Chemical Reaction Engineering I
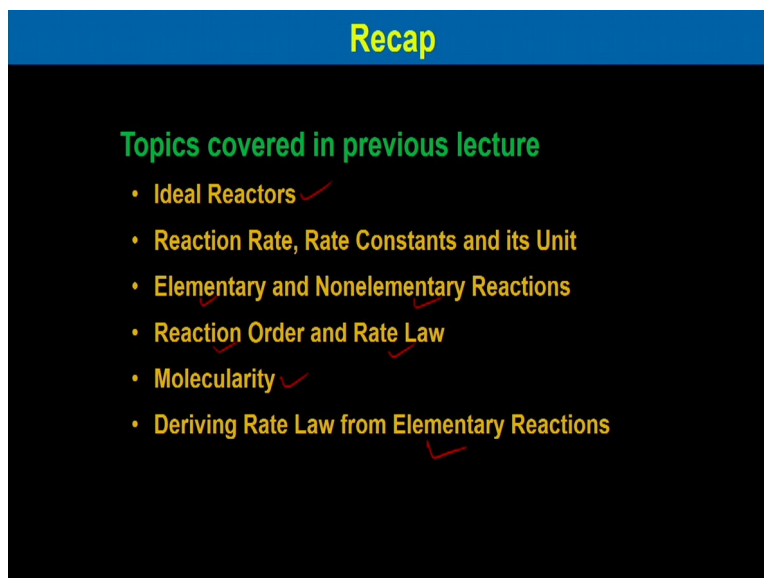**Professor Bishnupada Mandal**
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Lecture - 3
Kinetic Model and Temperature Dependency

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Welcome to the third lecture of module 1 on Chemical Reaction Engineering I. In this module we are discussing chemical kinetics and in this lecture we will discuss temperature dependency and testing of kinetic theories. Before going to this lecture, let us have brief recap on our previous lecture. The topic which we covered in our previous lecture is ideal reactors and we have seen there are three different types of reactors batch reactor, and then plug flow reactor and continuous stir tank reactor.

Then we have discussed reaction rates, rate constants and its unit. We have distinguished between elementary and non-elementary reactions. Then we have seen what is the concept of order of the reactions and different rate laws, then molecularity of the reaction and different rate law which derived from the elementary reactions.

Now, in this lecture we will consider kinetic models and temperature dependency. So the brief outline of this lecture are kinetic model for elementary reactions, kinetic model for non-elementary reactions. And then we will discuss the kinetic models and finally we will discuss the temperature dependency term of rate equation.
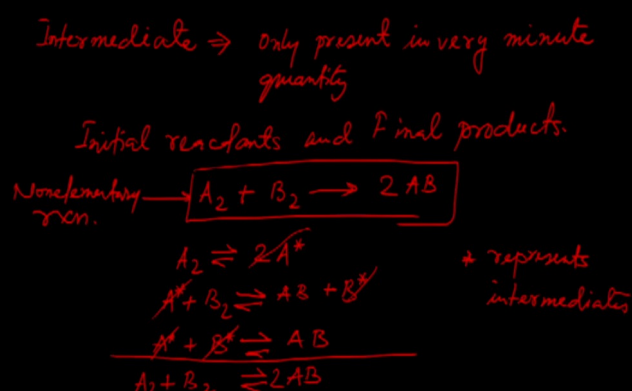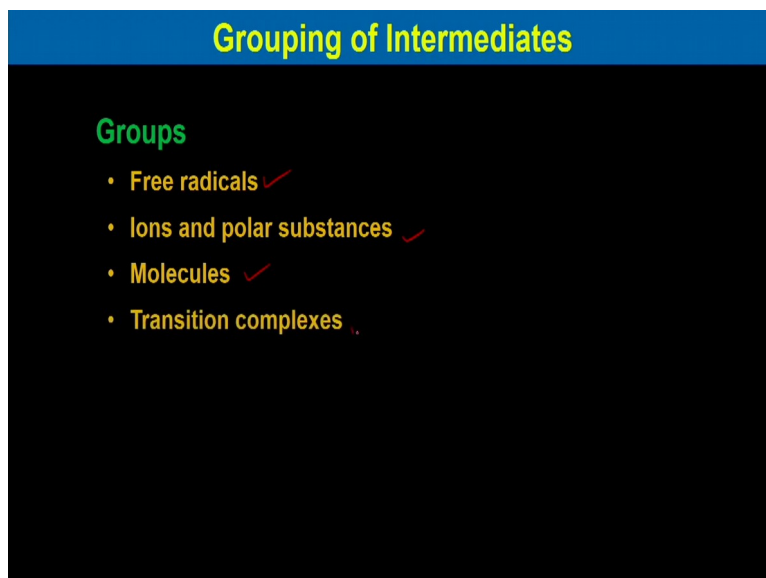
So, kinetic model for non-elementary reactions. As you know for elementary reactions, there are series of reactions which take place and finally we obtained the product. The some products we call the intermediate products, for which we do not see the change of concentration or that is not stable compound and then that disappears. So, its concentration present in the system is very minute quantity. So, intermediates only present in very minute

