

**Aspects of Biochemical Engineering**  
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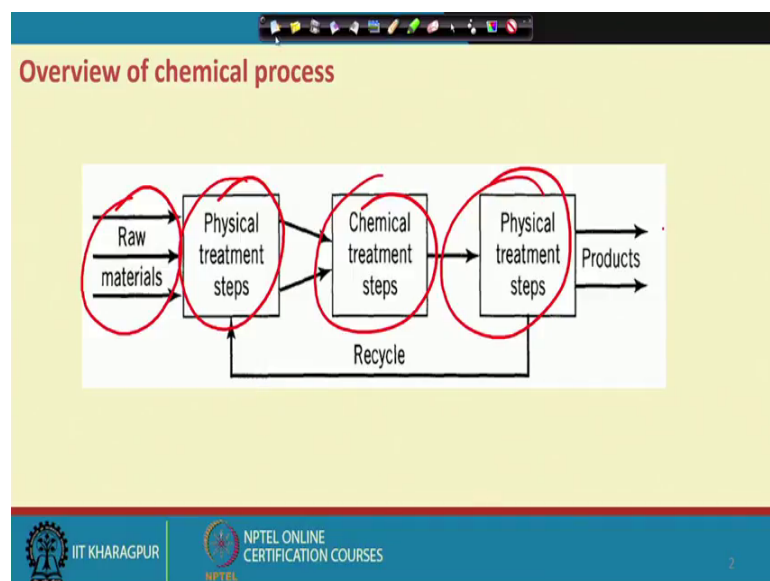
**Lecture – 11**  
**Kinetics of Homogeneous Chemical Reactions – I**

Welcome back to my course Aspects of Biochemical Engineering. Now, in this lecture we want to discuss the kinetics of the homogeneous chemical reaction and as we know that I told you previously that chemical engineering is kind of basis of the biochemical engineering.

So, we try to understand the chemical reaction how this chemical reaction we can express mathematically express, how different kinetic constant can be estimated and then we initially we discussed the irreversible reactions, and then we will discuss the reversible reaction, and after that we will also discuss the chain reaction. Because if you look at the biological process we have seen that mostly the biological reaction they are reversible in nature and they are chain reactions because if you look at the metabolic pathway stable steps of reaction take place a to b, b to c, c to d like this. So, those should be understood properly before we go to the biological process.

Now, if you look at this overall the chemical process how it looks.

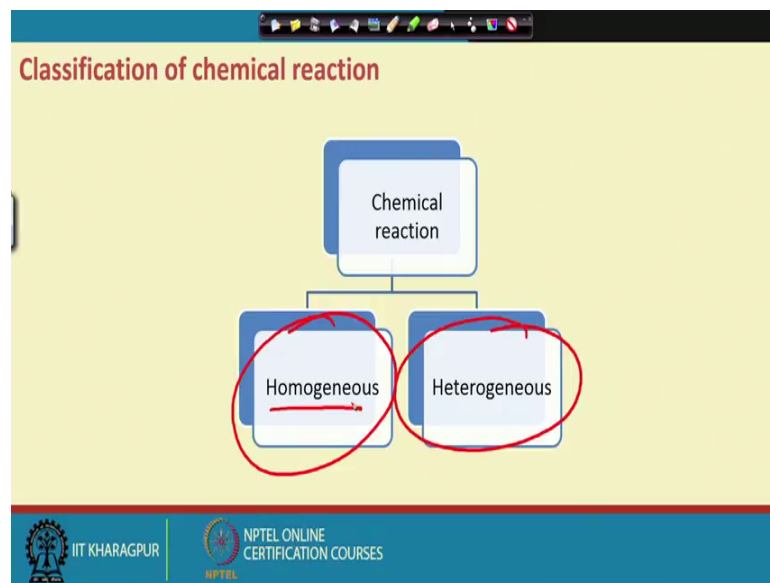
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Now, chemical process we have this raw materials, initially we have raw materials then these raw materials undergoes some kind of physical treatment before it goes to the chemical process.

And after chemical process we do some kind of purification what we call physical treatment steps, then we get the product and some of the things which is sometimes we recycle back to the system.

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Now, the chemical reaction can be classified in two different ways, one is called homogeneous reaction and then we call heterogeneous reaction. Homogeneous reaction means when the reaction take place in one particular phases. Though we have three different phases we have gas gaseous phase, liquid phase and solid phase, if the reaction take place in one particular phase we call it homogeneous reaction.

Now, mostly in case of homo homogeneous reaction and reaction take place either gas and liquid phase. Now, in case of heterogeneous system the reaction take place more than one phase; that means, either gas liquid, liquid solid like this in (Refer Time: 02:57) at least more than one phase present in this reaction.

