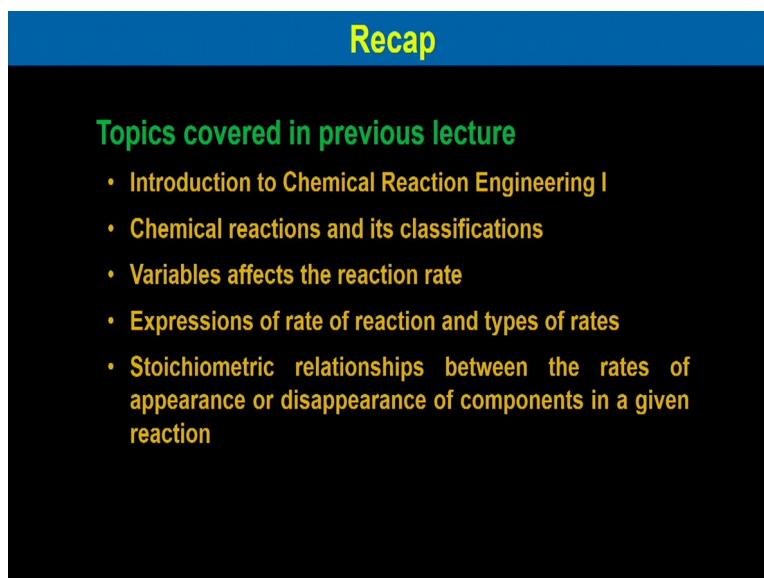


Chemical Reaction Engineering-I
Professor Bishnupada Mandal
Department of Chemical Engineering
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Lecture - 2
Kinetics of Homogeneous Reactions

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Recap

Topics covered in previous lecture

- Introduction to Chemical Reaction Engineering I
- Chemical reactions and its classifications
- Variables affects the reaction rate
- Expressions of rate of reaction and types of rates
- Stoichiometric relationships between the rates of appearance or disappearance of components in a given reaction

Welcome to the second lecture of module 2 on Chemical Reaction Engineering 1. Before going to this lecture, let us have a small recap on our previous lecture. In our previous lecture we have covered a few important topics, that is introduction to the chemical reaction Engineering 1, then we considered different reactions and their classifications. Different variables that affects the reaction rates. Here we have considered for homogeneous reactions and for heterogeneous reactions what are the variables that influence the rate of chemical reactions.

Like in the case of homogeneous reactions, we saw that the temperature, concentration, and these are the major variables which influence the rate of chemical reactions. In case of heterogeneous reactions, we have seen that the parameters which are temperature, pressure and composition, in addition to that we have seen the heat and mass transfer effects also affects the rate of chemical reaction.

Then we have different types of rates, and we have seen the correlations among them and also we have seen that the stoichiometric relationships between the rates of appearance or disappearance of the components in a given reaction.

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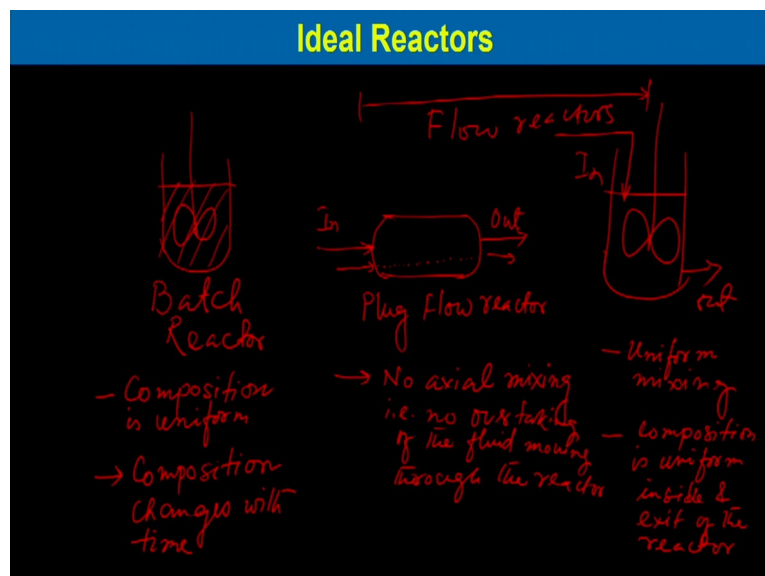
Lecture 2 : Kinetics of Homogeneous Reactions

