Theories of Reaction Rate
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Lecture No. # 11
Theories of Reaction Rate (contd…)

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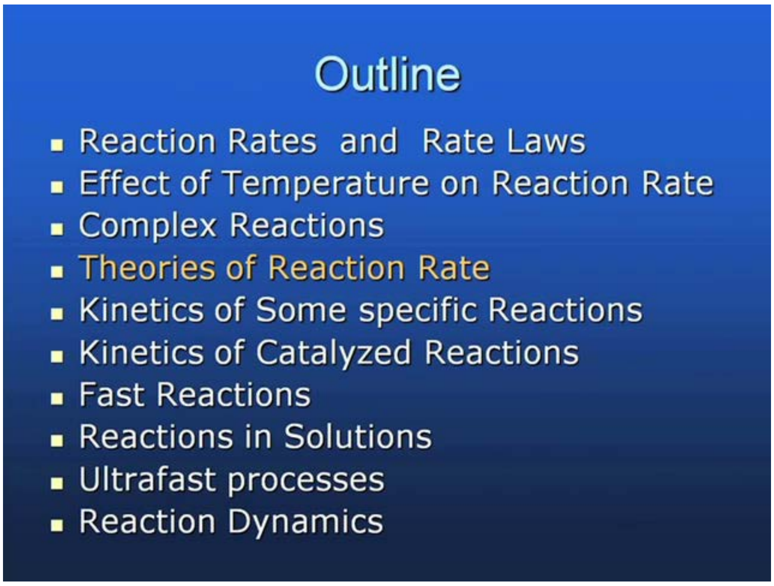

Outline

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

Hello, good morning everybody. So, we are discussing rate processes. So, under this heading we started to discuss theories of reaction rate. So, theories of reaction rate; so, last day we talked about this transition state theory before that we we talked about collision theory. So, now it is time to have a comparison of means whether we can make any comparison between these two theories.

Now, before that let us try to recap, about recap these two theories means basic like, basic postulates of something say - what is collision theory? So, collision theory is based on a hard-sphere model; that one molecule or an atom is there and reacting. Reacting means this reaction occurs via you know this collision occurs via collision. So, and this collision is purely purely based on the idea that these spheres are hard spheres that is molecule or atoms; those which are involved in collision process, so they are hard spheres, so it is a hard sphere collision theory.

And this collision theory is based on the concept of means it was borrowed from the concept of kinetic theory of gases that like in kinetic theory; you know this gas molecules. So, this basically this collision theory is applied to gas phase reactions. So, in kinetic theory it is postulated that these molecules are in a random to and flow motion within a container, and there is a collision between there is collision between you know molecules or atoms; and maybe this collision there is collision with the wall as well, wall of the container as well. Now, it is thought that this chemical reaction occurs as a result of this; this collision as a result of this collision.

So, if there is no collision then there is no chance of reaction to take place; so, this is a an a redistribution of atom or maybe if there is an exchange of atom between 2 interacting species is there through reaction. So, in that case these two species or these two parts should come in close contact at least once. So, that they will have a chance to exchange that is why collision is required and it is also explained in this way that not all the collisions are very effective, only those collisions which are having means the molecules those which are having some requisite amount of energy at least some minimum amount of energy; will be able to react further to produce your desired product.

But if your if the energy is you know less than a definite amount then the reaction will not take place, even if there is collision, those collisions are not effective. And also properly oriented properly oriented collision will lead to lead to product formation, but on in all these cases if is important to note that we do not have any idea of exactly; what is going on when two molecules are colliding with each other; when these two molecules are colliding with each other.

What is happening here in this in this region, in this in this region where there is a contact; so, we do not know we have no idea on that; what is exactly going on only the gross idea is that we have got two hard spheres, they are just doing this collision and then reaction is taking place. So, it is just you know a kind of qualitative idea; it does not give you know lot of insight. Now, in transition state theory what is there in transition state theory? Transition state theory says that an activated complex will be formed, during the codes of reaction. So, one molecule, there is one molecule, there is another molecule. They will from an activated complex, maybe something like that an activated complex.

And this activated complex will have higher energy compared to your reactant molecule or product molecule, and this higher energy state is called the activated state. So, once activated state is reached then the system, I mean system means this activated state has got the option to move forward to give you products or maybe it can come back it can come back to give you the reactants back. So, the thing is that you know in activated complex theory, there is a definitive there is a definitive option of you know structure; that maybe if A and B or maybe two interacting species which are undergoing a chemical reaction.

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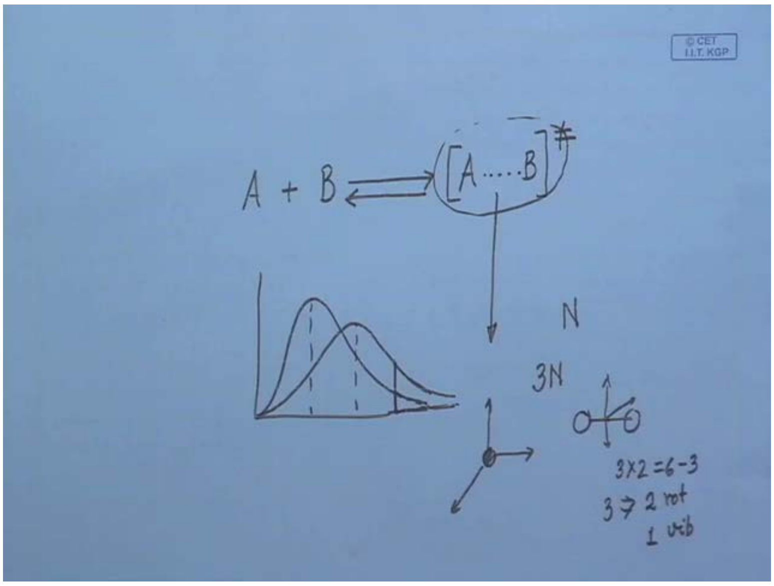

They will form say an additional linkage between them like say, like this say you have got A, you have got B and we can imagine that from this, it will form something like A, A weak interaction. So, this is your activated complex, then this activated complex will react further; it may go back to give you reactants as well.

So, there is a definitive you know option for the geometry or internal structure of this, and the thing is that there is a quick equilibrium established between A plus B with a reactivated. So, this is a fast equilibrium and then this activated complex is gradually depleted to give you your products. So, of course I can we can tell that your collision theory is not that much definitive, but it this activated complex theory or maybe your transition-state theory, you know it tries to talk about a structure a internal structure internal structure of this species, and also importantly it talks about you know a mode means out of the many modes out of the many modes say this is a multi-atomic species.

It will have 3 translation, then if it is a non-linear then it will have 3 rotational and remaining will be your vibrational modes; and out of these vibrational modes, a specific vibrational mode will have you know high amplitude and a low frequency. So, that high amplitude, low frequency, vibrational mode; so, that will be ultimately converted to a translational mode.

So, we have to take out one of the many vibrational modes of the molecule or or the complex and convert this to a translation, and this translation is responsible for passage from from one side to another, so this particle vibrational mode is responsible for passage from left hand side to right hand side out of the many vibrational mode and that is a weak vibration. And that happens in the it happens with your with your this activated complex. So, a definitive structure and also which particular mode could be responsible for this formation of the product, we can we can also you know deduce that means with the help of your this theory. So, definitely collision theory it it appears that collision theory is much more weaker than your transition-state theory.

