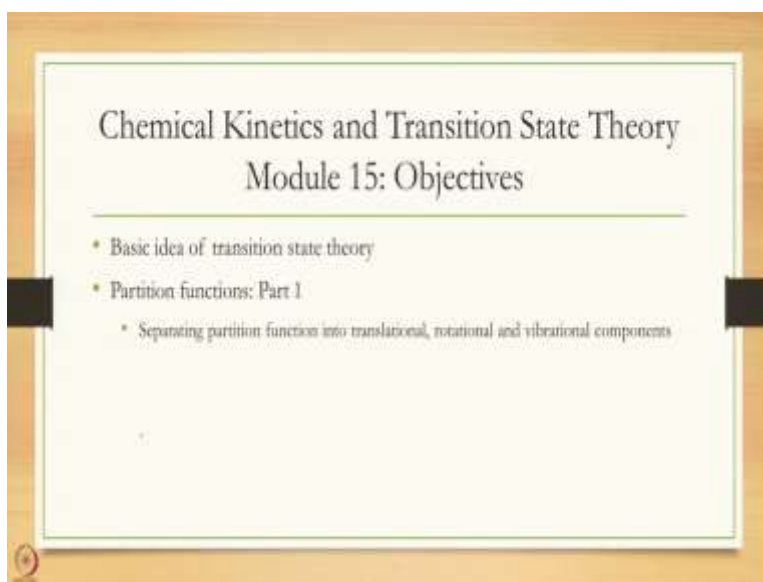**Chemical Kinetics and Transition State Theory**
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Lecture no. 15
Transition state theory and partition functions

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Hello and welcome to module 15 of Chemical Kinetics and Transition State Theory. Today we are going to start a new chapter. This course essentially focuses on 2 different theories: kinetic theory of collisions and transition state theory. We have looked in some detail the kinetic theory of collisions, but we have also looked into is the limitations of kinetic theory of collisions in the last module.

So, today we are going to build over a popular and more successful theory which is called the transition state theory. Today we will introduce the basic idea of transition state theory and then we will have to take a little detour of statistical mechanics particularly knowing partition functions. So, let us start.

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Transition state theory

"Some application of the transition
state method to the calculation of
reaction velocities, especially in
solution"
M. G. Evans and M. Polanyi
March, 1935

https://pubs.acs.org/doi/pdf/10.1021/cr60056a006

"The activated complex and the absolute rate of
chemical reactions"
Eyring
May, 1935

https://pubs.rsc.org/en/content/articlepdf/1935/tf/tf9353100875
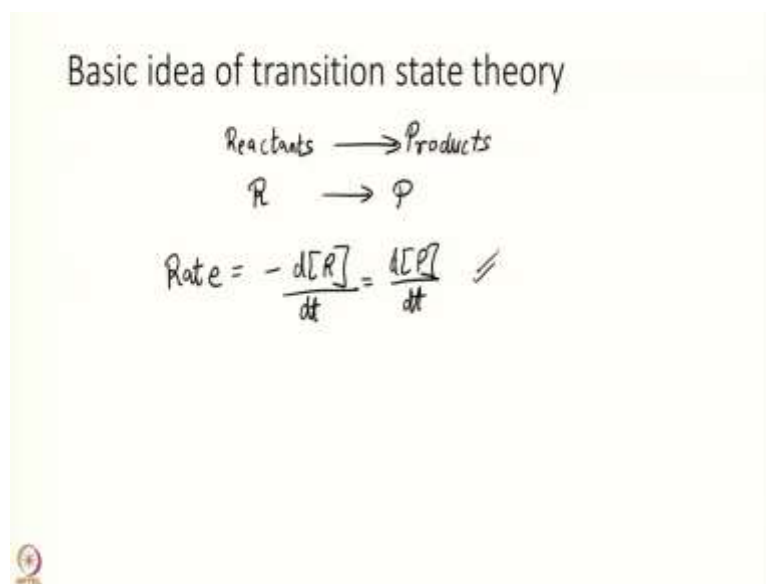
So, the transition state theory came about in 1935 there was a precursor to transition state theory in 1932 by Vigner, very nice paper but it had missed a few important factors. In 1935 there were 2 papers, 1 by Evans and Polyani, March of 1935, some applications on the transition state method to the calculation of reaction velocities. So, back in that day reaction velocity is the same as rate constant. And the second 1 was by Eyring, the activated complex and the absolute rate of chemical reactions, and the absolute rate again means the rate constant.