Lecture Outline

- Ideal Reactors
- Reaction Rate, Rate Constants and its Unit
- Elementary and Nonelementary Reactions
- Reaction Order and Rate Law
- Molecularity
- Deriving Rate Law from Elementary Reactions

So, in this lecture we will consider kinetics of homogeneous reactions. So, the brief outline of this lecture would be the ideal reactors, then reaction rate, rate constants and its unit, then we will discuss the elementary and non-elementary reactions, reaction order and rate law, molecularity and deriving rate law from different elementary reactions.

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So, let us start with ideal reactors. In general there are 3 ideal reactors, of which we generally considered in chemical reaction engineering. These 3 ideal reactors are, one of them is the batch reactor. So, you have a tank and you have a stirrer or impeller fitted into it. Here initially you have put some raw materials inside the reactor and there is, then you closed it, so there is no inlet outlet for this reactor. And you can stir it for a certain product time and then

you can take out the products. So, this is known as batch reactor. In this case, your composition everywhere is uniform. So, composition is uniform everywhere inside the reactor. But the composition changes with time.

So, these are batch reactors and another case is flow reactors, in which you have flow in and flow out. So, the other idealised reactor is the plug flow reactor, where you have a flow-in into the reactor and you have flow-out. You can think of a simple cylindrical pipe, so the fluid through which it enters and it flows through and there is no overtaking of the fluids which is behind. That means there is no back mixing in this case, that is why we call it plug flow. So, this is plug flow reactor.

So, in this case no axial mixing, that is there is no overtaking of the fluids, moving through the reactor. The other idealised reactor is continuous stir tank reactor. So, it is like a tank fitted with impeller and you have the feed in and you have the product out. So, raw material or the reactants in to the reactor, mixed it with an impeller and then you have an output. So, all these are, these two are flow reactors. So, this is in and this is out. So, in this case it is the mixing is uniform, homogeneous and at steady-state the composition inside the reactor as well as at outside are same.

So, the composition, uniform mixing, in this case composition is uniform at inside and exit of the reactor. So, the compositions would be same inside the reactor as well as which is coming out from the reactor. So, these are the three idealised reactors. We will consider more details on it while designing of the reactor.

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Reaction Rate and Rate Constant

In a perfectly mixed, closed, constant volume system (or in some region of space over which conditions are uniform) with the generic reaction

$$aA + bB \rightarrow cC + dD$$

Rate of disappearance

$$r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{moles of A disappearing}}{(\text{volume}) \times (\text{time})} \text{ m}^3 \text{ s}^{-1}$$

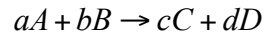
intensive measure

$$r = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$$= -\frac{1}{a} \frac{dA}{dt} = -\frac{1}{b} \frac{dB}{dt} = \frac{1}{c} \frac{dC}{dt} = \frac{1}{d} \frac{dD}{dt}$$

$-a, -b, c \text{ \& } d \Rightarrow$ stoichiometric coefficients

Now, reaction rate and the rate constants. So, in a perfectly mixed, closed, constant volume system or in some region of the space over which the conditions are uniform, we can write the generic correlations or the reaction, that is



So, we can write the rate of disappearance of A as

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

so which is equal to moles of A disappearing divided by volume into time. So, the unit we can write is mole per metre cube second. You could see the negative sign over here is the intensive measure. This indicates the rate of disappearance. That means the concentration is decreasing of the reactants. So, that is why the minus sign indicates the disappearance.