Although, collision theory can successfully explain can successfully explain your rate constant absorbed for many gas phase reactions, and also it can explain it can explain the temperature dependence. As I told you that if you think of Maxwell distribution of molecular velocities, and if we increase the temperature, then you will be seeing that the that the plot that is probability versus C that is the velocity or the speed of the molecule, if you increase the temperature the graph flattens, and your most probable velocity is shifted to the higher region.

And if you think of definitive amount of energy, the number of molecules with number of molecules having that amount of energy or more than that will be increased as a result of increase of temperature. So that means, you will have more number of you know, successful collisions and therefore, more reaction will take place. So, temperature dependence can be well explained with this theory, but it is rather a qualitative it can not explain exactly the the structure of your structure of your of the of the species which is responsible for the reaction to take place.

That is it does not think about any any species of this sort. And what is exactly going on during collision is not also very obvious here. So it can successfully explain the temperature dependence, but you know, it is weaker compared to your transition-state theory. And if you think of transition-state theory, your entropy of activation has got connection with your steric factor - steric factor of the reaction. And similar term is involved with collision theory, which is called also the probability factor that is not all the collisions are effective, only a certain fraction of this collisions are responsible for reaction to occur. That is with proper geometry. Therefore, therefore, collision theory you know, if we compare these two, so collision theory I mean a transition-state theory is on on the upper side compared to your collision theory.

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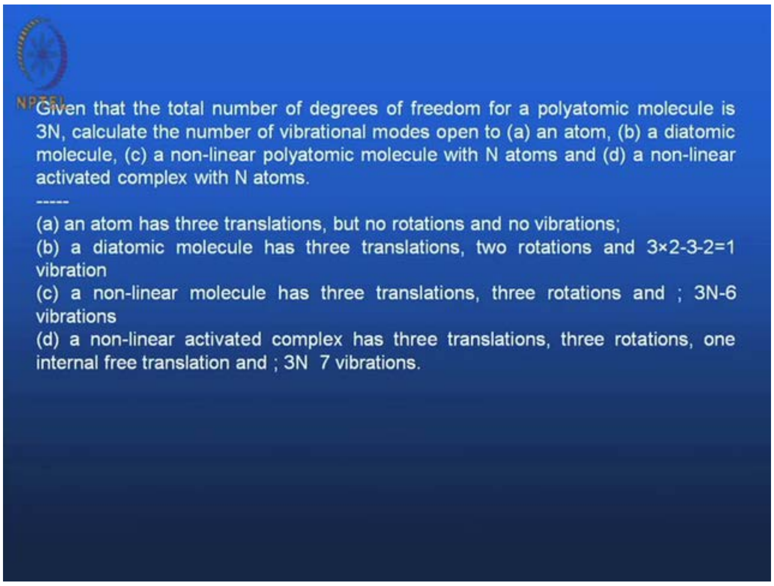

Given that the total number of degrees of freedom for a polyatomic molecule is $3N$, calculate the number of vibrational modes open to (a) an atom, (b) a diatomic molecule, (c) a non-linear polyatomic molecule with N atoms and (d) a non-linear activated complex with N atoms.

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(a) an atom has three translations, but no rotations and no vibrations;
(b) a diatomic molecule has three translations, two rotations and $3\times2-3-2=1$ vibration
(c) a non-linear molecule has three translations, three rotations and ; $3N-6$ vibrations
(d) a non-linear activated complex has three translations, three rotations, one internal free translation and ; $3N$ 7 vibrations.

Now, let us have some idea of the degrees of freedom, now these that given that the total number of degrees of freedom for a poly-atomic molecule is 3N.

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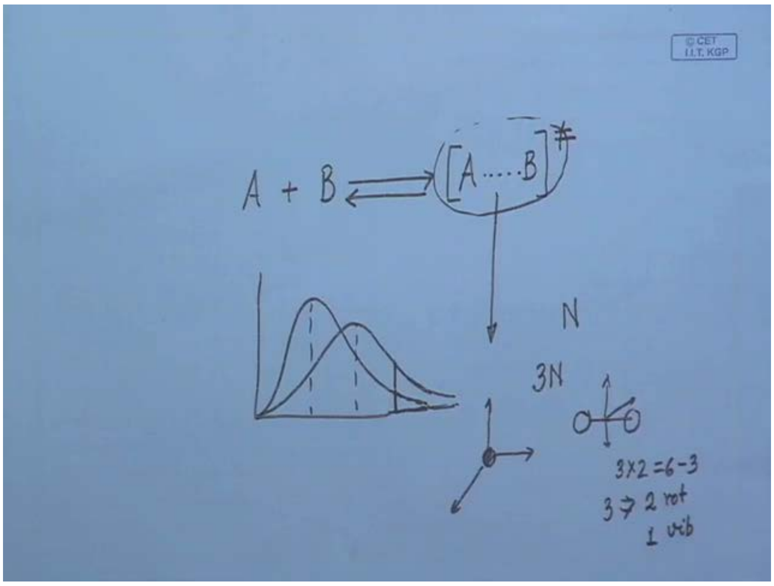

That is polyatomic molecule means, you have N number of atoms. So, polyatomic molecules. So, how many degrees of freedom for this molecule will be there; there will be total 3N degrees of freedom, for say for a Monoatomic case; say only 1 atom how many degrees of freedom it will have, it will have 3 three translation, in three mutually orthogonal axes.

Now, if we increase number of atoms by 2 that means if it is a diatomic system, then what will happen? To your diatomic molecule; so, how many translational degrees of freedom will be there, still it will be 3 translational degrees of freedom, because it can move in three you know intially orthogonal directions; that is a its center of mass can move in three mutually orthogonal direction like this.

Now, what about rotation? It will have so it will have since, this has 3 i 2 atoms; so, it will have 3 into 2 altogether 6 degrees of freedom of which of which 3 will be translation, so, minus 3; so, that means you have got rotation plus vibration to be equal to 3 of which let us try to find out how many rotational mode and how many vibrational modes are there? So, if you think of say this is a diatomic molecule say this is a diatomic molecule.

So, if you if you think of rotation about its axis; it does not give you a new configuration. New, new way of representation, So that means rotation about the internuclear axis is trivial; so, it does not contribute to the to the you know overall degrees of freedom now if you think of rotation about this axis, about this axis, it gives you new new configuration like this another is this.

So, rotation about this axis will contribute to your rotational degree of freedom; so, this is one rotational degree of freedom about this axis and there is another like this, about this axis, so total two therefore, 2 rotational degrees of freedom remaining how much 1 which will be vibrational, vibration means like this. This vibration, this vibration; so, that means it is a for a diatomic system, you will have you will have 3 translation, 2 rotation, 1 vibration.

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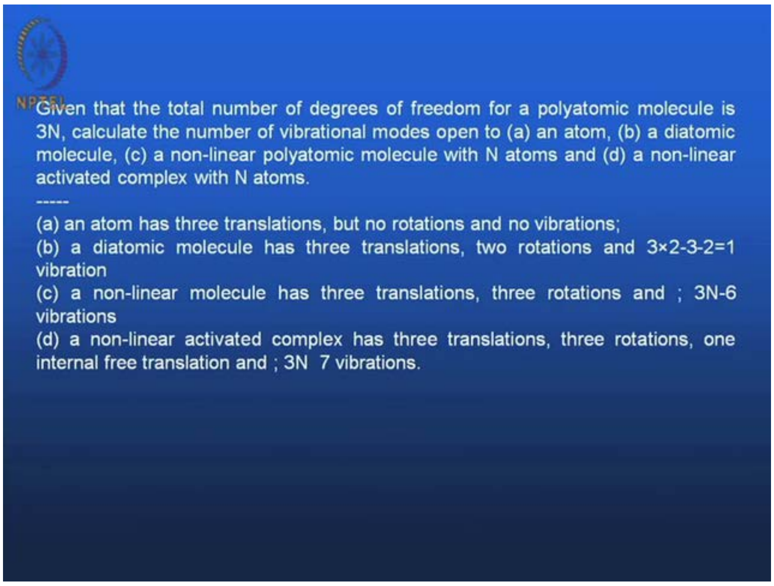

Given that the total number of degrees of freedom for a polyatomic molecule is 3N, calculate the number of vibrational modes open to (a) an atom, (b) a diatomic molecule, (c) a non-linear polyatomic molecule with N atoms and (d) a non-linear activated complex with N atoms.

