Chemical Kinetics and Transition State Theory
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Lecture 31
Problem Solving Session 4

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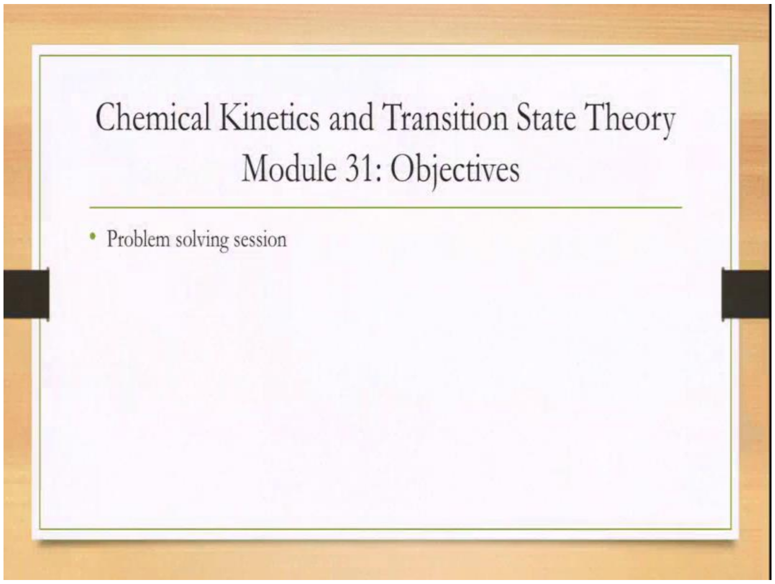

Chemical Kinetics and Transition State Theory
Module 31: Objectives

- Problem solving session

Hello and welcome to module 31 of Chemical Kinetics and Transition State Theory. In the last module, we solved a numerical problem. Today it is a continuation of that, we will continue solving more problems. Today our problems will although be more, not numerical, but more focused on concepts. So let us start the problems.

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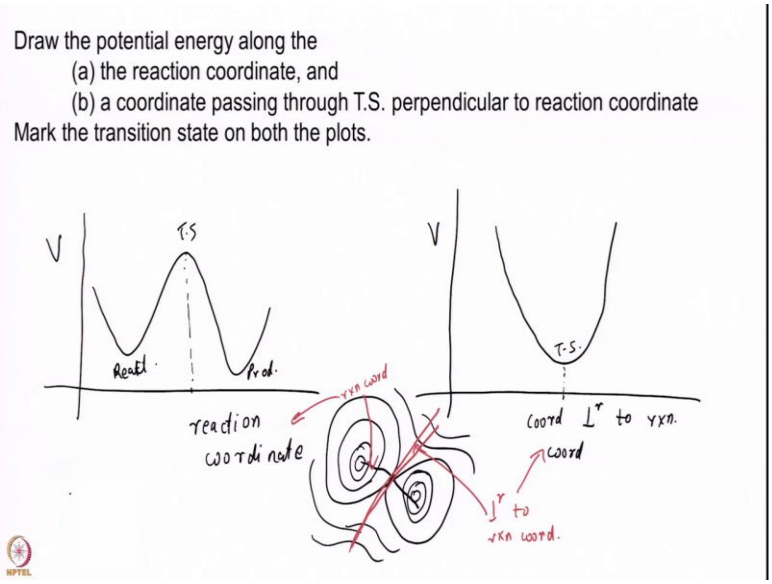

Draw the potential energy along the

(a) the reaction coordinate, and

(b) a coordinate passing through T.S. perpendicular to reaction coordinate

Mark the transition state on both the plots.

So, the first problem is a relatively simpler problem, but a conceptually very important problem. So, I really wanted to take a pause, draw the potential energy for along the reaction coordinate and a coordinate that is perpendicular to the reaction coordinate sitting at transition state. So, this, please do take a pause and you should be able to do these plots. Take a pause now.

Hopefully, you have taken a pause. So now let us solve it together. So, for the first one, we have to draw the potential energy along the reaction coordinate. So, this is the figure that you have commonly seen probably in every single textbook in kinetics. So, you get a figure like this where this is reactants, this is products and this is the transition state, the maximum struck point. So, this is your very familiar figure.