So, these 3 people had essentially developed transition state theory, both the papers developed very similar idea and combined together it is called transition state theory today. And by the way the formulas written in these papers are still used today. So, in the next several modules we are going to understand what was developed by in these papers. So, let us lo at what is, what is the idea, what are we doing.
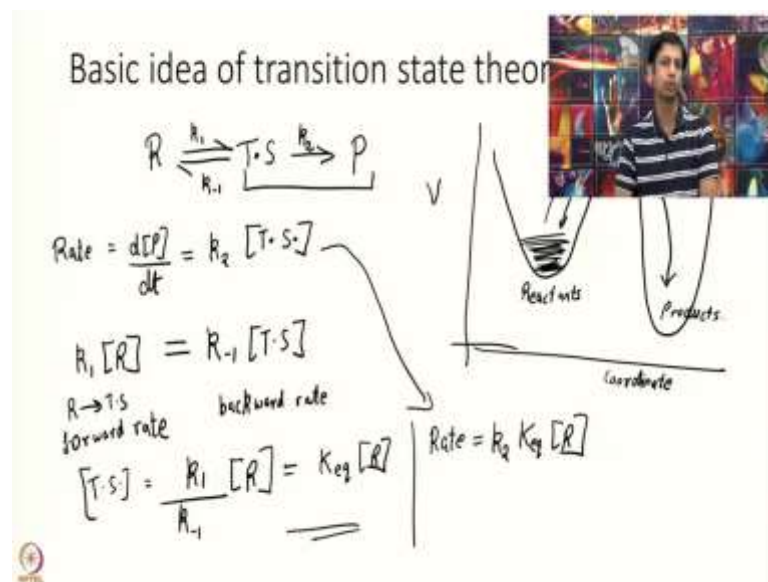
Basic idea of transition state theory

Reactants $\longrightarrow$ Products

$$R \longrightarrow P$$

$$Rate = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

So, remembering kinetic theory of collisions what is really missing is the idea of chemical bonding, the whole chemistry was missing. So, we want to get that in into the picture and we are essentially going to use the intuition that Arrhenius had provided. So, let us start, let us say I have some reactants going to some products, the most general reaction, reactants can be a combination, it can be bimolecular, unimolecular is any number of reactants to any number of products.

So, let me just write this in general as R going to P, I do not mean this to be unimolecular when I write R, R can be A plus B, R can be A plus B plus C, yeah, some R and eventually what we want to find is the rate which if you remember is defined to be this at constant volume. Please do note that in writing this definition of rate I am not assuming this step is elementary, this equation holds as long as volume is constant. So, this rate is what I want to find and the postulate, the transition state theory comes about is the following.

I have these reactants and I have these products and we bring in the idea of transition state that Arrhenius was talking about and so I have a transition state in between and the reaction between reactant and transition state is 1 at equilibrium. So, pictorially the idea is I have, I am drawing a 1D figure because that is easy to draw I have some coordinate here call it the reaction coordinate if you will, some potential energy here.

So, this is reactants, this is products and in between since the transition state. So, that is the main focus of transition state theory, the in between structure. So, what we assume is that initially I am at reactants, so I am initially here and I have an equilibrium with transition state, I am at thermal equilibrium with the transition state, so reactants can go to transition state, transition state can come back to reactants.

But transition state can also fall down to products and 1 of the critical assumptions of transition state is that going from transition state to product is 1 way, so there is no equilibrium, no back reaction from product to transition state, it is 1 of the critical assumptions and we are going to discuss these assumptions in great detail later on.

So, let us think about this model, I have a k 1 here and a k minus 1 here and I have some k 2 here and all these steps are assumed to be elementary. So, if I want to find the rate, rate was dp over dt but I can look at this elementary step, transition state going to product dp over dt will be equal to

k2 into concentration of transition state, so that is how we write rate loss, you can go back to our very first module where we defined this module 1 or module 2.