Now, basic difference between the homogeneous and heterogeneous reaction is that in case of homogeneous reaction the reactant they are freely interacting with each other give do give the product. Now, in case of heterogeneous system one phase supposed to

come in contact with the other phase and then an only then reaction take place and after the reaction is over the product has diffused from that phase to the other phase. So, that diffusion problem is the additional problem that we have in case of heterogeneous system.

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**Classification of chemical reaction**

- **Homogeneous reaction**
  - The reaction takes place in **one phase alone**  
(e.g. burning of LPG,  $\text{SO}_2$  to  $\text{SO}_3$ )  
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$$
- **Heterogeneous reaction**
  - **At least two phases** are required to proceed the reaction  
(e.g. burning of coal)  
$$\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$$
  - Simultaneous mass transfer and reaction occur
  - If  $\text{diffusion rate} > \text{reaction rate}$ , then reaction is controlling factor
  - If  $\text{diffusion rate} < \text{reaction rate}$ , Diffusion is controlling factor

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So, homogeneous I have a reaction we have the examples of this sulphur dioxide in presence of oxygen it produces sulfur trioxide. This is occurred particularly in the sulfuric acid production process. You might be knowing this sulfur trioxide in presence of water it produces either sulfuric acid.

Now, when sulphur dioxide is oxidized further to sulphur trioxide this all are gaseous phase this is gas, this is gas, so reaction occurred in the one particular phase. Since were reaction occurs in one particular phase we call it homogeneous reaction. We have another example is LPG, LPG is the liquified petroleum gas and when you part and it mostly contains the butane and when butane we burn it then it produce again carbon dioxide and water and carbon dioxide water also gas.

Now, heterogeneous reaction we have the examples of burning of coal and the coal is the solid material in presence of oxygen, oxygen is the gaseous material the ultimate product is carbon dioxide. So, the simultaneous the here, simultaneously mass transfer and the reaction occurred. As I pointed out before one phase has to come in contact with the other phase and then the reaction take place. So, two things simultaneously take place

here and if the rate of diffusion is more than rate of reaction then we call it a reaction controlling. So, if you want to improve upon the process then we still have to improve this rate of reaction. Now, if the rate of diffusion is less as compared to rate of reaction then diffusion is a controlling. So, we shall have to improve the diffusion rate.

Now, if you look at, if you look at the rate equations it is like this the  $aA + bB$  equal to  $rR + sS$ . Let us this is product and this is yours reactant.

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**The rate equation**

- Suppose a single phase reaction

$$aA + bB \rightarrow rR + sS$$

*Handwritten notes:*  $C_A \rightarrow \frac{dC_A}{dt}$ ,  $C_{ne} = \frac{\text{MASS}}{V} = \frac{\text{MOL}}{V}$

- The rate of disappearance of A =  $(-r_A) = -\frac{1}{V} \frac{dN_A}{dt}$
- For constant volume system

$$(-r_A) = -\frac{d(N_A/V)}{dt} = -\frac{dC_A \text{ mol}}{dt \text{ L.s}}$$

*Annotations:* Minus sign means disappearance,  $N_A \rightarrow$  moles of A,  $V \rightarrow$  Volume

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Now, rate of disappearance of A minus  $r_A$  it is usually expressed as minus the reason is that it is disappearing. Now, if you plot the concentration of product, concentration of raw material the substrate with respect to time always it will like this and why it is decreasing with respect to time; that means, rate of degradation of  $C_A$  that always should be negative because it is the negative profile that we have. So, this is why, that is why we you have written minus  $r_A$  this minus  $r_A$  equal to  $dN_A$ ;  $dN_A$  by A is the what moles of A. So, concentration, what is concentration? Concentration is nothing, but mass per unit volume or moles per unit volume moles per unit volume. So, this is here  $N_A$  is the moles of A. And  $b$  is the volume. So,  $b$  is the constant. So, it is comes out and this is  $d$  this is expressed as  $dN_A$  by  $dt$  into  $v$ . So, we can, if you when you put it like this then we can express in terms of concentration we can express minus  $dC_A$  by  $dt$  this is moles per liter per second.

Now, in the previous reaction that we have seen that is  $aA + bB \rightarrow rR + sS$ .  
 Now, here how you express the rate of the reactions that  $-\frac{r_A}{a} = -\frac{r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$ .

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**The rate equation**

- In addition, the rates of reaction of all materials are related to
 
$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$
- The rate of reaction is influenced by the composition and the energy of material. Energy means temperature, light intensity, magnetic field intensity, etc.

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The rate of reaction is influenced by the composition and the energy composition and the energy of the material. Energy means temperature light intensity and the magnetic field intensity. This is rate even industry any kind of reaction we can rate we can express like this.