However, what I want you to also understand from this course is that if I choose a coordinate perpendicular to reaction coordinate at the transition state, I will get a energy surface that is going to look like this and this is my transition state. This is a very important concept, transition state is a minima for any coordinate that passes perpendicular to the reaction coordinate.

So, once more a contour plot if I draw, these kind of contour plots that I have drawn a few times now. This is reaction coordinate. Let me just change the color in color red. This is a coordinate that is perpendicular to reaction coordinate. So, this is reaction, this is perpendicular to reaction coordinate. So, along the reaction coordinate you see a figure like this, along a direction perpendicular to reaction coordinate, which is if you are walking along this, you will get something like this. Get back to black color.

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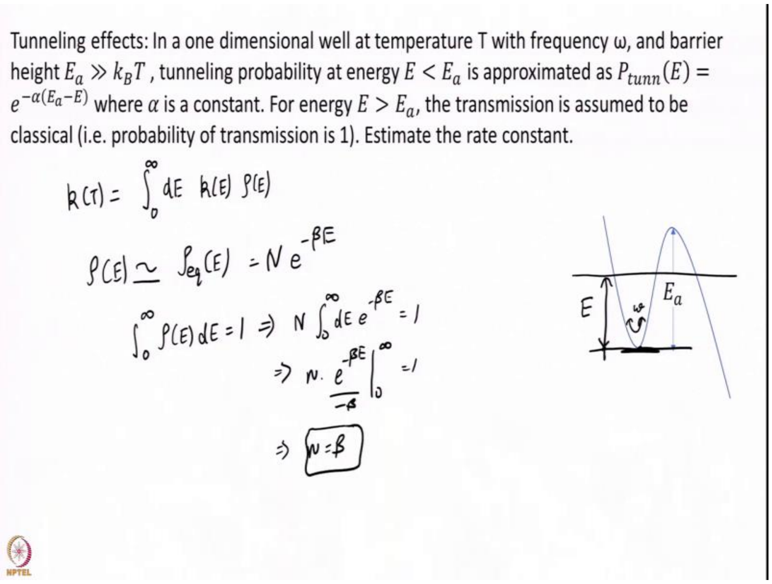

Tunneling effects: In a one dimensional well at temperature T with frequency ω, and barrier height $E_a \gg k_B T$, tunneling probability at energy $E < E_a$ is approximated as $P_{tunn}(E) = e^{-\alpha(E_a - E)}$ where α is a constant. For energy $E > E_a$, the transmission is assumed to be classical (i.e. probability of transmission is 1). Estimate the rate constant.

$$k(T) = \int_0^\infty dE \; k(E)\, \rho(E)$$

$$\rho(E) \simeq \rho_{eq}(E) = N e^{-\beta E}$$

$$\int_0^\infty \rho(E)\, dE = 1 \Rightarrow N \int_0^\infty dE\, e^{-\beta E} = 1$$

$$\Rightarrow N \cdot \frac{e^{-\beta E}}{-\beta}\Big|_0^\infty = 1$$

$$\Rightarrow \boxed{N = \beta}$$

Second problem is slightly harder, but it is an interesting problem and it shows you how to include quantum mechanical effects in transition state theory. So let us imagine I have only a one dimensional well and somehow the temperature is maintained at some temperature T. Let us say the frequency is given to you, omega here and the barrier height is much more than kT. This Ea is much greater than kT and we are going to include tunneling in this question now.

So, in a module, some modules ago, five, six modules ago, we solved this problem without any tunneling. So, you can go back to that module. See how we solved this problem. And now the question is can you also include tunneling effects in it. So, what I have provided you here is, at the probability of tunneling at an energy E less than Ea is given by this formula, where alpha is some constant, and for energy greater than Ea, you can assume that the transmission is 1. So, now, can you estimate the rate constant? You can make any approximations or assumptions that you want to make. Pause the video and attempt this problem on your own.

Hopefully you have paused the video and you have attempted the problem at least. This is not an easy problem, but you have to make at least attempts. So let us try to attack this problem. Well, we will have to go back to our fundamentals. How we solved this problem earlier? Well, idea is the same. This is what we are going to do. Let us say my, and I set some energy E. At that energy

E, what is the rate constant and what is the probability of being at that energy E. So if I integrate this together, I will get the total rate. And energy cannot be negative, because I cannot be lower than this minima. So, this is what I have to calculate.

