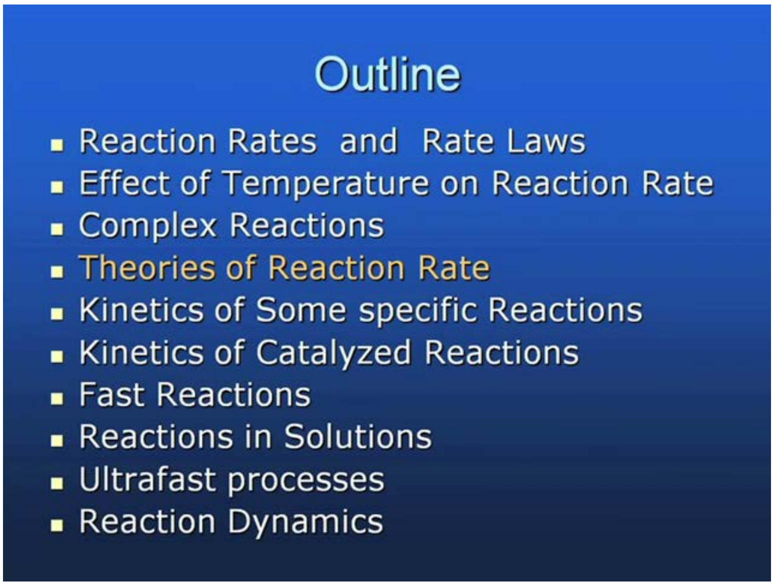
Rate Processes
Prof. M. Halder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Module No. # 01
Lecture No. # 10
Theories of Reaction Rate (contd…)

(Refer Slide Time: 00:26)

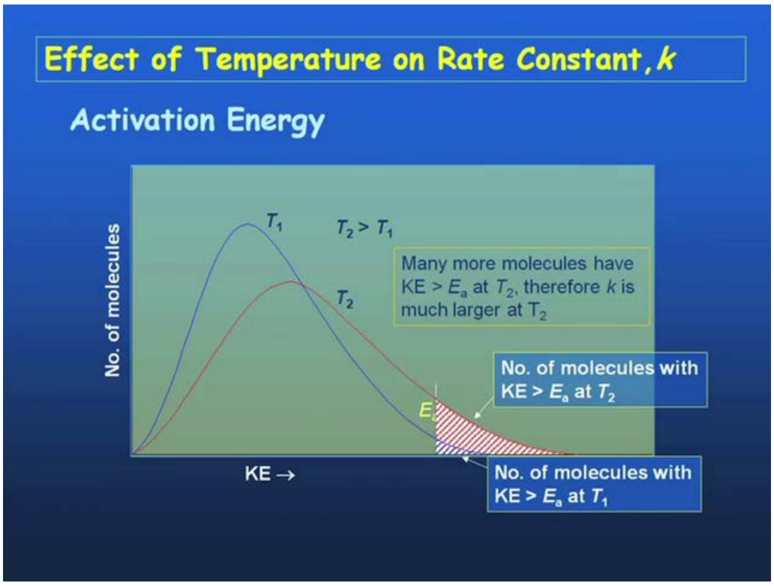


Outline

- 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, today we will continue with these theories of reaction rate. So, in our last lecture, we discussed this you know collision theory of for the chemical reaction rate.

(Refer Slide Time: 00:48)



Effect of Temperature on Rate Constant, k

Activation Energy

Many more molecules have KE > E_a at T_2, therefore k is much larger at T_2

No. of molecules with KE > E_a at T_2

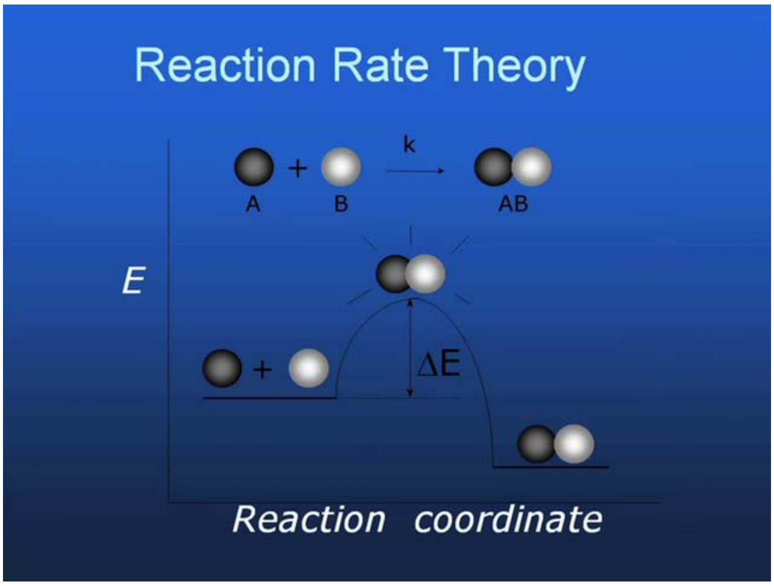
No. of molecules with KE > E_a at T_1

So, the last slide where we ended at was on the activation energy, was on the activation energy that is the effect of temperature on reaction rate constant. That you know we we were discussing this Maxwell distribution of molecular velocities, and that you know in collision theory; it is thought that the collision between molecules are responsible for a reaction to occur and there is a factor that with proper geometry and with proper with with a definitive amount of energy, the molecules can react through collision to produce your desired product.

So, here you see that this is the plot of the the number of molecules, that are the fraction of the total number of molecules, you can write it over here, it is better to write the probability function that is the fraction of total number of molecules present in the mixture and this side is your either it maybe you know in terms of kinetic energy or the overall energy or maybe your speed of the molecules. So, if you increase the temperature what you get is that this blue curve is getting flattened, and you see that you know this suppose, if this is your activation energy, if this line corresponds to the activation energy then when the gas molecules were at temperature T 1, absolute temperature T 1 then the area under the curve was like this.

And as you increase the temperature from T 1 to T 2 and as a result of which this plot gets flattened, then you see that this is more. So, more number of molecules are there in this region, because the integrated area is more. Therefore, this situation will have a better option for the molecule to react that is through through through collision. So, and that is you know based on purely the hard sphere collision model.

(Refer Slide Time: 03:02)

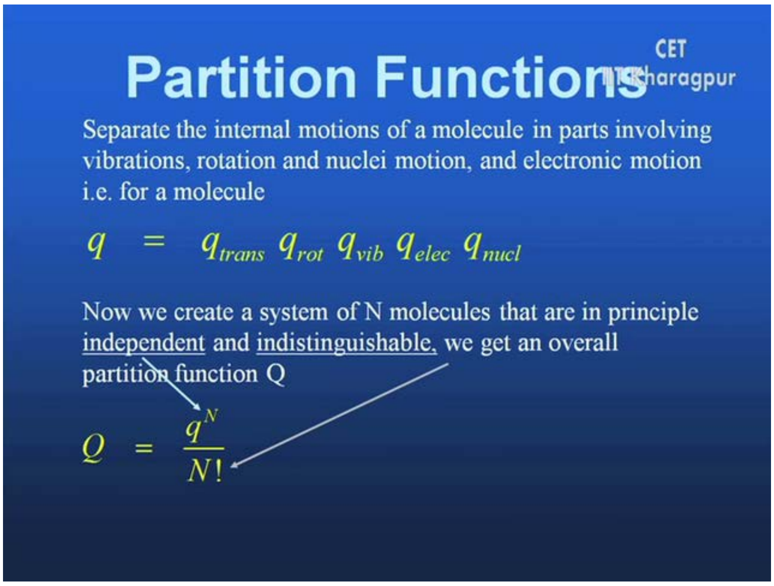


Reaction Rate Theory

Next, we will move onto you know another theory, which is the transition state theory. You see that this diagram - this is a typical diagram that A plus B with a rate constant producing AB. Now, this is your reactant side, and say and this is your, this is typical you know this it is it is depicted in the form that your reaction is an exothermic one. And this is your energy activation, delta is the energy of activation. So, you see these two are colliding as per your your collision theory, but here it is a different situation that these two will first form an activated complex of this about having energy higher compared to your reactants, and then this will move onto this side or maybe it will come back to this side.

So, this has got equal probability maybe of passing either to this right hand side or coming back to the left hand side. So, this is your activated complex; so, this activated complex will undergo further reaction to produce your your to give your product. So, that is the idea.

(Refer Slide Time: 04:35)



Partition Functions

Separate the internal motions of a molecule in parts involving vibrations, rotation and nuclei motion, and electronic motion i.e. for a molecule

$$q = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}\, q_{nucl}$$

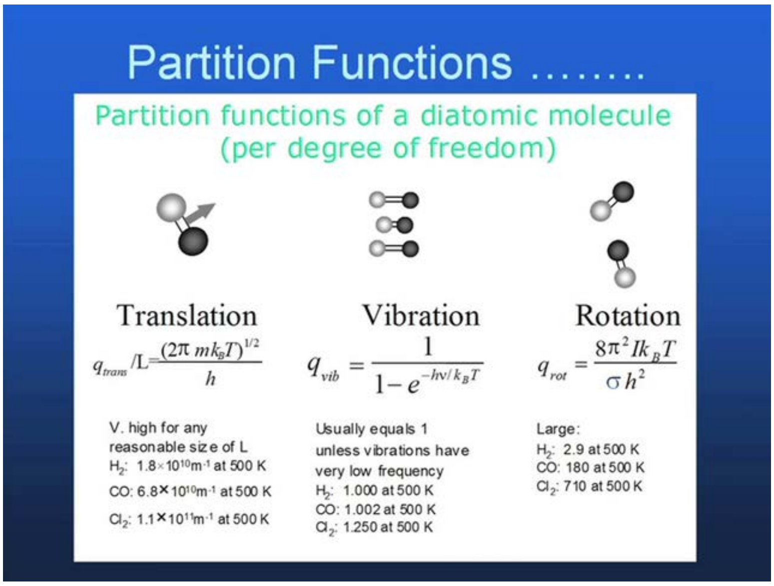
Now we create a system of N molecules that are in principle independent and indistinguishable, we get an overall partition function Q

$$Q = \frac{q^N}{N!}$$

And so, before going to the details, let us have a a quick look at this you know you know partition function, because we will require partition function. Now, molecules will have various motions. One can be translation, another can be rotation then third one is vibration, electronic motion and also your nuclear motions as a whole. So, these these are you know in terms of the total partition function of the molecule, you can write q is is a product of individual partition functions that is trans means translation, rotation, vibration, electronic and nuclear nuclear partition function.

So, and we create a system of n molecules that are in principle independent and indistinguishable, and we get an overall partition function q for the N such particle will be q to the power N divided by N factor that is that is, if you look into you know any standard textbook of statistical mechanics or statistical thermodynamics you will be finding this. So, these individual terms are you know individual partition functions; so, this is basically this whole to the power N whole to the power N; this whole to the power N divided by N factorial, N is the number of you know in indistinguishable independent molecules. So, this is your overall partition function for this N indistinguishable independent particle system.

(Refer Slide Time: 06:14)



Partition Functions ....