quantity. So that is why it is very difficult to observe in the reaction system. And only we observe the initial reactants and final products. If we consider a single reaction, say A_2 reacts with B_2 and produce twice AB. This reaction is non-elementary reaction.

So, to explain the kinetics of this non-elementary reaction, we can assume these reactions can take place with a series of reaction. Suppose the kinetics may be assumed like this, A_2 can dissociate reversibly to twice A^* and then A^* reacts with B_2 form AB plus B^* and A^* reacts with B^* for AB. So, if you look into the overall reaction, you can see that this, this cancelled out, this cancel out and you will get A_2 plus B_2 forming twice AB. And this star(*) represents intermediates.
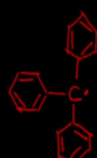
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Kinetics of this reaction, the intermediates can be grouped in four different categories. One is free radicals, then second one is Ions and polar substances, then molecules and then transition complexes.

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Now, free radicals, these are basically free atoms or fragments of molecules which contains one or more unpaired electrons, they are called free radicals. These free radicals sometimes, it may be stable compound or stable intermediates, sometimes they are not stable. In most of the cases free radicals are very very unstable.

One of the example of relatively stable intermediates is the triphenyl methyl. So this is triphenyl methyl and this dot represents the free radical. So, for free radicals, we generally represent it by dot. Okay. Some of the examples of highly reactive free radicals are methyl, CH_3 dot, C_2H_5 dot, H dot, CCl_3 dot, I dot and so on. So, these are highly reactive radicals.

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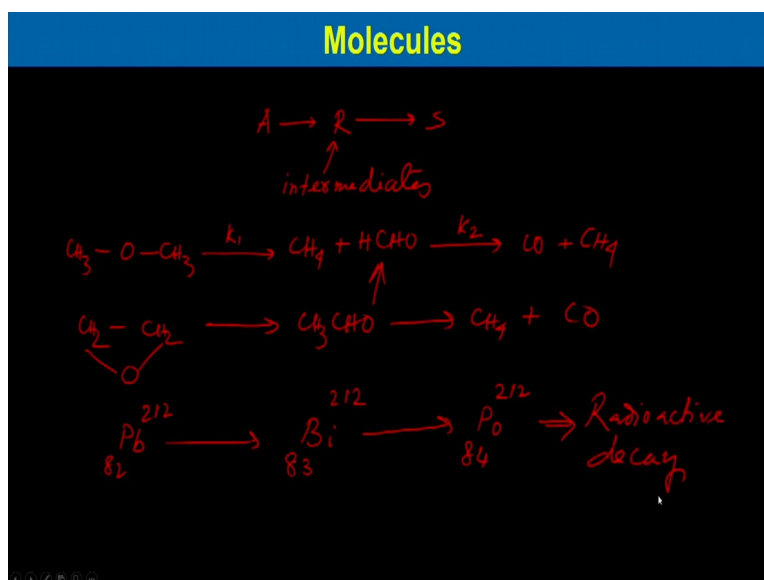
Now, ion and polar substances. Fragments of molecules and electrically charged atoms they are called ions or polar substances. Like Na^+, then OH^-, H_3O^+, NH_4^+, I^-, $CH_3OH_2^+$, so these are very active ions or molecules, or fragments of molecules, they can act as reaction intermediates.