So, the next thing we assume is that reactant and transition state are at thermal equilibrium which means that the forward rate k1 into R so this is R going to transition state this rate is equal to the backwards rate, so this is forward rate k minus 1 into transition state so this is the backward rate. So, at equilibrium which is an assumption, so we are making some assumptions to build a theory is equal to this.

So, from this I derive transition state concentration equal to k 1 over k minus 1 into R and k 1 over k minus 1 is what we call as k equilibrium, k equilibrium is the equilibrium constant of R with transition state. So, my rate is then so I use this equation here, k 2 into concentration of transition state which we have found here and so the after doing this basic analysis making all these assumptions what we have to do now is estimate k 2 and k equilibrium.

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Require statistical mechanics to calculate K_{eq} and k_2

$$K_{eq} = \frac{Q_P}{Q_R} e^{-E_0/RT} \quad \left\{ \text{Stat mechanics} \right.$$

Q_P and Q_R are partition functions

Need to study partition functions

So, to calculate this k equilibrium and k 2 we require a little bit of statistical mechanics, without that we cannot actually calculate this and as it turns out this k equilibrium particularly is related to what is called partition functions. So, these relations are very fundamental in statistical mechanics and to understand these relations we will need to study partition functions. So, that is what we are going to do in today's and next module and perhaps the next 1 as well is understanding partition functions, so that we can calculate this k equilibrium.

Resources

1. Chapter 15B, Atkin's physical chemistry, by Peter Atkins and Julio de Paula, 10th edition, Oxford publications

So, this partition functions you can read in the Atkin's book. I have provided you this particular edition, 10th edition chapter 15B, you have any other edition please do not worry, you will be able to find this particular content in some other chapter number, the content remains the same the chapter number changes, so you do not have to spend more money in getting the 10th edition, you will be able to find it in any other edition. Of course partition functions you can find in many other standard textbooks of statistical mechanics or even online.

Recap: Module 5

- Equilibrium density matrix: $\rho_{eq}(\vec{q}, \vec{p}) = \frac{1}{N} e^{-\beta H(\vec{q}, \vec{p})}$

- Normalization constant: $N = \int d\vec{q} \int d\vec{p} \, e^{-\beta H(\vec{q}, \vec{p})}$ dimensionless

  Units of N : $\vec{q} \, \vec{p}$ $q \, p \equiv m \frac{kgm}{s} \cdot \frac{kgm^2}{s} \equiv$ units of h
  $3N \, (q \cdot p) \equiv$ units as h^{3N}

- Partition function: $Q = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p} \, e^{-\beta H(\vec{q}, \vec{p})}$ → Dimensionless.

So, we will recap something very old, much about 10 modules ago, we derived something very fundamental that at equilibrium the classical density matrix looks like 1 over n into e to the power of minus beta h and my n which is the normalization constant we showed is equal to this. You can go back to this module where we derived did this partial derivation in phase space. We will build over it right now.

So, the point is first thing we note, what is the units of n. Well, its we see that this thing is dimensionless it is an exponential, so the units of n is the same unit as q into p. What is the dimension of 1 q into 1 p, that is equal to q is a unit of length, so in psi units its meter, p is momentum which is kilogram meter per second, which is kilogram meter square per second.

Does this unit remind you of any fundamental constant of nature? It should strike you something that is related to kilogram meter per square per second, if you guessed h or h bar you are exactly right, this is the same units of h the Planck's constant. So, q dot p this is **3** n q dot p, so q is a **3** n dimensional vector where n is the number of particles.

So, this thing is the same units as h to the power of 3 n, each q dot p gives me 1 h, I have 3 n q dot p so I get h to the power of 3 n. So, the first thing we do actually is to define a partition function q which is dimensionless, so we take this n and divide by h to the power of 3 n. So, this thing is dimensionless.

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Separation of energy and variables

- Partition function: $Q = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p}\, e^{-\beta H(\vec{q}, \vec{p})}$

$$H(\vec{q}, \vec{p}) \simeq H_{Translation} + H_{Rotation} + H_{vibration}$$

$$(\vec{q}, \vec{p}) \rightarrow (\vec{q}_{COM}, \vec{p}_{COM}) + (\vec{q}_{rot}, \vec{p}_{rot}) + (\vec{q}_{vib}, \vec{p}_{vib})$$

6N variables   3×2=6 variables

Linear : $2 \times 2 = 4\ var$ $6N - 4 = 10$

Non-linear : $3 \times 2 = 6\ variables$ $6N - 12$

So, we start with this partition function and what we do is this by itself is very large, very very complex to calculate, this is a 3 6 N dimensional integral, I have 3 n q's, I have 3 n p's, I do not want to do this integral, I do not know how to do this integral, we will simplify our life. What we do is, we note 1 important property of the Hamiltonian; this to a good approximation for most problems can be separated into Hamiltonian of translation plus Hamiltonian of rotation plus Hamiltonian of vibration.