Partition functions of a diatomic molecule
(per degree of freedom)

Translation

$q_{trans}/\mathrm{L} = \frac{(2\pi m k_B T)^{1/2}}{h}$

V. high for any
reasonable size of L
H_2: 1.8×10^{10} m^{-1} at 500 K
CO: 6.8×10^{10} m^{-1} at 500 K
Cl_2: 1.1×10^{11} m^{-1} at 500 K

Vibration

$q_{vib} = \frac{1}{1 - e^{-h\nu/k_B T}}$

Usually equals 1
unless vibrations have
very low frequency
H_2: 1.000 at 500 K
CO: 1.002 at 500 K
Cl_2: 1.250 at 500 K

Rotation

$q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$

Large:
H_2: 2.9 at 500 K
CO: 180 at 500 K
Cl_2: 710 at 500 K

Now, partition functions of a diatomic molecule; per degree of freedom, what do we mean by degree of freedom? Degree of freedom is the you know various types of motions that are associated in in you know in simplistic language. So, you know total number of independent ways you can realize. So, that is called your you know various motions like translation, rotation, vibration. So, these are the these are the various degrees of freedom.

Now, translational motion can be of like this molecule as a whole is moving means its center of mass is moving, center of mass is moving; so, that is why it is called the translational motion. So, center of mass is changing its coordinate with time. Vibration is basically you know your center of mass is fixed at a point. And and your these two masses for a diatomic molecule. I mean these two atoms they are changing their position maybe, it is you know doing like this, this, this motion.

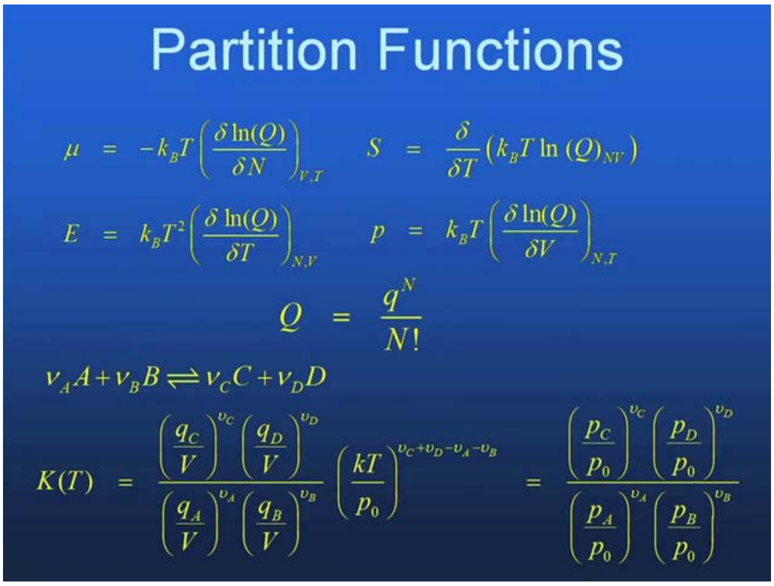
So, that is why you know, this is called your vibration. So, during vibration there is there should not be any change in your center of mass. So, center of mass is remaining fixed so, to keep your center of mass fixed these two molecules are the, I mean these two atoms will have to move in a definitive fashion; so, that there is no net change in the position of your center of mass. And in case of rotation, it is basically you know about some access about some access this molecule is you know rotating; so, this is changing its position this way and this other one is also doing like this.

So and translational partition function, you know it has got this expression, and where L is the box length. It is it is per degree of freedom. And it is generally very high for a reasonable size of L. L means box length for H 2, it is of this sort. I mean 10 to the power 10 per meter at 500 Kelvin, for C O it is 10 to the power 10, it is also 10 to the power 10 order, C l 2 it is also it is it is of the order of you know 10 to power 11. So, it is proportional to mass, directly proportional to mass; I mean to the power half, mass to the power half and temperature also to the power half. And it is you know in in reverse sense I mean although h is constant, so, it is a constant quantity and L will will is here, so basically it it depends on m and T that is why as m increases it is increasing here, also m increases, it is increasing H 2 m is less therefore, it is 1.8.

Next, is vibration it has got you know this expression one divided 1 divided by 1 minus e to the power minus h nu by k B T; where k B Boltzmann constant. And usually it is equal to one unless vibrations are of very low frequency - very low frequency means nu is high, means it is very less. So, if this is low or maybe if h nu, this h nu is much much smaller compared to k B T, then this term you know you know this has got some you know one by something. So, it is it is a this if it is much much smaller then practically, you can you can approximate this to something or maybe or maybe for for simplistic language. If this is you know very low low frequency mode, then you know this will have a value something little little more, because as you reduce this as I I was telling that if h nu is less then this will be less than one, this whole thing will be less than one.

So, that means this will be more than one. So, that is why it is increasing. So, low frequency vibration when it is introduced then this corresponding vibrational partition function increases. Rotational partition where it is large, it is you know for H 2, it is 2.9, C O it is 180, C l 2 it is 710. So, partition function for you know for degree of freedom, it is of this this order. But but you know it is higher than this one but, not higher than this one.

(Refer Slide Time: 11:04)



Partition Functions

$$\mu = -k_B T \left(\frac{\delta \ln(Q)}{\delta N} \right)_{V,T} \qquad S = \frac{\delta}{\delta T} \left(k_B T \ln (Q)_{NV} \right)$$

$$E = k_B T^2 \left(\frac{\delta \ln(Q)}{\delta T} \right)_{N,V} \qquad p = k_B T \left(\frac{\delta \ln(Q)}{\delta V} \right)_{N,T}$$

$$Q = \frac{q^N}{N!}$$

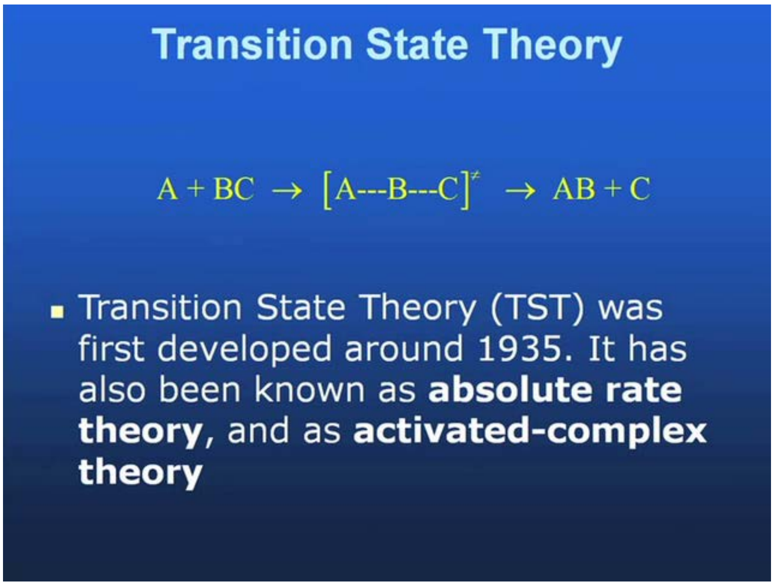
$$v_A A + v_B B \rightleftharpoons v_C C + v_D D$$

$$K(T) = \frac{\left(\frac{q_C}{V}\right)^{\upsilon_C} \left(\frac{q_D}{V}\right)^{\upsilon_D}}{\left(\frac{q_A}{V}\right)^{\upsilon_A} \left(\frac{q_B}{V}\right)^{\upsilon_B}} \left(\frac{kT}{p_0} \right)^{\upsilon_C + \upsilon_D - \upsilon_A - \upsilon_B} = \frac{\left(\frac{p_C}{p_0}\right)^{\upsilon_C} \left(\frac{p_D}{p_0}\right)^{\upsilon_D}}{\left(\frac{p_A}{p_0}\right)^{\upsilon_A} \left(\frac{p_B}{p_0}\right)^{\upsilon_B}}$$

Now, expression for various thermodynamic quantities, you know chemical potential. It is having this expression where Q is the total partition function is is having this one at constant volume, and temperature, here it is constant volume and number P, it is of this expression, internal energy is is having this expression, where Q is q to the power N by N factorial as I mentioned earlier. Now, move onto a reaction of this kind A plus B giving rise to C plus D with isometric coefficient nu A, nu B in the on the left hand side, and right hand side nu C and nu D.

So, equilibrium constant at a temperature T, you can write in this way, you can write you know q C partition function per unit volume of course, q C by V to the power this one q D by V to the power nu D divided by this into K T by P 0; why K T by P 0? You know, you can directly lets go back to the earlier slide; so, basically this will be having this expression P is basically your this one. So, if you if you write you know the appropriate expression, you will be getting this type of expression that it is P C by P 0 to the power nu C, P D by P 0 to the power nu D, P A by P 0 to the power nu A, P B by P 0 to the power nu B. So, it is a kind of you know activity P by P 0 it is a dimensionless quantity so, activity of C to the power nu C, activity of D to the power nu D, activity of A to the power nu A, activity of B to the power nu B. So, this is the expression for the equilibrium constant at a temperature T.

(Refer Slide Time: 13:20)



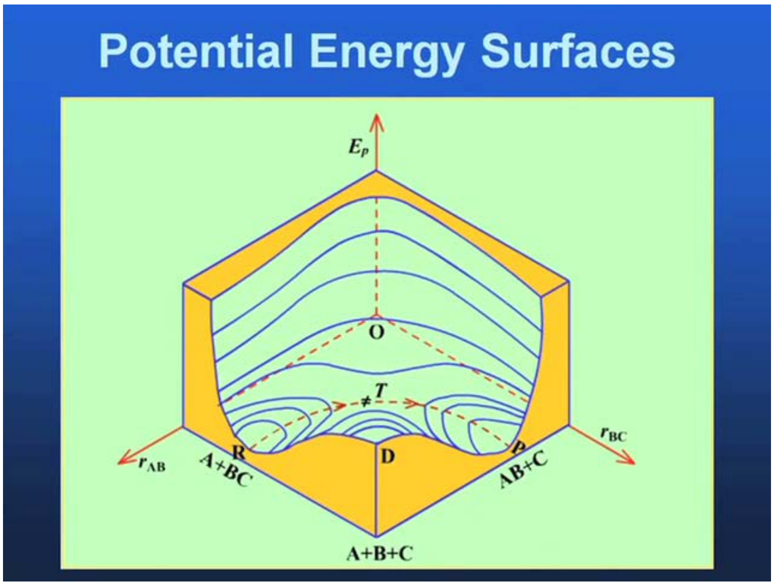
Transition State Theory

$$A + BC \rightarrow [A\text{---}B\text{---}C]^{\neq} \rightarrow AB + C$$

- Transition State Theory (TST) was first developed around 1935. It has also been known as **absolute rate theory**, and as **activated-complex theory**

Now, we will we will try to apply these expressions at the appropriate places. So, let us start with the transition state theory that a simple reaction A reacting with B C producing A B plus C that is an atom exchange reaction may be same. So, it is if it is going via an activated complex sorry, it it is going via a transition state. So, that is why it is called the Transition State Theory or TST and it was first developed around 1935, when it is it has also been known as absolute reaction rate theory also it is known as activated complex theory; although these two names are are outdated now, and transition state theory is you know now a days used this term is now a days used.