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Now, molecules. In some of the reactions, like series reactions, the intermediate molecules are not stable, it immediately dissociates to products. So the intermediate molecules is not observed or its concentration is difficult to measure because of the amount of intermediates observed at a particular time. So, a very minute quantity of the intermediate present which cannot be determined physically or experimentally that is why those are called the intermediate molecules.

Like if we consider the consecutive reaction $A \rightarrow R \rightarrow S$, here the reactions is multiple reactions and this R is called intermediates. One of the examples of this is dimethyl ether dissociates to CH_4 methane, plus formaldehyde and then it forms CO plus methane. So, this is K_1, this is K_2. So, these are very unstable intermediates. Another example is epoxides or ethylene oxide. It dissociates to form CH_3CHO and then it dissociates to CH_4 plus CO. So, this is one of the examples of molecular intermediates or reactive intermediates.

Another example of radioactive decay like lead, it forms bismuth and then it dissociates or decay to polonium. So, this is radioactive decay. So these are examples of reactive intermediates.

Now transition complexes, collisions among different reactant molecules lead to distribution of energies and molecules then either decompose to give products or can return to the normal state. Such unstable forms are called the transition complexes. That means when the molecules are in always the Brownian motion is in a particular system and they collide each other.

And once they collide with each other, they lead to distribution of the energies among the molecules present in the system. Some molecules, because of its energy states it is converted to the products or some molecules due to further collisions it comes down to the ground state or the normal state. The complex which forms due to the collisions is known as the transition complex. In most of the gas phase reactions occurs via transition complexes.

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This reaction scheme occurs via the 2 different mechanisms, the postulated reaction scheme involving four kinds of intermediates can occur with non-chain reactions and then chain reactions. So, non-chain reactions are basically molecular intermediates and transition complexes and then chain reactions are basically free radical reactions.

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So, in a non-chain reactions, the intermediate is first formed and then it disappears to give the products, like the reactants, it forms intermediates, then intermediates dissociates and gives products. One of the general examples of non-chain reaction is the enzyme catalytic reaction. Very well-known reactions, enzyme catalytic fermentation reactions, like if you have A and producing R and with the catalyst enzyme, the experimental rate can be obtained r_R would be

equal to K into concentration of A into initial concentration of the enzyme divided by C_M is a constant plus concentration of A. So, this reaction is viewed to proceed the following mechanism. A reacts with enzyme and forms A enzyme complex. And A enzyme complex dissociates to form R plus enzyme.

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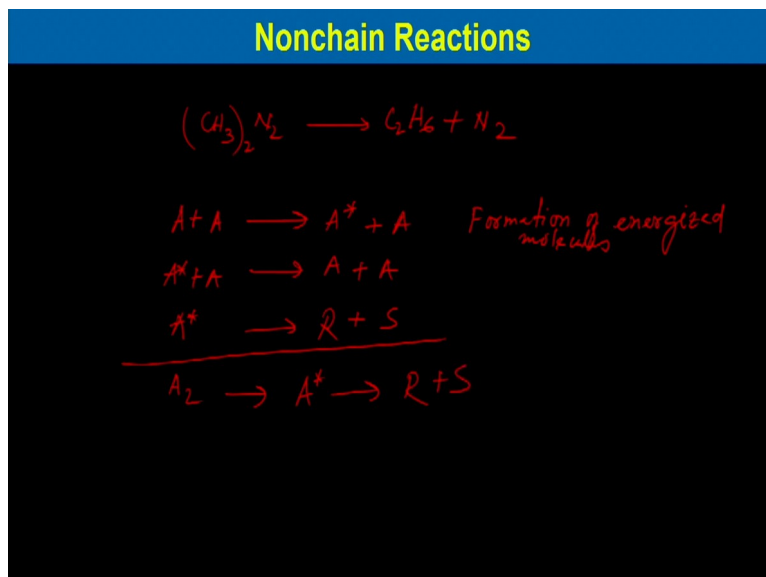
So, another example of non-chain reaction if the transition complex mechanism, like the decomposition of iso-methane. So, $(CH_3)_2 N_2$, it decomposes to form $C_2 H_6$ plus N_2. And the reactions can occur in various conditions, in one case it may be first-order, in other case it may be second order and so on. So, the reaction for this case is explained by Lindemann First in 1922 with the reactive intermediates.