Now, reaction rate for this reaction we can write r

$$r = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Or we can write this r is equal

$$= -\frac{1}{a} \frac{dC_A}{dt} = -\frac{1}{b} \frac{dC_B}{dt} = \frac{1}{c} \frac{dC_C}{dt} = \frac{1}{d} \frac{dC_D}{dt}$$

The coefficient as you can see -a, -b, c and d, these are the stoichiometric coefficients. And C_A , C_B , C_C and C_D or the concentrations of the different species.

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Reaction Rate and Rate Constant

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or rate law.

$$-r_A = k f(C_A, C_B, \dots)$$

↑
rate constants

Gas phase reactions - k depends on
- Catalyst conc
- Total pressure

Arrhenius Eqn $k = k_0 e^{-\frac{E_a}{RT}}$

Now, if we see the reaction rate, we can write

$$-r_A = kf(C_A, C_B, \dots)$$

The algebraic equation that relates $-r_A$ the species concentration is called the kinetic expression or rate law. So, in this case you could see this k is the kinetic constant, or known as rate constant. Essentially, this is not constant, this is independent of mostly concentrations. But in case of the gas phase reactions, for gas phase reaction, k depends on catalyst concentration and total pressure.

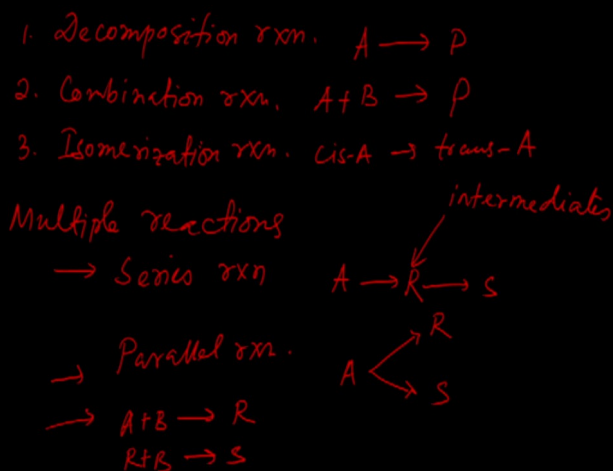
However, this dependency of k on catalyst concentration and the total pressure are very less as compared to the dependency with the temperature. So, k is a very strong function of temperature and which is related with the well-known equation of Arrhenius law. So Arrhenius relations, where k is dependent on the temperature as

$$k = k_0 e^{-\frac{E_a}{RT}}$$

So, k_0 is the frequency factor and E_a is the activation energy and R is the gas constant and T is the temperature. So, we will discuss more on the determination of the activation energy for different reactions in the later of our discussion.

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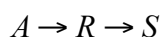
Elementary and Nonelementary Reactions



Now, we will discuss on elementary and non-elementary reactions. Before going to this elementary and non-elementary reactions, let us introduce you, which we have already discussed in the last lecture, that the different types of reactions. And we have seen there are three general categories of the reactions which happen, one is the decomposition reaction.

So, in this case we have seen a reactant decomposes to the product. And second thing we have seen, the combination reaction, where 2 reactants combine and produce a product P. And third one is the isomerisation reaction. And we have seen that Cis A converted to trans A. But when more than one reactions happen for a particular changes to happen from the reactants to the product, then we have the kinetic expression generally considered the changes of concentration which different components produces during the chemical reaction.

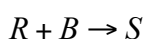
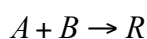
So, we call those reactions are multiple reactions. For multiple reactions we have two categories, one series reaction, like if we take



So, these are series reactions and this R we call intermediates. Now, another reaction is the parallel reaction. That means A can be decomposes to two different components, that is



Or



So, these are series-parallel reactions.