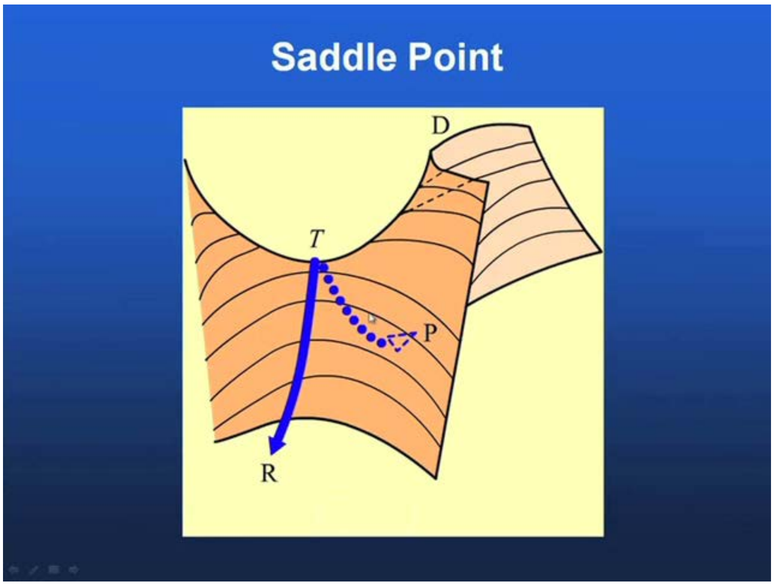
(Refer Slide Time: 14:12)



Potential Energy Surfaces

So there is a there there is a typical potential energy surface, that you know it is it is an you know cross section, you know this is a three dimensional description energy this way this side r A B, this side is r B C that is distance between B and C, and this is distance between A and B. So, you are plotting in a three-dimensional way that this side is your energy of the product or energy of the process overall energy of the process, and this side your distance for A B and this side is distance for B C, and this is called your the transition state where this A B C is located that is this one is located, this A B C is located.

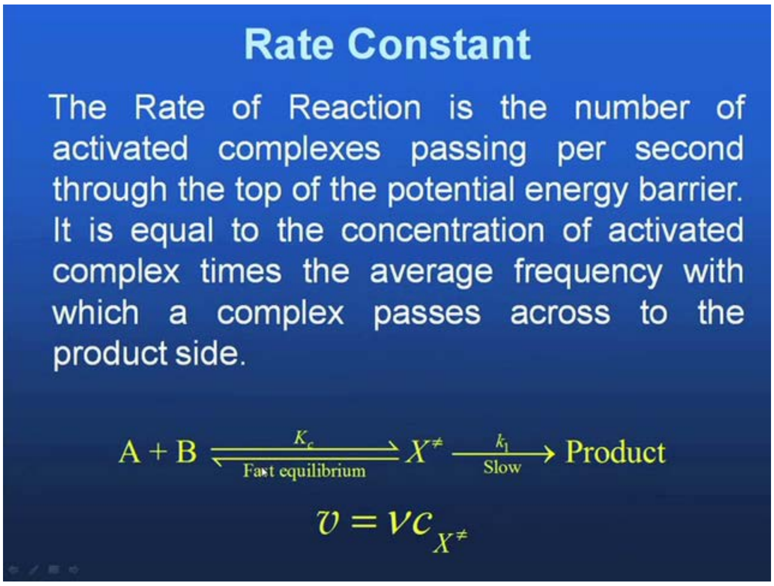
(Refer Slide Time: 15:09)



Saddle Point

This is the saddle point that is your, this is your transition state, this is your reactant side, this is the product side. It is just like a you know two mountains, you know separated by a by a you know a valley. So, this way product reactant will move this way to the transition state and then it will pass to the other side or maybe it will come back to the reactant side.

(Refer Slide Time: 15:34)



Rate Constant

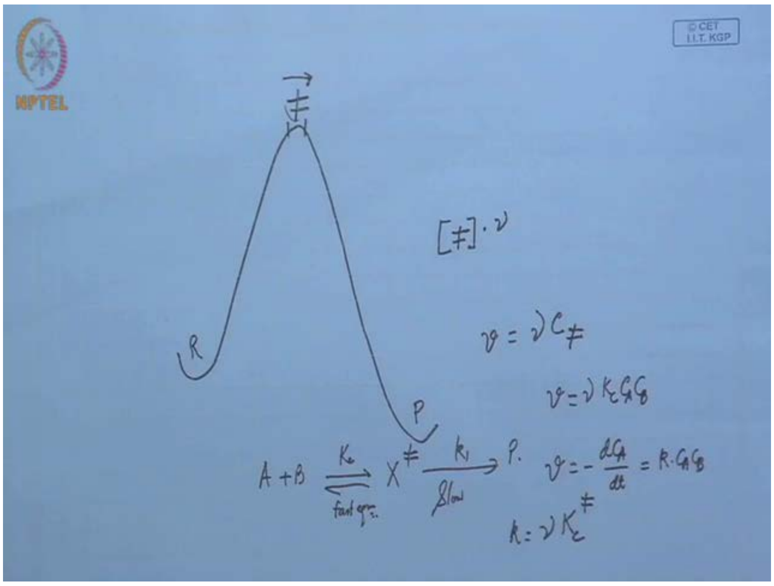
The Rate of Reaction is the number of activated complexes passing per second through the top of the potential energy barrier. It is equal to the concentration of activated complex times the average frequency with which a complex passes across to the product side.

$$A + B \underset{\text{Fast equilibrium}}{\overset{K_c}{\rightleftharpoons}} X^{\neq} \underset{\text{Slow}}{\xrightarrow{k_1}} \text{Product}$$

$$\upsilon = \nu c_{X^{\neq}}$$

It is just like yours like a you know, you find saddle in case of horse. Horse riders generally use this; anyway rate constant of the reaction what what is the rate constant how will you write; that rate constant of the reaction is the number of activated system that is activated complex, activated you can say that activated molecule. So, the number of activated molecule that are are activated molecule or maybe you can say that is A B C that I I was telling.

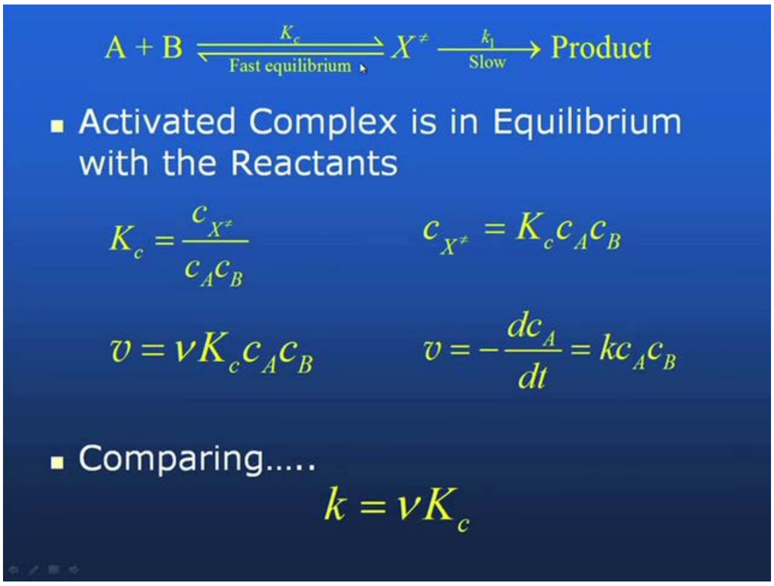
(Refer Slide Time: 16:23)



So, number of activated complexes passing per second through the top of the potential energy barrier say you are here like, you started from here and then you moved to this one and then you are here; so, this is your reactant side, this is your activated and this is your product side. So, it is basically reaction rate is nothing, but the but the number of these species - passing passing per second through the top of your potential energy barrier. And this is equal to the concentration of the activated complex times. So, this is equal to this rate is equal to equal to number of, I mean the concentration of the activated complex times, the frequency with which say nu is the frequency with which the activated complex is passing this one or the average frequency with which this activated complex is passing this top.

So, your velocity is equal to nu, times, concentration of the activated complex, concentration of the activated complex. So, basically it is A plus B it is a quick equilibrium I mean K c your it is a fast equilibrium, then giving rise to X double dagger, and then K 1 slow it is a slowest step then giving rise to product, for that I have written V is the reaction rate which is nothing, but equal to nu times C double dagger.

(Refer Slide Time: 18:07)



$$A + B \xrightleftharpoons[\text{Fast equilibrium}]{K_c} X^{\neq} \xrightarrow[\text{Slow}]{k_1} \text{Product}$$

- Activated Complex is in Equilibrium with the Reactants

$$K_c = \frac{c_{X^{\neq}}}{c_A c_B} \qquad c_{X^{\neq}} = K_c c_A c_B$$

$$\upsilon = \nu K_c c_A c_B \qquad \upsilon = -\frac{dc_A}{dt} = kc_A c_B$$

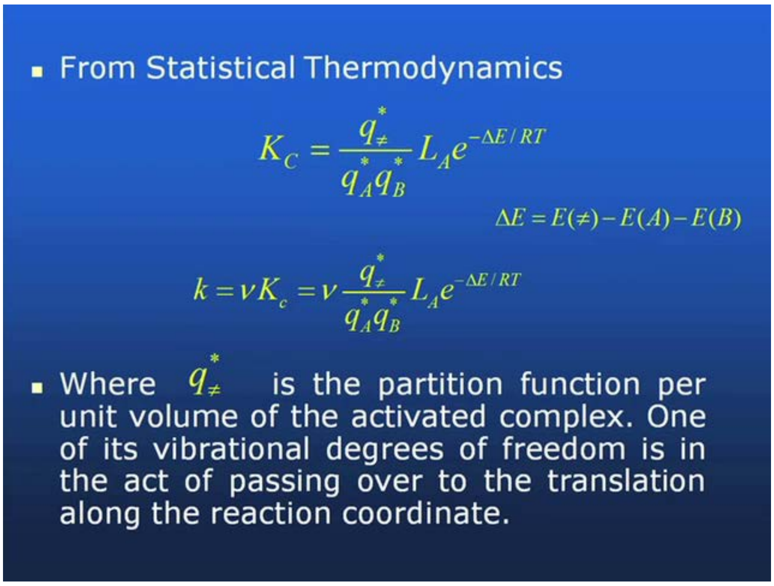
- Comparing.....

$$k = \nu K_c$$

So, the same thing that this is your scheme, this is a scheme; now, this activated complex this one is in equilibrium with reactants. So, equilibrium constant K c can be written as this divided by this in terms of concentrations. Concentration of the activated complex divided by the concentration of A and concentration of B. So, you can write c that is the concentration of the activated complex equal to K c into C A into C B. So, you just write then the appropriate expression that velocity of the reaction is equal to nu is the frequency with which it is passing the top of the barrier times K c, times C A, times C B.

And we know that V is equal to minus d C A d t which is equal to K times C A, C B. Therefore, you can write rate constant K is equal to nu, times K c. K c means it is basically equilibrium constant for this activated complex formation; so, you can also put a double dagger on K c. So, we are involving this activated complex in this equilibrium process with your reactant side.

