Chemical Kinetics and Transition State Theory
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Lecture 29
Thermodynamic formulation of TST

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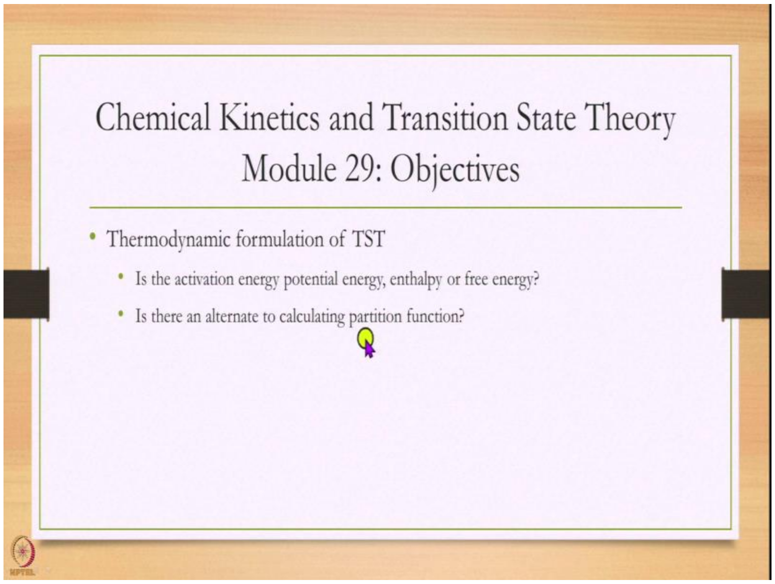

Chemical Kinetics and Transition State Theory
Module 29: Objectives

- Thermodynamic formulation of TST
  - Is the activation energy potential energy, enthalpy or free energy?
  - Is there an alternate to calculating partition function?

Hello, and welcome to module 29 of Chemical Kinetics and Transition State Theory. So, this is formally going to be the last module on transition state theory. We might discuss more problems later on, but the theory wise this will be the last. And the final thing I want to discuss in transition state theory are two important questions.

First one which is a very common question, the activation energy that we talk about, is it a difference of potential energy, enthalpy or free energy? Secondly, we are also going to look at today, is there an alternate to calculating partition functions? Is there is some other way we can write the transition state theory?

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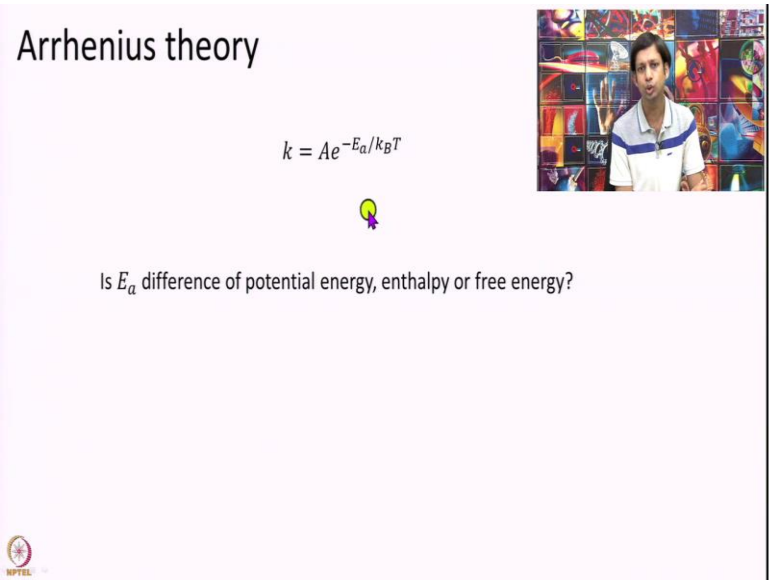

Arrhenius theory

$$k = Ae^{-E_a/k_BT}$$

Is E_a difference of potential energy, enthalpy or free energy?

So, let us start with this question, Arrhenius had originally written this formula. Well, went off head and Arrhenius had interpreted this as some activated state. But what exactly is Ea, exactly?

