Chemical kinetics and transition state theory
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Lecture No. 03
Arrhenius equation: what's the fuss about?

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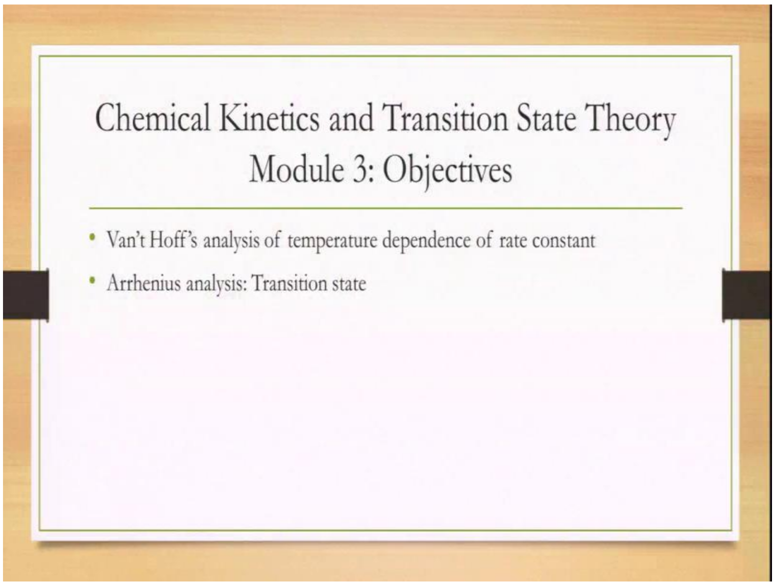

Chemical Kinetics and Transition State Theory
Module 3: Objectives

- Van't Hoff's analysis of temperature dependence of rate constant
- Arrhenius analysis: Transition state

Hello and welcome to the 3rd module of chemical kinetics in transition state theory. So, in the first 2 modules, we have covered the prerequisites, a brief summary of the prerequisites. Today, we will start with understanding how rate constant changes with temperature and we will look at 2 analysis, done by 2 giants of physical chemistry. The first by Van't Hoff, he is considered to be the father of physical chemistry. He started chemical kinetics, he started chemical thermodynamics, many other fields and he got the first ever Nobel Prize in chemistry in 1901.

So, we will look at work he analysed, how he thought of temperature dependence of rate constant and then we will look at what Arrhenius, had to say on that. Arrhenius was another giant. He was the Nobel Prize winner in 1903 by the way. And chemical kinetics is essentially attributed to Arrhenius. So, let us start. I will start by writing what is called the Arrhenius equation to get started and we will get into its more details.

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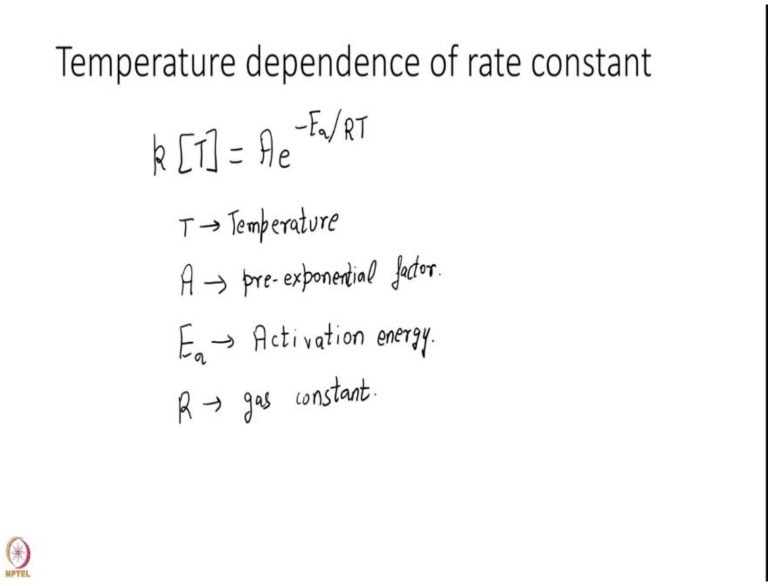

Temperature dependence of rate constant

$k[T] = Ae^{-E_a/RT}$

$T \rightarrow$ Temperature

$A \rightarrow$ pre-exponential factor.