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**The rate equation**

Suppose the  $n$ th order reaction  
 $A \rightarrow \text{product}$

the rate equation

$$(-r_A) = k C_A^n = A e^{-E_a/RT} C_A^n$$

*Handwritten notes:*  
 Rate constant (circled around  $k$ )  
 order of reaction (circled around  $n$ )  
 Activation energy (points to  $E_a$ )  
 Order of reaction (points to  $n$ )  
 Temperature dependent (points to  $e^{-E_a/RT}$ )  
 Composition dependent (points to  $C_A^n$ )  
 From Arrhenius equation (points to  $k$ )  
 Rate constant  $\left\{ \frac{\text{mol}}{\text{L}} \right\}^{(1-n)} \cdot \text{s}^{-1}$

*Handwritten equation:*  
 $k = A e^{-E_a/RT}$

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Now, here that you know suppose we have we have taken a very simple reaction A to product, A is the reactant and give the what is the how you can express the rate equation minus r A equal to k, k is called the rate constant, this is called rate constant and this is called order of reaction order of reaction. So, these are the two constant that we have. So, k into, now k again k depends on temperature and the k depends on temperature that can be expressed by the Arrhenius equation this is minus E a by RT. So, if we put it here. So, the whole equation looks like this. So, this is the Arrhenius equation we put it here this equation looks like this.

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**Arrhenius' Law**

Temperature dependent term, rate constant ( $k$ ) can be expressed using Arrhenius' equation as follows

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

where,  $A$  → frequency factor  
 $E_a$  → activation energy of the reaction  
 $R$  → universal gas constant

At the same concentration

$$(-r_A) \propto k \propto \frac{1}{t}$$

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Now, this is the Arrhenius equation I told you, this is Arrhenius equation. Now, the rate of reaction again directly proportional with k, since rate of reaction is proportional to the this is inversely proportional with t, 1 by t is the same concentrated time that is inversely proportional with this.

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**Arrhenius' Law**

Therefore, at the same concentration but at two different temperature

$$\ln \left( \frac{(-r_A)_2}{(-r_A)_1} \right) = \ln \left( \frac{k_2}{k_1} \right) = \ln \left( \frac{t_1}{t_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Subscripts 1 and 2 indicate two different reaction at temperature  $T_1$  and  $T_2$  respectively.

*Handwritten notes:*  
 $-r_A = k C_A^n$   
 $E = A e^{-E_a/RT}$

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Now, if you take this Arrhenius equation into consideration then we will find two rates this  $\ln$  minus because since it is proportional to  $k$  because as I told you this minus  $r_d$  equal to it  $k$  into  $C_A$  to the power  $n$ , am I right. So, it is proportional to this. So, this in the Arrhenius equation we have also written this equation  $k$  equal to  $A e$  to the power,  $e$  to the power  $E_a$  by  $RT$ .

So, I can write that  $r_{A2}$  by  $r_{A1}$  equal to  $\ln k_2$ ,  $k_2$  by  $k_1$  because this is that the particular different temperatures differ and this is equal to  $T_1$  by  $T_2$  this since it is inversely proportional with time and this is if you take this into account then we will we will get this particular relation  $a$  by  $r$  equal to  $1$  by  $T$  a minus  $1$  by  $T_2$ .

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### Temperature sensitivity of reactions

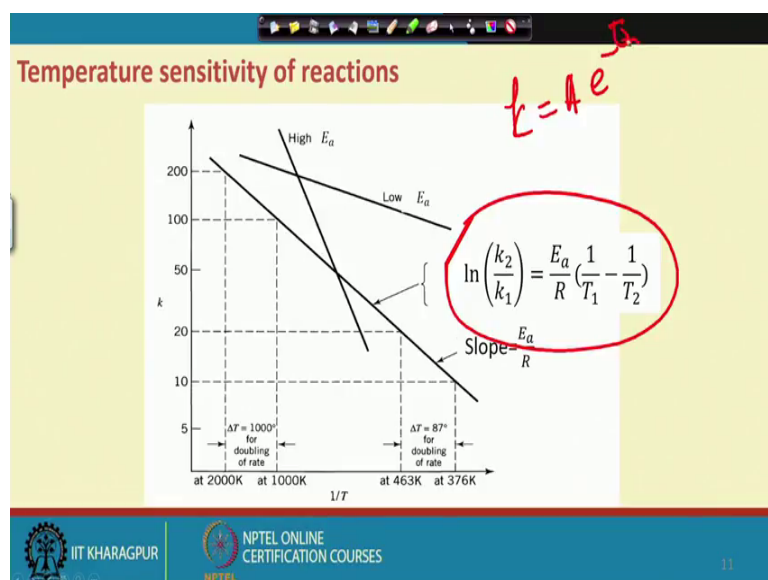
✓ The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction

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Now, temperature dependence on the reaction is determined by the activation energy, energy and temperature level of the reaction. So, this is very much clear from this form the next slide that I can show you here we have plot this is the log plot you can see that this is 10, then this is 100 like this and a double we can do that this is not normal plot this, and this is the normal centimeter plot that we can have.