(a) an atom has three translations, but no rotations and no vibrations;

(b) a diatomic molecule has three translations, two rotations and 3×2-3-2=1 vibration

(c) a non-linear molecule has three translations, three rotations and ; 3N-6 vibrations

(d) a non-linear activated complex has three translations, three rotations, one internal free translation and ; 3N 7 vibrations.

Now, the question is calculate the number of vibrational modes open to a, an atom b for a diatomic molecule as I explained to you c, for a non-linear polyatomic molecule with N atoms, and you know there is a non-linear activated complex with N atoms. So how to look into that as I told you for an atom it will have no vibrational degrees of freedom just translation; just simple translation like this, this way or that way or maybe the other way.

So, it will not have any rotation or any vibration, because it is a spherically symmetric the atomic system is thought to be spherically symmetric. Now, for a diatomic molecule you will have as I told you you will have 1, 1 vibrational degree of freedom that is only it will have this, this motion, this vibrational motion this; that is it will lengthen and it will shrink this motion.

And for a non-linear molecule; so, for a non-linear molecule say this this is a say this is a non-linear molecule like this. So, it will have 3 translation as it is obvious that this will have a center of mass mass maybe located somewhere over here; so, it will move this way or maybe that way or maybe this way. Now, what about rotation means if you think of rotation about this axis say for example, then this rotation will lead to something else so, it will not lead to you know any indistinguishable configuration.

So, maybe it will have a rotation like this axis maybe that axis and maybe another orthogonal axis. So, since this is a non-linear system, you will have 3 rotational degrees of freedom. You will have 3 rotational degrees of freedom therefore, you have 3 N minus 3 and minus 3, so that means 3 N minus 6. So, 6 will be counted for 3 translation, 3 rotation. So, remaining will be 3 n minus 6, so 3 n minus 6 will be the the vibrational degrees of freedom or or such number of vibrational modes are there. What about a non-linear activated complex? What about the non-linear activated complex that since it is a non-linear activated complex like it is a complex, you know maybe you think that it it is something some aggregate kind of thing.

So, it will move like this maybe this way or maybe that way; so, it will have 3translation in the same way like your non-linear molecule, it will have it will have 3 rotation as well; now the question is now the question is what about your vibrational mode? Can you guess guess what will be the number of vibrational modes. So, you in that case in order to find out that you have to you have to take help of transition-state theory. It says that for the reaction to take place, because your non-linear activated complex will for sure undergo reaction to give you products or maybe it will come back to give you reactants.

So, to give you products what you have to have in order to get your product out of many vibrational degrees of freedom; one will be will be taken out and that will be converted to translation and your rate of barrier passage will be equal to K T by h that is the K T is the thermal energy divided by the Planck’s constant. So, that is the frequency with which it will pass the the barrier, it will pass the barrier is the rate with which it is reacting.

So, that means out of many vibrational degrees of freedom one will be taken off and you add that to your total translation; that is initially it had 3 translation plus 1 you call that it is internal free translation on internal translational mode that internal translational mode is responsible responsible for the reaction to occur, internal free translation. So therefore, you have altogether 3 N minus 7 minus is somehow dropped; so, 3 N minus 7 vibrations are there for a non-linear activated complex.

So if we apply transition-state theory to find out you know, find out the number of degrees of freedom that is vibrational degrees of freedom remaining for an activated complex, then you have to think of that out of the many vibrational modes out of the many vibrational modes, one will be taken off one will be taken off and that should be added to the translation and the one which is added to translation should not be called as a direct translational mode but, in turn it can be called as an internal free translation.

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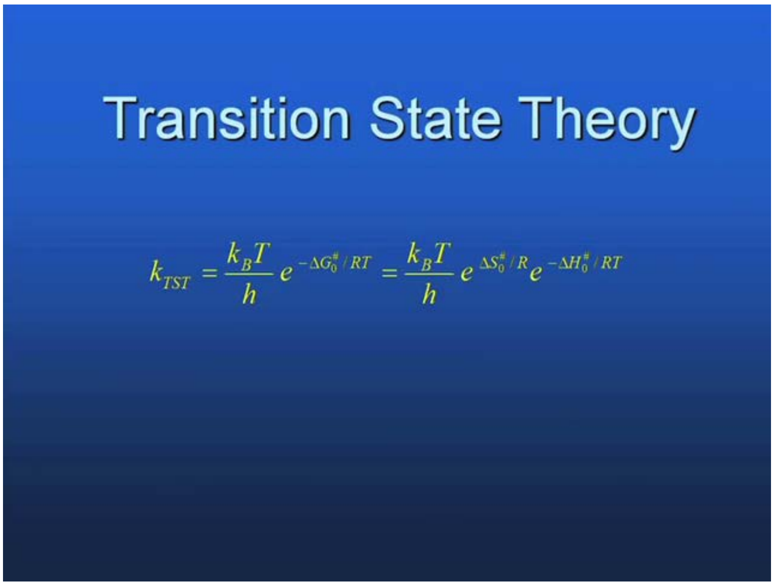

Transition State Theory

$$k_{TST} = \frac{k_B T}{h} e^{-\Delta G_0^{\ddagger}/RT} = \frac{k_B T}{h} e^{\Delta S_0^{\ddagger}/R} e^{-\Delta H_0^{\ddagger}/RT}$$

Next, so transition state theory and now this is the rate constant for your transition state theory it is K T by h you know e to the power minus delta G double dagger zero by R T which is which has got your exponential this entropic term, and this is your enthalpic term; so, it is a simple you know a bulk phase reaction, but what happens if the reaction occurs occurs on surface; do you think that the you know expressions are different, so let us try to try to look into that.

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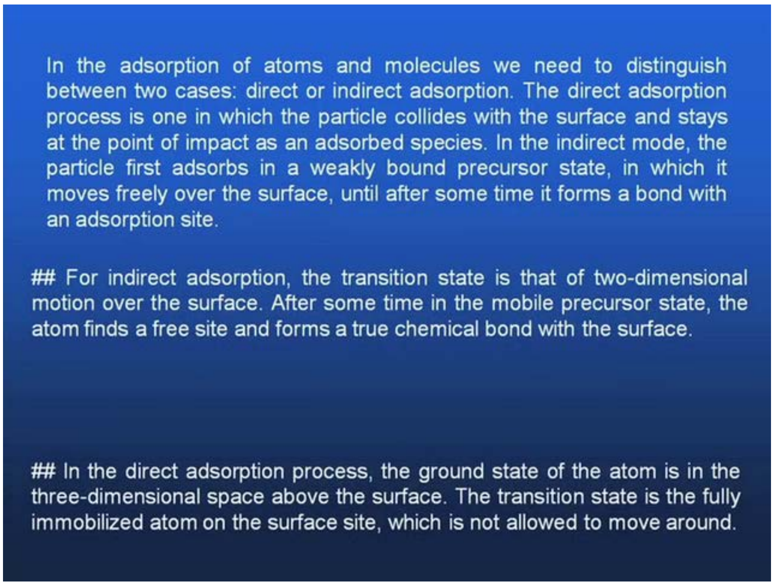

In the adsorption of atoms and molecules we need to distinguish between two cases: direct or indirect adsorption. The direct adsorption process is one in which the particle collides with the surface and stays at the point of impact as an adsorbed species. In the indirect mode, the particle first adsorbs in a weakly bound precursor state, in which it moves freely over the surface, until after some time it forms a bond with an adsorption site.