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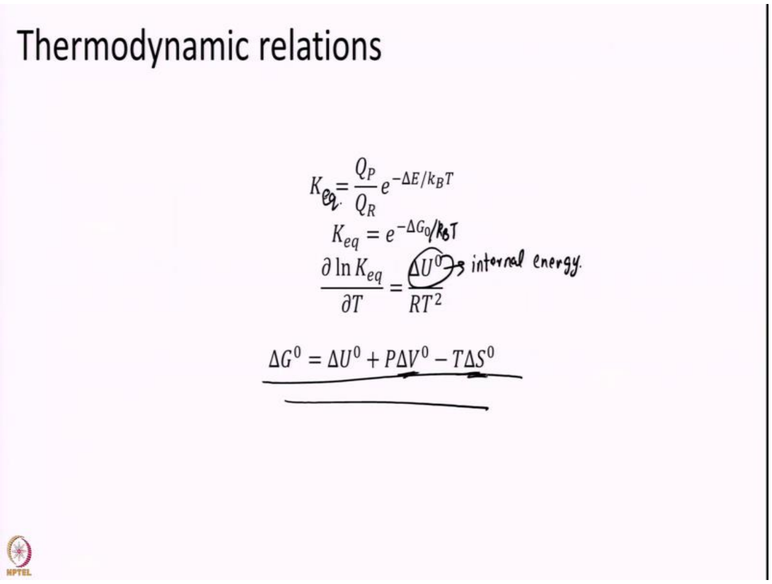

Thermodynamic relations

$$K_{eq} = \frac{Q_P}{Q_R} e^{-\Delta E/k_BT}$$

$$K_{eq} = e^{-\Delta G_0/k_BT}$$

$$\frac{\partial \ln K_{eq}}{\partial T} = \frac{\Delta U^0}{RT^2} \rightarrow \text{internal energy.}$$

$$\underline{\Delta G^0 = \Delta U^0 + P\Delta V^0 - T\Delta S^0}$$

So, to answer that, let us analyze our theory a little bit, but to do that I will need a few thermodynamic relations today. One that we had already derived that this is supposed to be K equilibrium is ratio of partition functions into exponential of delta E over kT, where delta E is difference of potential energies. K equilibrium can be written as minus delta G naught over kT. That is another relation from thermodynamics that we are not deriving. We are just stating. So, if

I just take derivative of lnK equilibrium with temperature, I will get delta U naught over RT square, where delta U naught is your internal energy. Sorry, this is your internal energy.

And finally, you perhaps already know the definition of delta G itself, it is delta U naught, the internal energy plus pressure into delta V minus T into delta S. So, these relations I will be needing today.

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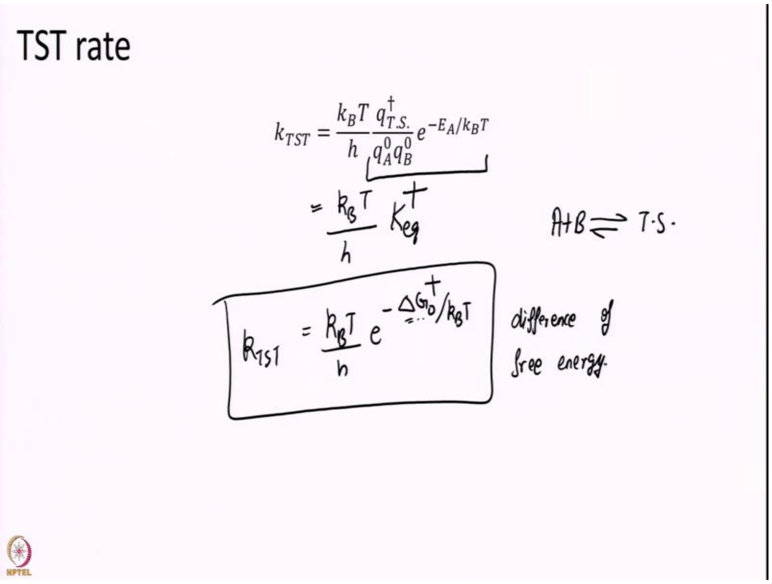

TST rate

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

$$= \frac{k_B T}{h} K^{\dagger}_{eq}$$

$A+B \rightleftharpoons T.S.$

$$\boxed{k_{TST} = \frac{k_B T}{h} e^{-\Delta G^{\dagger}_0/k_BT}}$$

difference of free energy.

So, let us look at our KTST relation that we have derived. Now, what I am going to say is this is equal to, now this thing is nothing but K equilibrium of the transition state where this is nothing but A plus B in equilibrium with transition state. Remember, this is how we actually started. So, this has to be true. But K equilibrium is nothing but e to the power of minus delta G naught over kT.