Once we bring in quantum mechanics we will also have an electronic part but that I am not writing right now. So, this is an approximation, this is not always separable, translational part can always be separated but rotation and vibration in principle can be mixed but we will make this simplification for now for this course.

How do we make this simplification let us say we will have to provide 1 more thing, the q, comma p these are 6 N variables, this itself is partitioned into translational which is nothing but center of mass so these are 3 coordinates, 3 into 2, 6 variables, so the entire center of mass of the my molecule, so x, y, z and say of center of mass and p x, p y, p z of my center of mass plus I have also coordinates and momentum describing rotation, so that tells me how the molecule is oriented and what is the angular momentum of my molecule, of the overall molecule, how it is rotating around.

So, I have a q rotation, comma p rotation, so this is a slightly more complex for linear molecule, there are only 2 rotations possible we will discuss this in a moment, so 2 into 2, 2 angles and 2 corresponding angular momenta, so 4 variables. For non linear, we will discuss this in the next slide please do not worry, we can have 3 possible rotations.

And finally we have q, comma p of vibrations so not only do we separate out the Hamiltonian we have also separated outer coordinates and momentum we have coordinates describing translation, coordinates describing rotation and coordinates describing vibrations. So, again for linear vibrations will essentially become 6 N minus 4.

Remember the total has to be 6 N, I had 6 N variables here I should have 6 N variables on the right, 6 have been taken for translation, 4 for rotation, so I am sorry my max should become 6 N and minus 10 for linear. And for non-linear this will become 6 N minus 6 plus 6 is 12 minus 12.

So, I will have 6 N minus 10 vibrations vibrational degrees of freedom for linear molecules and 6 N minus 12 for non-linear. So, let us look at an example, things will become clearer.
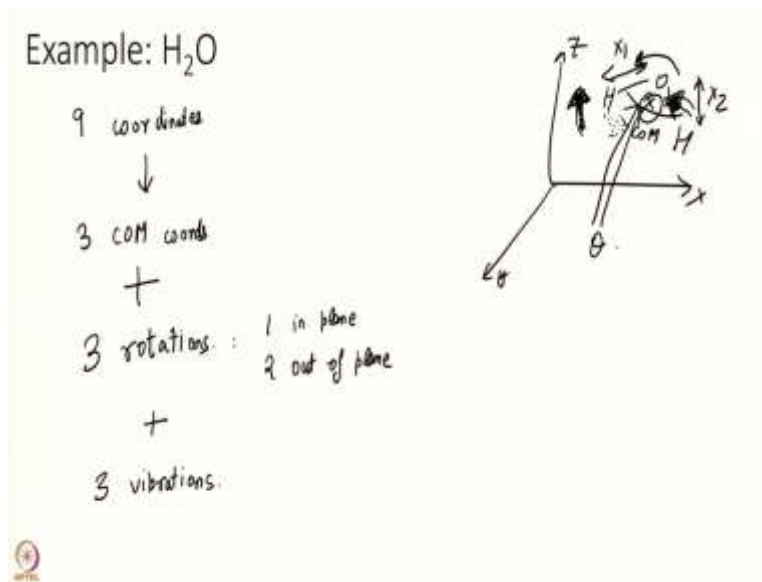
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So, let us start with a very simple linear molecule h2, so let me just draw x, y, z and let us say I have some h2 molecule oriented somewhere here so I have x1, y1, z1 of the first and x2, y2 and z2 of the second hydrogen yeah so I have a 6 coordinates which is basically x 1, y 1, z 1, x 2, y 2, z 2 and we transform this into 3 center of mass so we find a center of mass here, 3 center of mass coordinates.