And the mechanism is proposed as follows. A plus A form A^* plus A, that is formation of energised molecules, then A^* reacts with A, it form A plus A, that is forming the stable compound and we can view it, the reverse reaction of these, the first one. That means the activated complex or active energised molecules again collide with A molecules and coming back to A plus A. So, it is the reverse one.
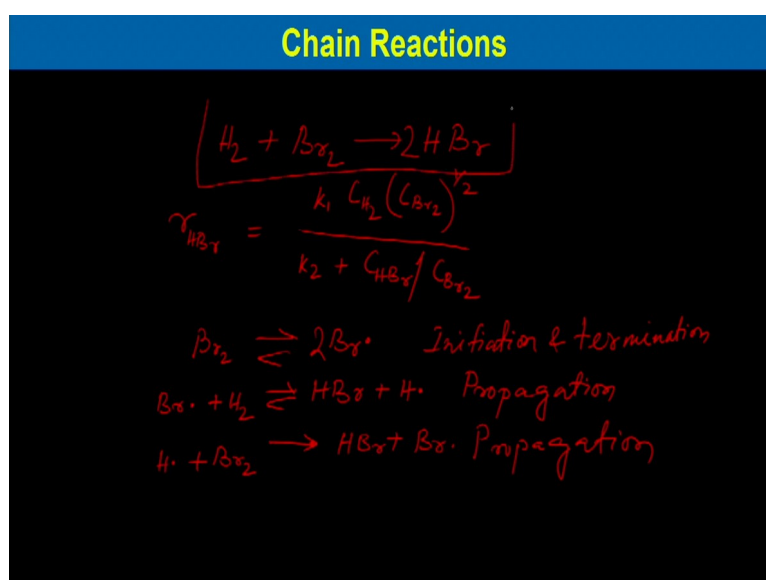
And then the third step is the spontaneous one, that is A^* decomposes or giving the products R plus S. So, this overall reactions can be viewed as A_2, so A_2 is forming A^* and then forming R plus S.
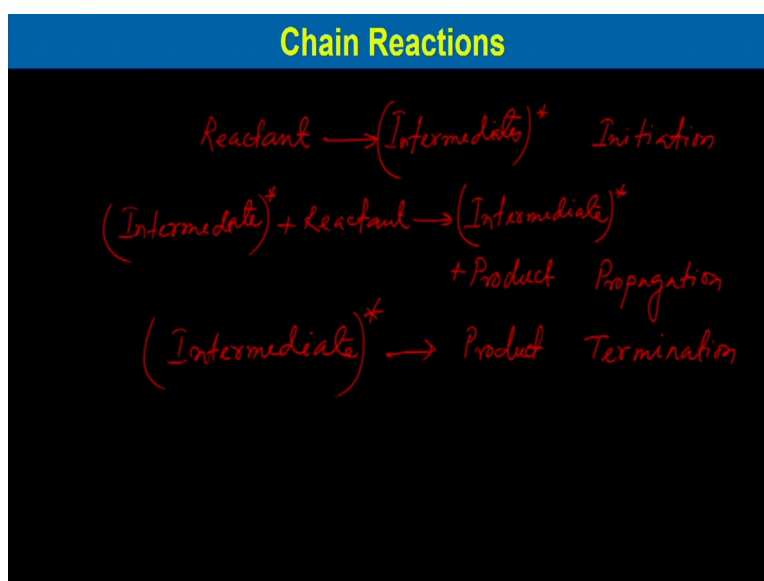
Chain Reactions