(Refer Slide Time: 19:32)



- From Statistical Thermodynamics

$$K_C = \frac{\overset{*}{q}_{\neq}}{\overset{*}{q}_A \overset{*}{q}_B} L_A e^{-\Delta E/RT}$$

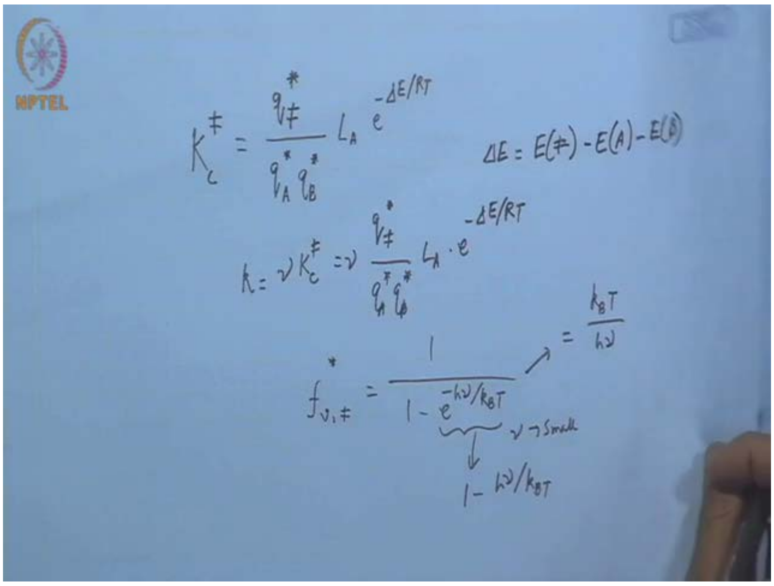
$$\Delta E = E(\neq) - E(A) - E(B)$$

$$k = \nu K_c = \nu \frac{\overset{*}{q}_{\neq}}{\overset{*}{q}_A \overset{*}{q}_B} L_A e^{-\Delta E/RT}$$

- Where $\overset{*}{q}_{\neq}$ is the partition function per unit volume of the activated complex. One of its vibrational degrees of freedom is in the act of passing over to the translation along the reaction coordinate.

Next, from statistical thermodynamics.

(Refer Slide Time: 19:45)



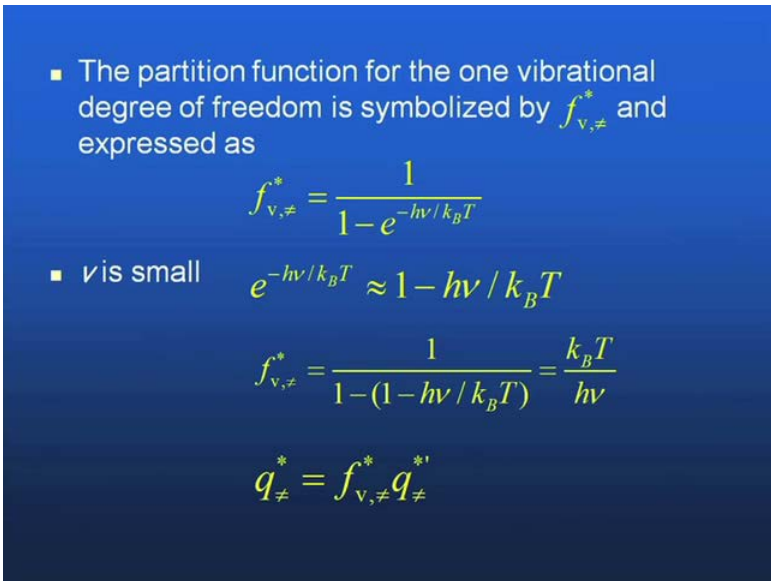
We can write your equilibrium constant K c is equal to K c double dagger or maybe you can write K c as well; so, q double dagger it is star divided by q A star then q B star and Avogadro Number L A e to the power minus delta E by R T. So, ultimately k is equal to nu times K c nu q q A L A minus delta E by R T where delta E is E delta E is E double dagger minus E A minus E B. So, here this q double dagger with star is the partition function per unit volume of the activated complex.

And of course, it is one of its vibrational degrees of freedom is in the act of passing over to the to the translation along the reaction coordinate. So, one of its vibrational degree of freedom, suppose if it is a complicated molecule - molecule or maybe complicated you know, entity; the idea is that out of many vibrational degrees of freedom. Only one vibrational degree of freedom will be responsible for making this activated complex to pass the you know the top of the barrier; that is why one of its vibrational degrees of

21 52

freedom is in the act of passing over to the translation that is that vibrational degrees of degree of freedom is supposed to be a lose vibration, and that will be converted to a translational motion unless it is converted to a translational motion, it cannot in principle pass the barrier. So, it is in the act of passing over to the translation along the reaction coordinate.

(Refer Slide Time: 22:23)



- The partition function for the one vibrational degree of freedom is symbolized by $f^*_{v,\neq}$ and expressed as

$$f^*_{v,\neq} = \frac{1}{1-e^{-h\nu/k_BT}}$$

- ν is small $e^{-h\nu/k_BT} \approx 1 - h\nu/k_BT$

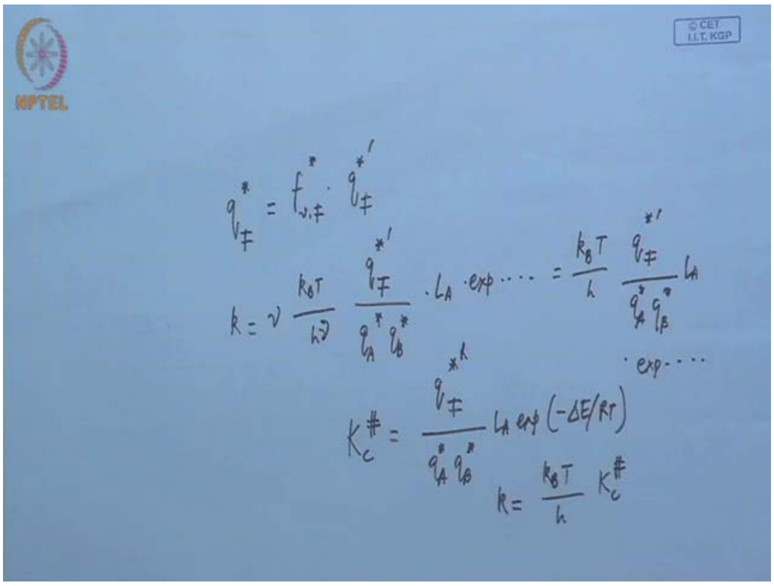
$$f^*_{v,\neq} = \frac{1}{1-(1-h\nu/k_BT)} = \frac{k_BT}{h\nu}$$

$$q^*_{\neq} = f^*_{v,\neq}\, q^{*'}_{\neq}$$

So, the partition function for the only vibrational degree of freedom that is responsible for you know such passage from one side to the other. So, you know that that we can write in this way, that f v double dagger star which is equal to 1 by 1 minus e to the power minus h nu, suppose its frequency its corresponding frequency vibrational frequency is nu therefore, we can write and since nu is very small, we can approximate this to we can approximate, if nu is small as I told you that generally this vibrational degree you know partition function; these are generally unity close to unity but, if these modes are I mean this frequency is low then e u you know it will be, it will not become 0, but it will be you know some something else, something else it is more than more than 0.

Therefore, your number will be this denominator will be less you know less than unity 0 and 1 between 0 and 1; therefore, this overall f nu double dagger star will be will be basically, your it will be more it little more than 1.So, you can you know you can write in place of this approximate this to when nu is small, you can write your this one to be equal to 1 minus h nu divided by K B T. Therefore, this will be basically this will come out to be basically equal to K B T by h nu.

(Refer Slide Time: 24:18)



$$q^{*}_{\ddagger} = f^{*}_{v,\ddagger} \cdot q^{*'}_{\ddagger}$$

$$k = \nu \frac{k_B T}{h\nu} \frac{q^{*'}_{\ddagger}}{q^{*}_{A} q^{*}_{B}} \cdot L_A \cdot \exp \cdots = \frac{k_B T}{h} \frac{q^{*'}_{\ddagger}}{q^{*}_{A} q^{*}_{B}} L_A \cdot \exp \cdots$$

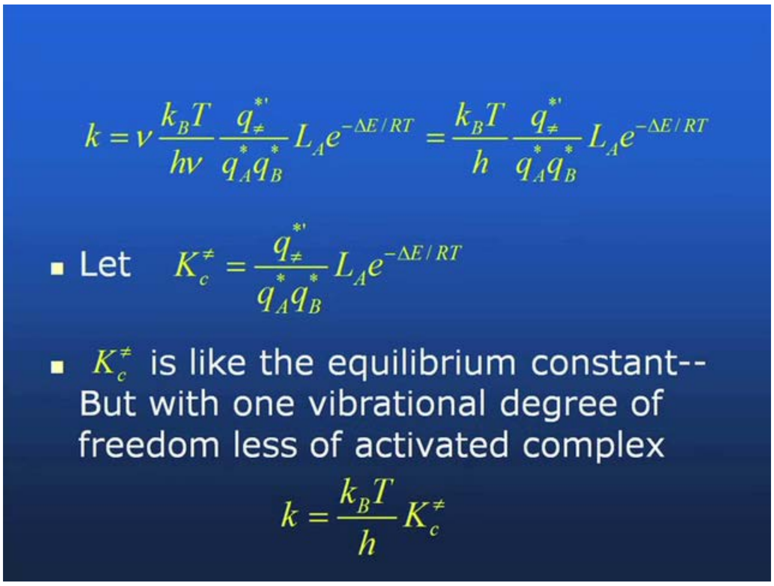
$$K^{\#}_{c} = \frac{q^{*'}_{\ddagger}}{q^{*}_{A} q^{*}_{B}} L_A \exp(-\Delta E/RT)$$

$$k = \frac{k_B T}{h} K^{\#}_{c}$$

So, your q star double dagger will be equal to one vibrational mode less so, it will be f v double dagger star times q star prime, this prime means you know one mode less. So, therefore therefore, k you can write k equal to nu into K B T by h nu then q double dagger star primed divided by q A star, q B star, because these are the and one thing these these do not have any lose vibrational mode, because maybe these are atoms; so, there is a position of lose vibrational mode into L A times exponential quantity.

So, this gives you this gives you K B T by h into q divided by q A q B star L A times exponential quantity. Now, if you take K c double dagger is equal to, now if you take this one primed divided by q A, q B star L A exponential minus delta E by R T, then you can simply write k rate constant is equal to K B T by h into K c this one.