For indirect adsorption, the transition state is that of two-dimensional motion over the surface. After some time in the mobile precursor state, the atom finds a free site and forms a true chemical bond with the surface.

In the direct adsorption process, the ground state of the atom is in the three-dimensional space above the surface. The transition state is the fully immobilized atom on the surface site, which is not allowed to move around.

So transition-state theory applied to you know, applied to surfaces. Now, when there is a surface reaction when there is a surface reaction means, surface means it is a region, again region of in homogeneity; if you think of a glass of water over here. You can have two regions: one is inside the glass which is called your bulk phase, and the top of you know layer, water layer you have got your you know interface you have got your interface interface.

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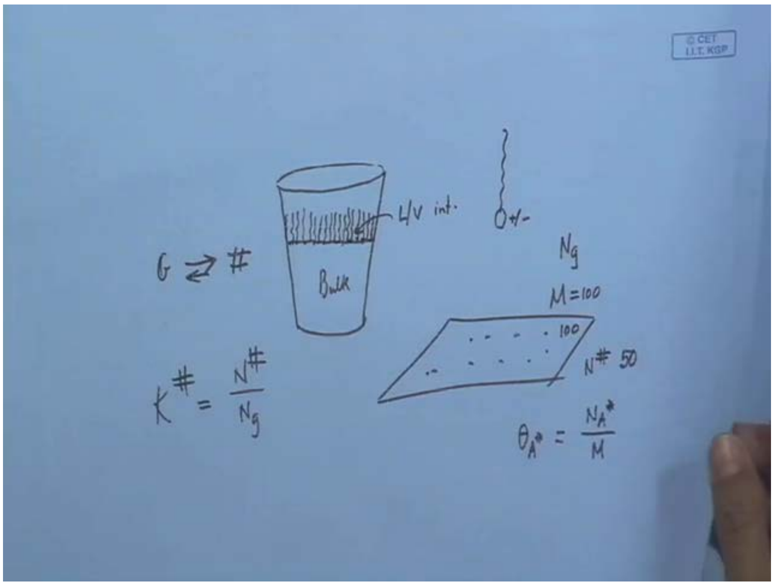

So like this say you have got a glass of water, and water is up to here; so, this is your bulk and this is your water, water vapor interface, liquid vapor interface liquid vapor interface and this is called the region of inhomogeneity, here it is homogeneous in this region it is homogeneous.

So, if you think of the composition then composition everywhere same. But here you see the moment you cross this boundary, you will be seeing you know density is reduced a lot and also number of density of water molecules will also change that is will also reduce enormously; so, this is called the region of inhomogeneity and lot many things may happen over here.

Suppose, you put some surfactant molecule that is like you know detergent and what will happen this detergent molecules having like tail and a hydrophobic group. So, this I mean tail hydrophobic tail with with a polar group plus or minus or maybe uncharged with some polar character; so, what will happen this charged one or the polar one will will be directed this way, and the tail will be like this so adsorption of this you know this molecule, the surfactant molecules will be there.

So, when there is a there is a question of region of inhomogeneity or surface, then appropriate substances may get adsorbed onto the surface; so, that the bulk concentration maybe different for your surface concentration for the same substance; so, when you think of a surface reaction. So, that surface reaction must have a component that your reactant will adsorb onto onto the surface on which the reaction is taking place the maybe on the metal surface.

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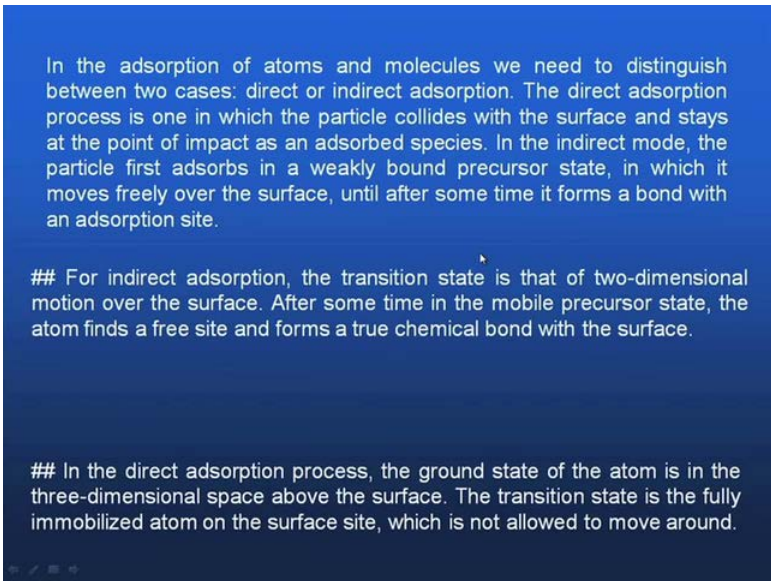

In the adsorption of atoms and molecules we need to distinguish between two cases: direct or indirect adsorption. The direct adsorption process is one in which the particle collides with the surface and stays at the point of impact as an adsorbed species. In the indirect mode, the particle first adsorbs in a weakly bound precursor state, in which it moves freely over the surface, until after some time it forms a bond with an adsorption site.

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In the direct adsorption process, the ground state of the atom is in the three-dimensional space above the surface. The transition state is the fully immobilized atom on the surface site, which is not allowed to move around.

So, in the adsorption of atoms and molecules; you need to distinguish between two cases two cases may happen: one is called the direct adsorption another is called the indirect adsorption. The direct adsorption process is one in which the particle collides with the surface - surface means your maybe the metal surface and stays at the point of impact as an adsorbed species. So, that means the moment the molecule or the atom hits the surface it gets a position, it gets a position means it gets one chair - a vacant chair where it will have its you know have its sit.

So it will be sited over there and it will stays at the point that is at the point of impact, but in the indirect mode, what is happening? That the particle first adsorbs in a weakly bound precursor state that is initially it will just maybe get adhered to the surface of the metal, but there is no you know strong strong linkage, it is a weakly bound situation.

So, it is a weakly bound precursor state in which in which what is happening? That it will have the option, it will have the freedom to move around over the surface, it will have the freedom to move around over the surface until until it gets some permanent position, permanent means like although nothing is permanent like, a it will have better sit where which is basically vacant for for the for this incoming particle. That is it will it will get some vacant space where it will it will make a you know make a bond.

So, that means the moment so for your your indirect adsorption, it comes onto the surface then it moves around it it looks for some position some some sit; where it will means if it gets a gets a sit then it will definitely from a bond, but initially when it it has sit the surface there is a weak linkage. Weak linkage means it sits the surface, but it remains adhered to the surface, it will not it will not you know go out; it will just move around move around the surface until it is it can find out a space for its for its sit.