$E_a \rightarrow$ Activation energy.

$R \rightarrow$ gas constant.

So, the very famous Arrhenius equation that you must have seen before looks like this. Sometimes people use k_b instead of R. Here, let me just define the constants T is temperature, A is called pre exponential factor for the lack of better word, we chemists are (2:27) not very creative so, we just see it is before the exponents, we call it pre exponential factor. We have E_a that is the very important term. That is called activation energy and we will discuss this in some detail and R is the gas constant that you are well familiar with. So, today we will look at the origins of this equation.

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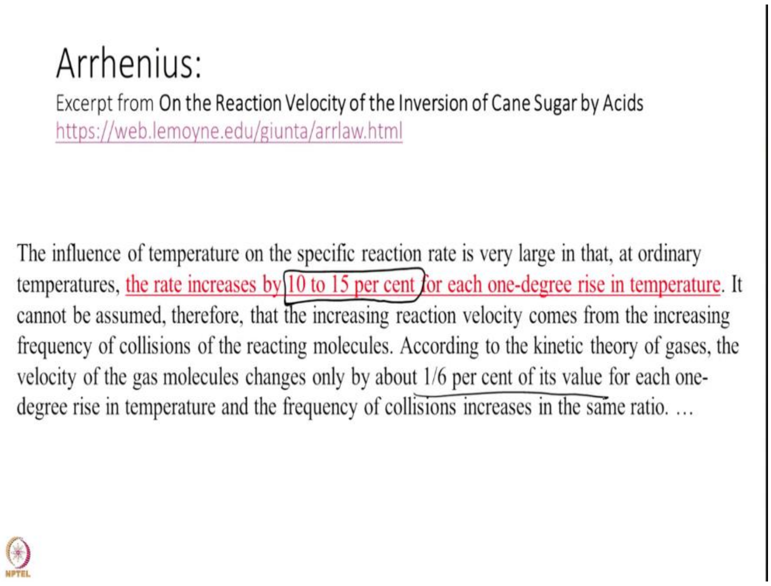

Arrhenius:

Excerpt from On the Reaction Velocity of the Inversion of Cane Sugar by Acids

https://web.lemoyne.edu/giunta/arrlaw.html

The influence of temperature on the specific reaction rate is very large in that, at ordinary temperatures, the rate increases by 10 to 15 per cent for each one-degree rise in temperature. It cannot be assumed, therefore, that the increasing reaction velocity comes from the increasing frequency of collisions of the reacting molecules. According to the kinetic theory of gases, the velocity of the gas molecules changes only by about 1/6 per cent of its value for each one-degree rise in temperature and the frequency of collisions increases in the same ratio. …

So, let's start by reading excerpts from what Arrhenius wrote in a very famous paper. A translation of the paper written by Arrhenius can be found in the link above. So, let me read on what Arrhenius is saying. Arrhenius notes that for most reactions that were observed in that time, each increase in temperature by 1 kelvin or 1^{o}C changes the reaction rate by 10 to 15%, 1 kelvin that’s it. You go from 25^{o}C to 26^{o}C, and it has been noted that the reaction rate is changing by 10%.

So, what he says is how do I understand this? What is going on the atomic level or molecular level that can explain this and that’s what is the genius of Arrhenius. The 1st thing he note is, well one argument perhaps I can make is that at a higher temperature, the thermal speed increases. Boltzmann has told us as much. So, maybe I can say that with increase in temperature, molecules are simply moving faster and therefore reacting faster.

But Arrhenius very beautifully argues against it. Arrhenius says that cannot be true. He says that it cannot be assumed that the increasing reaction velocity, reaction velocity by the way is the same as reaction rate. In 1800s it was simply called reaction velocity. The increasing reaction velocity comes from increasing frequency of collisions of the reacting molecules. According to kinetic theory of gases which we will study in this course, the velocity of the gas molecules changes by only one sixth percent of its value. So, that cannot explain an increase of 10%. We have to do something else.