(Refer Slide Time: 26:26)



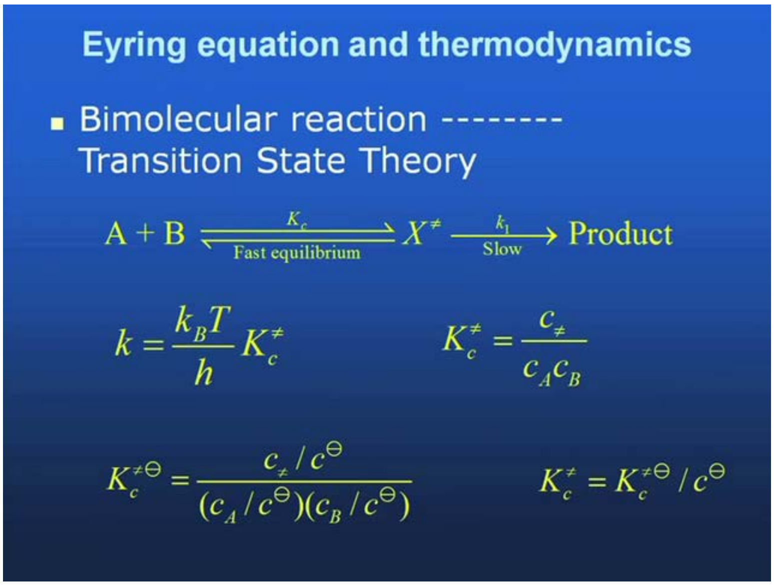
$$k = \nu \frac{k_B T}{h\nu} \frac{q_{\neq}^{*'}}{q_A^* q_B^*} L_A e^{-\Delta E/RT} = \frac{k_B T}{h} \frac{q_{\neq}^{*'}}{q_A^* q_B^*} L_A e^{-\Delta E/RT}$$

- Let $K_c^{\neq} = \frac{q_{\neq}^{*'}}{q_A^* q_B^*} L_A e^{-\Delta E/RT}$
- $K_c^{\neq}$ is like the equilibrium constant-- But with one vibrational degree of freedom less of activated complex

$$k = \frac{k_B T}{h} K_c^{\neq}$$

So, K c double dagger is like the equilibrium constant, but with one vibrational degree of freedom less of the activated complex. So, this one is having one degree of freedom less, because that degree of freedom you know is responsible for the reaction to take place. So, that is converted to a translational mode and that translational mode will help in making your activated complex to pass the top of your barrier.

(Refer Slide Time: 26:59)



Eyring equation and thermodynamics

- Bimolecular reaction -------- Transition State Theory

$$\mathrm{A + B} \underset{\text{Fast equilibrium}}{\overset{K_c}{\rightleftharpoons}} X^{\neq} \xrightarrow[\text{Slow}]{k_1} \text{Product}$$

$$k = \frac{k_B T}{h} K_c^{\neq} \qquad K_c^{\neq} = \frac{c_{\neq}}{c_A c_B}$$

$$K_c^{\neq\ominus} = \frac{c_{\neq}/c^{\ominus}}{(c_A/c^{\ominus})(c_B/c^{\ominus})} \qquad K_c^{\neq} = K_c^{\neq\ominus}/c^{\ominus}$$

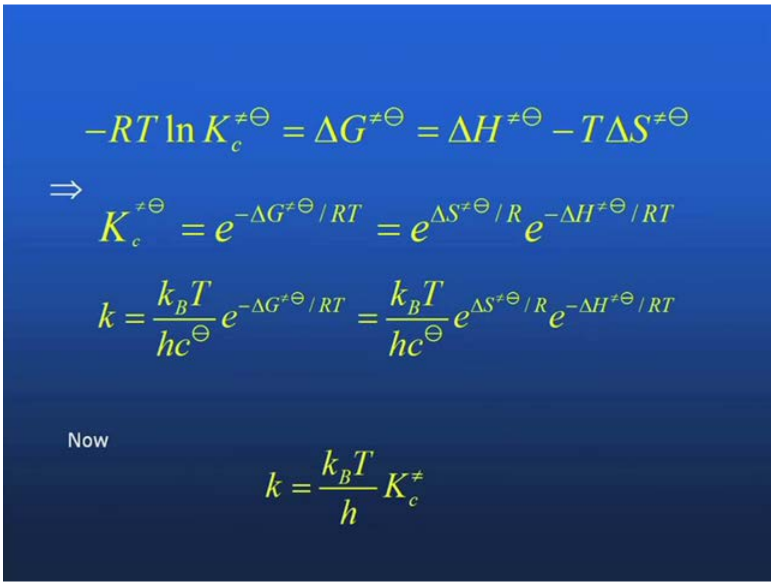
Next, this Eyring equation... So, this last equation you know this one. Eyring equation and relation with you know thermodynamics. Let us consider the bimolecular reaction under transition transition state theory, such that A and B they are in equilibrium with your activated complex X double dagger; the forward forward equilibrium you know this

this one is having the equilibrium constant K c, and it is a this equilibrium is established very fast and then this X double dagger slowly passes to the product side with a rate constant k 1. So, k rate constant is equal to K B T by h into K c double dagger as we just have deduced deduced it, where K c double dagger is equal to C double dagger divided by C A and C B it is simple concentration equilibrium constant.

If we want to convert this to activity equilibrium constant that is to thermodynamic equilibrium constant, then we have to we have to you know use the corresponding activity term that is we have to divide C double dagger by corresponding standard concentration and also these two by standard concentration like this.

So, K c double dagger with zero-bar it is zero bar is equal to this. Therefore, you can write that for this type of reaction A plus B giving rise to X and then X giving rise to product, we can write K c double dagger which is equal to K c double dagger zero-bar divided by C zero-bar; so, this this is the relation between you know concentration equilibrium constant and the activity equilibrium constant, that is you are you are diving this concentration to make it dimensionless you are dividing by you know C, I mean C zero-bar you are dividing by that.

(Refer Slide Time: 29:14)



$$-RT\ln K_c^{\neq\ominus} = \Delta G^{\neq\ominus} = \Delta H^{\neq\ominus} - T\Delta S^{\neq\ominus}$$

$$\Rightarrow K_c^{\neq\ominus} = e^{-\Delta G^{\neq\ominus}/RT} = e^{\Delta S^{\neq\ominus}/R}e^{-\Delta H^{\neq\ominus}/RT}$$

$$k = \frac{k_B T}{hc^{\ominus}}e^{-\Delta G^{\neq\ominus}/RT} = \frac{k_B T}{hc^{\ominus}}e^{\Delta S^{\neq\ominus}/R}e^{-\Delta H^{\neq\ominus}/RT}$$

Now

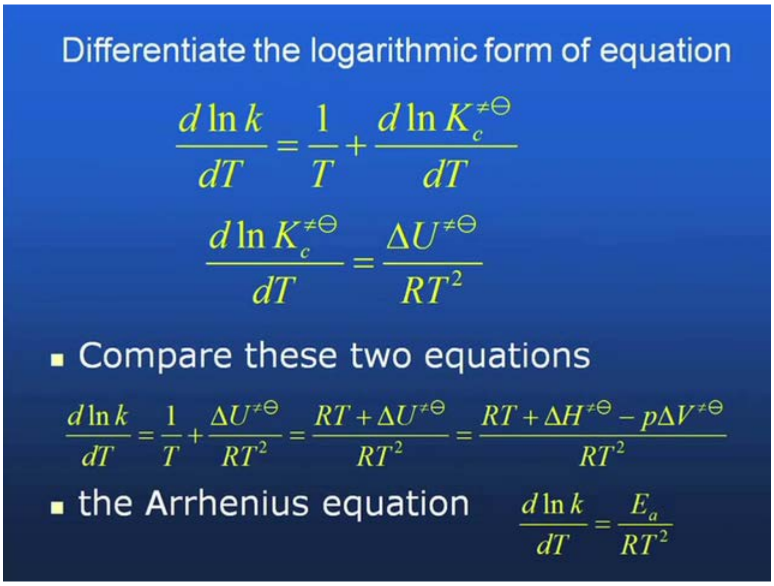
$$k = \frac{k_B T}{h}K_c^{\neq}$$

So you have got you know you know that delta G you know this is this simple thermodynamic expression delta G zero-bar with double dagger is equal to minus R T l n K c this bar; so, because we will be using this expression over there is equal to delta H minus T delta S with double dagger and zero-bar, this gives you K c double dagger-bar is equal to minus e to the power minus delta G double dagger zero-bar divided by R T which is equal to e to the power delta S double dagger 0 by R into e to the power minus delta H double dagger 0 by R T. So, therefore, we have come to a relation that your equilibrium constant that that describes the equilibrium between your reactant and the activated complex.

So, that is that is K c double dagger with zero-bar is equal to e to the power that is you know this there are two exponential quantities - one is this one, it is it does not have explicit temperature dependence and it has got an explicit temperature dependence. So, it has you know this entropic term; so, standard entropy of activation, it is a standard entropy of activation, this is a standard heat of formation for the activated complex. So from this we can write k is equal to K B T by h divided by c zero-bar, because you go back to the earlier slide this one, because you have got K c double dagger is equal to K c double dagger zero-bar by c zero- bar that is why this one divided by c zero-bar.

So, this gives you K B T by h c zero-bar into e to the power delta S. So, this exponential to the power delta S quantity and exponential to the power delta H quantity that is an entropic term and this is an enthalpy term. Now now we have this k is equal to K B T by h into K c this one, this one we have got this one this expression. So, we will be using it again; so, what we have to do is we have to take logarithm of both the sides.

(Refer Slide Time: 32:05)



Differentiate the logarithmic form of equation

$$\frac{d\ln k}{dT} = \frac{1}{T} + \frac{d\ln K_c^{\neq\ominus}}{dT}$$

$$\frac{d\ln K_c^{\neq\ominus}}{dT} = \frac{\Delta U^{\neq\ominus}}{RT^2}$$

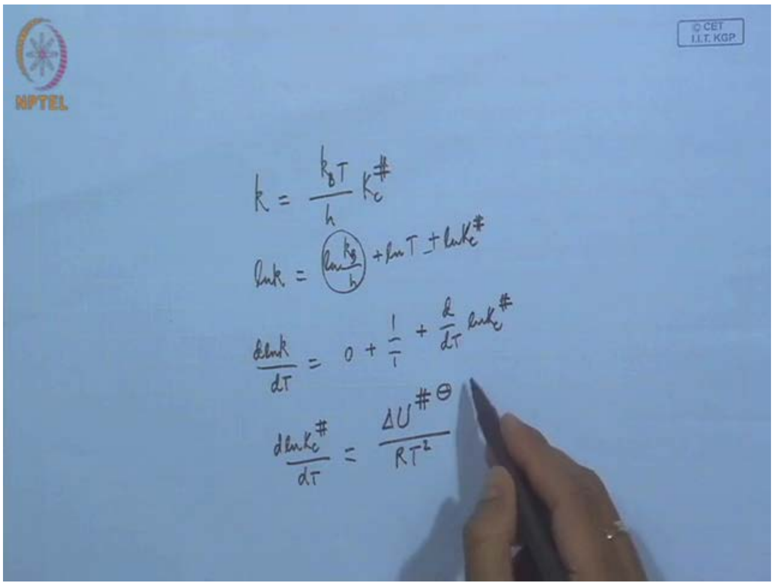
- Compare these two equations

$$\frac{d\ln k}{dT} = \frac{1}{T} + \frac{\Delta U^{\neq\ominus}}{RT^2} = \frac{RT + \Delta U^{\neq\ominus}}{RT^2} = \frac{RT + \Delta H^{\neq\ominus} - p\Delta V^{\neq\ominus}}{RT^2}$$

- the Arrhenius equation $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

Taking logarithm of both the sides, and then we have to we will differentiate it. So, what should be we getting basically we take logarithm of this both sides; so, l n K is equal to l n K B by h then plus l n T plus l n K C double dagger.