Rho, I am going to approximate as we have always done in transition state theory, as the equilibrium, so that is given by e to the power of minus beta E in one dimension. So, we will find this N, as always, as 0 to infinity. This should be 1. So now this is easy to integrate. This if I integrate, I get something like this. So, you can quickly show this easily enough. The first part, I am good, I know rho of E.

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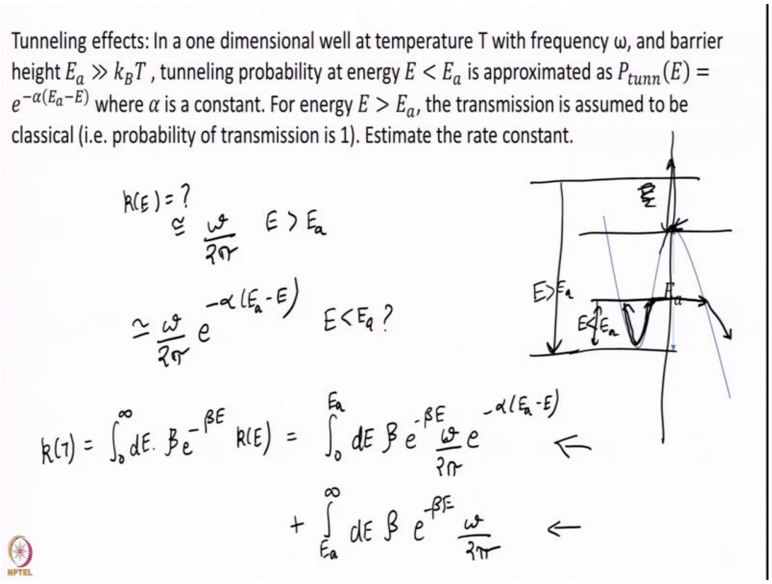

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$$k(E) = ?$$

$$\cong \frac{\omega}{2\pi} \quad E > E_a$$

$$\simeq \frac{\omega}{2\pi} e^{-\alpha(E_a - E)} \quad E < E_a\,?$$

$$k(T) = \int_0^\infty dE.\, \beta e^{-\beta E} k(E) = \int_0^{E_a} dE\, \beta e^{-\beta E} \frac{\omega}{2\pi} e^{-\alpha(E_a - E)} \leftarrow$$

$$+ \int_{E_a}^{\infty} dE\, \beta\, e^{-\beta E} \frac{\omega}{2\pi} \leftarrow$$

Second part, how do I calculate this k of E. Well, let us start by saying that this is equal to at least, for less than E and E greater than Ea. We will calculate them separately. So, this is equal to nothing but omega over 2 pi for E greater than Ea. So, if my energy is above this point, then my rate is omega over 2 pi and once back, we argued this in some more detail in our module, it is omega over 2 pi, because omega over 2 pi is the frequency of hitting the transition state. So, this is my transition state. I am sitting here. The probability that I will hit this point is one time period. In every one time period I will hit this exactly once in the forward direction.

So again, this is approximate, I am making the transition state approximations here. So, transition state approximation is that I only look at rate in the forward direction. And in the forward direction, I will hit this transition state once in one time period. What about E less than Ea? So, we are going to approximate that as omega over 2 pi that is for my energy is let us say here, I am sorry, this was E for E greater than Ea and this is E less than Ea.

Well, in one time period, I am going to assume I tunnel once. So, I come here and then I have some probability of leaking through. So again, this is somewhat open-ended problem, it is doing estimates. And so, this I am going to say is E to the power of minus alpha Ea minus E. So that is our way to estimate things.

So, k of T then becomes 0 to infinity dE rho of E, which we showed is beta e to the power of minus beta E, into k of E. Now k of E is divided into 0 to Ea into omega over 2 pi e to the power of minus alpha Ea minus E plus Ea to infinity dE beta. So, what we had discussed several modules ago was that we ignored this part, the first part, because we were assuming no tunneling and we had only this second part. But now we have the tunneling contribution as well.