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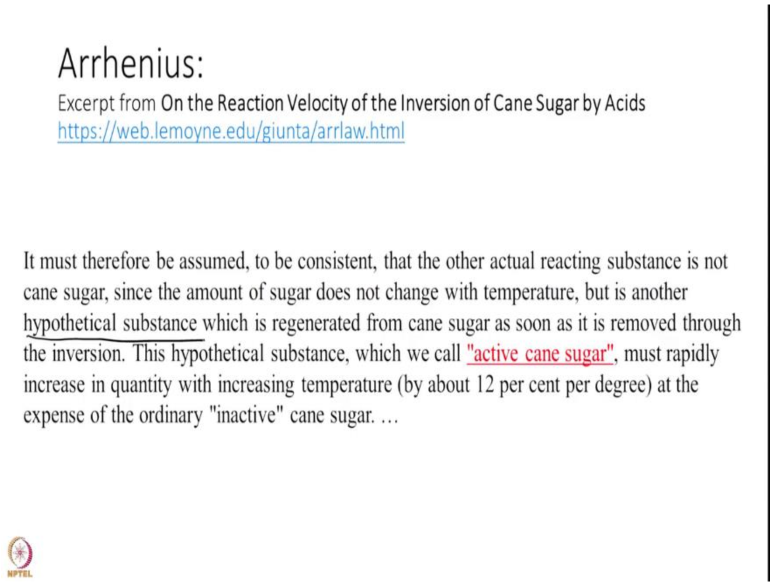

Arrhenius:

Excerpt from On the Reaction Velocity of the Inversion of Cane Sugar by Acids

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It must therefore be assumed, to be consistent, that the other actual reacting substance is not cane sugar, since the amount of sugar does not change with temperature, but is another hypothetical substance which is regenerated from cane sugar as soon as it is removed through the inversion. This hypothetical substance, which we call "active cane sugar", must rapidly increase in quantity with increasing temperature (by about 12 per cent per degree) at the expense of the ordinary "inactive" cane sugar. …

So, Arrhenius points out, we have to assume something different. And he says and I let me read verbally here the translation. It must therefore be assumed, to be consistent, that the other actual reading substance is not cane sugar. He was looking at the inversion of cane sugar a specific example. Since the amount of sugar does not change with temperature, but is another hypothetical substance which is regenerated from cane sugar as soon as it is removed through the inversion.

This hypothetical substance which we call “active cane sugar”. This is the origin of transition state, this hypothetical substance is active cane sugar is what we understand as transition state. And remember in those times there was no notion of a structure which we have not measured and it was simply the genius of Arrhenius. When he hypothesise that such a substance must exist otherwise, how do I explain the chemical data? We have taken so much data as the function of temperature and I cannot explain it any other way.

And, however improbable it may seem, this is the only hypothesis that it fits. It was a very radical idea for the day and it is exactly right and that’s why Arrhenius is given the credit for getting this Arrhenius equation right and the idea of activated state correct.

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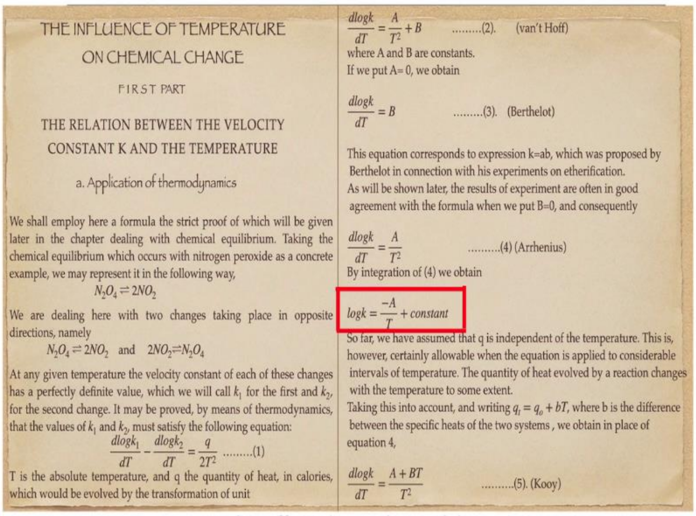

THE INFLUENCE OF TEMPERATURE
ON CHEMICAL CHANGE

FIRST PART

THE RELATION BETWEEN THE VELOCITY
CONSTANT K AND THE TEMPERATURE

a. Application of thermodynamics

We shall employ here a formula the strict proof of which will be given later in the chapter dealing with chemical equilibrium. Taking the chemical equilibrium which occurs with nitrogen peroxide as a concrete example, we may represent it in the following way,

$$N_2O_4 \rightleftharpoons 2NO_2$$

We are dealing here with two changes taking place in opposite directions, namely

$$N_2O_4 \rightleftharpoons 2NO_2 \quad \text{and} \quad 2NO_2 \rightleftharpoons N_2O_4$$