(Refer Slide Time: 32:32)



$$k = \frac{k_B T}{h} K_c^{\#}$$

$$\ln k = \ln \frac{k_B}{h} + \ln T + \ln K_c^{\#}$$

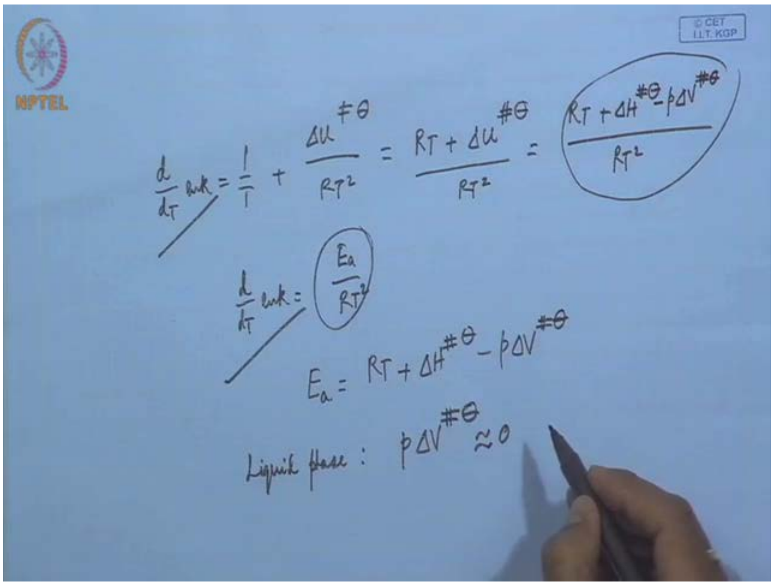
$$\frac{d \ln k}{dT} = 0 + \frac{1}{T} + \frac{d}{dT} \ln K_c^{\#}$$

$$\frac{d \ln K_c^{\#}}{dT} = \frac{\Delta U^{\# \ominus}}{RT^2}$$

So, then lets lets do it so, K is equal to K B by T h k c double dagger. So, l n K that is your rate constant is equal to l n K B by h plus l n T plus l n K c double dagger. So, this is a constant quantity; so, if we do differentiation with respect to T that is the temperature then d l n K d T, because we we will ultimately relate this with or we will ultimately compare this with your famous or well known Arrhenius equation.

So, d l n K d T is equal to this one will be 0 plus this is d d T of l n T is 1 upon T plus d d T of l n K c double dagger. So, we can write, so, we can write you know d l n K c double dagger d T is equal to delta E or delta U whatever this is called your iso-core. So, we have got this expression this is another van't off expression. Now what we will do we will plug in this expression over here, and then we will try to simplify it; so, this is one van't off expression and this is the expression after differentiating the logarithmic form of this expression this one.

(Refer Slide Time: 34:31)



$$\frac{d}{dT}\ln k = \frac{1}{T} + \frac{\Delta U^{\neq\ominus}}{RT^2} = \frac{RT + \Delta U^{\neq\ominus}}{RT^2} = \frac{RT + \Delta H^{\neq\ominus} - p\Delta V^{\neq\ominus}}{RT^2}$$

$$\frac{d}{dT}\ln k = \frac{E_a}{RT^2}$$

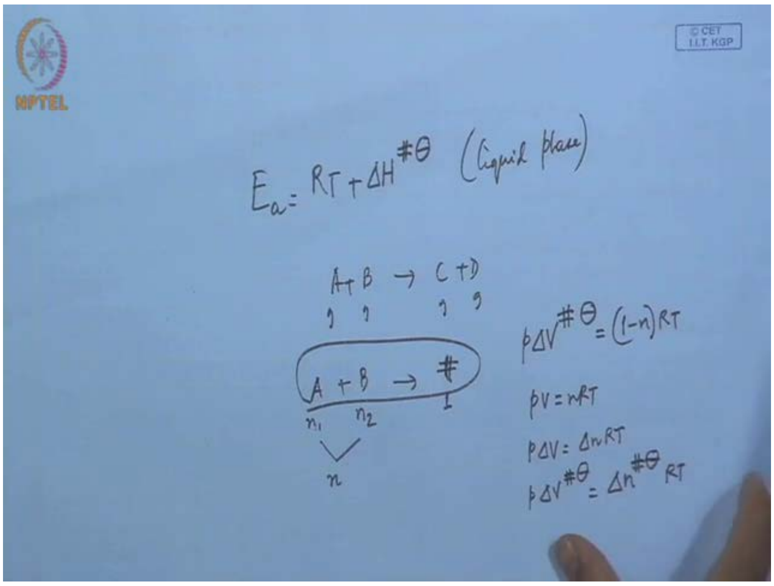
$$E_a = RT + \Delta H^{\neq\ominus} - p\Delta V^{\neq\ominus}$$

Liquid phase : $p\Delta V^{\neq\ominus} \approx 0$

So, comparing these two what we are getting is this d d T of l n K is equal to 1 upon T plus delta U zero-bar divided by R T square is equal to R T plus delta U zero-bar divided by R T square is equal to your R T plus delta H 0 minus p delta V zero-bar divided by R T square. So, what is that we have to find it out, find it; now, we let us write the well known you know all of you know or all of us know this Arrhenius equation d d T of l n K is equal to E A by R T square.

Now, we are in a position to compare this with this one, because left hand side this one and this one these two are identical; so, we are in a position to compare. So, what do we get that E a is equal to R T minus delta H sorry plus delta H double dagger zero-bar minus P delta V. So, this is enthalpy of activation, this is volume of activation, standard volume activation, this is standard enthalpy of activation. Now what happens that there are situations - one situation is for you know liquid phase reaction, liquid phase reactions where you know you are changed this P delta V, this volume activation may be neglected for all practical purposes.

(Refer Slide Time: 37:01)



$E_a = RT + \Delta H^{\#\ominus}$ (liquid phase)

$A + B \rightarrow C + D$

$A + B \rightarrow \#$

$p\Delta V^{\#\ominus} = (1-n)RT$

$pV = nRT$

$p\Delta V = \Delta n RT$

$p\Delta V^{\#\ominus} = \Delta n^{\#\ominus} RT$

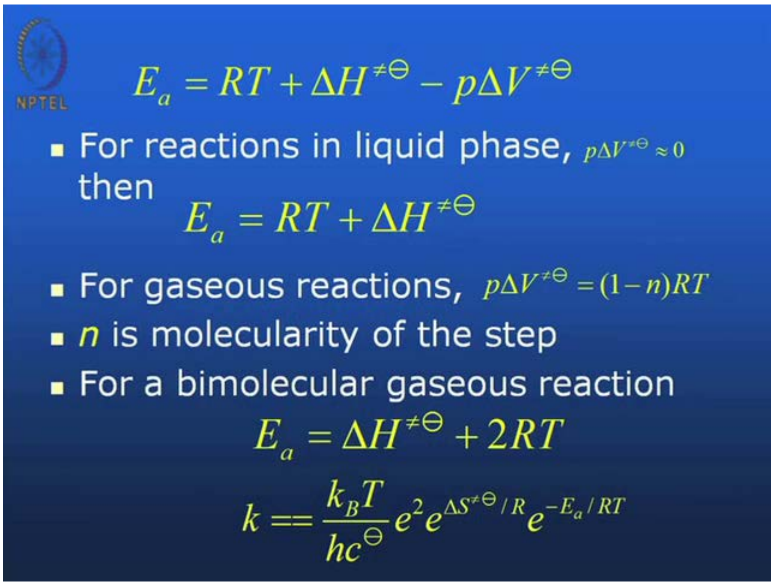
So, that means for liquid phase; we have a very simple relation that E a is equal to R T plus delta H double dagger zero-bar. Next what happens for your gaseous reaction, this is your liquid, liquid phase what happens for gaseous reaction? That is reaction that is your left hand side A plus B all are gas giving rise to C plus D all are gas. So, what is the situation. So, for that we have to apply you know this ideal gas principle, we have to assume that these gases behave ideally, these gases behave ideally.

So, basically you know you have say n 1 mole of A plus B of n 2 giving rise to you know say say for example, say one mole of activated complex say one mole of activated complex. So, basically your right hand side is less right hand side is one and left hand side is n 1 plus n 2; so, let us write in place of n 1 plus n 2 equal to n. So, left hand side total number of moles will be n and right hand side total number of moles will be n, because out of these, these two species A and B your activated complex will be produced that means n 1 mole of A and n 2 mole of B producing one mole of the activated complex.

So, your for your you know gas phase reaction your p delta V term double dagger zero term will be is will be equal to 1 minus n into R T; that is at a given temperature p V is equal to n R T. That is that you have to use; so, that is p delta V is the delta V that is the change in volume, because of these activated state formation, activated complex formation there is a change in volume; so, that change in volume can be computed this way, assuming these gas molecules are behaving ideally from your P V is equal to n R T this expression. So, basically P delta V is equal to delta n R T at a given temperature, because you are carrying out this reaction at a fixed temperature. So, that is why P delta V; so, P delta V double dagger zero-bar is equal to your delta n double dagger zero-bar R T.

Now, this delta n is nothing, but your final minus initial final is 1 initial is n, where n is the you know this step – so, this is this step you can call this as, this step you can call as an like an elementary step - in this elementary step your activated complex is formed. Therefore, molecularity of this particular step that is the step in which your A plus B giving rise to activated complex will be n 1 plus n 2 or maybe n molecularity n that is n number of molecules are involved in the production of 1 mole of your activated complex. Therefore, if it is a it it is the case of a you know bimolecular gas phase reaction.