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So, this is the plot this is the equation that we have that  $\ln k_2$  by  $k_1$  equal to  $E_a$  by  $R$ ,  $1$  by  $T_1$  minus  $T_2$ . That we can do it very easily because if you know  $k$  equal to  $Ae$  to the



power minus, I can show you another way that if you consider the  $k_1$  equal to  $Ae$  to the power minus  $E_a$  by  $RT_1$ . Let us assume this is the  $T_1$  temperature and  $k_2$  equal to  $Ae$  to the power minus  $E_a$  by  $RT_2$ , This is  $T_2$ , am I right.

(Refer Slide Time: 12:43)

The image shows handwritten mathematical work on a whiteboard. It starts with the Arrhenius equation for  $k_1$  and  $k_2$ , then divides  $k_2$  by  $k_1$  to derive the relationship between the two temperatures  $T_1$  and  $T_2$ .

$$k_1 = A e^{-E_a/RT_1}$$

$$k_2 = A e^{-E_a/RT_2}$$

$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

$$= e^{-\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Now, if you divide  $k_2$  by  $k_1$  then what I can write  $e$  to the power minus  $E_a$  by  $RT_2$  this is  $E_a$  sorry this is  $E_a$   $RT_2$  by  $e$  to the power minus  $E_a$  by  $RT_1$ . So, we can now, this is equal to what we can write this is equal to  $e$  to the power minus  $E_a$  by  $RT_2$  plus  $E_a$   $RT_1$  am I right then you can take it (Refer Time: 13:46). Then  $\ln$ , if you take  $\ln k_2$  by  $k_1$  equal to then I can write this is equal to you can  $E_a$  by  $R$ , you can take common though this will be  $1$  by  $T_1$  minus  $1$  by  $T_2$  like this. We can easily write this equation it is not very difficult. This is how this equation has come.

Now, here we want to focus one particular point that we are interested to show you this portion. Now, if you look at this (Refer Time: 14:22), this is  $1$  by  $T$  am I right, if  $1$  by  $T$  this is this is  $1$  by  $T$  is higher; that means, is the lower temperature. At low temperature that if you look at here that is the  $\Delta T$  is 87 degree centigrade for doubling the rate of reaction is this. Now, here if within the higher temperature the  $k$  value changes more as compared to this value. Here at the low temperature your rate of the  $k$  value does not change much, you know that, if you see that for eighty seven degree centigrade you have this much of change, but in higher temperature this you require more temperature to

change the k value as compared to this. This has been found that this from this particular Arrhenius plot that we can easily find out this.

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**Temperature sensitivity of reactions**

- ✓ From Arrhenius' law a semi-log plot of  $k$  vs  $1/T$  gives a straight line, with large slope for large  $E_a$  and small slope for small  $E_a$ .
- ✓ Reactions with high activation energies are very temperature-sensitive; reactions with low activation energies are relatively temperature-insensitive.
- ✓ Any given reaction is much more temperature-sensitive at a low temperature than at a high temperature.
- ✓ From the Arrhenius' law, the value of frequency factor does not affect the temperature sensitivity.

Handwritten diagram: A coordinate system with a vertical axis labeled  $k$  and a horizontal axis labeled  $1/T$ . A straight line with a negative slope is drawn. The slope is labeled as  $\text{slope} = -E_a/R$ .

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Now, temperature sensitivity to of reaction that is determined with the help of Arrhenius law by semi log plot I have already shown you. This is if you plot  $\ln k$  versus  $1/T$  that gives you the simple type about this slope will give you the value of slope will give you the value of  $E_a$  by  $R$  and here  $R$  is the gas constant. So, if you put this value you can easily find out the value of  $A$ .

The reaction with the high activation energy are very heated temperature sensitive and reaction with low activation energy beautifully temperature insensitive. So, if the activation energy plays very important role as per chemical reactions is concerned any given reaction is much more temperature sensitive at low temperature than the high temperature that we have seen previously, that at low temperature their change of  $k$  value is more as compared to high temperature and from Arrhenius law the value of frequency factor does not affect with the temperature because that remain constant with respect to temperature.

(Refer Slide Time: 16:49)

**Differential method for estimation of  $k$  and  $n$  from experimental data**

□ The rate equation

$$(-r_A) = -\frac{dC_A}{dt} = kC_A^n$$

□ Taking exponential log both side

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + n \ln C_A$$
$$\ln\left(-\frac{dC_A}{dt}\right) = n \ln C_A + \ln k \quad y = mx + c$$

*Handwritten notes on the slide:*

- $A \xrightarrow{k} B$
- A graph showing  $\ln\left(-\frac{dC_A}{dt}\right)$  on the y-axis and  $\ln C_A$  on the x-axis. A straight line is drawn through the data points with the label "Slope = n".
- The word "Intercept" is written near the y-axis.
- The word "Rate" is written at the bottom right.