At any given temperature the velocity constant of each of these changes has a perfectly definite value, which we will call k_1 for the first and k_2, for the second change. It may be proved, by means of thermodynamics, that the values of k_1 and k_2, must satisfy the following equation:

$$\frac{dlogk_1}{dT} - \frac{dlogk_2}{dT} = \frac{q}{2T^2} \quad ....(1)$$

T is the absolute temperature, and q the quantity of heat, in calories, which would be evolved by the transformation of unit

$$\frac{dlogk}{dT} = \frac{A}{T^2} + B \quad ....(2). \quad \text{(van't Hoff)}$$

where A and B are constants.
If we put A= 0, we obtain

$$\frac{dlogk}{dT} = B \quad ....(3). \quad \text{(Berthelot)}$$

This equation corresponds to expression k=ab, which was proposed by Berthelot in connection with his experiments on etherification.
As will be shown later, the results of experiment are often in good agreement with the formula when we put B=0, and consequently

$$\frac{dlogk}{dT} = \frac{A}{T^2} \quad ....(4) \text{ (Arrhenius)}$$

By integration of (4) we obtain

$$\boxed{logk = \frac{-A}{T} + constant}$$

So far, we have assumed that q is independent of the temperature. This is, however, certainly allowable when the equation is applied to considerable intervals of temperature. The quantity of heat evolved by a reaction changes with the temperature to some extent.
Taking this into account, and writing $q_t = q_o + bT$, where b is the difference between the specific heats of the two systems , we obtain in place of equation 4,

$$\frac{dlogk}{dT} = \frac{A + BT}{T^2} \quad ....(5). \text{ (Kooy)}$$

van’T Hoff: Studies in chemical dynamics
https://archive.org/details/studiesinchemica00hoffrich/page/122

I also want to show you an excerpt from the work of Van't Hoff. This is slightly older than what Arrhenius had written, but I note, as I noted before, Arrhenius equation was not written by Arrhenius originally. It’s a very interesting trivia for you. Van't Hoff wrote that equation earlier. So, this equation that you see here that is there in Van’t Hoff's paper. This equation actually Van’t Hoff wrote in 1884 before Arrhenius wrote it.

And don’t get me wrong, Arrhenius gave full credit for this to Van’t Hoff. And Van’t Hoff gave full credit to Arrhenius for identifying this reaction and connecting it to the idea of an activated state. So, this equation is the same as Arrhenius equation as you can quickly observe. So, let us look at the, what Van’t Hoff essentially argued, what was the intuition of Arrhenius?

How Van’t Hoff was able to write this equation? So, this analysis you can find in the Ladlers book section 2.9.

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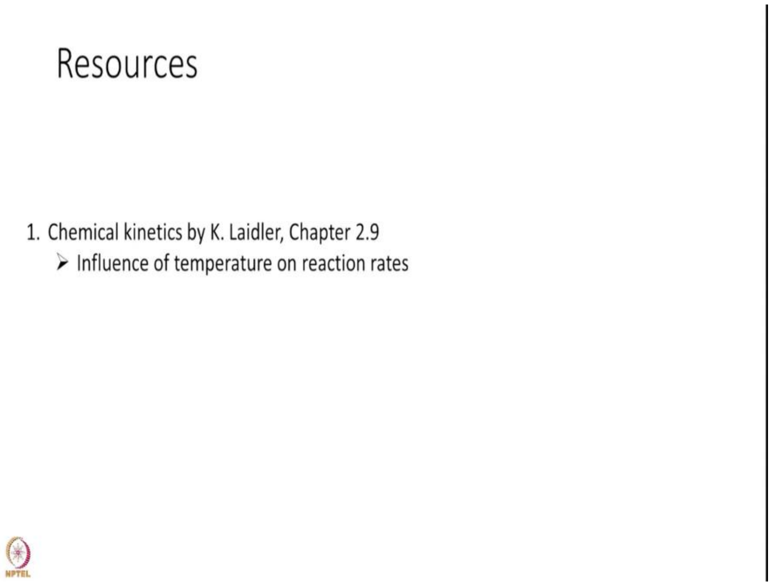

Resources

1. Chemical kinetics by K. Laidler, Chapter 2.9
   - ➤ Influence of temperature on reaction rates

I am writing the name of the section here as well which is quite the Influence of temperature on reaction rates. The reason is if you have a different edition than mine, mine is edition 3, you can still find it in some other chapter number, chapter number will change but not the content. So, let’s look at what’s Van’t Hoff’s analysis.