(Refer Slide Time: 41:04)



$$E_a = RT + \Delta H^{\neq\ominus} - p\Delta V^{\neq\ominus}$$

- For reactions in liquid phase, $p\Delta V^{\neq\ominus} \approx 0$ then

$$E_a = RT + \Delta H^{\neq\ominus}$$

- For gaseous reactions, $p\Delta V^{\neq\ominus} = (1-n)RT$
- n is molecularity of the step
- For a bimolecular gaseous reaction

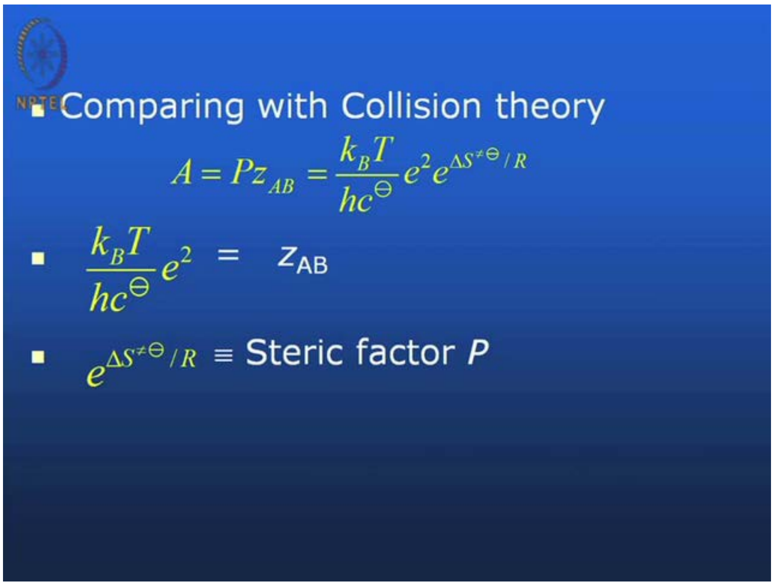
$$E_a = \Delta H^{\neq\ominus} + 2RT$$

$$k == \frac{k_B T}{hc^{\ominus}} e^2 e^{\Delta S^{\neq\ominus}/R} e^{-E_a/RT}$$

Gaseous reaction then you can write E a is equal to delta H double dagger zero-bar plus so, 1 minus n one minus n one minus n R T and there is another R T term plus R T. so far, your bimolecular case it is two. Therefore, delta H zero-bar is equal to I mean delta H E a equal to delta H zero-bar plus R T plus R T that is equal to 2 R T plus delta H zero-bar. Therefore, we can write what can we write is this. So, let us again go back to the expression of k expression of k will be expression of k will be, k is equal to k B T by h C zero-bar e to the power delta S double dagger zero bar by R into e to the power minus delta H zero- bar by R T; this is your expression for k. So, what you have to do, we have to now plug in this appropriate expression.

Since, it is 2 R T since it is 2 R T .So additional e to the power two terms will come into picture. So, that is why your expression will be your k will be k B T divided by h c this one into e to the power delta S whatever was there is there zero-bar by r e to the power minus delta H zero-bar by R T times e to the power 2 R T by R T. So, that will give you e square. Therefore, your k is equal to k T by h divided by c zero-bar e to the power this e to the power delta H, e to the power delta S term, e to the power delta H term times, e square. So far a bimolecular gas phase reaction you are getting an expression of this sort.

(Refer Slide Time: 44:00)



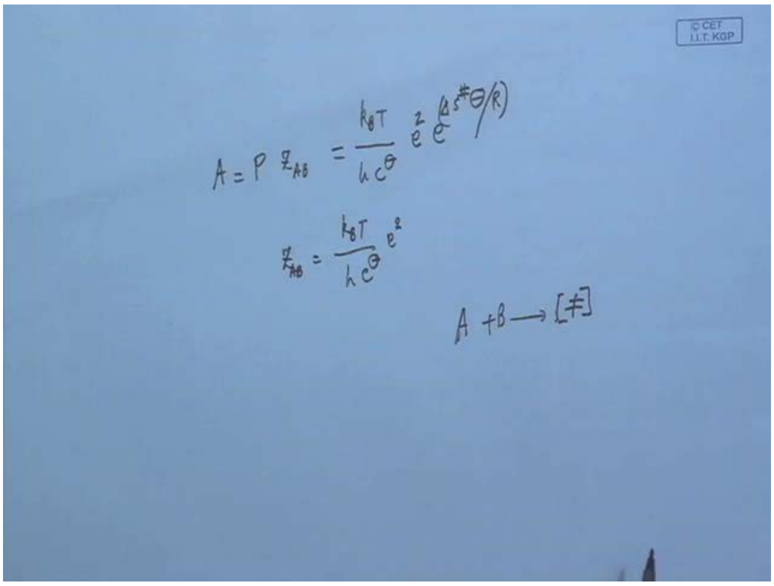
- Comparing with Collision theory

$$A = Pz_{AB} = \frac{k_B T}{hc^{\ominus}} e^2 e^{\Delta S^{\neq\ominus}/R}$$

- $\frac{k_B T}{hc^{\ominus}} e^2 = z_{AB}$
- $e^{\Delta S^{\neq\ominus}/R} \equiv$ Steric factor *P*

Next, is your we have to compare this with collision theory, because we already have started collision theory that collision theory is purely based on hard sphere - hard sphere approximation. That these hard sphere molecules are reacting via collision with one another like this.

(Refer Slide Time: 44:40)



So, therefore, therefore, if we look into the pre-exponential term that is A that we already have talked about A is equal to p is the probability or or you know Steric factor into z A B small z A B which is equal to k B T divided by h c zero-bar e square, then e to the power delta S double dagger zero-bar by R. If we compare compare this with this one.

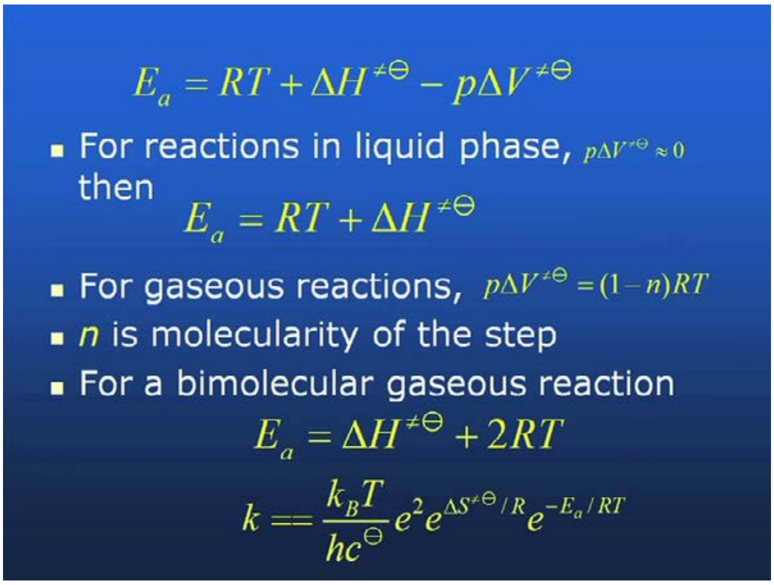
Then, what do we get. We get z A B small z A B is equal to k B T by h c zero- bar into e square. So, therefore, this frequency term this frequency term is basically this term and you see that frequency term increases with increase of temperature and it occurs in a linear fashion. Now, what about the other term, this other term is e to the power delta S double dagger zero by R. So, which is which you can just equate to your P that is your Steric factor; therefore, this Steric factor you see that if you if you if you write that the your Steric factor Steric factor is this equal to delta S double dagger zero by R this Steric factor.

Then, you can see that this exponential to the power delta S activation. That is entropy of activation has got a relation with the Steric factor. So, entropy of activation means standard entropy of activation of course, so, standard entropy of activation means you have got your reactant that is A and B, and you have got your product or product means your your activated complex. So, if you just look into this situation that your A plus B giving rise to your activated complex, then if this is giving rise to activated complex, then it is basically you are having 2 2 atoms over here or 2 molecules over here and you are generating a single molecule, single means only one species on the right hand side; so, there is a net there is a net decrease in entropy of the system, just if we if we concentrate onto the system.

So, this factor has got enormous importance onto onto this onto the behavior of this reaction that is that is whether whether, if if we have if we have a collision like, if we try to you know have a link with the your collision theory, and absolute reaction rate theory. Then if there is a collision between these 2 molecules then and if they are not properly oriented, if they are not properly oriented then they will not make any product, they will not give rise to any product.

So, that is very important; so, this entropy factor has got also a a an important role important role in determining, your this pre-exponential term. So, pre-exponential term has got this your frequency term another is your Steric factor or maybe entropic term. So, this entropic term is very important; so, and you see that as a as as such this entropic term e to the power delta S double dagger zero-bar does not have an explicit temperature dependence this exponential term; it does not have any temperature over here, may be delta S double dagger-bar this quantity is having some maybe it will it will have some temperature dependence, but no that is not the it is not directly you know or maybe explicitly showing anything.

(Refer Slide Time: 49:47)



$$E_a = RT + \Delta H^{\neq\ominus} - p\Delta V^{\neq\ominus}$$

- For reactions in liquid phase, $p\Delta V^{\neq\ominus} \approx 0$ then

$$E_a = RT + \Delta H^{\neq\ominus}$$

- For gaseous reactions, $p\Delta V^{\neq\ominus} = (1-n)RT$
- *n* is molecularity of the step
- For a bimolecular gaseous reaction

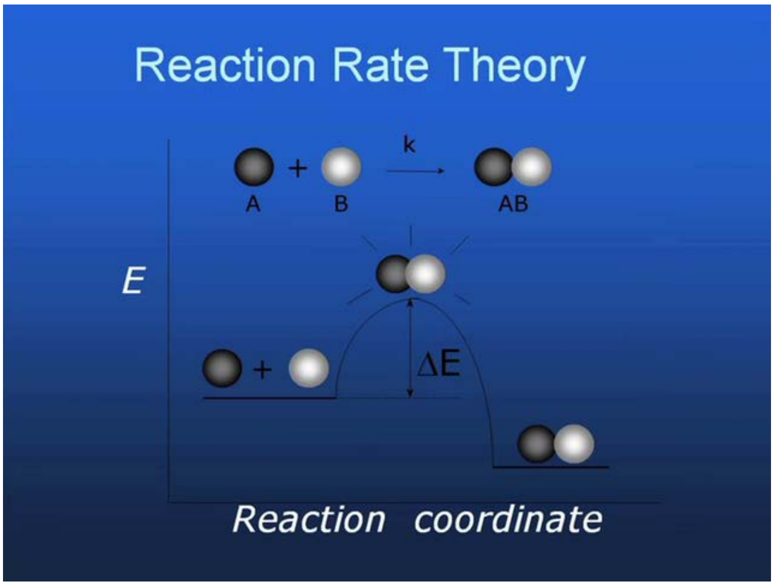
$$E_a = \Delta H^{\neq\ominus} + 2RT$$

$$k == \frac{k_B T}{hc^{\ominus}} e^2 e^{\Delta S^{\neq\ominus}/R} e^{-E_a/RT}$$

So, comparing with collision theory we get that your this if we if we again go back to the to the earlier slide that you see that your activation energy has got an R T term, and enthalpy term and also a kind of pressure volume where kind of term p delta V kind of term. So, if there is an activated complex formation then there is a reduction in you know number of moles and these reduction in number of moles is ultimately related to you know a maybe a reduction in in the you know work done by the system. And for your liquid phase this one this p delta V this this volume of activation term times p is very close to zero.