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Now, question comes how you can determine the value of rate constant and the order of reaction. So, this is the equation that we have.

The rate of reaction can be just A to B, if there is a rate of reaction and  $k$  is the rate constant it can be expressed like this am I right. Now, if you take a log, nature log  $\ln$  minus  $dC_A$  by  $dt$  this comes at the  $\ln k$  plus this. Now, in case if you plot this is log log graph paper this is  $\ln$  minus  $dC_A$  by  $dt$  and this is  $\ln k$ ;  $\ln C_A$  sorry  $\ln C_A$  if you plot then you will get a slope and this slope will give you the value of  $n$  am I right and this intercept will give you the value of  $\ln k$ . So, you can find out your  $k$  value as well as your  $n$  value, both  $k$  value and  $n$  value you can find out any kind of chemical reaction.

(Refer Slide Time: 18:02)

**Differential method for estimation of  $k$  and  $n$  from experimental data**

- Plotting  $\ln y$  vs  $x$  yields slope  $= m = n = \text{order of reaction}$

intercept  $= c = \ln k = e^c$   $\rightarrow$

- Central differential method is used to get the value of  $\left(-\frac{dC_A}{dt}\right)$

$$\frac{dy}{dt} = \frac{y_{n+1} - y_{n-1}}{t_{n+1} - t_{n-1}}$$

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This is what we explained in this. So, here also you see that similarly we can find it out from the slope we can find out the  $n$  order of reaction and intercept, we can find out the value of  $k$ . So, central differential method that this is the another very interested the differential technique suppose we want to find out the substrate concentration at a rate of substrate degradation. I can give the example, I can give the example suppose in a reaction suppose  $C_A$  is decreases with respect to time you have profile like this. Now, if you want to find out minus  $dC_A$  by  $dt$ , how you can calculate? You can calculate the  $C_A^{n+1} - C_A^{n-1}$  divided by  $2 \Delta T$ .

So, suppose you have  $T_1$ ,  $T$  is that the  $T$  value and  $C_A$  value. So, you have different value here. So, you can find out this is the number of sampling point  $n$  this is 1 2 3 4 like this. So, you can see a  $n+1$  suppose you want to find out this; that means, you have to take the value here and minus 1 means 0 hour you have some value you have to take the value of 0 hour and  $\Delta T$  is the time difference. This is the 1 2 that may be in hour, may be in minutes, that difference you have to give you can easily find out the rate of change of substrate concentration, rate of change of product formation or you can estimate with the help of difference here technique. This is called the differential technique.

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**Irreversible uni-molecular 1<sup>st</sup> order reaction**

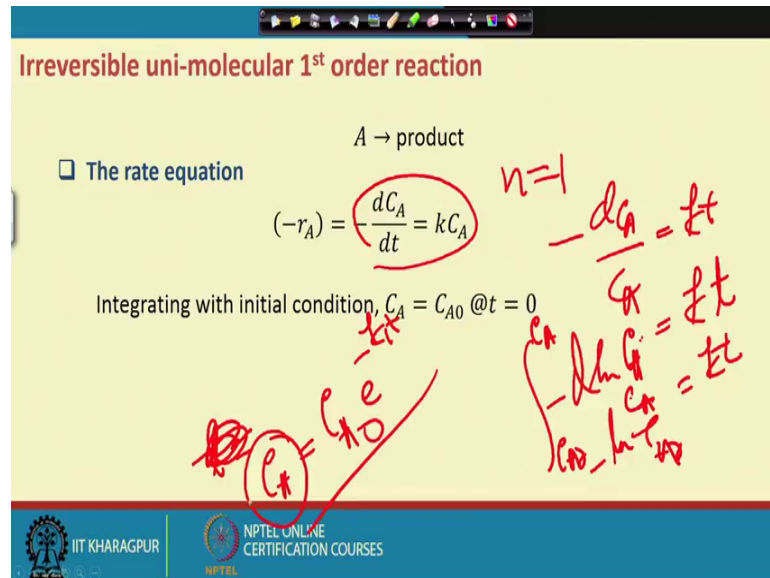
$A \rightarrow \text{product}$

□ The rate equation

$$(-r_A) = \frac{dC_A}{dt} = kC_A$$

Integrating with initial condition,  $C_A = C_{A0}$  @  $t = 0$

*Handwritten notes:*  $n=1$ ,  $-\frac{dC_A}{C_A} = k dt$ ,  $\ln \frac{C_A}{C_{A0}} = -kt$ ,  $C_A = C_{A0} e^{-kt}$