So, now chain reaction. The chain reactions in which the intermediate which forms first and then it initiates the process of the next step. So, the reactions proceed via different steps that is reactant, its first forms intermediates and this step is called initiation. Then intermediates reacts with reactant again, it forms intermediate plus product and this step is called propagation. And the 3rd step is intermediate forming products and this step is known as termination. So, most of these chain reactions goes via free radical mechanism.
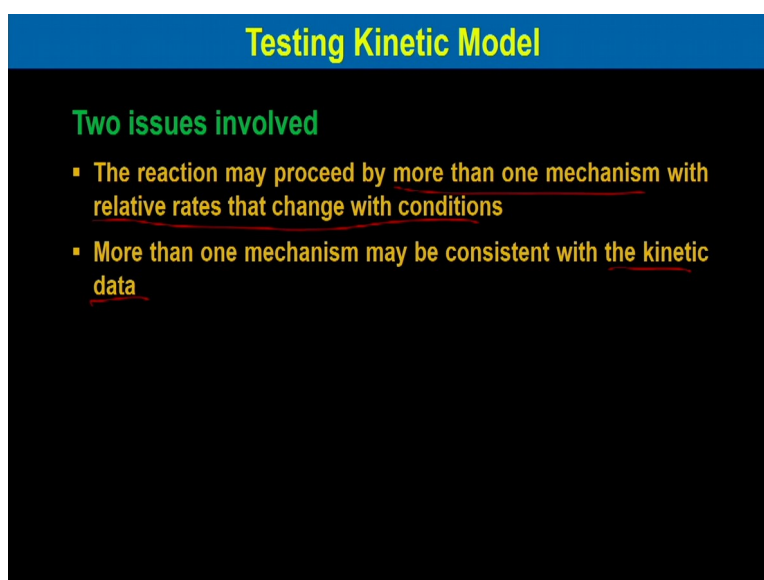
Chain Reactions

Let us consider the reaction mechanism for the reactions of bromine with hydrogen forming hydrogen bromide. So the reactions of hydrogen plus bromine is forming twice HBr and the experimental rate for this reaction is observed as r_{HBr} is equal to K_1 concentration of

hydrogen into concentration of bromine to the power half divided by K_2 plus concentration of HBr divided by concentration of Br_2. And the reaction involves the following mechanisms. Bromine first dissociates into Br radical, this is also initiation and termination, Br dot reacts with hydrogen, it forms HBr plus H dot, this is called propagation.

And the 3rd step H dot plus Br_2, it forms HBr plus Br dot. So, this is also propagation. So, the example of formation of hydrogen bromide from hydrogen and bromine is one of the examples of chain reactions which goes through the free radical mechanism.

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So, now we will discuss the testing of kinetic models. There are two issues involved for the testing of kinetic models. They are the reactions may proceed by more than 1 mechanisms, with reactive rates that may change with the conditions. And the second one is more than one mechanism may be consistent with the kinetic data. So, resolving these issues is quite difficult and let us not consider these issues over here and let us consider a simple system based on our knowledge, if we developed a kinetic model and whether that is valid with our experimental observations. So, let us look into that part first.
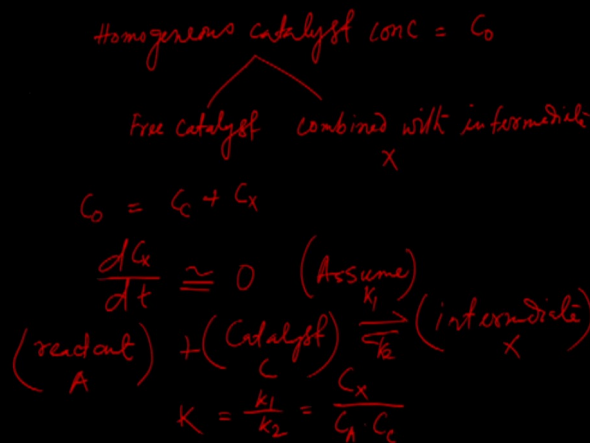
So, there are two types of intermediates we can consider or two types of elementary reactions we can propose for any kinetic model. In type one, the intermediates is unseen and unreserved, because of its quantity present into the system, it is very less. Suppose if we consider an intermediate X which is present in very small quantity. So, it is rate of change of concentration of this particular intermediate can be taken as 0. That means $\dfrac{dC_X}{dt}$ would be equal to 0 when concentration of X is small. And this is called steady-state approximation.

To understand this mechanism or that kinetic model, please go through the book of Kuny and Levenspiel, and try to there is some example given and try to understand this model.

