distinguish two extreme cases.

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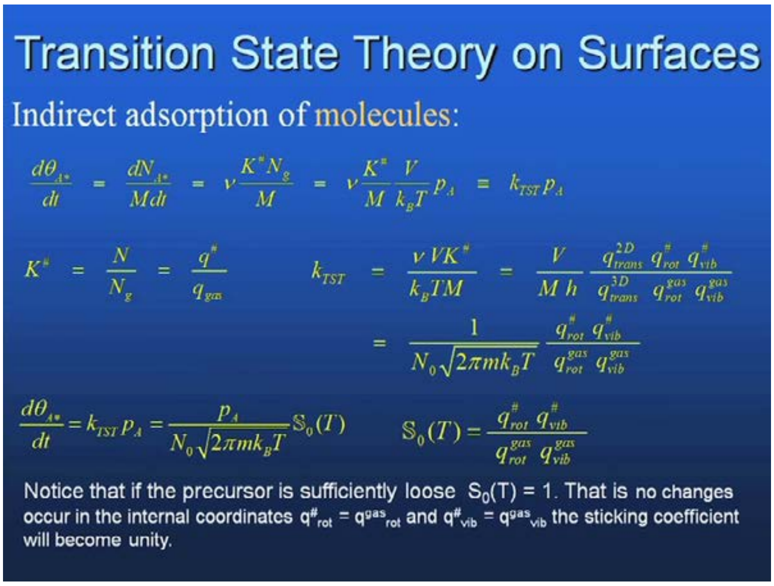

Transition State Theory on Surfaces

Indirect adsorption of molecules:

$$\frac{d\theta_{A^*}}{dt} = \frac{dN_{A^*}}{M\,dt} = \nu\frac{K^{\#}N_g}{M} = \nu\frac{K^{\#}}{M}\frac{V}{k_BT}p_A = k_{TST}\,p_A$$

$$K^{\#} = \frac{N}{N_g} = \frac{q^{\#}}{q_{gas}} \qquad k_{TST} = \frac{\nu VK^{\#}}{k_BTM} = \frac{V}{M\,h}\,\frac{q^{2D}_{trans}\;q^{\#}_{rot}\;q^{\#}_{vib}}{q^{3D}_{trans}\;q^{gas}_{rot}\;q^{gas}_{vib}}$$

$$= \frac{1}{N_0\sqrt{2\pi mk_BT}}\,\frac{q^{\#}_{rot}\;q^{\#}_{vib}}{q^{gas}_{rot}\;q^{gas}_{vib}}$$

$$\frac{d\theta_{A^*}}{dt} = k_{TST}\,p_A = \frac{p_A}{N_0\sqrt{2\pi mk_BT}}\,\mathbb{S}_0(T) \qquad \mathbb{S}_0(T) = \frac{q^{\#}_{rot}\;q^{\#}_{vib}}{q^{gas}_{rot}\;q^{gas}_{vib}}$$

Notice that if the precursor is sufficiently loose $S_0(T) = 1$. That is no changes occur in the internal coordinates $q^{\#}_{rot} = q^{gas}_{rot}$ and $q^{\#}_{vib} = q^{gas}_{vib}$ the sticking coefficient will become unity.

Now indirect adsorption of molecules we will be using the similar expression as we did for as we did for you know indirect adsorption of atoms we use the similar expression that d theta a start d t is equal to d N A star d t divided by M is equal to nu K double dagger N g divided by M and ultimately this is equivalent to k T S T into P A gas pressure and K double dagger is N by N g your q q double dagger by q gas. So, this gives you like. So, rate constant after transition state theory is this nu divided by K V into T into V K double dagger divided by M. So, V M and h is here. So, ultimately what we got is your q translation in two dimension and your you see this is your double dagger rotation and vibration these are the internal modes Internal modes in the activated state and of course, there is a translation in two dimension. So, this way they will translate in two dimension. So, your expression is this and divided by q translation in three dimension because it is in gas its partition function corresponding to the gas phase into q rotation in gas phase q vibration in gas phase. So, if we put the you know respective expression you see it is 2 D it is 3 D. So, we will be getting this expression. So, we we are not in a position right now to you know go into the expression of this we just simplified this term and taking these together we got this expression so; that means, your K double I mean k T S T is this overall d theta A star d t which is equal to k T S T into P