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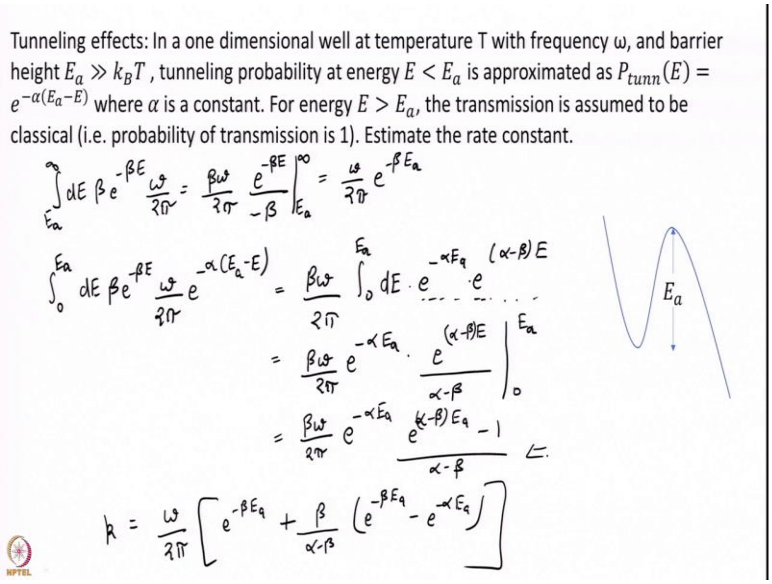

Tunneling effects: In a one dimensional well at temperature T with frequency ω, and barrier height $E_a \gg k_B T$, tunneling probability at energy $E < E_a$ is approximated as $P_{tunn}(E) = e^{-\alpha(E_a-E)}$ where α is a constant. For energy $E > E_a$, the transmission is assumed to be classical (i.e. probability of transmission is 1). Estimate the rate constant.

$$\int_{E_a}^{\infty} dE\, \beta e^{-\beta E} \frac{\omega}{2\pi} = \frac{\beta\omega}{2\pi} \left.\frac{e^{-\beta E}}{-\beta}\right|_{E_a}^{\infty} = \frac{\omega}{2\pi} e^{-\beta E_a}$$

$$\int_0^{E_a} dE\, \beta e^{-\beta E} \frac{\omega}{2\pi} e^{-\alpha(E_a-E)} = \frac{\beta\omega}{2\pi} \int_0^{E_a} dE \cdot e^{-\alpha E_a} \cdot e^{(\alpha-\beta)E}$$

$$= \frac{\beta\omega}{2\pi} e^{-\alpha E_a} \cdot \left.\frac{e^{(\alpha-\beta)E}}{\alpha-\beta}\right|_0^{E_a}$$

$$= \frac{\beta\omega}{2\pi} e^{-\alpha E_a} \frac{e^{(\alpha-\beta)E_a} - 1}{\alpha-\beta} \leftarrow$$

$$k = \frac{\omega}{2\pi}\left[e^{-\beta E_a} + \frac{\beta}{\alpha-\beta}\left(e^{-\beta E_a} - e^{-\alpha E_a}\right)\right]$$

So let us solve these two integrals. The second integral is easier so that I will start with, beta e to the power of minus beta E omega over 2 pi. So, this is beta omega over 2 pi which are constants. I integrate e to the power of minus beta E. So, this will be equal to omega over 2 pi. So, this you can quickly verify, this is not hard at all. E to the power of minus beta infinite is 0, and so you are left with only Ea part.

So, let us also do the first part now. E alpha Ea minus E. Well, this is also not hard really. Beta omega over 2 pi. You have to just be careful. 0 to Ea dE e to the power of minus alpha Ea into e to the power of alpha minus beta E. So, I have just taken the exponential, separated this term out, because it is a constant and taken the parts that had e in common and taken them together. So, this is nothing but beta omega over 2 pi e to the power of minus alpha Ea into e to the power of alpha minus beta E over alpha minus beta from 0 to Ea. So, this is nothing but beta omega over 2 pi e to the power of minus alpha Ea into e to the power of alpha minus beta Ea minus 1.