So for indirect adsorption process for indirect adsorption process: the transition state is that of a two-dimensional motion over the surface. So, it is very interesting, if we think of an indirect adsorption process then as I told you that the first first process what is happening is that there is a there is a weak linkage formation. Weak linkage means weakly bound to the metal surface and the moment it is weakly bound, it just moves around your surface.

So, it is a kind of you know two-dimensional motion. So, another this dimension is taken off, although in gas phase reaction it has got the option, if you think of collision theory again then it is colliding so, it is moving to and flow in all possible directions like in three dimension, but here the moment it is weakly bound to the metal surface or to the surface then it does not any longer go this way perpendicular to the metal surface it is not doing that.

So, only it is moving this way in in two dimension; so, that is indirect adsorption the transition state is that of a two-dimensional motion over the surface. So, it is a it is a kind of transition state. So, it did not did not have any specific position so, that is why it is moving around it so the transition state is with a two-dimensional motion. After sometime this mobile precursor state why it is a mobile, because it is moving around.

Mobile, mobile precursor state after sometime this atom finds this atom finds a position a site, which is free for its occupancy and a possible chemical linkage maybe formed at the surface. So, this is the situation with indirect adsorption process. Now, the other option the direct adsorption process, the ground state of the atom. Since, before the atom gets adsorbed onto the surface.

The atom is in the ground state; so, the ground state of the atom is in the three-dimensional space over the surface, that means here it is 3 rd that you have got the metal surface and on top of that metal surface, there is a little you know slice, three-dimensional space in which this you know these atoms are moving around. So, it is thought that ground state of the atom is in the three-dimensional space over the surface of the metal, and the transition state is fully mobilized atom on the surface side which is not allowed to move around.

And the transition state is a fixed state, it does not have the option to move here and there; unlike your indirect adsorption which is a case of for which your transition state is a is in a in a two-dimensional motion over the metal surface, but here no it is not the case. It does not have the option to move in a two two-dimensional space, only thing is that there is a slice over slice volume space over your metal surface.

So, the the atoms are initially there and then eventually it will it will stick onto the metal surface. So, this way the other option that is the direct adsorption process occurs; so, that means when there is a question of surface reaction then the question of adsorption comes into picture and the adsorption means it maybe a weakly bound situation, like it maybe a physisorption or maybe weakly bound situation or maybe a strongly bound situation which is generally, which is taught to be to be the case for your direct adsorption process.

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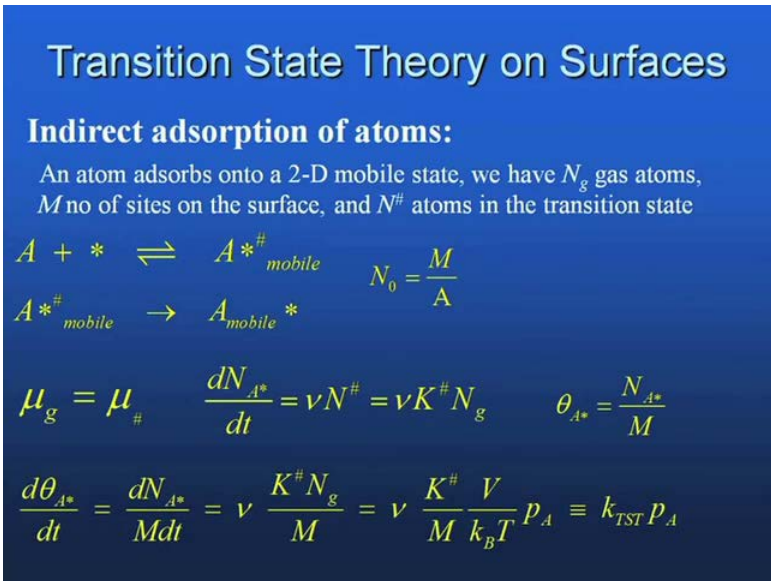

Transition State Theory on Surfaces

Indirect adsorption of atoms:

An atom adsorbs onto a 2-D mobile state, we have N_g gas atoms, M no of sites on the surface, and $N^{\#}$ atoms in the transition state

$$A + * \rightleftharpoons A*^{\#}_{mobile} \qquad N_0 = \frac{M}{A}$$

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

$$\mu_g = \mu_{\#} \qquad \frac{dN_{A*}}{dt} = \nu N^{\#} = \nu K^{\#} N_g \qquad \theta_{A*} = \frac{N_{A*}}{M}$$

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

So, lets lets go for indirect adsorption process. So, think of an atom which adsorbs onto a 2-D mobile state. Mobile state means it is moving around; so, that is why it is a 2-D mobile state; it is in two dimension, no this dimension is not allowed, only this dimension or maybe that way it is allowed; over the metal surface so, it binds here on the metal surface a weakly bound precursor that is transition state and then it is moving around like this, and then eventually it gets a position.

So atom adsorbs onto a 2-D mobile state and suppose we have got N g number of gas atoms, gaseous atoms. So, N g number of gaseous atoms and M number of sites on the surface; so, you have got the site M number of such sites and N g number of gaseous atoms. The mechanism is that the atom this is the surface, the star is the surface making a mobile you know situation.

So, it is a mobile precursor - that is this precursor is moving around and per unit area, this is the number of sites available per unit area, this is M is the total number of sites on the surface and A is the area; so, if you divide by area then it will be giving you number of sites per unit area. So, this mobile then gets converted to mobile, but it is the right one that is your that is your a star state; so, after it has got some position, maybe maybe you know one vacant position where the the your a atom is adhering to.

And also the idea is that we have to apply here, the since it is an it it is a case of the equilibrium; so, chemical potential of the atoms in gas phase and in the in your in your double dagger state, that is your that is your activated state. These two are identical thought be identical; so, rate of formation or I mean yes rate of formation of this this a star this a star which is nothing but the frequency with which it is formed and your N number of means number of atoms in the dagger state, this N star and where K double dagger is your is the equilibrium constant is your is your N double dagger divided by N g; so, it is g to double dagger kind of thing.

So, therefore d N A star d t is equal to nu K double dagger N g and also the fractional coverage, fractional coverage due to A star is your N A star divided by total number of you know, total number of M sites that is sites available for the for adsorption. So this is your theta A star so, suppose you have got like say 100 over here.

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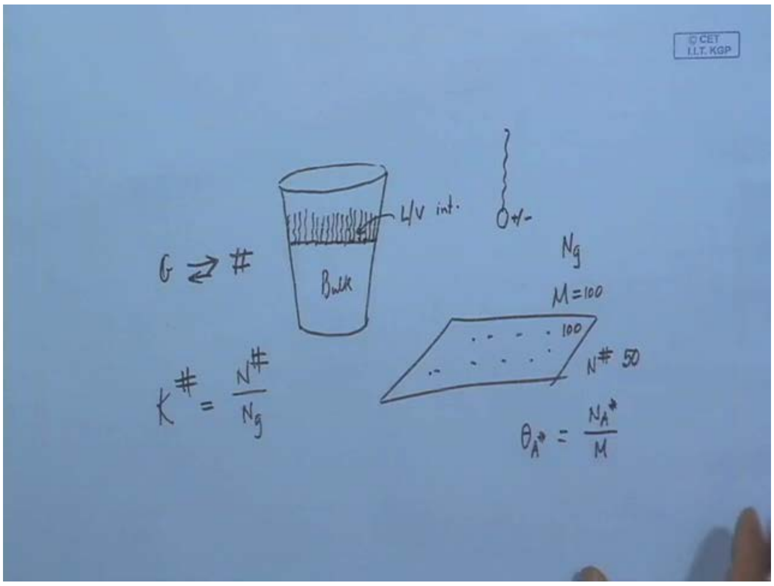

Say, 100 means M is equal to say 100 and suppose that N double dagger is fifty that is maybe 50 percent is occupied then what will be theta, occupied means after the dagger state is getting converted to some confirmed you know position that is not like A mobile it is moving here and there and looking for some some position to occupy; so, it is a confirmed state, so theta A star is equal to N A star divided by M.