The slide features a yellow background with a blue header and footer. The header contains the title 'Irreversible uni-molecular 1<sup>st</sup> order reaction'. Below the title, the reaction  $A \rightarrow \text{product}$  is shown. A box labeled 'The rate equation' contains the differential equation  $(-r_A) = \frac{dC_A}{dt} = kC_A$ , with the fraction circled in red. To the right, handwritten red text shows  $n=1$  and  $-\frac{dC_A}{C_A} = k dt$ . Below this, another handwritten derivation shows  $\ln \frac{C_A}{C_{A0}} = -kt$  and  $C_A = C_{A0} e^{-kt}$ . The footer includes the IIT Kharagpur logo and the text 'NPTEL ONLINE CERTIFICATION COURSES'.

Now, a simplest reaction is the first order reaction when n value is 1. First order reaction means n value is 1, then we can write this equation like this. Now, this equation I can write like minus dC A by C A equal to k into t am I right. So, this is what, this is equal to d ln C A, this is equal to k into t. So, this is minus. So, we can do the integration C A to; 0 to C A. So, we can write this as ln C A by C A 0 minus equal to k into t. So, I can write t equal to (Refer Time: 20:47) whatever I can write dt equal to will be what not; I can sorry I can write C A equal to this is e to the power minus k 1 t. So, I can write C A 0 e to the power minus k 1 t. So, we can easily at any time for any point of time if we want to find out the concentration of A, that you can find out this correlation. So, this is like this.

(Refer Slide Time: 21:34)

**Irreversible uni-molecular 1<sup>st</sup> order reaction**

$A \rightarrow \text{product}$

□ The rate equation

$$(-r_A) = -\frac{dC_A}{dt} = kC_A$$

Integrating with initial condition,  $C_A = C_{A0}$  @  $t = 0$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$
$$-\ln \frac{C_A}{C_{A0}} = kt$$

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So, this correlation we have, what I have shown you this you can solve it very easily.

(Refer Slide Time: 21:41)

**Irreversible uni-molecular 1<sup>st</sup> order reaction**

In terms of conversion

$$\frac{dX_A}{dt} = k(1 - X_A)$$

Integrating with initial condition  $X_A = 0$  @  $t = 0$

Conversion,  $X_A =$   
 $(1 - \frac{C_A}{C_{A0}})$   
So,  
 $C_A = C_{A0}(1 - X_A)$

*Handwritten notes:*  
 $-\frac{dC_A}{dt} = k C_A$   
 $= k C_{A0} (1 - X_A)$   
 $dC_A = -C_{A0} dX_A$

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Then again this conversion I can express in the other term also with respect to  $X_A$  is the fraction of A that is converted this is the  $X_A$ ,  $X_A$  is the expresses 1 minus  $C_A$  by  $C_{A0}$  that means,  $C_A$  by  $C_{A0}$  is the fraction that remains after time t. The 1 minus means fraction that is converted with that respect I gave you convert the same equation we can convert it like this. How we can convert? By suppose  $dC_A$  by  $dt$  I have written what k into  $C_A$  am I right. So, what is the  $C_A$ ? Here we have seen that k equal to  $C_{A0}$  initial

concentration of substrate 1 minus  $X_A$  and what is that. Now, if you here if you do that  $dC_A$  then what will be this is 0. So, I can write  $C_{A0}$  is constant. So, this is equal to  $dX_A$ . Now, here if you put this value here  $dX_A$ , the  $C_{A0}$   $C_{A0}$  cancel will get this equation.

(Refer Slide Time: 22:57)

**Irreversible uni-molecular 1<sup>st</sup> order reaction**

In terms of conversion



$$\frac{dX_A}{dt} = k(1 - X_A)$$

Integrating with initial condition  $X_A = 0$  @  $t = 0$

$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

$$-\ln(1 - X_A) = kt$$

Conversion,  $X_A =$   
 $(1 - \frac{C_A}{C_{A0}})$   
 So,  
 $C_A = C_{A0}(1 - X_A)$

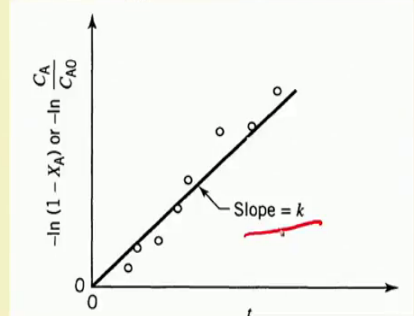





So, this is the final equation we will get in this form.