Well, so the total rate is nothing but the sum of these two. Beta over alpha minus beta. And I just take this thing inside so I get e to the power of minus beta Ea minus e to the power of minus alpha Ea. So, I have just simplified the second part a little bit here. But that is not very important, like the important is the concept how to set it up. And so, the set up was we calculate the rate constant as integral over all energies. And for E less than Ea, we estimated it to be omega over 2 pi multiplied by tunneling probability. For E greater than Ea, we simply took omega over 2 pi. And once you have that, the rest is just numericals.

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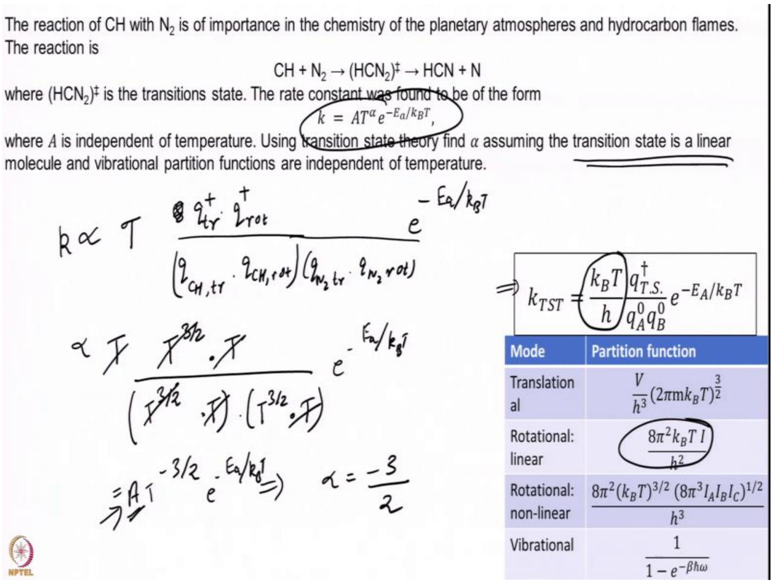

The reaction of CH with N_2 is of importance in the chemistry of the planetary atmospheres and hydrocarbon flames. The reaction is

$$CH + N_2 \rightarrow (HCN_2)^{\ddagger} \rightarrow HCN + N$$

where $(HCN_2)^{\ddagger}$ is the transitions state. The rate constant was found to be of the form

$$k = AT^{\alpha} e^{-E_a/k_BT},$$

where A is independent of temperature. Using transition state theory find α assuming the transition state is a linear molecule and vibrational partition functions are independent of temperature.

$$k \propto T \frac{q^{\dagger}_{tr} \cdot q^{\dagger}_{rot}}{(q_{CH,tr} \cdot q_{CH,rot})(q_{N_2,tr} \cdot q_{N_2,rot})} e^{-E_a/k_BT}$$

$$\propto \cancel{T} \frac{\cancel{T}^{3/2} \cdot \cancel{T}}{(\cancel{T}^{3/2} \cdot \cancel{T}) \cdot (T^{3/2} \cdot \cancel{T})} e^{-E_a/k_BT}$$

$$= AT^{-3/2} e^{-E_a/k_BT} \Rightarrow \alpha = \frac{-3}{2}$$

$$\Rightarrow \boxed{k_{TST} = \frac{k_BT}{h} \frac{q^{\dagger}_{T.S.}}{q^0_A q^0_B} e^{-E_A/k_BT}}$$

Mode	Partition function
Translational	$\frac{V}{h^3}(2\pi m k_BT)^{\frac{3}{2}}$
Rotational: linear	$\frac{8\pi^2 k_BT I}{h^2}$
Rotational: non-linear	$\frac{8\pi^2 (k_BT)^{3/2} (8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$
Vibrational	$\frac{1}{1-e^{-\beta\hbar\omega}}$

So now the next problem I have for you is that I have a particular reaction which is of importance for atmospheric chemistry CH plus N2 going to some transition state to HCN plus N and people experimentally found that the rate constant finds this formula. So, you use transition state theory and estimate what alpha must be. We have given you a few things to assume. You can assume transition state to be linear and vibrational and electronic partition functions to be independent of temperature. So, take a pause and calculate alpha.

Hopefully, you are back. You have a value of alpha with you. We will calculate it together and see if our results match. So, we are going to use this formula and we are going to look only at the temperature part. So, I am going to use proportional to, first I have this T coming from this, then I have q transition state. So, that q transition state, well, will be q translational into q rotation divided by q CH translational into q CH rotational into q N2 translational into q N2 rotation. I have gotten rid of vibrational part or electronic part. So, this is proportional to temperature.