Now, this molecule can rotate in 2 ways, 1 is this rotation in plane, 1 in plane rotation plus 1 out of plane rotation. So, for this molecule I have to tell you theta and phi essentially is what I am saying you give me center of mass and you give me how the molecule is oriented in space which can be described by theta and phi.

So, for a linear molecule only 2 are enough, so 1 is in plane rotation and the other is imagine this h2 coming out of plane like this, so it is a hard thing to draw but you can imagine something like this and this h is going under the plane something like this, so the whole thing is rotating around like this. And plus I have 1 vibration, h2 can have only 1 vibration which is this length let me call this x. So, you see I have a total of 6, 3 center of mass, 2 rotation, 1 vibration.

Example: H$_2$O

9 coordinates

↓

3 COM coords

+

3 rotations : 1 in plane
2 out of plane

+

3 vibrations.

Let us lo at a slightly more complex example which is non-linear, let us look at water so I have some orientation of water sitting here, again I have x, y, z so now I have 9 total coordinates, x 1, y 1, z 1 of hydrogen, x 1, y 1, z 1 of the second hydrogen, x 3, y 3, z 3 of the oxygen. So, again I will always get 3 center of mass so wherever the center of mass lies plus this time I will have 3 rotations.

Why? Because you also have to describe how the water itself is oriented, so theta and phi tells me the overall structure but beyond that as well the molecule has internal structure, so I can have a 1 more degree of freedom, more physically, essentially you have 1 in plane and 2 out of plane. So, I can rotate the whole molecule in this manner but I can also rotate the whole molecule in this manner.

So, 1 is in the plane 1 is out of the plane like this and I can also rotate it like this, so I have 3 possible rotations. For h2 this was not possible because your h2 is rotating around the 1 axis, it is yeah, so it that does not rotate at all, so that is ratio. And I have 3 vibrations so for water I can have this stretch x 1, I have this stretch x 2, and finally I have the angle theta. So, I have 3 vibrations possible, so the match will always work out.

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Separation of energy

- $H \approx H_{tr} + H_{vib} + H_{rot}$

$$H_{Tr.} = \frac{\vec{P}_{coM} \cdot \vec{P}_{coM}}{2M}$$

$M = $ mass of con of all atoms.

$$H_{rot} = \text{Angular momentum.}$$

$$H_{vib} = \frac{p^2}{2\mu} + \frac{1}{2}\mu r^2$$

So, we have separated the energy, let me just tell you a little bit more so the translational energy is essentially that of center of mass. So, this basically los like momentum of centre of mass square divided by 2 M where M is the sum of all masses so M is the sum of all atoms, sum of sorry masses of all atoms. So, that is your translational energy just the kinetic energy of your centre of mass.

Rotation gets a little bit more complex, so I will not write the complex descriptions here which is not necessary for this course. This essentially is the angular momentum which is like l square over 2 y and finally is the vibration which essentially looks like harmonic oscillators, so you have a something like a p square over 2 mu plus half mu R square something like that where R is your vibrational degree of freedom.

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So, we have this separation of Hamiltonian whatever the Hamiltonians are let us not get into what the Hamiltonian are right away but let us lo at this structure and let us put the separation of variable and the separation of Hamiltonian here. So, remember my q and p are now separated out so I will write integral of d q d p in terms of q and p of translational rotational, sorry and vibrational and Hamiltonian also I am separating out.

And then what we do is we this depends only on center of mass and this depends on this and this depends on this. So, I can write this as 1 over h cube dq center of mass dp center of mass e to the power of minus beta h translation 1 over h square for linear and h cube for non-linear you understand that now, it does not matter.

And finally vibrations and depending on linear or non-linear I will have 1 over h to the power of 6 N minus 5, sorry 3 N minus 5 or 3 N minus 6. Now, this should be d p vib so we call this 1 q translational, we call this 1 q rotation whatever it is h cube or h square and this 1 will be called q vibration.

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So, in summary what we have done today is we first looked into the introduction to transition state theory and what we realize is if we want to solve transition state theory we need to know a little bit about partition functions so we are going to cover that and to study partition functions we divide the partition function into 3 components, translation, rotation, vibration, we separate our Hamiltonian into these 3 as well as R variables.

And finally we derive a formula for q translation rotation and vibration. A concrete expression for these translation, vibration and rotation will be derived in the next module. Thank you.