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**Irreversible uni-molecular 1<sup>st</sup> order reaction**

A plot of  $-\ln(\frac{C_A}{C_{A0}})$  or  $-\ln(1 - X_A)$  vs  $t$  yields the slope= $k$

Now, if you plot the  $\ln$ , this 1 minus  $X_A$  of versus  $t$  will get straight line plot and slope will give you the value of  $k$ , slope will give you the value of  $k$ . So, we can easily in case

of first order reaction we can find out that k value of the chemical reactions. Now, question comes what will happen when we have the fractional this, when we have the nth order reaction. We talk about the first order reaction.

(Refer Slide Time: 23:52)

**Fractional life method**

Consider a nth-order reaction rate equation

$$(-r_A) = -\frac{dC_A}{dt} = kC_A^n$$

Rearranging

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^n} = -k \int_0^t dt$$

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt \quad n \neq 1$$

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Now, nth order reaction we have the expression like this and this we can write in this form. This is where n is not equal to 1. This way we can have this expression we can write differentiate, we can write this expression like this.

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**Fractional life method**

If  $F = \frac{C_A}{C_{A0}}$  = fraction of reactant converted in time  $t_F$

So,

$$(FC_{A0})^{1-n} - C_{A0}^{1-n} = (n-1)kt_F$$

Rearranging

$$t_F = \frac{(F^{1-n} - 1)}{k(n-1)} C_{A0}^{1-n}$$

This expression can also be used to determine the order of reaction.  
**Note: this expression is not valid for 1<sup>st</sup> order reaction.**

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Now, this equation may be simplified in this form and finally, we can write this equation in this form. This is the, F is the fraction that is the F is defined as the  $C_A$  by  $C_{A0}$  fraction of reactant converted at time t F.

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**Half life method**

For half life of reaction  $F = \frac{0.5C_{A0}}{C_{A0}} = \frac{1}{2}$  at half life time  $t_{1/2}$

Therefore,

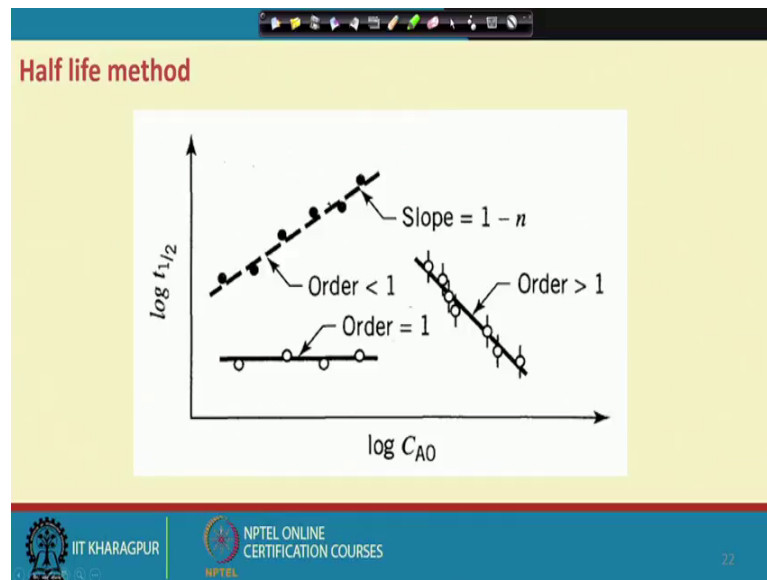
$$t_{1/2} = \frac{(0.5^{1-n} - 1)}{k(n-1)} C_{A0}^{1-n}$$

This expression can also be used to determine the order of reaction.

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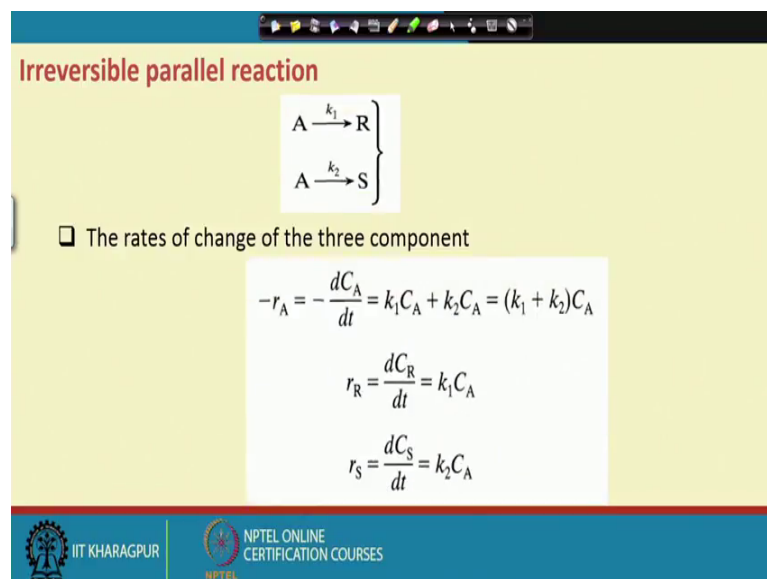
Now, in case of F if we substitute F by t half, what is t half? Is the half life of a chemical reaction, half life of a chemical reaction how you define? That where the half of the substrate that is converted into product and that time if we put in this equation we will get this particular equation. Now, this is very interesting because if you look at this that you know when order of reaction n equal to 1.