So, this relation, this activation energy is really a difference of free energy. Your entropy is important, remember that. You have a free, your enthalpy as well as entropy. So that is the first question. The free energy, the energy difference is that of free energies, not enthalpy, not potential.

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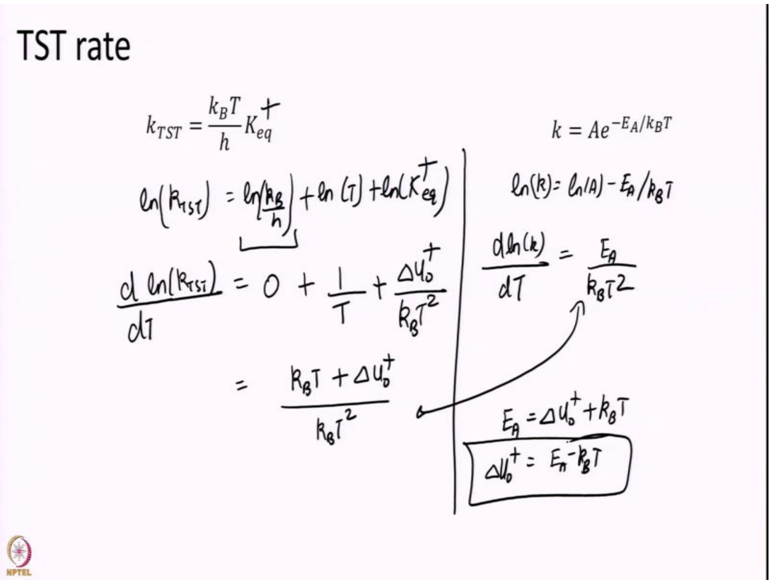

TST rate

$$k_{TST} = \frac{k_B T}{h} K_{eq}^{\dagger}$$

$$\ln(k_{TST}) = \underbrace{\ln\left(\frac{k_B}{h}\right)} + \ln(T) + \ln(K_{eq}^{\dagger})$$

$$\frac{d\ln(k_{TST})}{dT} = 0 + \frac{1}{T} + \frac{\Delta U_0^{\dagger}}{k_B T^2}$$

$$= \frac{k_B T + \Delta U_0^{\dagger}}{k_B T^2}$$

$$k = Ae^{-E_A/k_B T}$$

$$\ln(k) = \ln(A) - E_A/k_B T$$

$$\frac{d\ln(k)}{dT} = \frac{E_A}{k_B T^2}$$

$$E_A = \Delta U_0^{\dagger} + k_B T$$

$$\boxed{\Delta U_0^{\dagger} = E_A - k_B T}$$

But let us analyze this a little bit more. So, in the last slide we had written this KTST as kT over h into K equilibrium. Let us just play around with it, let us take the ln of this, this will be ln of this constant plus ln of T plus ln of K equilibrium. If I take a derivative of this with temperature, well, this is a constant, so I do have 0 here, ln of T the derivative of that is 1 over temperature and the derivative of K equilibrium is delta U naught, this again is dagger over kT square.

In some slides, you might see is R or in some slides you might see kB that is the same thing, it is just a matter of units. I try to use kB at all places. But if you see R somewhere, do not get worried, it is not a mistake really. It is just a different dimension. So, let me just rewrite this as kT plus delta U naught over kT square. But if I compare this with the Arrhenius equation, so if I do the same thing here and dlnk over dT, the first term will vanish and I will get is EA over kT square. And if I compare these two, what I get is EA is delta U naught dagger plus kT or delta U naught is EA minus kT.

So, remember this fact actually, internal energy is not exactly the same as potential energy. Internal energy also remember, has average kinetic energy included in it. And because of that average kinetic energy, you get this factor of kT. So, EA and delta U naught are not same. That is number one point.