Testing Kinetic Model

Type 2

Homogeneous catalyst conc = C_0

Free catalyst — combined with intermediate X

$C_0 = C_c + C_x$

$\frac{dC_x}{dt} \cong 0$ (Assume)

$\left(\text{reactant}\atop A\right) + \left(\text{Catalyst}\atop C\right) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left(\text{intermediate}\atop X\right)$

$K = \frac{k_1}{k_2} = \frac{C_x}{C_A \, C_c}$

In type two, consider the homogeneous catalyst concentration is C_0. So, this is present in two forms, free catalyst or combined with intermediate X. Now, we can consider the total concentration of catalyst would be equal to the free catalyst concentration plus the concentration of the catalyst with the intermediate.

And in this case also we can assume $\frac{dC_X}{dt}$ is approximately equal to 0. So, the reactant A reacts in presence of catalyst and forms intermediate X, where the equilibrium constant can be denoted as K_1 by K_2, which is equal to concentration of the intermediate divided by the concentration of A into concentration of the catalyst.
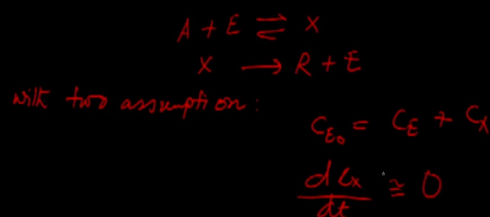
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Example 1

A substrate, A is converted to product, R by the action of an enzyme as per the following: $A \xrightarrow{enzyme} R$

Many of these reactions exhibit the following behaviour:

- A rate proportional to the concentration of the enzyme introduced in the mixture, C_{E0}.
- At low concentration the rate is proportional to the reactant concentration, C_A.
- At high reactant concentration the rate levels off and becomes independent of reactant concentration.

Propose a reaction mechanism to account for this behaviour.

$A + E \rightleftharpoons X$

$X \longrightarrow R + E$

with two assumption:

$C_{E_0} = C_E + C_x$

$\frac{dC_x}{dt} \cong 0$

Now, let us take an example to test this kinetic model of type 2. A substrate, A is converted to product R by the reaction of an enzyme as per the following. A to R in presence of enzyme. Many of these reactions exhibit the following behaviour. A rate proportional to the concentration of the enzyme introduced in the mixture, that is C_{E0}. At low concentration the rate is proportional to the reactant concentration C_A and at high concentration the rate levels off and becomes independent of the reactant concentration. So, these are the typical behaviours observed in most of the enzymatic reactions.

So, now we need to propose a reaction mechanism to account for this behaviour. This is one of the examples which is solved first by Michaelis and Menten in 1913. And Michaelis got Nobel Prize in chemistry. So, they proposed the reaction scheme like this, A in presence of the catalyst forms the intermediate X, then X forms R plus E. <mark>With the two assumptions, we can write concentration of E naught would be equal to concentration of E plus concentration of X. And d concentration of X / dt could be equal to 0.</mark>

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Now, if we write for this reaction $X \rightarrow R + E$, if we write the rate equation, it would be $\dfrac{dC_R}{dt}$ would be equal to, suppose this is K_3, so this would be K_3 into C_X and $\dfrac{dC_X}{dt}$ would be equal to K_1 into C_A into C_E minus K_2 into C_X minus K_3 into C_X would be equal to 0. So, the first reaction is $A + E$ which reacts reversibly form intermediate X. So, this is K1 and this is K2.

Now, from these two we can write the C_X would be equal to K_1, concentration of A into C_{E0} divided by K_2 plus K_3 plus K_1 into C_A.

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Now, if we introduce the C_X in the earlier equation, that is $\dfrac{dC_R}{dt}$ is equal to K_3 into C_X and we have obtained C_X is equal to K_1 into C_A into C_{E0} divided by K_2 plus K_3 plus K_1 into C_A. So now, if we substitute this C_X over here, we would get K_1 K_3 C_A into C_{E0} divided by K_2 plus K_3 plus K_1 into C_A.

So, we can write, this is K_1, K_3 into C_A into C_{E0} divided by K_2 plus K_3 divided by K_1 plus C_A. Which we can write as K_3 into C_A into C_0 divided by C_M plus C_A. This C_M is nothing but K_2 plus K_3 by K_1 and is known as Michaelis constant.