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Elementary and Nonelementary Reactions

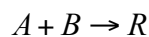
$$\textcircled{A} + \textcircled{B} \rightarrow \textcircled{R}$$
$$\textcircled{-r_A} = k C_A C_B$$

Such reactions in which the rate equation corresponds to a stoichiometric equation (i.e. the reaction order of each species is identical with the stoichiometric coefficient of the of that species for the reaction as written) are called elementary reactions.

$$H_2 + I_2 \rightarrow 2HI$$

Rate Law: $-r_{H_2} = k C_{H_2} C_{I_2}$

So, now further elementary reactions. So, if we consider the stoichiometric relations

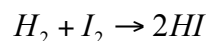


and we postulate that one mole of A reacts with one mole of B and produce R. So, in that case the rate of reaction we can write as

$$-r_A = k C_A C_B$$

So, in such reactions in which the rate equations corresponds to the stoichiometric equation, that means the stoichiometric coefficient for A is 1 and stoichiometric coefficient for B is 1. So, power of the concentration term raised to 1 for both A and B. So, if that is happens, that means the stoichiometric equation and the rate equations are same.

So, in that case we can say these reactions is elementary reactions. One good example of elementary reactions is that the hydrogen reacts with iodine and it produces HI



The rate law we can write

$$-r_A = k C_{H_2} C_{I_2}$$

So, that means these relations correspond to the stoichiometric coefficient of the overall reaction.

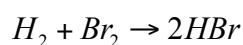
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Elementary and Nonelementary Reactions

When there is no direct correspondence between stoichiometry and rate, then we have nonelementary reactions.

$$H_2 + Br_2 \rightarrow 2 HBr$$
$$r_{HBr} = \frac{k_1 [H_2] [Br_2]^{1/2}}{k_2 + [HBr] / [Br_2]}$$

When there is no direct correspondence between the stoichiometry and the rate, then we call that the reaction is a non-elementary reaction. That means, one such example is the production of HBr from reactions between hydrogen and bromine. So, if we react hydrogen plus bromine, it produces hydrogen bromide twice HBr.



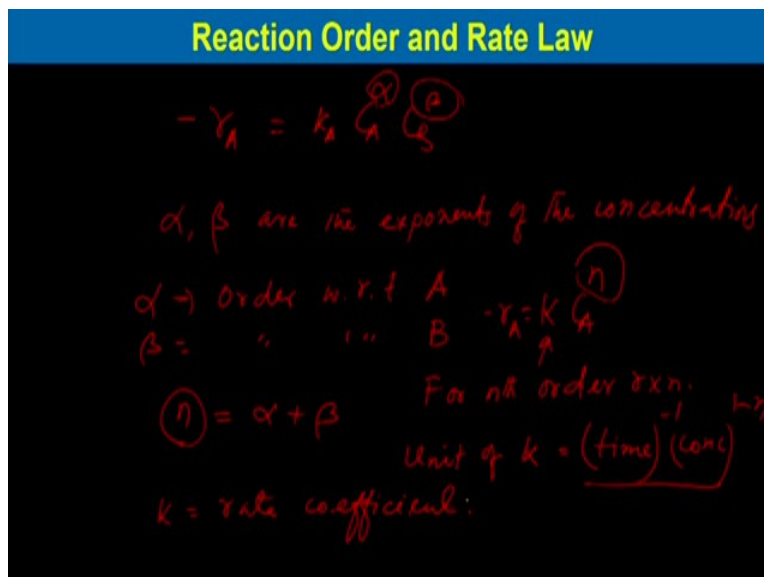
And the rate expression is

$$r_{HBr} = \frac{k_1 [H_2] [Br_2]^{1/2}}{k_2 + [HBr] / [Br_2]}$$

So this reaction does not correspond to the stoichiometric relations shown over here. So that is why this reaction is known as a non-elementary reaction.

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Reaction Order and Rate Law



Now, we will discuss about some other fundamentals of reactions, one is reaction order and rate law. So, the rate equations is generally derived from the experimental measurements. And that is based on the change of concentration of reactants or the products which are produced. So, if we consider the general rate equations

$$-r_A = k C_A^\alpha C_B^\beta$$

the exponent over here represents the order of the reaction. So, here α and β are the exponents of the concentrations. So, α is the order with respect to A and β is the order with respect to component B.