A where P A is over here and you write this this where you put put this over here with S 0 T is equal to ratio of this partition function's that is rotation vibration for your transition state and you know gas phase rotation vibration. So, rotation vibration double dagger state and gas phase. So, notice that if the precursor is sufficiently loose loose means loose means it is not very you know very much sticking onto the surface that is no change occurs in the internal coordinates. So, and the sticking coefficient will be will be very close to unity; that means, if it is very loosely bound if it is very loosely bound onto the surface then as if we can think for all practical purposes that you know fate of your partition function is not much you know there is not much change in the fate of your partition function so; that means, you can you can write for all practical purposes. So, this rotational one this one is close to this one and this one close to this one as a result of which S 0 T is very close to unity. So, for your loose precursor if the precursor is loosely bound then the situation is like this.

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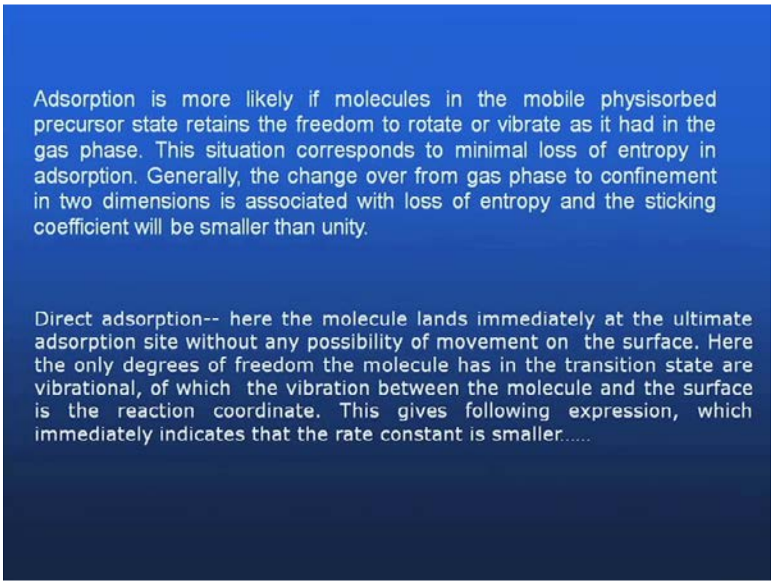

Adsorption is more likely if molecules in the mobile physisorbed precursor state retains the freedom to rotate or vibrate as it had in the gas phase. This situation corresponds to minimal loss of entropy in adsorption. Generally, the change over from gas phase to confinement in two dimensions is associated with loss of entropy and the sticking coefficient will be smaller than unity.

Direct adsorption-- here the molecule lands immediately at the ultimate adsorption site without any possibility of movement on the surface. Here the only degrees of freedom the molecule has in the transition state are vibrational, of which the vibration between the molecule and the surface is the reaction coordinate. This gives following expression, which immediately indicates that the rate constant is smaller......

So, so adsorption is more likely molecules are in the mobile physisorbed precursor state and retains the freedom to rotate and vibrate as it had in the gas phase this situations corresponds to minimal loss of entropy in the adsorption process as if there is you know not much strong linkage there although it is a kind of it is these molecul[es]- gas molecules are inclined towards the surface, but but they are they are not means the[re]- there there is not much change in their in their you know mobile state or maybe in their internal internal modes. So, that is why there is a minimal loss of entropy while the gas molecules are adsorbed. So, that is why your sticking coefficient that is S 0 T is close to unity. So, this happen in case of your indirect adsorption now what happens to direct adsorption here the molecules land immediately immediately at the ultimate adsorption site. So, this they are they are landing onto the surface wherever they will land that is their immediate that is their immediate position they will not move around any further. So, here the molecule lands immediately at the ultimate adsorption site without any possibility of movement on the surface. So, here the only degree of freedom that the molecule has in the trans transition state are vibrational. So, this is the only only mode that is the vibration. So, so this is the reaction coordinate it is vibrating. So, once it is adsorbed it will not move this way that way or whatever it will do only say this this it has the option only this way like this suppose this is your adsorbed one so; that means, on on the surface. So, it will do like this this this motion this motion is you know like this. So, it does like this. So, kind of this this is your one. So, this vibration. So, so this gives the expression which immediately indicates that the rate constant is you know smaller