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Example 1

A substrate, A is converted to product, R by the action of an enzyme as per the following: $A \xrightarrow{\text{enzyme}} R$

Many of these reactions exhibit the following behaviour:
- A rate proportional to the concentration of the enzyme introduced in the mixture, C_{E0}.
- At low concentration the rate is proportional to the reactant concentration, C_A.
- At high reactant concentration the rate levels off and becomes independent of reactant concentration.

Propose a reaction mechanism to account for this behaviour.
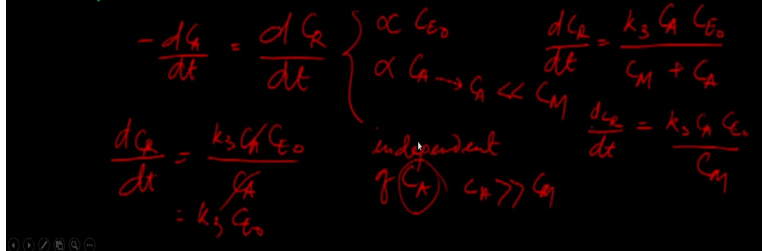
So, by comparing with the experiments, it can be observed that $-\dfrac{dC_A}{dt}$ would be equal to dCR / dt, which would be proportional to C_{E0} as can be seen from this equation. So, if we write $\dfrac{dC_R}{dt}$ is equal to K_3, C_A into C_{E0} divided by C_M plus C_A. This would be proportional to C_{E0} and it would be proportional to C_A, when C_A is very very greater than C_M.

So, if this is very very greater from this, we can write $\dfrac{dC_R}{dt}$ would be equal to K_3 into C_A into C_{E0} naught by C_M. That means K_3 into C_{E0} by C_M can be clubbed to a constant and it would be proportional to C_A. So, that is valid when C_A is very very less than C_M. And it would be independent of concentration of A, when C_A is very very greater than C_M. That means when this is very very greater, so this can be written as $\dfrac{dC_R}{dt}$ is equal to K_3 C_A C_{E0} by C_A. So, then this will cancel out and it would be $K_3 C_{E0}$, so that makes it would be independent of concentration C_A.

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Now, the temperature dependent term of the rate equation, as we have seen particularly for the elementary actions the rate expression can be written as the function of temperature as well as composition that means R is equal to function of temperature into function of composition. Or we can write this function of temperature is included with the term K, the rate coefficient into function of composition.

The temperature dependent term can be related with the activation energy and the equation is K is equal to K_0 into $e^{-\frac{E_a}{RT}}$, where K_0 is the Arrhenius frequency factor and E_a is activation energy, R is the universal gas constant and T is the temperature.

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Now, if we take the logarithmic of this relation, that is K is equal to $K_0 e^{-\frac{E_a}{RT}}$. If we take

logarithmic of this, it will be ln K is equal to $-\frac{E_a}{R}$ into $\frac{1}{T}$ plus ln K_0. Now, if we plot ln K

versus $\frac{1}{T}$, this will lead to a straight line. And slope would be $-\frac{E_a}{R}$, the value of R is 8.314

joules per mole Kelvin.

So, the activation energy, that is E_a can be calculated using the 2 values of rate constants, say

at temperature T_1 and temperature T_2. So, we can use the expression ln K_2 by K_1 would be

equal to $-\frac{E_a}{R}$ into $\frac{1}{T_2}$ minus $\frac{1}{T_1}$ or ln K_1 by K_2 would be equal to $\frac{E_a}{R}$ into $\frac{1}{T_2}$ minus $\frac{1}{T_1}$,