So, the overall order of this reaction, if we consider n is the overall order, then n would be equal to $\alpha + \beta$. So, this is the overall order of the reaction. Or if the rate of reaction

$$-r_A = k C_A^n$$

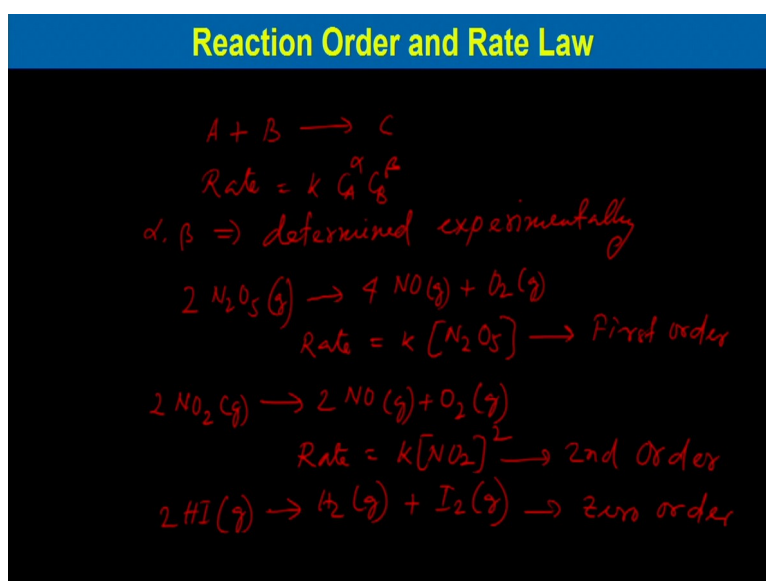
so then the order of the reaction is n. If nth order reaction the unit of rate constant k we can write would be equal to

$$k = (\text{time})^{-1} (\text{conc})^{1-n}$$

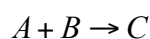
So, this is a unit of k.

As I said earlier the k is the rate constant only when we consider at a particular temperature. But essentially k is a function of temperature, so the better term to use for k is the rate coefficient instead of rate constant. So, k we can call rate coefficient.

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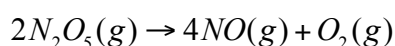
Now, if we consider a general reaction



And the rate law, we can write

$$\text{rate} = k C_A^\alpha C_B^\beta$$

And this α and β , they are determined experimentally. For example, if we consider



And the rate is given as

$$\text{rate} = k[N_2O_5]$$

That is the reaction is first-order. That means if we double the concentration of N_2O_5 , the rate of reaction will double. So, if we triple the concentration at the rate of reaction will triple.

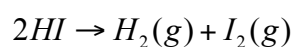
Now, if we consider another reaction



And the rate is equal to

$$\text{rate} = k[NO_2]^2$$

That means the reaction is second order. So, in this case if we double the concentration of NO_2 , the rate of the reactions will enhance to quadruple. Another reaction is



and this reaction is found to be 0 order. That means the reactions is independent of the concentration of the species.

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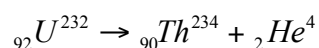
Molecularity

The molecularity is the number of atoms, ions, or molecules involved (colliding) in the rate-limiting steps of the reaction.

$${}_{92}U^{232} \longrightarrow {}_{90}Th^{234} + {}_2He^4$$

Radioactive Decay
reaction of spontaneous in nature.

Now, we will discuss another important topic which is molecularity of the reaction. The molecularity is defined is a number of atoms, or ions, or molecules involved in the rate-limiting steps of the reaction. Based on the number of molecules involved for a rate-limiting steps, we can define it as unimolecular, bimolecular, and termolecular and so on. But the unimolecular and bimolecular are common, but termolecular reactions are very rare. One common example of unimolecular reaction is the conversion of the uranium to thorium and helium.



So, this is the reaction of the radioactive decay and this reaction in spontaneous in nature.