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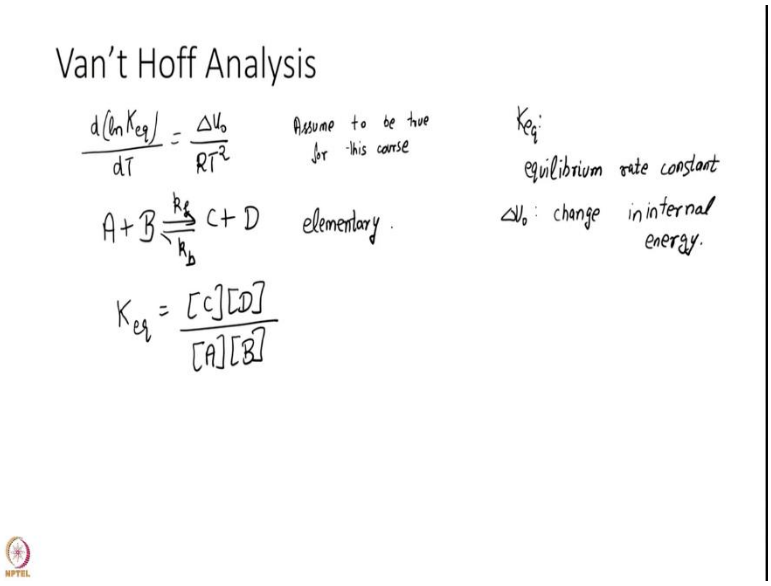

Van’t Hoff Analysis

$$\frac{d(\ln K_{eq})}{dT} = \frac{\Delta U_0}{RT^2}$$

Assume to be true for this course

K_{eq}: equilibrium rate constant

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

elementary.

ΔU_0 : change in internal energy.

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

We will start with a 1 equation that Van’t Hoff had already derived. As I have noted, Van’t Hoff is the father of physical chemistry. He just knew every single thing and he had derived several equations in chemical thermodynamics as well. So, 1 particular equation that he had already derived was the following.

In this course, we are not going to derive this equation, this we assume to be true for this course. Here, K_{eq} is the equilibrium rate constant and ΔU_0 is the change in internal energy. We do not need to get into to understand what is internal energy mean, it is some form of energy that is sufficient for the purposes of this module. So, let us look at a specific example of a reaction and for simplicity let's assume that the stoichiometry (9:58) is all 1. The argument will not change 1 bit even if the stoichiometry (10:03) is not 1.

So, for this K_{eq}, how is K_{eq} defined? It is defined to be product of, product concentrations divided by product of reactant concentrations. We are also assuming here that this is elementary. If that is true, what do we get or what kind of figure? Let's write a few more equations and let's try to use the Van't Hoff's equation to see where we go to and then you will realize a genius of Van't Hoff.

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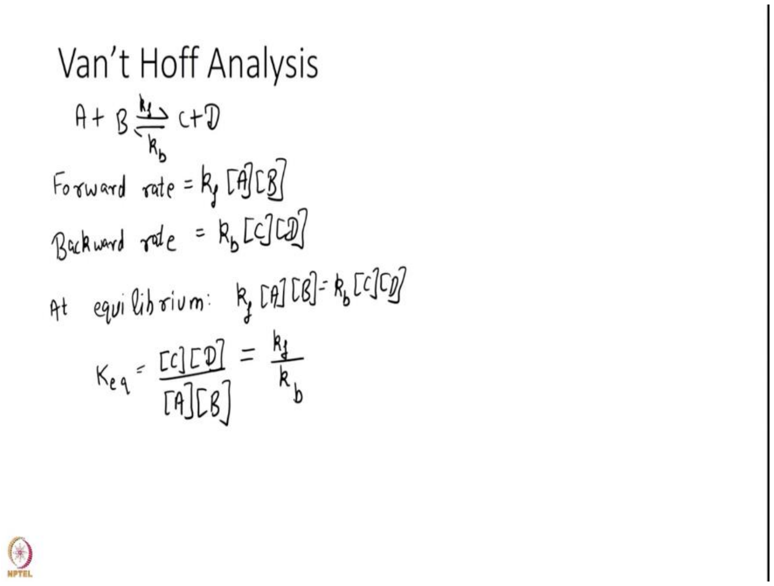