And again, I am not going to look at any other factor other than temperature. Translational part that is dependent on T to the power of 3 half. Rotational part, rotational part we are assuming the transition state to be linear. For linear, I use this formula, so I get T divided by CH translational. Well, all translationals are 3 half. Rotational of CH, CH is also linear into translational into rotational, all linear molecules proportional to T. So, this cancels with this, this cancels with this, this cancels with this, this cancels with this, and I am left with T to the power of minus 3 half. This implies alpha is…

Remember, I still have that exponential factor that I simply chosen not to write so far. And all other common factors there that I have been not writing all the mass and 2 pi and m and all that. So, if I compare this formula with this, you can easily see alpha is minus 3 half.

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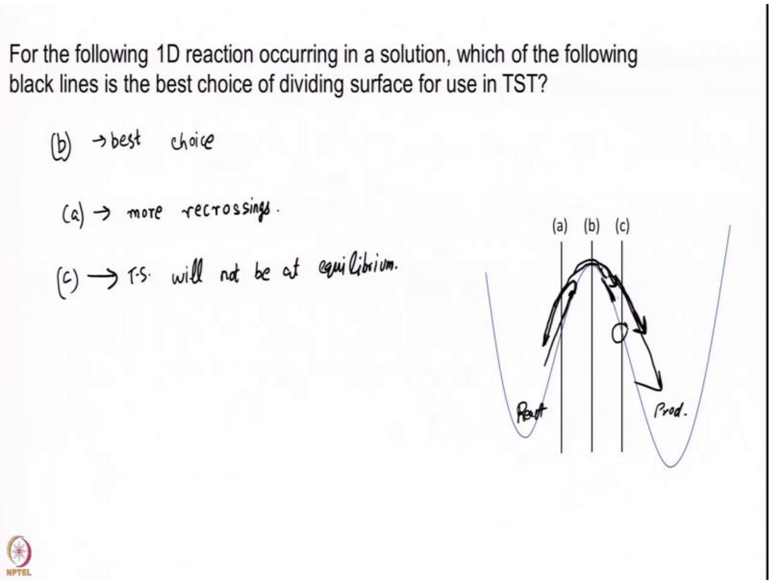

For the following 1D reaction occurring in a solution, which of the following black lines is the best choice of dividing surface for use in TST?

(b) → best choice

(a) → more recrossings.

(c) → T.S. will not be at equilibrium.

This is a conceptual question. For the following one-dimensional surface, I really like one dimensional surfaces, in solution at some temperature T, where should I draw the transition state, which is the best line representing transition state, is it a if I draw it here and do my transition state theory with this dividing surface, should I draw it at b and do my transition state theory with this dividing surface or should I do my transition state theory with the c dividing surface? So, take a pause, think about it and come up with your own answer.

So, hopefully, you have thought about it. So let us discuss it together now. So, the correct answer is b, this is the best choice. Why? So, we have to look into the assumptions made in the transition state theory. This is what this question about. A, this is my reactant, this is my product. If you draw the dividing surface at a, you can have trajectories that are going up and they just have a more chance of reverting back compared to b. You can have that happening at b as well. But at b, a trajectory that crosses here, sees a force that looks like this. So, this is more inclined to keep on moving forward.

So, at a, a trajectory that is going up might not have enough energy and it just turns back. So, a more re-crossings, which is not good. In transition state theory, remember our assumption is no re-crossing. So, the best choice is where the re-crossings are minimal. And a has more re-crossings compared to b.

What about c though? In c I have this kind of energy surface. I have my trajectories coming here and they are simply falling down, is not c better there? No. Here the other assumption comes in picture. The equilibrium assumption will be bad. Remember that we also assumed that transition state is at equilibrium with the reactants. So, transition state will not be at equilibrium. Well, again, you can think of it intuitively. You have these trajectories that are coming up. And they are just forward crashing into the products like this.

So, there is no reason that at c you can expect a good Boltzmann ratio, good Boltzmann distribution, e to the power of minus beta h, where the velocities are much more, faster, because trajectories are coming up and then crashing like this. So, the transition state will not be at equilibrium. So, the other assumption does not hold very well. So, b is the optimal point where you will get minimum re-crossings as well as the equilibrium assumption will hold better.