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Elementary Steps and Molecularity

- Elementary steps or elementary reactions are simple steps that together make up the reaction mechanism for a given reaction.
- An elementary reaction is characterized by its molecularity, which is the number of particles/molecules involved in the formation of transition-state complex.
- An elementary reaction may be characterized as unimolecular, bimolecular, or termolecular.
- Unimolecular and bimolecular reactions are considered the most common elementary processes.

So, elementary steps or elementary reactions are simple steps that together make up the reaction mechanism for a given reaction. An elementary reaction is characterised by its molecularity, which is the number of molecules or particles involved in the formation of the transition state complex. An elementary reaction may be characterised as unimolecular, bimolecular or termolecular, which I have explained before.

So, if we consider elementary reactions, then it would be easy to find out the rate of the reaction and the molecularity will be based on the elementary steps of the reaction. Unimolecular and bimolecular reactions, as I said, is the most common in the processes.

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Rate Law from Elementary Steps

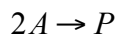
<u>Elementary Rens</u>	<u>Molecularity</u>	<u>Rate</u>
$A \rightarrow P$	Unimolecular	$k C_A$
$2A \rightarrow P$	Bimolecular	$k C_A^2$
$A+B \rightarrow P$	Bimolecular	$k C_A C_B$
$2A+B \rightarrow P$	Termolecular	$k C_A^2 C_B$

$2O_2 + N_2 \longrightarrow O_3 + O + N_2$

Now we will consider rate law from elementary steps. So, if we consider elementary reaction say

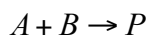


then we call the molecularity as unimolecular. And the rate law if we can obtain from here, it would be kC_A . If 2A produces products,

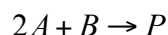


then we call bimolecular. And we can write the rate of the reaction kC_A^2 . So, this is the bimolecular reaction.

Now, if A plus B produce P,

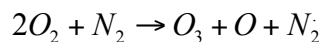


this is also two different reactants reacts together producing product P, this is also a bimolecular reaction. And the rate we can write $kC_A C_B$. And another one if twice A reacts with B and forms product,



then we can write, tell this reaction as termolecular and the rate would be $kC_A^2 C_B$. So, as we said that the termolecular reactions are very rare. One example of termolecular reaction is assumed to happen for the conversion of oxygen to ozone.

So,



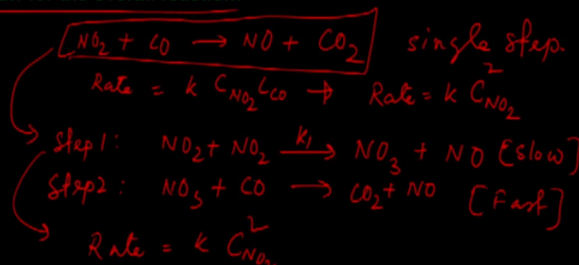
So, this reaction is considered as termolecular reactions, but in general the termolecular reactions are very rare.

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Rate Law from Rate-Determining Step

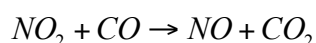
➤ If a proposed mechanism consists of more than one elementary steps, then the one with the slowest rate will determine the overall rate of reaction.

➤ It is called the rate-determining step, which step represents the rate law for the overall reaction.



Now, we will consider from rate determining step, how to obtain the rate equation or the rate law from the rate determining step. If the proposed mechanism consists of more than one elementary steps, in that case the slowest steps or the steps where the rate is the slowest of the overall reactions is considered as the rate determining step. So, it is called the rate determining step, which step represents the rate law of the overall reaction.