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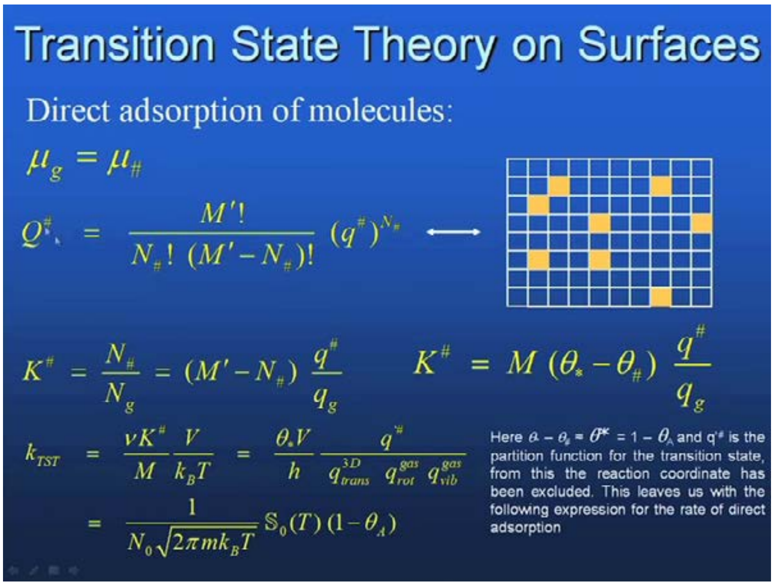

Transition State Theory on Surfaces

Direct adsorption of molecules:

$$\mu_g = \mu_\#$$

$$Q^{\#}_{*} = \frac{M'!}{N_\#!\,(M'-N_\#)!}\,(q^\#)^{N_\#}$$

$$K^\# = \frac{N_\#}{N_g} = (M'-N_\#)\,\frac{q^\#}{q_g} \qquad K^\# = M\,(\theta_* - \theta_\#)\,\frac{q^\#}{q_g}$$

$$k_{TST} = \frac{\nu K^\#}{M}\,\frac{V}{k_B T} = \frac{\theta_* V}{h}\,\frac{q^\#}{q^{3D}_{trans}\,q^{gas}_{rot}\,q^{gas}_{vib}}$$

$$= \frac{1}{N_0\sqrt{2\pi m k_B T}}\,S_0(T)\,(1-\theta_A)$$

Here $\theta_* - \theta_\# = \theta^* = 1 - \theta_A$ and $q^{\#}$ is the partition function for the transition state, from this the reaction coordinate has been excluded. This leaves us with the following expression for the rate of direct adsorption

Let us go to that direct adsorption of molecules. So, you as as usual some of the sites are occupied with respect to the molecules and your your overall partition function q in the transition state is this and you know you you are you are putting the similar treatment as we did for direction adsorption of atoms. So, k T S T will come out to be like this q primed double dagger divided by q trans 3 D because situation is different that in case of your indirect adsorption we could have retained you know q D trans then q double dagger you know double dagger rotation q double dagger vibration, but here we cannot write and also out of these we we have to take out one mode which is responsible for this movement. So, here you know theta start minus theta dagger is close to theta star which is equal to one minus theta A A as usual and q primed double dagger is the partition function of the transition state from this the reaction coordinate has been excluded this is the reaction coordinate I have talked about it is not the total partition function, but one one coordinate I mean one mode is excluded. So, this leaves us with the following expression for the rate of direct adsorption. So, this is the rate constant and you know similar, but the thing is that this is S 0 T S 0 T is something different.