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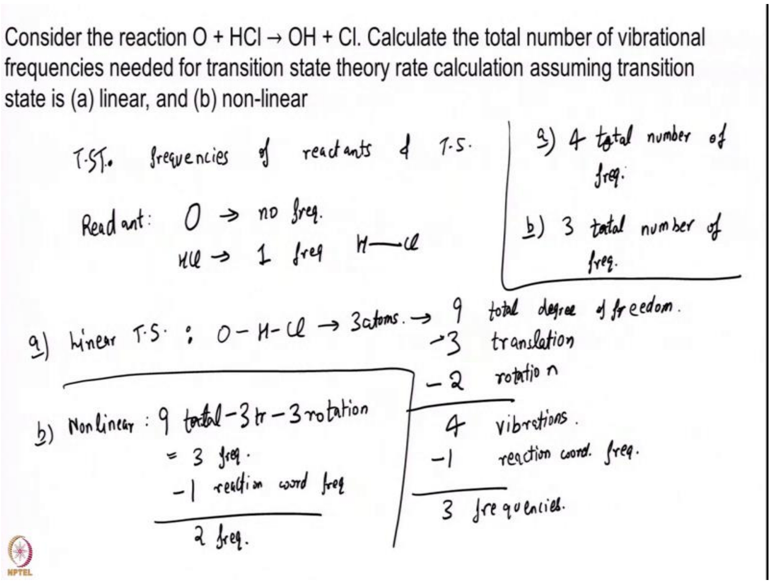

Consider the reaction O + HCl → OH + Cl. Calculate the total number of vibrational frequencies needed for transition state theory rate calculation assuming transition state is (a) linear, and (b) non-linear

T.S.T. frequencies of reactants & T.S.

Reactant: O → no freq.
HCl → 1 freq H—Cl

a) 4 total number of freq.

b) 3 total number of freq.

a) Linear T.S. : O – H – Cl → 3 atoms. → 9 total degree of freedom.
–3 translation
–2 rotation
4 vibrations.
–1 reaction coord. freq.
3 frequencies.

b) Nonlinear : 9 total – 3 tr – 3 rotation
= 3 freq.
–1 reaction coord freq
2 freq.

The final question for today, you think of a reaction like O plus HCl going to OH plus Cl. And this is again a conceptual question. Calculate the total number of frequencies that are needed assuming transition state to be linear versus non-linear. Again, take a pause. Solve this problem on your own. This is an important problem as far as this course is concerned and get an answer. Pause this video now and solve this problem on your own.

Hopefully you are back. So let us solve this problem together. Remember that for transition state I need frequencies of reactants and transition state. I do not worry about products. Reactants here O, well, that is an atom. Atom does not have frequencies, there is no vibration there, no frequency. HCl, 1 frequency, the stretch. So HCl can vibrate. 1 frequency only. Linear transition state, how many frequencies are required for a linear transition state is the question.

So, I have O, H, Cl, three atoms. For three atoms, I have 9 total degrees of freedom. X, y, z corresponding to each atom. Out of which, I have three translationals and 2 rotations. Remember that a linear molecule only has 2 rotations. So whatever remains are the number of vibrations. Now, there is still a little bit of trick.

At transition state, we need 1 frequency less compared to the total number of frequencies. Why, because in transition state theory the frequency of the reaction coordinate is not considered. So minus 1 reaction coordinate frequency which is an imaginary frequency, so 3 frequencies. So, if the transition state is linear, I need to calculate 1 frequency for HCl and 3 frequencies for OHCl.

Now, for b, non-linear, I will do the same math. I will have 9 total minus 3 translational minus 3 rotations. So, a non-linear molecule has 3 rotations, instead of 2. So, I get 3 frequencies and I subtract 1 reaction coordinate frequency, so I get 2 frequencies. So, for a, I will need 4 total number of frequencies, 3 for transition state, 1 for reactant. And for b, I will need 3 total number of frequencies, 2 for transition state and 1 for reactants.

So, we will stop with this problem session now. Hope you got to learn and you hope you tried these problems on your own. Thank you very much.