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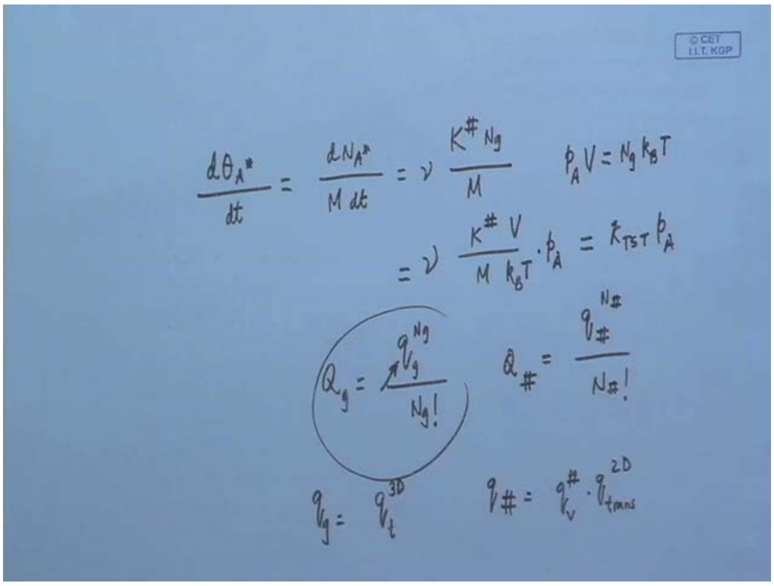

Therefore, therefore, you can write you can write d theta A star so rate, time rate of theta A that is your after it is it has from the precursor, activated precursor to you know adsorbed state to the adsorbed state; so, that is equal to d N A star d t divided by M. So, that is equal to nu K double dagger N g divided by M which is equal to nu K double dagger by M. Now, you have to write in terms of P A gas pressure of a P A, then V is equal to is equal to N g then N g K B T.

So you can write in this way; so, if you if you substitute this, this is this is your number density it is your number of it is not the mole; it is the number density N g. So, you can write for this you can write V K B T into P A which is equal to you know transition state theory K TST P A. So, that means we started with this indirect adsorption mechanism, adsorption of atom and the idea is that your mechanism as I as…

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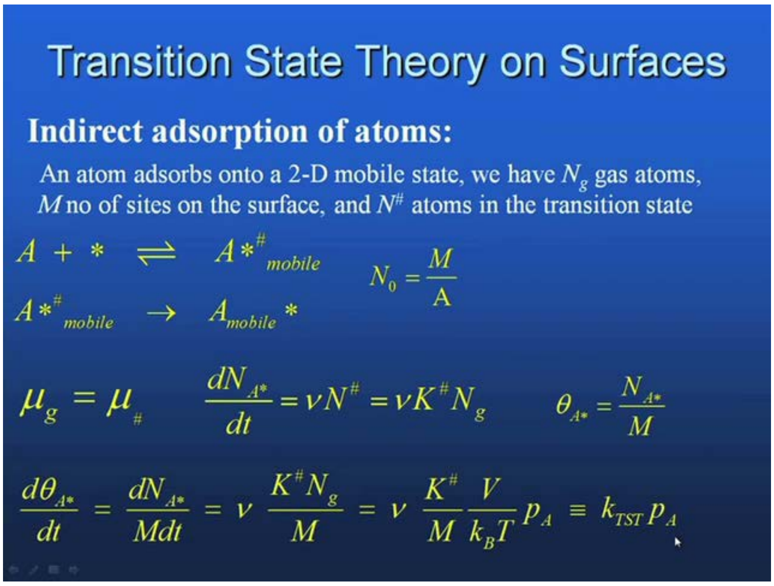

Transition State Theory on Surfaces

Indirect adsorption of atoms:

An atom adsorbs onto a 2-D mobile state, we have N_g gas atoms, M no of sites on the surface, and $N^{\#}$ atoms in the transition state

$$A + * \rightleftharpoons A*^{\#}_{mobile} \qquad N_0 = \frac{M}{A}$$

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

$$\mu_g = \mu_{\#} \qquad \frac{dN_{A*}}{dt} = \nu N^{\#} = \nu K^{\#} N_g \qquad \theta_{A*} = \frac{N_{A*}}{M}$$

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

I explained here that a with the surface producing a a weakly bound a mobile mobile phase and then this mobile phase is converted to your adsorbed phase, and once this adsorbed phase is produced then this adsorbed phase undergo you know some reaction. So, that is why your rate of change of N A star with time is written in this way where theta is the coverage, fractional coverage and from this we arrived at this relation d theta A star d t is equal to K TST into P A.

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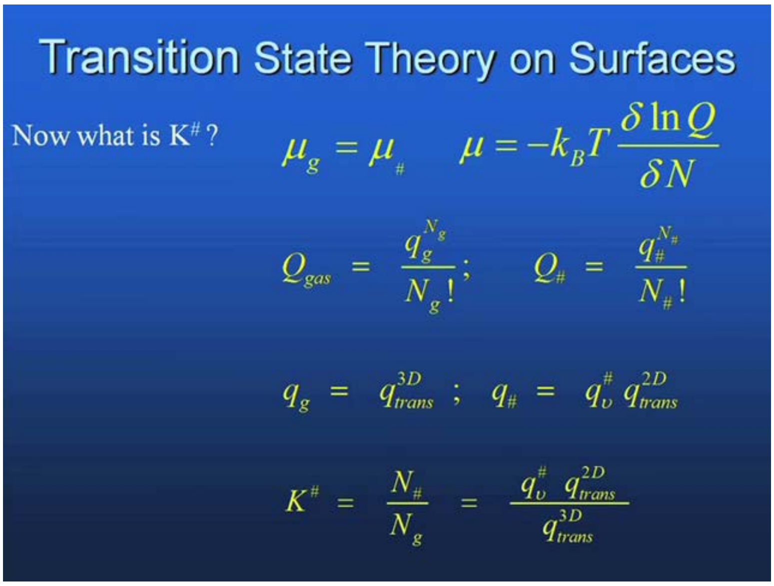

Transition State Theory on Surfaces

Now what is K$^{\#}$?

$$\mu_g = \mu_{\#} \qquad \mu = -k_B T \frac{\delta \ln Q}{\delta N}$$

$$Q_{gas} = \frac{q_g^{N_g}}{N_g!}; \qquad Q_{\#} = \frac{q_{\#}^{N_{\#}}}{N_{\#}!}$$

$$q_g = q_{trans}^{3D} \; ; \quad q_{\#} = q_{\upsilon}^{\#} \, q_{trans}^{2D}$$

$$K^{\#} = \frac{N_{\#}}{N_g} = \frac{q_{\upsilon}^{\#} \; q_{trans}^{2D}}{q_{trans}^{3D}}$$

Next is what is K double dagger? K double dagger is since, it is you know this activated state and your gas gaseous atoms are in equilibrium; first they will form an equilibrium like, if you you know think of this step you see this is an equilibrium therefore, therefore, you know you apply mu g is equal to mu double dagger, and you know if you apply your statistical mechanical expressions from partition function then mu is equal to minus K B T del l n Q del n, and Q gas is equal to…