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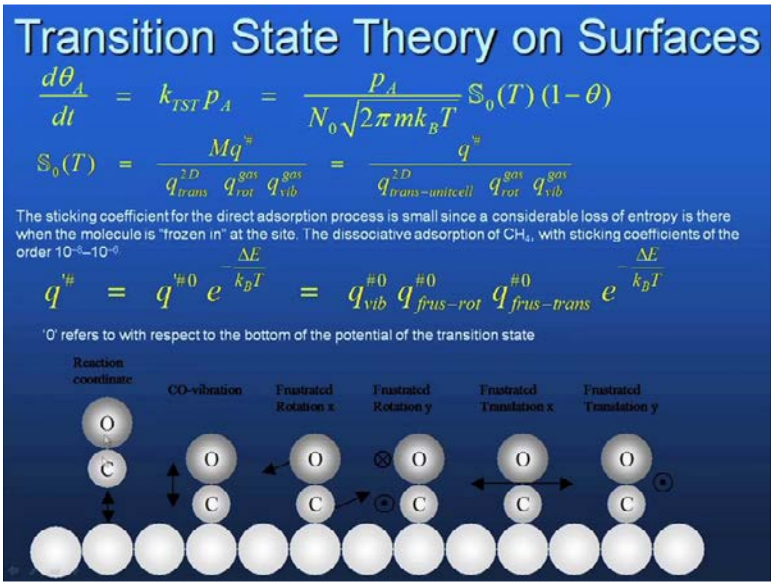

Transition State Theory on Surfaces

$$\frac{d\theta_A}{dt} = k_{TST}\,p_A = \frac{p_A}{N_0\sqrt{2\pi m k_B T}}\,\mathbb{S}_0(T)\,(1-\theta)$$

$$\mathbb{S}_0(T) = \frac{Mq^{'\#}}{q_{trans}^{2D}\;q_{rot}^{gas}\;q_{vib}^{gas}} = \frac{q^{'\#}}{q_{trans-unitcell}^{2D}\;q_{rot}^{gas}\;q_{vib}^{gas}}$$

The sticking coefficient for the direct adsorption process is small since a considerable loss of entropy is there when the molecule is "frozen in" at the site. The dissociative adsorption of CH_4, with sticking coefficients of the order 10^{-8}–10^{-6}.

$$q^{'\#} = q^{'\#0}\,e^{-\frac{\Delta E}{k_B T}} = q_{vib}^{\#0}\,q_{frus-rot}^{\#0}\,q_{frus-trans}^{\#0}\,e^{-\frac{\Delta E}{k_B T}}$$

'0' refers to with respect to the bottom of the potential of the transition state