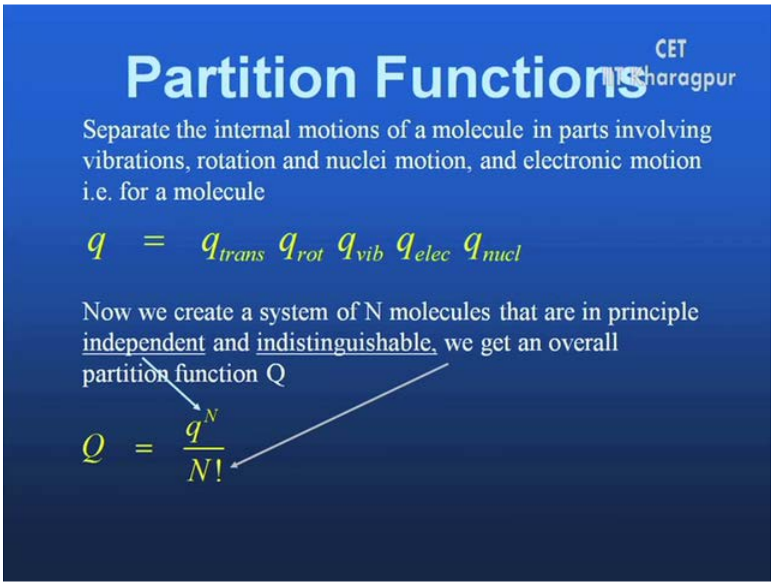
Therefore, it is it is you know, it is getting simplified to this type of expression, but your gas phase reaction your since it is a it is a huge volume change during reaction. Therefore, your this term this particular term really matters to the overall energy of activation term. And where where if you if you call this particular you know you know there your activated complex formation as as an elementary step, then your left hand side number of species that is if there are 2 species 2 molecules then you will be it will be a Bi-molecular reaction, Bi-molecular elementary reaction. So, by if a for a Bi-molecular gas phase reaction, gaseous reaction your activation energy will be your delta H is 0 zero-bar double dagger plus 2 R T; so,1 R T was there and another R T is coming as a result of your work done, work done by the system.

(Refer Slide Time: 52:25)


Reaction Rate Theory

So, ultimately we get this expression. So, what have we learnt from this lecture that that your that your this is a typical typical reaction - a Bi-molecular reaction maybe maybe if we think of a Bi-molecular. So, it is a typical Bi-molecular reaction. These are activated complex is forming this side is a reaction code that maybe as a function of some distance between say A and B.

(Refer Slide Time: 52:47)



Partition Functions

Separate the internal motions of a molecule in parts involving vibrations, rotation and nuclei motion, and electronic motion i.e. for a molecule

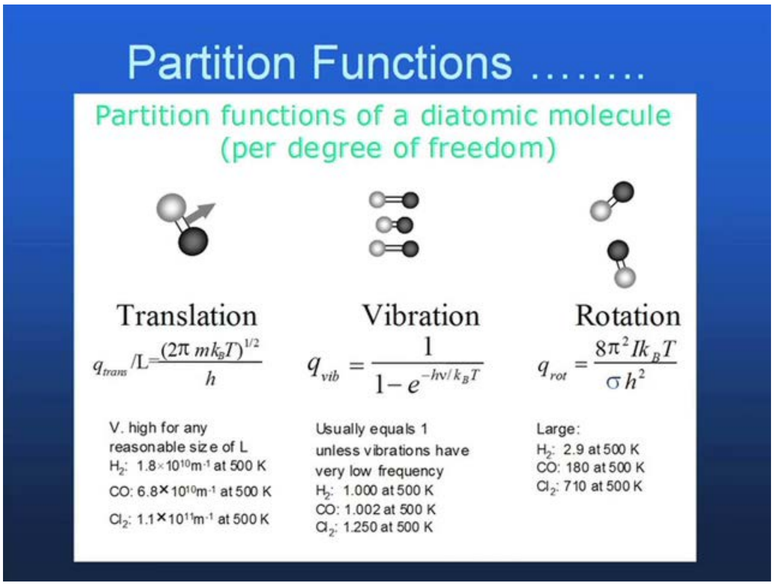
$$q = q_{trans}\, q_{rot}\, q_{vib}\, q_{elec}\, q_{nucl}$$

Now we create a system of N molecules that are in principle <u>independent</u> and <u>indistinguishable,</u> we get an overall partition function Q

$$Q = \frac{q^N}{N!}$$

We talked a little about partition function and it is partition function is basically combination of your various, you know terms arising out of various motion; so, one is translation, another is rotation, vibration, electronic and of course, nuclear partition function. This partition function is basically representing a number it is basically a number. So, how the particles are you know partition between various level at a different temperature and you know at some temperature.

(Refer Slide Time: 53:28)



Partition Functions ……..

Partition functions of a diatomic molecule (per degree of freedom)

Translation

$q_{trans}/L = \frac{(2\pi m k_B T)^{1/2}}{h}$

V. high for any reasonable size of L

H_2: 1.8×10^{10}m^{-1} at 500 K

CO: 6.8×10^{10}m^{-1} at 500 K

Cl_2: 1.1×10^{11}m^{-1} at 500 K

Vibration

$q_{vib} = \frac{1}{1-e^{-h\nu/k_BT}}$

Usually equals 1 unless vibrations have very low frequency

H_2: 1.000 at 500 K

CO: 1.002 at 500 K

Cl_2: 1.250 at 500 K

Rotation

$q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$

Large:

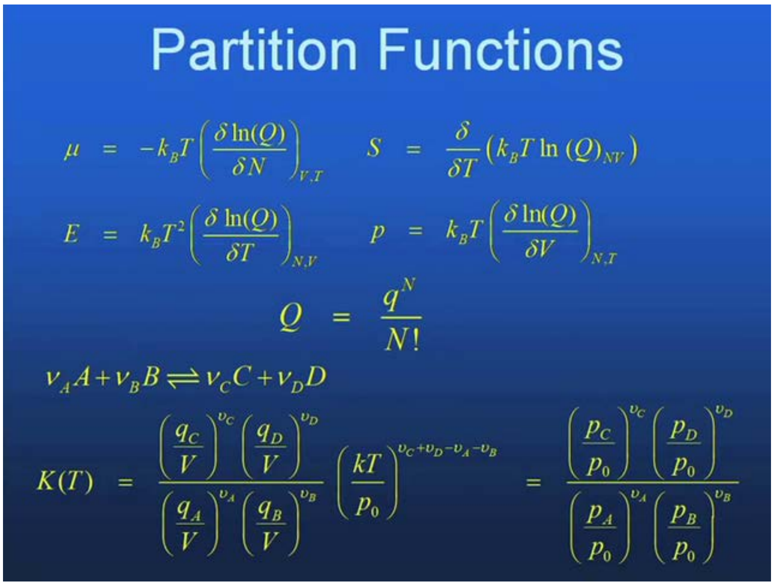
H_2: 2.9 at 500 K

CO: 180 at 500 K

Cl_2: 710 at 500 K

Now, we have given some estimate of partition function per degree of freedom for a Di-atomic molecule.

(Refer Slide Time: 53:39)



Partition Functions

$$\mu = -k_BT\left(\frac{\delta \ln(Q)}{\delta N}\right)_{V,T} \qquad S = \frac{\delta}{\delta T}\left(k_BT\ln(Q)_{NV}\right)$$

$$E = k_BT^2\left(\frac{\delta \ln(Q)}{\delta T}\right)_{N,V} \qquad p = k_BT\left(\frac{\delta \ln(Q)}{\delta V}\right)_{N,T}$$

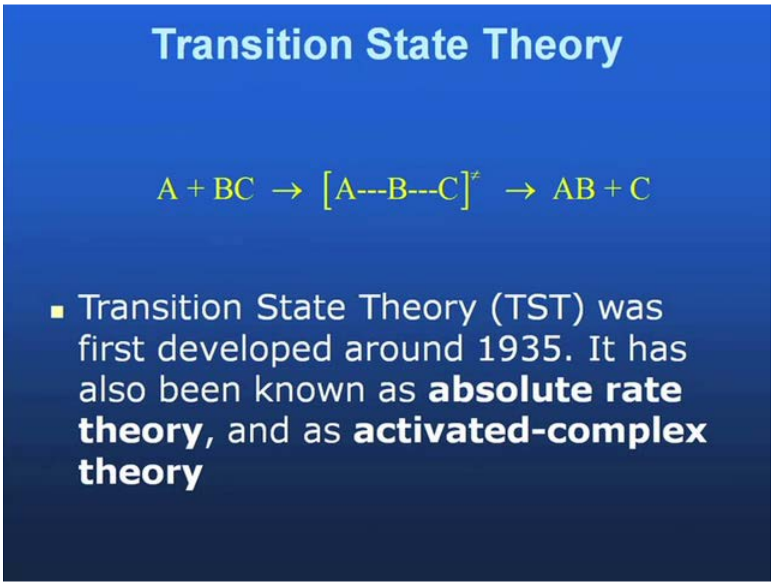
$$Q = \frac{q^N}{N!}$$

$$v_AA + v_BB \rightleftharpoons v_CC + v_DD$$

$$K(T) = \frac{\left(\frac{q_C}{V}\right)^{\upsilon_C}\left(\frac{q_D}{V}\right)^{\upsilon_D}}{\left(\frac{q_A}{V}\right)^{\upsilon_A}\left(\frac{q_B}{V}\right)^{\upsilon_B}}\left(\frac{kT}{p_0}\right)^{\upsilon_C+\upsilon_D-\upsilon_A-\upsilon_B} = \frac{\left(\frac{p_C}{p_0}\right)^{\upsilon_C}\left(\frac{p_D}{p_0}\right)^{\upsilon_D}}{\left(\frac{p_A}{p_0}\right)^{\upsilon_A}\left(\frac{p_B}{p_0}\right)^{\upsilon_B}}$$

Next is expressions we just wrote the expressions for you know various thermodynamic functions like chemical potential, entropy, internal energy and pressure and with that we we wrote an expression for your equilibrium constant at a at a temperature T.

(Refer Slide Time: 54:05)



Transition State Theory

$$A + BC \rightarrow [A\text{---}B\text{---}C]^{\neq} \rightarrow AB + C$$

- Transition State Theory (TST) was first developed around 1935. It has also been known as **absolute rate theory**, and as **activated-complex theory**

Then we started with Transition State Theory. Now, this transition state theory is idea is that there is an activated complex of this type is formed, and then it will dissociate or it will give rise to product. And the idea is that that in this activated complex. Since, this is this is a kind of aggregate say A B C aggregate, it will have you know vibrational various vibrational modes of which one is a weak vibrational mode and that vibrational mode will will be converted to a translational mode. That is that vibrational mode it is a it is a low frequency and lalarge maybe a large amplitude vibration, that is responsible for the rupture of a particular bond or the rearrangement of a particular bond giving rise to A B plus C, and that we did in this fashion that you know this is your scheme then we wrote the equilibrium constant, then is this equilibrium constant is written in terms of various partition functions then and also we have taken out one particular vibrational mode.

So, these vibrational mode and corresponding partition function and therefore, we wrote your partition function for reactivated complex in terms of another partition function times one vibrational partition function. Then we got this expression and finally, we compared with your with compared with collision theory. And this says that you know your your this entropic term and this term k B T by h c. This term is you know similar to your is similar to your a term similar to your a means pre-exponential term, and your Steric factor is in principle you know related to your entropy of activation.

So, in this discussion we have you know, we have learnt how learnt the treatment of your reaction rate based on transition state model. So, next day we will have you know the extension of the same theory for surface reactions and some other aspects as well. So, till then have nice time and see you in the next lecture, thank you.