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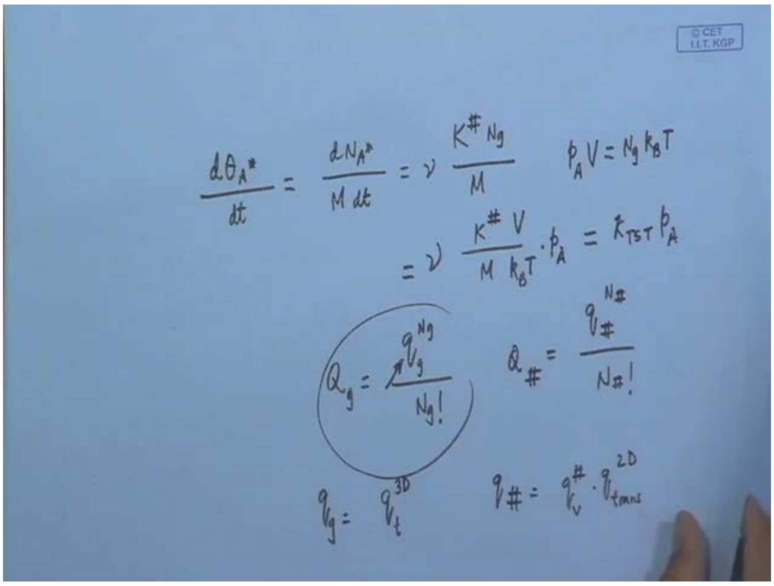

$$\frac{d\theta_A^*}{dt} = \frac{dN_A^*}{M\,dt} = \nu \frac{K^{\#} N_g}{M} \qquad p_A V = N_g k_B T$$

$$= \nu \frac{K^{\#} V}{M\, k_B T} \cdot p_A = k_{TST}\, p_A$$

$$Q_g = \frac{q_g^{N_g}}{N_g!} \qquad Q_{\#} = \frac{q_{\#}^{N_{\#}}}{N_{\#}!}$$

$$q_g = q_t^{3D} \qquad q_{\#} = q_v^{\#} \cdot q_{trans}^{2D}$$

you know total Q gas is equal to individual particle gas particle to the power N g divided by N g factorial and in the same way q total q double dagger is equal to q double dagger to the power N double dagger divided by N double dagger factorial and for this q g this q g q g is is equal to q translation, because it is a gas phase case so, this gas molecules, since these are not adsorbed.

These gas molecules are not adsorbed; so, it will have these gas molecules will have have the option to move around in, in three-dimensional space, so this will be basically you know it it will have translation, only translation degrees of freedom. So, q t to the power in in 3 D, and for double dagger it will be your q trans in 2 D times q v that is we have taken out we have taken out one you know, one vibrational mode out of this many many modes.

So, that means why 2 D, because now as soon as the as the gas is confined gas atoms or gaseous atoms are confined; they will have the option to move in two dimension only this way or maybe that way in two dimension only. So, this third dimension this third dimension that is moving to this way that is that is to the top this way, this movement is not there; therefore, we have taken out this vibrational one out of this, this translational modes one is taken as your vibration.

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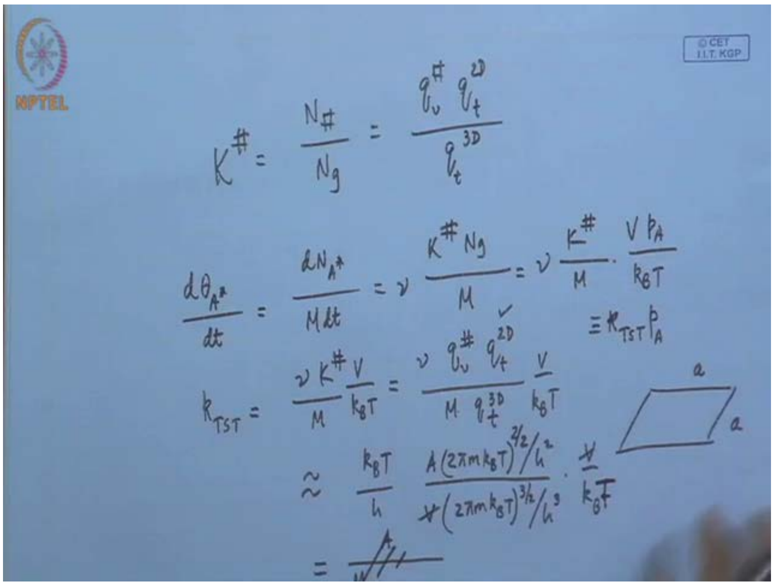

$$K^{\#} = \frac{N^{\#}}{N_g} = \frac{q_v^{\#}\, q_t^{2D}}{q_t^{3D}}$$

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

$$k_{TST} = \frac{\nu K^{\#}}{M}\frac{V}{k_B T} = \frac{\nu\, q_v^{\#}\, q_t^{2D}}{M\, q_t^{3D}}\,\frac{V}{k_B T}$$

$$\approx \frac{k_B T}{h}\,\frac{A(2\pi m k_B T)^{2/2}/h^2}{\cancel{V}(2\pi m k_B T)^{3/2}/h^3}\cdot\frac{\cancel{V}}{k_B \cancel{T}}$$

Therefore, K double dagger is equal to N double dagger divided by N g is equal to q v double dagger q translation 2 D divided by q translation 3 D. So, one degree of freedom is taken out as a product; so, so, what you can write d theta A star, d t is equal to d N A star by M d t which is equal to nu K double dagger N g divided by M is equal to nu into K double dagger by M into V P A by K B T which is equal to equivalent to K TST P or P A.

So, K TST is equal to nu; so, K TST you have to you know just this part, excepting p a this part. So, K TST is equal to nu K double dagger V by K B T and divided by M is equal to V now, q V double dagger then q translation 2 D divided by q M into q translation 3 D into V by K B T, then then if you put the respective expression, because it is a 2 D it is a 3 D and simply if you simplify that this dimension means. if you have this plate or the surface like say a, this is a then your two dimension will be area will be a square, third dimension will be a cube like that; so, if you put this you can if you put the respective expression for your translational mode, if you put this expression for your translational mode then you can write for your translation it will be 2 phi m K B T to the power to the power 3 by 2.

Since, it is 2 D therefore, 2 by 2 2 by 2 means 1 by h square so for this part; we wrote like this and here it will be 2 phi m K B T to the power 3 by 2 divided by h cube of course, V by K B T K B T what will happen to this 1 now now and of course, you have to write and here one term will be there a, and here it will be V V means volume it will be area, because it is it is two dimension; now, what will you write for this this one this nu.

So, you can write for this one to be equal to equal to for this case it you can write express this one means this remaining part you can write your K B K T by h, basically K B T by h, because this represents this represents your the partition function for your vibrational thing. So, what you end up at is is your this is equal to since V is there, this V gets canceled this a is remaining and this h this h square, with h will give you h cube, so this h cube gets canceled. So, ultimately what you get is a divided by M; let me write it in a separate page.