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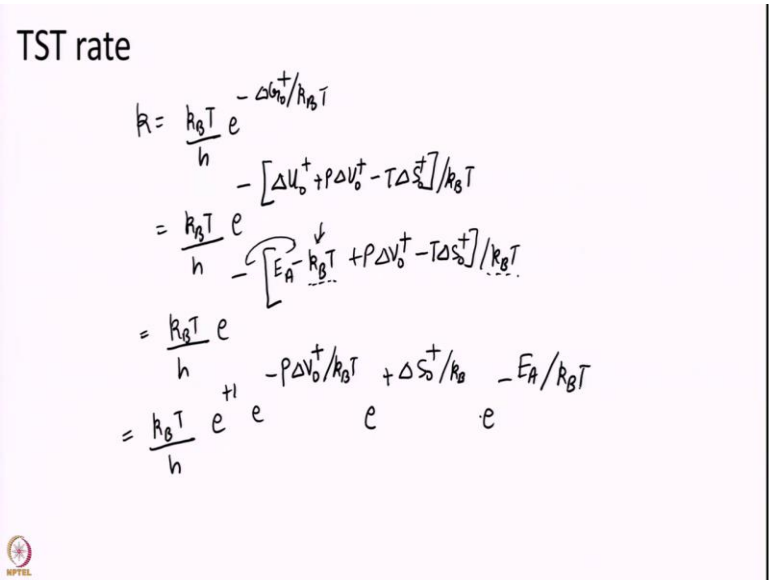

TST rate

$$k = \frac{k_B T}{h} e^{-\Delta G_0^{\ddagger}/k_B T}$$

$$= \frac{k_B T}{h} e^{-[\Delta U_0^{\ddagger} + P\Delta V_0^{\ddagger} - T\Delta S_0^{\ddagger}]/k_B T}$$

$$= \frac{k_B T}{h} e^{-[E_A - \overset{\downarrow}{\underline{k_B}} T + P\Delta V_0^{\ddagger} - T\Delta S_0^{\ddagger}]/\underline{k_B T}}$$

$$= \frac{k_B T}{h} e^{+1} e^{-P\Delta V_0^{\ddagger}/k_B T} e^{+\Delta S_0^{\ddagger}/k_B} \cdot e^{-E_A/k_B T}$$

But, well, so what? So, K we had shown is equal to kT over h, e to the power of minus delta G naught over kT, but delta G is given by delta U naught plus P delta V minus T delta S, but delta U naught, in the last slide we showed is related to activation energy. So, delta U naught we showed is equal to EA minus kT. So, we are going to put that here. EA minus kT, I will, minus kT plus P delta V naught minus T delta S naught over kT.

So, I will just simplify this a little bit, I will write this term first. So, you see I have kT over kT that gives me 1 and minus into minus gives me plus 1, then I will write e to the power of minus P delta V naught over kT and then I will write e to the power of minus, plus delta S naught over kB and finally e to the power of minus EA over kBT.

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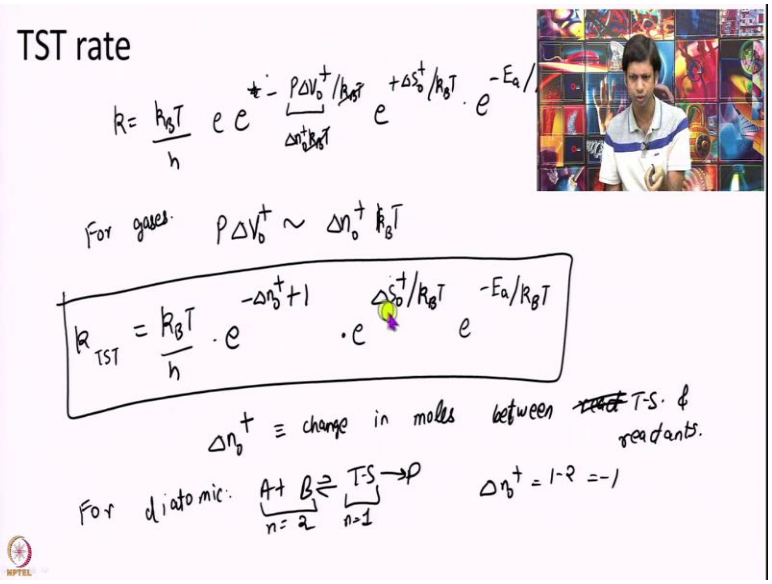

TST rate

$$k = \frac{k_BT}{h}\, e\, e^{-\underbrace{P\Delta V_0^{\ddagger}}_{\Delta n_0^{\ddagger} k_BT}/k_BT}\, e^{+\Delta S_0^{\ddagger}/k_BT} \cdot e^{-E_a/}$$

For gases. $P\Delta V_0^{\ddagger} \sim \Delta n_0^{\ddagger} k_BT$

$$\boxed{k_{TST} = \frac{k_BT}{h} \cdot e^{-\Delta n_0^{\ddagger}+1} \cdot e^{\Delta S_0^{\ddagger}/k_BT}\, e^{-E_a/k_BT}}$$

$\Delta n_0^{\ddagger}$ ≡ change in moles between T-S. & reactants.