Van't Hoff Analysis

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

Forward rate = $k_f [A][B]$

Backward rate = $k_b [C][D]$

At equilibrium: $k_f [A][B] = k_b [C][D]$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{k_f}{k_b}$$

We will consider this reaction and we will write the rate law. We will write the forward rate. Forward rate is simply k_f *A* B and the backward rate = k_b *C* D. Well, this equation is always true if it is elementary. This is also true at equilibrium then, but at equilibrium, forward rate equal to backward rate. So, at equilibrium, I get k_f A B = k_b C D. You will seen through note of few interesting relations. Note that K_{eq} is CD/AB, but from the above equation, this = k_f/k_b. Let's use the Van't Hoff's equation now.

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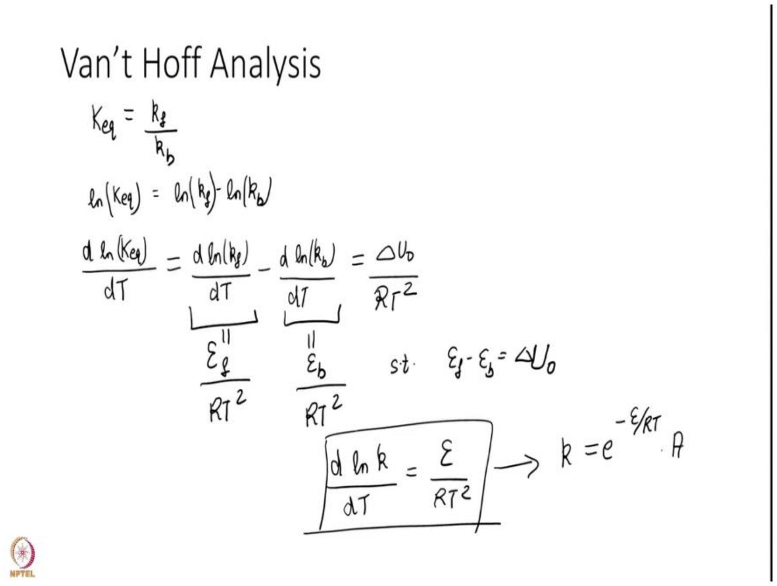

Van't Hoff Analysis

$$K_{eq} = \frac{k_f}{k_b}$$

$$\ln(K_{eq}) = \ln(k_f) - \ln(k_b)$$

$$\frac{d\ln(K_{eq})}{dT} = \underbrace{\frac{d\ln(k_f)}{dT}}_{\overset{||}{\frac{\mathcal{E}_f}{RT^2}}} - \underbrace{\frac{d\ln(k_b)}{dT}}_{\overset{||}{\frac{\mathcal{E}_b}{RT^2}}} = \frac{\Delta U_0}{RT^2} \quad \text{s.t. } \mathcal{E}_f - \mathcal{E}_b = \Delta U_0$$

$$\boxed{\frac{d\ln k}{dT} = \frac{\mathcal{E}}{RT^2}} \longrightarrow k = e^{-\mathcal{E}/RT} \cdot A$$

So, what we have got is K_{eq} is k_f / k_b. Well $\ln(K_{eq})$ is then $\ln(k_f) - \ln(k_b)$. Van't Hoff equation relates $\frac{d\ln(k_{eq})}{dt}$. This is then $= \frac{d\ln(k_f)}{dt} - \frac{d\ln(k_b)}{dt}$ and this is $= \frac{\Delta U_0}{RT^2}$. Good. At this point, Van't Hoff basically looked at this equation and he said, well, this looks like too much of a coincidence to be true always true.