Like, if we consider reactions



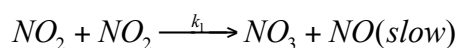
And the reaction happens in a single step. So, in that case we can write the rate is equal to

$$rate = k C_{NO_2} C_{CO}$$

However, the experimental measurement shows that the rate is actually

$$rate = k C_{NO_2}^2$$

So, now if we propose this step into 2 elementary steps, this reactions if we propose into 2 elementary steps, we can write step 1,



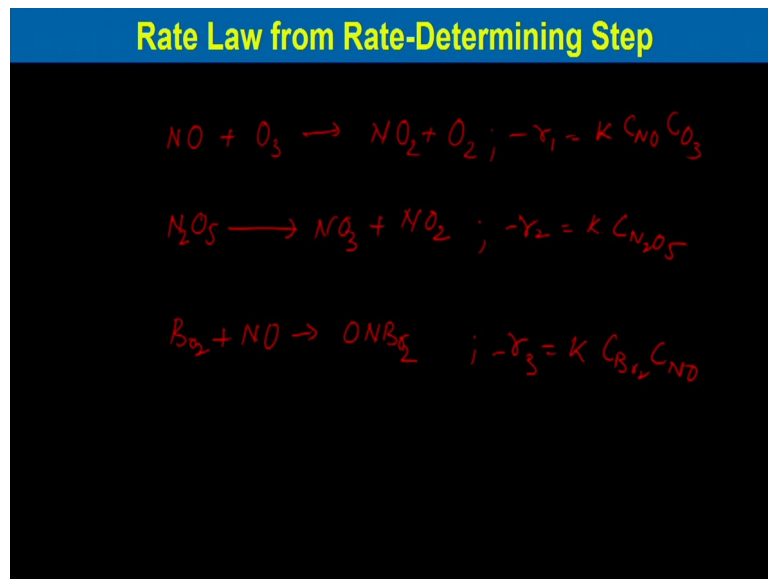
and step 2,



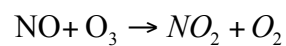
So, this reaction is actually slow and this reaction is fast. So, this is the rate determining step, so from here we can write the rate is equal to $kC_{NO_2}^2$.

So, as we have said, the overall reaction rate must be determined experimentally or the rate law must be obtained from the experimental measurements. And if there is elementary reaction, then the rate equations can be obtained directly from the elementary reactions or from the molecularity of the reaction.

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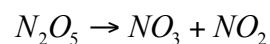
Like for following examples, it forms



and we can write the rate

$$-r_1 = k C_{NO} C_{O_3}$$

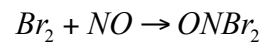
Similarly, if



we can write as

$$-r_2 = k C_{N_2O_5}$$

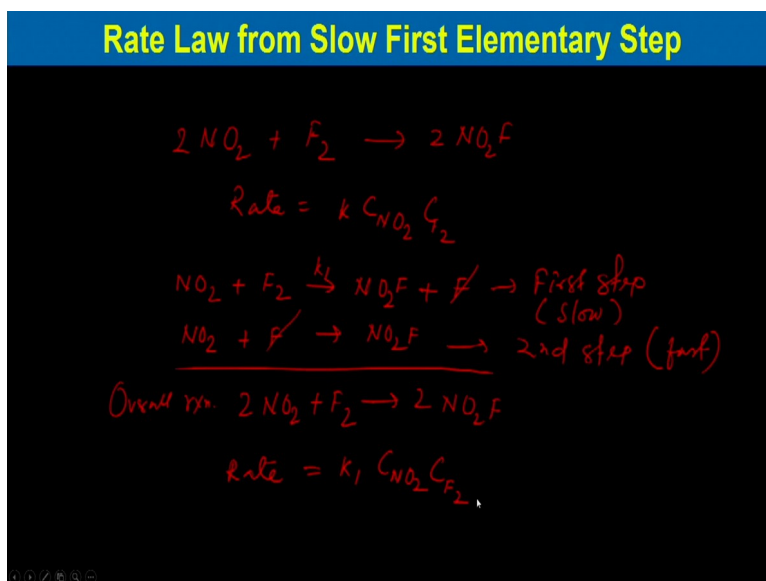
Similarly,



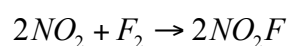
the rate can be written as

$$-r_3 = kC_{\text{Br}_2}C_{\text{NO}}$$

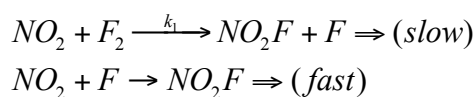
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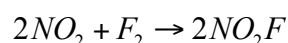
Now, we can also obtain the rate law from the slow first elementary step. Like, if we consider the reaction



and the rate we can write $\text{Rate} = k C_{\text{NO}_2} C_{\text{F}_2}$. The proposed mechanism for this we can write