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Now, if you come back here, if your n equal to 1 this will be this will be 0 am I right this will be 0 n equal to 1. This C A will be 0 and if C A to the power 0 is there then t half is independent of C A am I right. So, here ln is C A 0 it will be constant like this.

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Now, in case this is more than one then it will be negative, more than 1 negative then it will be inversely proportional with this t half and in case of positive it will be I told you if n is positive then.

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**Autocatalytic reaction**

□ Product itself acts as a catalyst

$$A + R \rightarrow R + R$$

The rate equation

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R$$

Total numbers of moles remain constant

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

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Now, here if n is less than 1, in case of n is less than 1 then what will happen this will be positive then (Refer Time: 26:03) t half is directly proportional to the t half; what I can write that here t half will be directly proportional to C A.

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**Half life method**

For half life of reaction  $F = \frac{0.5C_{A0}}{C_{A0}} = \frac{1}{2}$  at half life time  $t_{1/2}$

Therefore,

$$t_{1/2} = \frac{(0.5^{1-n} - 1)}{k(n-1)} C_{A0}^{1-n}$$

This expression can also be used to determine the order of reaction.

*t\_{1/2} \propto C\_A*

*t\_{1/2} \propto C\_A*

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So, as the as the t half changes then with C A values then this also will changes like this. So, this is what I want to point out this is very good relationship that we have. Then we have the other type of reaction we have side the parallel reaction that can be expressed

like this, this is given minus  $dC_A$  by  $dt$  equal to rate of this conversion of the R and rate of conversion of S.

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**Irreversible parallel reaction**

$$\left. \begin{array}{l} A \xrightarrow{k_1} R \\ A \xrightarrow{k_2} S \end{array} \right\}$$

□ The rates of change of the three component

$$-r_A = -\frac{dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A$$

$$r_R = \frac{dC_R}{dt} = k_1C_A$$

$$r_S = \frac{dC_S}{dt} = k_2C_A$$

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That can be expressed like this. We can take out common  $C_A$  we can write this.

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**Autocatalytic reaction**

□ Product itself acts as a catalyst

$$A + R \rightarrow R + R$$

The rate equation

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R$$

Total numbers of moles remain constant

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

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Now, in case of auto catalytic reaction you see that, what is auto catalytic reaction? Where the product acts as a catalyst, where product acts as the catalyst and it is an example of our microbial system. In the microbial system when we get the product the microorganism itself again it produce more products. So, it is kind of what catalytic

reaction. Now, here how we express that? This can be expressed like this you see that  $r_A$  equal to  $k$  in to  $C_A$  plus  $C_R$  because it is proportional to like this, what is  $C_0$ ,  $C_0$  if we assume the concentration of a plus concentration of R. So, we can write this  $C_A$  plus  $C_A$  and  $C_R$  that should be equal to constant.

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**Autocatalytic reaction**

Thus the rate equation become

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

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So, this expression we can write in this form final expression this is equal to  $C_R$ ,  $C_R$  equal to  $C_0$  minus  $C_A$ . So, my rate of substrate conversion we can express like this.

So, in conclusion of what I want to tell that in the reaction kinetics what we basically deal with that, I told you that whatever reactions we have it broadly it can be classified into two ways, one is called that homogeneous reaction and they will call heterogeneous reaction. Now, homogeneous reaction where the reaction take place in one particular trails. We have three phases we have gas phase, we have liquid phase, we have solid phase. Now, mostly the reaction take place either gas phase or the liquid phase in homogenous reaction. But heterogeneous reaction where the reaction take place more than one phase, then major limitation of this process is that one phase should come in contact with the other phase then and only then reaction takes place. So, this is the limitation of the.

So, diffusion is a very important aspect of this heterogeneous. So, diffusion reaction both simultaneously act; when where the rate of diffusion is less then as compared to reaction then diffusion is a controlling factor, when rate of diffusion is more as compared to rate

of reaction then rate of reaction is a controlling factor. Then question comes that we how we can write the expression of the chemical reaction, that we come across two different constant rate constant  $k$  and order of reaction we discussed how it can be determined. Then, but different types of this irreversible reactions we have side reaction, we have auto catalytic reaction how mathematical expression can be done, how you can determine different rate constant about  $k$  value both in case of first order reaction and  $n$ th order reaction I try to explain.

Thank you very much.