So, he said well most likely this itself, this is a rate constant remember, not thermal equilibrium. This it itself is equal to some energy over RT^2 and this itself is equal to some energy over RT^2 such that $E_f - E_b$ is ΔU_0. So, he is just hypothesised it, he is not proving anything. But this equation suggested that to him. Ok so, he in general wrote d ln of any k over d temperature must equals some energy over RT^2.

So, this you can simplify and show $k = e^{-\epsilon/RT} * A$, which is the Arrhenius equation. Ok so, that's the argument Arrhenius had put forward. Note, this is a completely mathematical argument and E is just some energy, he is not telling you what energy.

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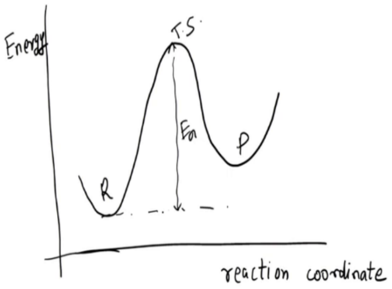
Arrhenius's activated state

$$k_f = Ae^{-\frac{E_a}{RT}}$$



$$R \longrightarrow \underbrace{T.S.} \longrightarrow P$$

Enters Arrhenius now. Arrhenius looks at this equation and now I have already shown you the excerpt from Arrhenius. Arrhenius says, well what can be this E_a, this energy that was there in Van't Hoff's equation and he essentially argued that there is a hypothetical active state between reactant and product. So, he hypothesised that a transition state exists in between transition, reactant and product. And this E_a must be the energy required to go from R → T.S.

So, what he is talking of although he didn't drew this figure, but what you have famously seen is this kind of a energy profile. And, what Arrhenius was pointing out although not in a diagrammatic way is that this is E_a and this is your transition state and this we very well know to be true today.

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Can we calculate rate constant k from an atomistic picture?

So, the question that we ask in this module, in this course, how do we calculate this rate constant k? How do we, we have an Arrhenius equation, but we do not know how to calculate A for example. So, is there a way for us to calculate these quantities from an atomistic picture? At the end of the day, all we have is a dance of molecules happening and this dance is governed by a certain laws of physics. We know the laws of physics, can we use these laws of physics to calculate this rate constant? So, that’s going to be the focus of this course.

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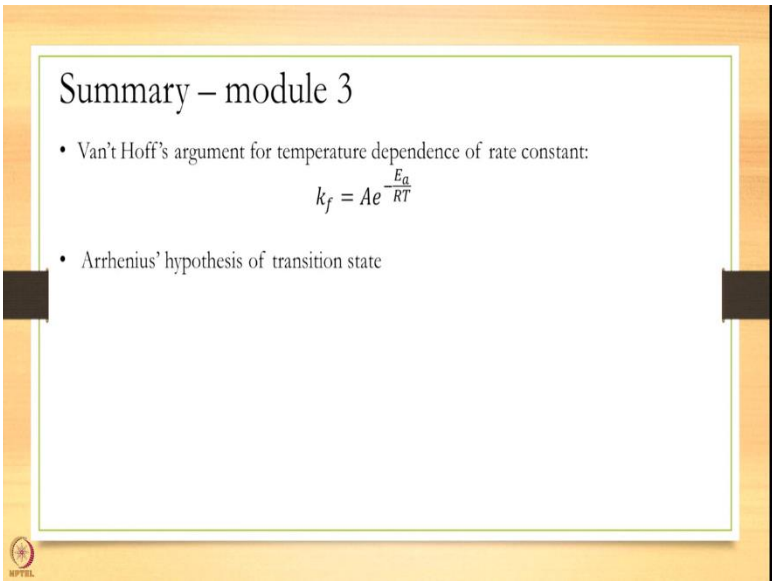

Summary – module 3

- Van’t Hoff’s argument for temperature dependence of rate constant:

$$k_f = Ae^{-\frac{E_a}{RT}}$$

- Arrhenius’ hypothesis of transition state

So, in summary for this module, we have looked at the analysis given by Van't Hoff, his argument on how we got the rate constant to be something like $A*e^{\frac{\text{sum energy}}{\text{RT}}}$. And we also looked at how Arrhenius looked at that equation and presented a physical picture out of it. Specifically, he hypothesised the existence of transition state which is critical in our understanding of rate laws. So, with that we end today. Thank you very much.