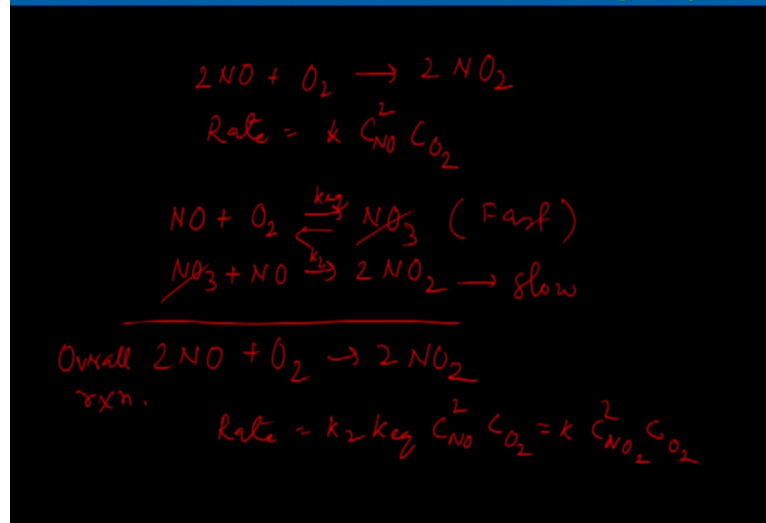
if we sum it up, then this will cancel out and we will have



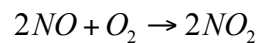
So this is the first step and it is considered as slow and rate determining and this is the second step and considered as fast. So, the rate of reaction for this we can write k_1 , say this is $k_1 C_{\text{NO}_2} C_{\text{F}_2}$

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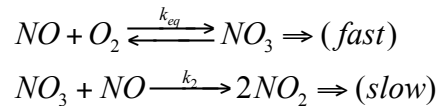
Rate Law from Slow Second Elementary Step



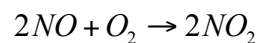
Now, rate law can also be obtained from the second step which is slow reaction. Like if we consider



The rate is $k C_{NO}^2 C_{NO_2}$. So, in this case the mechanism we can propose as



So, if we sum it up, so this will cancel out, we will have



So, this is the overall reaction. So, from here the slowest step is the second step and this is fast.

So, rate of reaction we can write, so this reaction, the first reaction is considered to be the equilibrium reaction and hence, this rate is written as $k_2 k_{eq} C_{NO}^2 C_{NO_2}$, which is equal to $k C_{NO}^2 C_{NO_2}$. So, the rate can be obtained from the slow elementary, second elementary step.

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Correlation of Reaction Mechanism with Rate Law

- The elementary steps must add up to give the overall equation.
- Elementary steps must be physically reasonable i.e. proposed step can occur with reasonable probability and they are either unimolecular or bimolecular. A termolecular elementary step is considered unlikely.
- The mechanism must correlate with the rate law i.e. the rate law derived from rate-determining step must agree with the actual rate law obtained experimentally.

So, there is correlation between the reaction mechanism and the rate law. The elementary steps must add up to give the overall equation. And also elementary steps must be physically reasonable, that is proposed step can occur with a reasonable probability so that they are either unimolecular or bimolecular. As we said a termolecular elementary step is considered unlikely.

The mechanism must correlate with the rate law that is the rate law derived from the rate determining step must agree with the actual rate obtained experimentally. Thank you for hearing this lecture and we will continue our discussion on the reaction kinetics in our next lecture.