where T is in Kelvin.
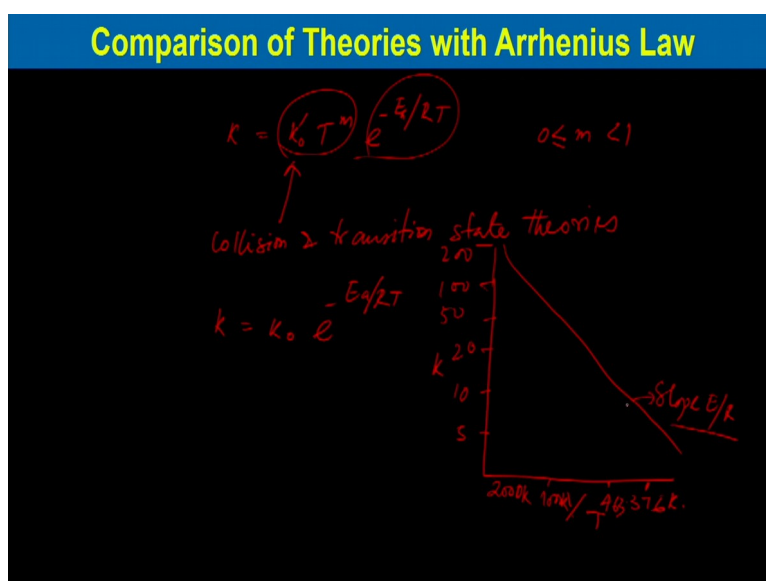
Now, let us compare the temperature dependency of the Arrhenius equation with the different theories. Like if we consider theories, they generally represent the rate constant K is equal to

$K'_0 T^M e^{-\frac{E_a}{RT}}$, where m is greater than or equal to 0 and less than 1. So, this equation predicts most of the cases for the rate from collision and transition state theories. These are temperature dependency on the rate constant.

Now, the temperature dependency of the pre exponential factor is too sensitive and so the exponential term of temperature dependency is too more sensitive than the pre-exponential factor. So, that means which is shown over here, this is not so sensitive compared to the temperature sensitivity of the exponential term. So, this can be expressed again with K is

equal to $K_0 e^{-\frac{E_a}{RT}}$.

Now, if we plot, it will give K versus 1 by T and this is say at low temperature, say at 375 Kelvin, 376, this is that 463 and this is in the range of 2000 and 1000. And this is the K values, that is 5, 10, 20, 50, then 100 and 200. So, if we plot the Arrhenius equation, it would

be like this, this is with slope $\dfrac{E}{R}$, so this is the slope.

Now, activation energy and temperature dependency. From the Arrhenius plot it can be seen that the plot of ln K versus $\dfrac{1}{T}$ gives straight line with large slope for large E_A, activation energy and small slow for small E_A. Secondly, reaction with high activation energy is very sensitive and reactions with low activation energy is less sensitive. Third thing is that at any reaction is much more temperature sensitive at low temperature compared to at high temperature. Reaction is more sensitive at high temperature than low temperature.

And the frequency factor, the pre-exponential factor is not much temperature sensitive. So, these are the relations of the sensitivity of the activation energy with the temperature.

Now, let us calculate the activation energy for a simple example. A second-order reaction was observed and the reaction rate constant at 10 degree was found to be 1.5 into 10 to the power minus 2 litre per mole per second and the other temperature at 40 degree centigrade 8.5 into 10 to the power minus 2 litre per mole per second. And we need to calculate the activation energy of this reaction.

So, step 1, we need to just calculate or convert the temperature into Kelvin, that is T is equal to degree centigrade plus 273.15, so it would be 10 plus 273.15, so it is 283.15 Kelvin. And T_2, this is T_1, T_2 would be 40 plus 273.15, so it would be 313.15 Kelvin.

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Now, we need to find activation energy. So, to do that, use the equations ln K2 by K1 would be equal to Ea by R into 1 by T1 minus 1 by T2. So, if we substitute, this is ln 8.5 into 10 to the power minus 2, divided by 1.5 into 10 to the power minus 2, so this will lead to Ea divided by 8.3145 joules per Kelvin mole into 1 by 283.15 Kelvin minus 1 by 313.15 . So, if we solve it, it will be ln 5.67 would be equal to Ea by 8.3145 into 3.38 into 10 to the power minus 4.

So, from here you can calculate Ea is equal to 4.263 into 10 to the power 4 joules per mole which is equal to 42.63 kilojoules per mole. So this is how we can calculate the activation energy knowing the rate constant at two different temperatures. So thank you for hearing this lecture, and we will continue our discussion on the kinetics and the reactor design in our next lecture.