So, what is that now you see that for your direct adsorption what we get d d t of theta is k T S T P A which is equal to this much into S 0 T into 1 minus theta and S 0 T is this where one degree of freedom less. So, this divided by q trans 2 D in unit cell translational partition function in the unit cell and of course, the rotational code partition function for the gas and vibrational partition function for the gas let us take an idea about the you know about this sticking coefficient what is the typical value the sticking coefficient for the direct adsorption process is small since a considerable loss of entropy is there. So, if there is not not a considerable amount of loss in entropy is there then your sticking coefficient will be will be high. So, there is a considerable amount of loss of entropy is there and when the molecules are frozen at this site it is a kind of frozen once it gets a site it remains over there for time. So, it is a frozen it'll not move anything it has the option to just do this one along the reaction coordinate example is the dissociative adsorption of methane has the sticking coefficient of the order of 10 to the power of minus 8 to 10 to the power of minus 6 it is a very very small it is a very very small small quantity now what is this q primed double dagger q primed double dagger can be written as q primed double dagger 0 with with you know an exponential term with an exponential quantity and of course, there is vibration frustrated rotation and frustrated transition these are all arising out of the internal internal modes into exponential and energy term now this 0 refers to with respect to the bottom of the potential of the transition state. So, so you know this is the reaction coordinate this is the reaction coordinate. So, you see we we think of your carbon monoxide adsorption onto some metal surface you see that this is the reaction coordinate along with this this can vibrate ok. So, C O this is your C O vibration that may happen that vibration may be responsible for some for further reaction to occur. So, this is your you know this is this is one normal typical carbon monoxide vibration. So, actually the reaction coordinate is this one. So, it is bound. So, like this. So, this is your molecule this is your surface. So, this where this is where you know in this region you know it is changing in distance this is your frustrated rotation x rotation this is frustrated y rotation like this this one the other one initially frustrated x rotation is this y rotation is this like this and frustrated translation is kind of you know as a whole this one is moving frustrated translation and frustrated y translation is in this direction. So, so. So, what do we get out of this discussion now it is important to note that it is important to note that we we are discussing here the adsorption process and you know we are trying to apply transition state theory onto onto surface adsorption now it is typically categorized into two like one is your is your indirect adsorption another is your direct adsorption now for indirect adsorption your what happens that it is loosely bound. So, loosely bound means it has got the option to move around onto the surface. So, it is loosely bound and corresponding sticking coefficient is is high enough. So, it moves around the around you know in in a two dimensional surface and for your calculation of this partition function you know you have to take out one mode which is responsible for your for your reaction to occur that is the mode which is the the mode which will be converted to a translation mode. So, at par with your transition state theory and when it is the case of direct adsorption and and also one thing that one is the case for your atomic adsorption another is your molecular adsorption. So, atomic adsorption means it is the single atomic entity that is getting adsorbed and the molecule in case of molecule you can treat the whole whole thing that is theoretical treatment will be identical only thing is that that you have to you have to take into account that for molecules there are additional internal modes translation not translation I mean rotation and vibration. So, these are the internal modes that you have to you know consider on top of what you have considered in case of atoms. So, internal modes are to be considered are to be considered here also for your molecular adsorption. So, so like if we go back again that if it is the case of direct adsorption even if it is molecule or even if it is atom you see that if you look into the two dimensional surface that maybe maybe initially some of them are occupied and remaining. So, your gas molecules or gaseous atoms which are going to be adsorbed onto this they will be distributed among these available adsorption sites and your adsorption ah available adsorption site and another thing is that that maybe for direct adsorption hundred percent you know hundred percent you know reaction is not possible hundred percent reaction means suppose hundred molecules are colliding not hundred molecules will be adsorbed maybe a certain fraction will be excluded they will come out and we we have to you know for this we have to write the you know corresponding partition function and then we have to we have to treat them appropriately. So, so we see and also importantly when temperature is very high then maybe if we are in a region ranging between direct and indirect adsorption then if temperature is very high or the potential force which binds your atom which binds your atom atom or molecule together on onto the surface which binds your atom or molecule onto metal surface if this potential force is weak is not very strong that it binds it is a very weak force or if your temperature is high if temperature is high then you know their thermal motion thermal you know ah motion will compete with your attractive pull. So, what will happen they will move around this thermal motion is. So, prominent that although initially they they stick to one position, but what will happen if temperature increases they will start to you know do some wiggling like this and ultimately your your firm position the position which was which was fixed will no longer remain there it will just you know you know it will just to move around start to move around like this. So, so this becomes you know this case of indirect adsorption which is associated with some weak force. So, so this lecture you know this particular piece of lecture which where we talked about direct adsorption or indirect adsorption of atoms of molecule give you an idea of how you know how transition state can be applied applied to to explain you know surface reactions and how does it depend on gas pressure how should it depend on temperature how the entropic factors are important in determining whether your sticking coefficient is will be will be close to unity or will be very less that is when it is the case of direct adsorption then you see I have shown that value is less, but if it is not a direct adsorption if it is an indirect adsorption it becomes higher because higher because you know it is not attended by a huge loss of entropy, but when it is the case of when it is the case of direct adsorption then you know it has to surmount its additional you know degrees of freedom because once it is firmly fixed over there then its other modes are now you know not in action.