For diatomic: $\underbrace{A + B}_{n=2} \rightleftharpoons \underbrace{T\text{-}S}_{n=1} \rightarrow P$ $\quad \Delta n_0^{\ddagger} = 1-2 = -1$

So, let me just write this once more and simplify this a little bit. So, my K is kT over h e, e to the power of minus P delta V over kT, e to the power of plus delta S naught over kT into e to the power of minus EA over kT. Now, for gases, even for liquids it can be partially true, P delta V naught we will approximate as, by ideal gas.

So, PV equal to n kT, ideal gas law. So that is what we are going to do. It is just a crude approximation really. And so, I will get is P delta V I will write as delta n naught kT and kT will cancel here, so I will get is e to the power of minus delta naught dagger plus 1 into e to the power of delta S naught dagger over kT into e to the power of minus Ea over kT.

So, this is another common relation people often use to calculate rate constants. Here you do not have to calculate partition functions. Here you have to calculate free, this enthalpy, I am sorry, here we have to calculate this entropy difference, activation energy and delta n. So, if you can calculate that somehow experimentally, then you can calculate the KTST, while partition functions require a bit more rigorous numerical calculation. You have to be much, much more careful with partition functions. It is just an alternate way. I am not saying this is the better way, but a different way of calculating rate constant.

And delta n naught again let me just define very clearly, delta n naught is the change in moles between reactants, sorry, between transition state and reactants. So, for diatomic A plus B go into transition state, your n here is 1, your n here is 2. So, delta n naught is 1 minus 2 equal to minus

1. For monoatomic, similarly, delta n naught will be 0, because you have one reactant and one transition state, one mole of each. So, depending on what your, how much reactant, number of reactants are, you can calculate this delta n naught so this is usually trivial, delta n naught. So, the harder part is delta S naught and Ea.

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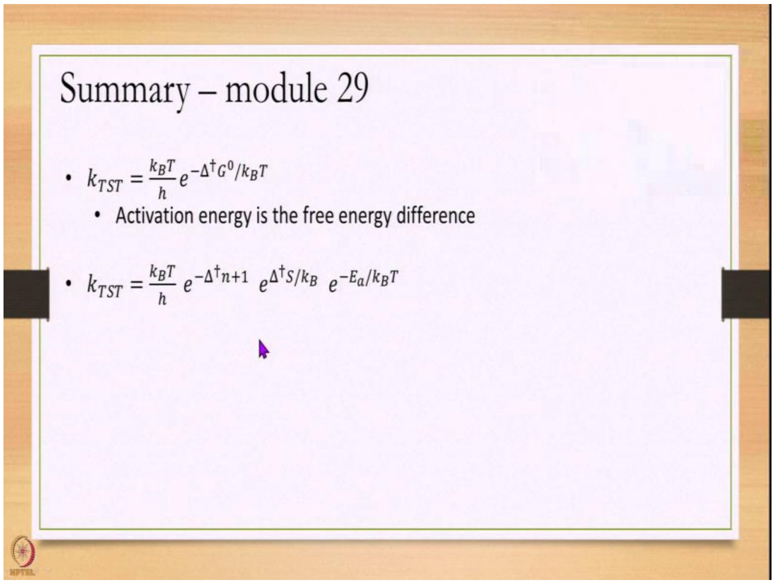

Summary – module 29

- $k_{TST} = \frac{k_B T}{h} e^{-\Delta^{\dagger} G^0 / k_B T}$
    - Activation energy is the free energy difference
- $k_{TST} = \frac{k_B T}{h} e^{-\Delta^{\dagger} n+1} \; e^{\Delta^{\dagger} S / k_B} \; e^{-E_a / k_B T}$

So today we have just briefly looked at a thermal formulation of transition state theory and we have looked at two important points. One that transition state rate is really a free energy difference, the activation energy. And second, we can write transition state rate in the language of thermal quantities delta S, Ea and delta n. So next time we will solve few problems and then move on to molecular dynamics. Thank you very much.