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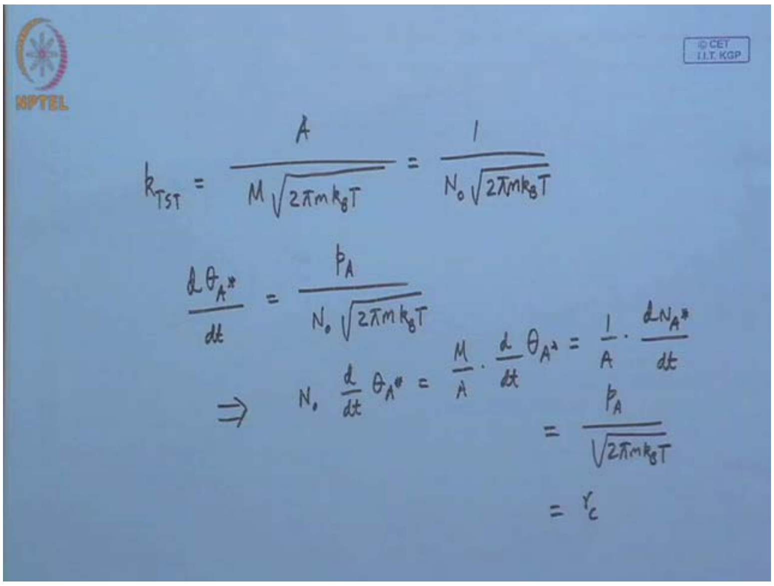

$$k_{TST} = \frac{A}{M\sqrt{2\pi m k_B T}} = \frac{1}{N_0\sqrt{2\pi m k_B T}}$$

$$\frac{d\theta_{A^*}}{dt} = \frac{P_A}{N_0\sqrt{2\pi m k_B T}}$$

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

$$= \frac{P_A}{\sqrt{2\pi m k_B T}}$$

$$= r_c$$

So ultimately K TST will be equal to A area divided by M; M is the total number of sites into square root of 2 phi m K B T; so, this is equal to 1 by N 0 per unit area M by A is N 0 into square root of 2 phi M K B into T. So, that means d theta A star d t will be equal to P A into K TST that means P A by N 0 square root of 2 phi m K B into T. So, this is your fractional coverage rate of fractional coverage change; so, from this we can write N 0 d d t of d d t of theta A star is equal to M by A d d t of theta A star which is equal to 1 by A d N A star d t which is equal to your P A by square root of 2 phi m K B T which is nothing but your rate for the you know collisional mechanism.

Collision the that that you are getting from collision theory; so, are collision so if you think of this indirect adsorption mechanism, then you get you know similar to a rate expression, similar to what you get for the collision based on collision theory of surface reaction.

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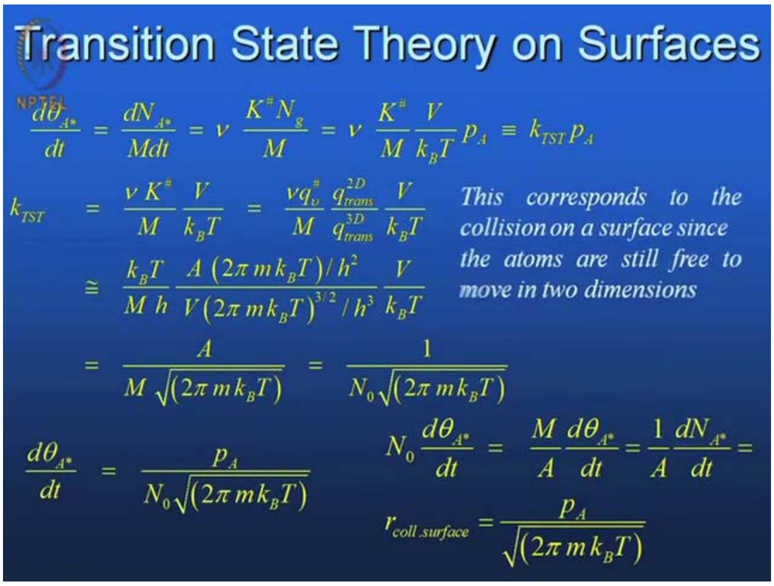

Transition State Theory on Surfaces

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

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

$$\cong \frac{k_B T}{M h} \frac{A (2\pi m k_B T)/h^2}{V (2\pi m k_B T)^{3/2}/h^3} \frac{V}{k_B T}$$

$$= \frac{A}{M \sqrt{(2\pi m k_B T)}} = \frac{1}{N_0 \sqrt{(2\pi m k_B T)}}$$

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

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

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

$$r_{coll.surface} = \frac{p_A}{\sqrt{(2\pi m k_B T)}}$$

So this corresponds to collision on a surface. Since, the atoms are still free to move in two dimension; so, it is basically this corresponds to as I told you that surface collision. So, ultimately we ended up to a very simplified expression that your that your d d t of theta A star has got you know, your P A divided by N 0 into square root of 2 pi m K B T. So it is this corresponds to the collision on a surface, since the atom are still free to move in two dimension, because it is it is similar to you know what you get in other other theories that they are move around they are they are moving around in the on the surface although the third dimension is off this dimension is off but, they are moving around so there is option for them to collide onto the on on the surface.

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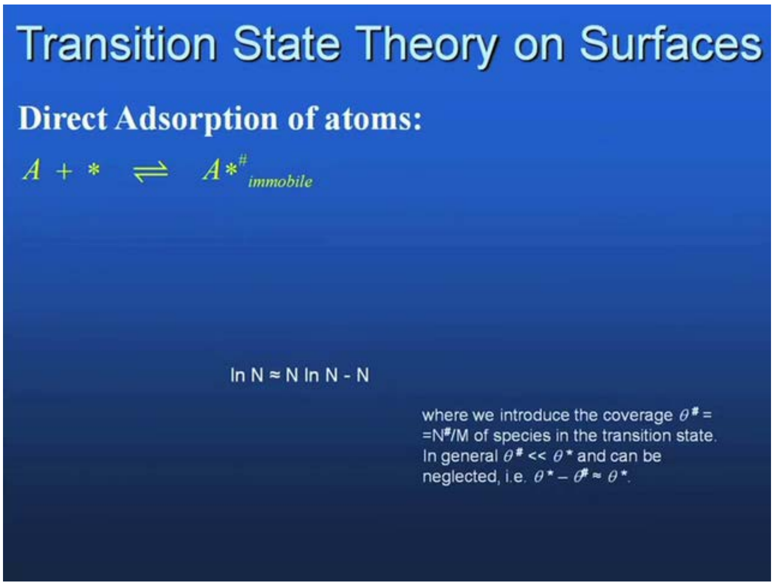

Transition State Theory on Surfaces

Direct Adsorption of atoms:

$A + * \rightleftharpoons A*^{\#}_{immobile}$

$\ln N \approx N \ln N - N$

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

So, today I guess I should stop and in the next lecture, we will talk about direct adsorption mechanism. Now, so what have we learnt out here that in this particular lecture, we started to discuss this transition state theory applied to surface reactions and there are 2 modes of reaction: one is your indirect adsorption, another is your direct adsorption.

So, today we talked about this indirect adsorption and ultimately we came to a conclusion that even if it is if even if the you know, your reactant is bound to the surface although maybe it is a by by a weak force but, they have the option to move around you know on onto the surface, and maybe they will make collision. So a gives you a similar to you know collision rate, and we also discussed you know this with taking taking some example taking some example about this your degrees of freedom specially, you know a non-linear activated complex how many vibrational degrees of freedom are there; it is actually one less than a corresponding corresponding you know molecule that is same number of atom continuing molecule or the molecule containing the same number of atoms as your activated complex.

So in the next lecture, we will talk about your direct adsorption mechanism and we will try to find out the expression of rate out there. So, till then have nice time we will see you in the next lecture thank you.