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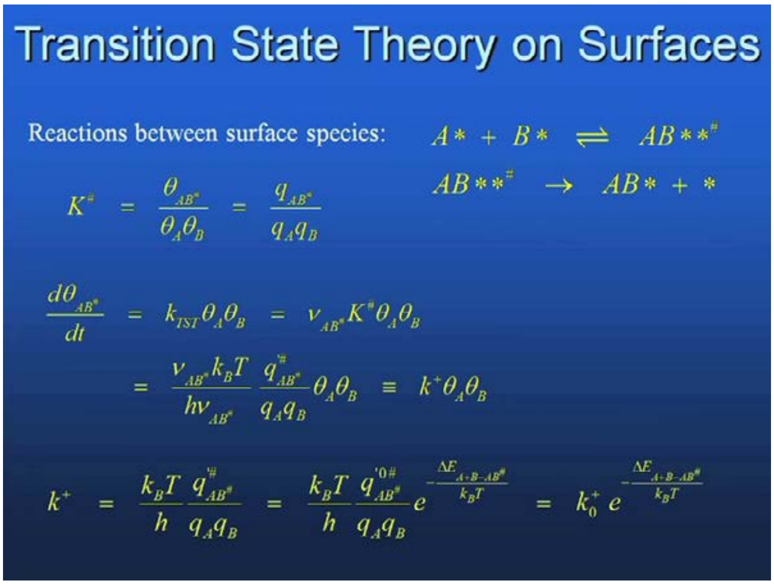

Transition State Theory on Surfaces

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

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

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

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

$$= \frac{\nu_{AB^*}k_BT}{h\nu_{AB^*}}\frac{q^{\#}_{AB^*}}{q_Aq_B}\theta_A\theta_B \equiv k^{+}\theta_A\theta_B$$

$$k^{+} = \frac{k_BT}{h}\frac{q^{\#}_{AB^{\#}}}{q_Aq_B} = \frac{k_BT}{h}\frac{q'^{0\#}_{AB^{\#}}}{q_Aq_B}e^{-\frac{\Delta E_{A+B-AB^{\#}}}{k_BT}} = k_0^{+}\,e^{-\frac{\Delta E_{A+B-AB^{\#}}}{k_BT}}$$

So, you know in next lecture we will you know we will extend a little bit a little further in in our next lecture and we will close this transition state theory you know maybe in next lecture. So, after that after we we are done with this transition state theory and theories of reaction rate we will move onto let us go back to you know what is there in the you know in the in the list let us see let us see.

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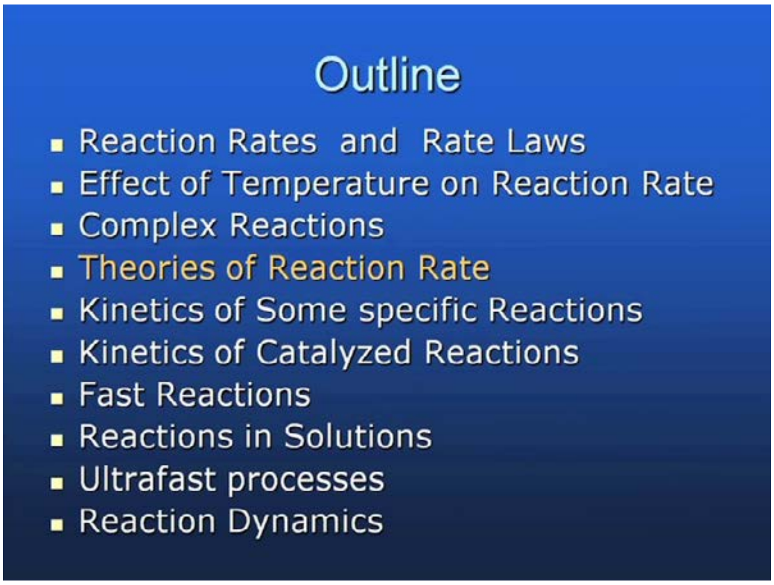

Outline

- 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, after you are done with this there is there is little portion to left to be talked about with respect to surface reaction we will move onto kinetics of some specific reactions we will we will move onto kinetics of some specific reactions like maybe. So, in under the under this heading maybe some catalyzed reaction maybe some photochemical reaction like that we will we will talk on that some specific reaction we will take up some specific reaction and then maybe we will move onto kinetics of catalyzed reaction like (( )) that is enzyme catalyzed reaction and other reactions. So, this much for today. So, in the next lecture we will maybe we will conclude this theories of reaction rate portion and we will maybe start with kinetics of some specific reaction. So, till then have a nice time see you in the next lecture .